Innovative Drilling muds for High pressure and High temperature (HPHT) Condition Using a Novel Nanoparticle for Petroleum Engineering Systems

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Abbreviations and Nomenclatures

WBMs	Water based muds
OBMs	Oil based muds
DLS	Dynamic light scattering
Pac	Polyanionic-Cellulose
HPHT	Hight pressure/High temperature
LPLT	Low pressure/Low temperature
SiO_2	Silica dioxide
SNPs	Silica nanoparticles
NPs	Nanoparticles
API	American Petroleum Institute
PSI	Pounds per square inch
YP	Yield point (100 Ib/ft^2)
PV	Plastic viscosity (cP)
BHR	Before hot rolling
AHR	After hot rolling
R	Reference bentonite mud
ABDACI	Alkylbenzyldimethylammonium
TEOS	Tetraethyl orthosilicate
Pac	Polyanionic-Cellulose
SNPs	Silica nanoparticles
NPs	Nanoparticles
θ_{300}	300 RPM Dial Reading
θ_{600}	600 RPM Dial Reading
K	Fluid Consistency Index
n	Flow Behaviour Index
YP/PV	Ratio of Yield Point to Plastic Viscosity
TD	Total depth
SI	SI unit
(MΩ-cm)	Megaohm
S. G	Specific Gravity
ROP	Rate of penetration
HPWBM	High Performance Water Based Mud
RPM	Revolutions per minute
SBM	Synthetic Based Mud
ECD	Equivalent Circulating Density
MS	Modified silica
US	Unmodified silica
S	Sand nanoparticles
Rs	Indian Rupee

Unit Conversion Factors

Viscosity

1 Centipoise = 0.001 Pascal Seconds = 0.01 Poise

Shear Rate

Ib/100ft^2 = 0.4788 N/m^2 = 0.4788 Pascal

Shear rate (S^{-1}) = 1.703 RPM

Declaration

I CASTER PRINZ MARTIN, here by declare that this dissertation is my own work. Any part, section of phrasing of more than 20 consecutive words that is copied from any other work or publication has been clearly referenced at the point of use and fully described in the reference section of this thesis.

Signed……………………………………………

CASTER PRINZ MARTIN

Supervisors

Sign……………………	Sign......................................
Dr Amir Nourian	Prof. Ghasem Nasr

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List of Publications and Conferences

1. Martin, C., Babaie, M., Nourian, A., and G. G. Nasr. "Rheological Properties of the Water-Based Muds Composed of Silica Nanoparticle Under High Pressure and High Temperature." SPE J. 27 (2022): 2563–2576. https://doi.org/10.2118/209786-PA
2. Martin, C., Babaie, M., Nourian, A., & Nasr, G. G. (2023). Designing Smart drilling muds using modified nano silica to improve drilling operations in Geothermal wells. Geothermics, 107, 102600. https://doi.org/10.1016/j.geothermics.2022.102600.
3. Martin, C. Comparing the Rheological Properties of Water-Based Mud Fluids Containing Nanoparticles Under High Pressure and High Temperature (HPHT) Conditions. 2022 SPARC Book of Abstracts.pdf (salford.ac.uk) – SPARC conference
4. C. Martin, A. Nourian, M. Babaie, G.G. Nasr, Environmental, health and safety assessment of nanoparticle application in drilling mud – Review,Geoenergy Science and Engineering,Volume 226,2023,211767,ISSN 2949-8910,https://doi.org/10.1016/j.geoen.2023.211767.(https://www.sciencedirect.com/science/article/pii/S2949891023003548)
5. Martin, C., Nourian, A., Babaie, M., & Nasr, G. G Innovative drilling mud containing a cheap novel additive capable of drilling high pressure and high temperature petroleum and geothermal wells – Pending submission

Abstract

The negative environmental impacts of drilling muds, particularly oil-based muds, are a cause for concern to regulators and governments worldwide. As a result, rules regarding the discharge and disposal of drilling muds have tightened globally. Recent drilling muds formulation research has concentrated on the development of high-performance water-based drilling muds that are economically viable, environmentally friendly, remain stable when exposed to high temperatures, and can avoid the problems associated with reactive shale. Despite of the fact that water-based fluid systems are environmentally friendly, their instability when subjected to high temperatures continue to be a major challenge. Polymers have been used to supplement and stabilize water-based muds, but they degrade when exposed to extremely high temperatures and therefore, their usage is limited to a certain temperature. Nanotechnology has widely been applied in drilling mud technology and many advantages have been registered. However, the technology has been found to be very expensive leading to increased drilling operational costs and its toxicity has not been properly documented. As a result, the industry is still looking for a low-cost substitute that can provide the same benefits as nanoparticles.

In this experimental study, an attempt has been made to investigate whether nanoparticles could increase the stability of water-based drilling muds under high temperatures. Unmodified silica nanoparticles, modified silica nanoparticles and nano sand were investigated in water-based formulations. The properties of the drilling mud formulations were measured using Model 1100 viscometer before and after aging in a roller oven dynamically for 16 hours. The stability temperature of the mud system was defined as the temperature at which the mud retains 50% of its original viscosity after aging for 16 hours. Experimental data indicated that water-based mud stability temperature after aging for 16 hours was at 121 ^{o} C. Addition of nanoparticles in water-based muds enhanced mud rheology and filtration properties. Filtration characteristics of water-based formulations containing unmodified nano silica, modified nano silica and nano sand were improved on average by 9.7%, 19.5% and 22.9% respectively. Experimental data also indicated that modifying the surface of silica nanoparticles improves the rheology though it adds to the cost of drilling operation. Nano sand exhibited stable rheological properties and filtration characteristics when compared to silica nanoparticles. The new mud fluid system which is economically viable and environmentally friendly can therefore meet the requirements of high pressure and high temperature drilling operations.

Chapter 1: Introduction

This chapter outlines the background and significance (section 1.1), problem statement (section 1.2) of the research, and contribution and relevancy (section 1.3). It also discusses the research aim and objectives (Section 1.4) and presenting the a brief outline and structure of the remaining Chapter in the thesis (section 1.5).

1.1. Background and Significance

The growing demand of energy worldwide and the depletion of existing reserves has resulted in a big gap between supply and demand. This situation has led to the exploration and development of unexplored, unconventional reservoirs with deeper wells in harsh and extreme environments to meet the need for affordable energy. Drilling to reach such deeper wells with very high temperatures and pressures (HPHT) involves several technical and environmental challenges. The three key early technologies that contributed to the success of a well and later the drilling industry were the rotary drive, roller cone bits and drilling mud. Therefore, to drill safely, successfully, and economically in such volatile harsh environments, a drilling mud whose properties stay stable is a key parameter.

Conventional drilling by all accounts began at Spindletop, near Beaumont Texas in 1900. Today, conventional drilling circulation flow path now begins in the mud pit, where drilling mud is pumped through the drill string to the downhole, through the drill bit, up to the annulus, and exits to the top of the wellbore open to the atmosphere via a bell nipple, then through the flow line to the separation and solid control equipment, and back to the mud pit [1].

Because of their technical performance, oil-based mud (OBM) systems have been used successfully in HPHT conditions [2]. However, environmental, and economic concerns have restricted its use. Oil-based muds can contaminate the water table, cause fires, and cause significant environmental damage during disposal. As a result of strict environmental regulations, high costs of disposal, treatment of cuttings from the use of OBMs, and formulation costs, the oil industry's current effort and research has shifted focus to designing high-performing water-based fluids (HPWBFs) that are less costly and environmentally friendly but can perform like OBMs in terms of performance, stability and efficiency [3]. Even though water-based mud (WBM) systems are considered environmentally friendly, their thermal instability when exposed to high pressure and high temperature (HPHT) conditions remains a big problem [4]. Very high temperatures affect the hydration of components, filtration properties and clay dispersion, thus causing degradation of additives in WBM [5].

Researchers have been evaluating the use of nanoparticles (NPs) in different oil and gas applications including drilling muds [6, 7]. Nanoparticles can be defined as particles with a diameter size less than 100 nm [8]. It is thought that nano-sized particles can plug shale nanopores, reducing the factors that cause wellbore instability [9, 10]. To evaluate the use of nanomaterial potential in WBMs, the stability and dispersion abilities of nanoparticles in WBMs must be thoroughly investigated and understood in detail. The best approach is to use a methodology that characterises nanomaterial sizes, then select the appropriate nanoparticle size and evaluate it under real-HPHT drilling conditions, and finally analyse the overall drilling mud performance based on rheology, filtration and dispersion properties. This will then serve as a benchmark for understanding nanomaterial performance hence basing on the findings, design a stable mud system.

1.2. Problem Statement

Well-drilling operation success depends on many factors and one of the most important factor is a drilling mud system. Despite ongoing efforts to explore and develop HPHT wells in a cost-effective, safe, and environmentally friendly manner, development has been hindered by persistent environmental implications associated with drilling operations such as environmental contamination, mud fluid disposal after use, and maintaining mud fluid stability under HPHT conditions. Borehole instability, hole cleaning, and rate of penetration, all of which are major wellbore construction issues in HPHT wells have persisted as major global concerns in the petroleum industry. Drilling operations contribute a large amount of wastewater which may contain dissolved chemicals and other contaminants that require treatment before reuse or disposal. The application and use of chemicals in drilling muds that are potentially hazardous means that any release of these fluids can lead to the contamination of the surrounding areas including sources of drinking water and can negatively affect the natural habitats.

Therefore, developing a high performance environmentally friendly and economically viable drilling mud could be one of the promising ways to solve the problem. Drilling muds cool and lubricate the drill bit, prevent formation damage, carry the cuttings to the surface, suspend the cuttings and weighting materials when circulation is stopped etc. Oil-based muds have always been the preferred choice especially in highly technical and challenging formations such as HPHT formations. This has been due to their excellent properties including excellent thermal stability, good borehole control, high lubricity, high penetration rate and great cleaning abilities with less viscosity and improved shale inhibition which is critical in shale formations. Such properties may lead to reduction in operational costs. However, there are environmental issues associated with the disposal and hazards to personnel. Therefore, this has continued to present challenging issues due to the strict environmental regulations over the disposal of waste.

The drilling mud industry has tried to introduce other OBMs using alternative base oils to diesel and mineral oils that have been deemed to be environmentally friendly while maintaining high technical efficiency. Throughout the years, different plant oils such as Sesame oil, rapeseed oil, Soya bean oil, palm oil, canola oil, Jatropha oil and many more have been used as diesel replacement. However, there has been conflicting issues with maintaining the mud properties such as good rheology, low fluid loss, high stability and compatibility of the chemical additives with the vegetable oil continuous phase [3]. As a result, there is still unanswered questions about how to design stable, environmentally friendly drilling mud systems while keeping costs low. Research has shown that it is often impossible to reduce filtrate loss into the formation successfully with micro and macro type fluid loss additives due to their physio-chemical and mechanical characteristics e.g. size, surface charge etc., thus raising the economic consequences on non-productive drilling time [11, 12].

Although nanoparticles (NPs) have been widely adopted in the industry, the cost of NPs is a major impediment in preparation of large volumes of nanofluids for drilling operations. In this study, a novel additive will be introduced and tailored to interact with the rest of the drilling mud components resulting in good dispersion properties, reduced fluid loss during drilling, and improved drilling mud functionality under a variety of conditions, including high temperature, high pressure drilling environments and formations. This will reduce the amount of additives used in drilling mud formulations resulting in reduced overall cost of drilling operations.

1.3. Contribution and relevancy

This project poses a great deal of significance to the oil and gas industry. The demand of oil is increasing every day while many wells are reaching maturity, so oil and gas companies are venturing in environments once deemed unreachable, unexplorable with HPHT conditions. In this project, the author therefore intends to use theoretical and practical knowledge in petroleum engineering to suggest a solution to the problem of drilling mud additive cost, environmental pollution, and drilling mud stabilization.

Results of this research will encourage the adoption and use of a novel, cheap and environmentally friendly WBM for drilling in HPHT wells due to its ability to reduce filtrate loss, improve rheology as well as provide good bore hole cleaning abilities. This experimental study presents a detailed procedure of formulating a novel WBM fluid for HPHT drilling operations. Since WBM fluids degrade at high temperatures, the research findings of this study will greatly contribute to knowledge and literature as this present study seeks to develop a novel nanoparticle WBM fluid. This study will also help to unveil and answer some contradictions in the current literature regarding to the effects of silica nanoparticles in drilling mud rheology.

1.4. Research Aim and objectives

The aim of this research is to design a novel WBM using a nanoparticle that is cost effective and environmentally friendly for high-performance drilling in HPHT wells. The thesis aim will be achieved through the objectives below:

- Establish the base mud (R) characteristics with and without nanoparticles by analysing its rheological properties before and after aging at HPHT conditions.
- Establish the optimum concentration of nanoparticles
- Synthesize and characterise NPs and test their performance and effect on water-based mud before and after aging at HPHT conditions.
- Functionalization of nanoparticles and analyse their behaviour in WBM before and after aging at HPHT conditions.
- Analyse the rheological properties of the novel mud before and after aging at HPHT conditions
- Study the effect of nanoparticles on thermal and rheological stability of WBM through aging tests at different temperatures (18 ^{o}C, 100 ^{o}C, 121 ^{o}C, 149 ^{o}C, 176 ^{o}C, 204 ^{o}C, and 232 ^{o}C) and examine nanoparticle ability to reduce degradation rate of polymers at high temperatures.

1.5. Thesis Outline

This thesis is organised into five chapters as presented below:

- **Chapter 1** presents an introduction of the research background, including the aim and objectives of the research. It also presents the significance and the research contribution.

- **Chapter 2** presents an extensive literature review on the drilling muds, nanoparticles, nanoparticle-based drilling muds, filtration mechanisms, governing equation used in filtration process and the effect of high temperature on WBMs containing nanoparticles are presented. More to the above, previous works including problems associated with the use of nanoparticles as additives in drilling muds was reviewed. This chapter also discusses previous research on the subject and what other researchers have reported on it.

- **Chapter 3** explains the methodology used in this research work. The laboratory equipment and test procedures used in the research work are detailed in full.

- **Chapter 4** discusses and analyses the results of the experiments and laboratory findings. It also presents the significance of the experimental data and presents the cost analysis of the mud systems.

- **Chapter 5** presents the conclusion drawn from the work, limitations and a detailed plan for the future.

Chapter 2: Literature Review

This chapter presents four sections. The first section addressed an overview on drilling mud types and functions. The second section addressed high-performance water-based muds. The third section considered the performance of nanoparticles in water-based muds, nano drilling muds general functions and their challenges, nanoparticle properties and previous experimental studies on drilling mud properties using nanoparticles with reference to those directly relevant to the subject under investigation. The fourth section focused on nanoparticle synthesis, nanoparticle dispersion in colloidal mixtures, stabilisation of nanoparticle in fluid mixtures, zeta potential and other nanofluids such as hybrid nano fluids.

2.1. Overview

The literature review considered the effect of HPHT conditions on the performance of WBM fluids. From the early developments of water-based mud fluids (WBMFs), water was the first ever drilling mud used in any drilling operation [13]. Back in the third millennium, the Egyptians used water to remove cuttings from the holes drilled using hand-driven rotary bits [14]. According to the current WBMF formulation trends, water-based drilling muds that simulate the performance of oil-based drilling muds are referred to as high performance water-based fluids (HPWBFs) [15]. The advantages of HPWBMFs include the lowering down costs associated with cuttings and fluid disposal and the reduction of environmental impacts. Selecting additives capable of giving a WBM fluid the properties needed in HPHT drilling operations is still a big challenge the industry is facing. Therefore, a detailed understanding of WBM formulations that can perform like oil-based muds is important for further enhancement of WBMFs.

Though the main objective of this research was to investigate the effect of a novel nanoparticle in water-based bentonite mud system, it was of importance to identify the other additives that stabilise WBMs under HPHT. More attention was given to those additives that enhanced the technical performance of WBMs at high temperatures. As a result, experimental studies relevant to this current research were prioritised.

2.2. Drilling mud

A drilling mud is a term used for the different types of fluids used in the drilling of oil and gas wells. Throughout this thesis, drilling mud and drilling fluid are being used interchangeably. A drilling muds is defined as a fluid that is used in a drilling operation in which the fluid is pumped through the drill string from the surface down the hole and back to the surface via the annulus with the capacity of performing certain functions [16, 17]. These functions include, maintaining wellbore stability, removal of drilled cuttings, suspend and release of cuttings, cool the drill bit and more. Drilling mud is one of the most important components of well construction process. It is designed to perform in the best way possible under predicted wellbore conditions. Technology made it possible to come up with highly efficient and cost-effective drilling muds that are suitable for different sections in the well. Drilling muds costs around 10% of the total tangible costs of the well. Its performance can heavily affect the overall cost of the well construction process. An efficient drilling mud can keep the cost under control by maximizing the rate of penetration (ROP), reducing possible loss of circulation, maintaining well bore stability, minimizing formation damage and keeping HSE compliance requirements [18].

2.2.1. Basic functions of drilling muds

Drilling mud serves many functions during drilling as well as other operations such as cementing, tripping, logging and many others. Some of them were mentioned in this section.

- **Minimize formation damage:** Producing formations have a continuous exposure to drilling mud. Drilling muds tends to lose the filtrate and solids into the formation which sometimes affects productivity. Therefore, a careful design of a mud system can minimize this formation damage and can be validated by testing it onto the core samples.
- **Transport cuttings to surface:** The basic function of drilling mud is to transport the cuttings from beneath to the surface. The fluid is designed with such properties that help to carry the cuttings. Different solids are usually added to achieve those properties. Correct chemical properties are also necessary to avoid the dispersion of drilled solids or it might lead to generation of ultrafine particles which can affect drilling efficiency and productivity of the pay zone.
- **Prevent Well-control issues:** The hydrostatic head of drilling mud creates well bore pressure. The pressure should either balance or exceed the pore pressure of the formation to be drilled under normal conditions. As drilling proceeds, pore pressure of the formation usually increases and sometimes it can go to abnormal pore pressures.

The density of the drilling mud must be altered accordingly so that any possible well control situation can be avoided. Therefore, selection of proper mud weights for each interval is important to minimize kick.

- **Preserve Wellbore stability:** Maintaining well bore stability is very vital for a successful drilling operation. Drilling mud density and proper composition can result in a stable well bore which is very important for tripping drill string, running logging tools, conducting casing running and cementing operation.
- **Cool and lubricate the drill string:** Circulation of drilling mud acts as a heat exchanger for bit and drill string and reduces the friction between tools and hole wall. The generation of heat is natural process dependent on the geothermal gradient of the area. Lubricity is required due to the directional trajectory of the wells as well as tight spots. A mud utilizing oil as its base fluid offers high lubricity and finds its application in high angle directional wells.
- **Provides information about the wellbore:** Drilling mud also provides information about the wellbore. Mud pulse telemetry is the basic principle of measurement for transferring downhole survey and logging data during drilling. It also serves as a transferring medium during wireline logging operation. Preservation of cutting by drilling mud and its efficient transfer to surface allow the geologists to analyse the cutting accurately [18].

2.2.2. Types of drilling muds

There are different types of drilling mud systems (as shown in Figure 2.1) which includes, saltwater systems, freshwater systems, oil or synthetic based systems, and pneumatic (mist, form, air, gas) systems [19]. Oil or water-based drilling muds are made up of clays, water and chemical additives. In addition, drilling muds are important for any drilling operation and make up a large portion of drilling cost system [19]. With WBMs, the solid materials are mixed with in water or brine without chemicals or with chemicals with a percentage of oil. The solid materials used commonly are clay, weighting agents, and organic materials. When oil is dispersed in water, the water in the mud will be the continuous phase but when water is dispersed in oil, the oil will be the continuous phase. Oil based muds (OBMs) consist of mineral oils, chemical additives and barite though they are not environmentally friendly [20]. The base fluids used in OBMs are usually, diesel, kerosene, and fuel oils but in synthetic -based muds, an oil like substance might be used as the base fluid [21-23].

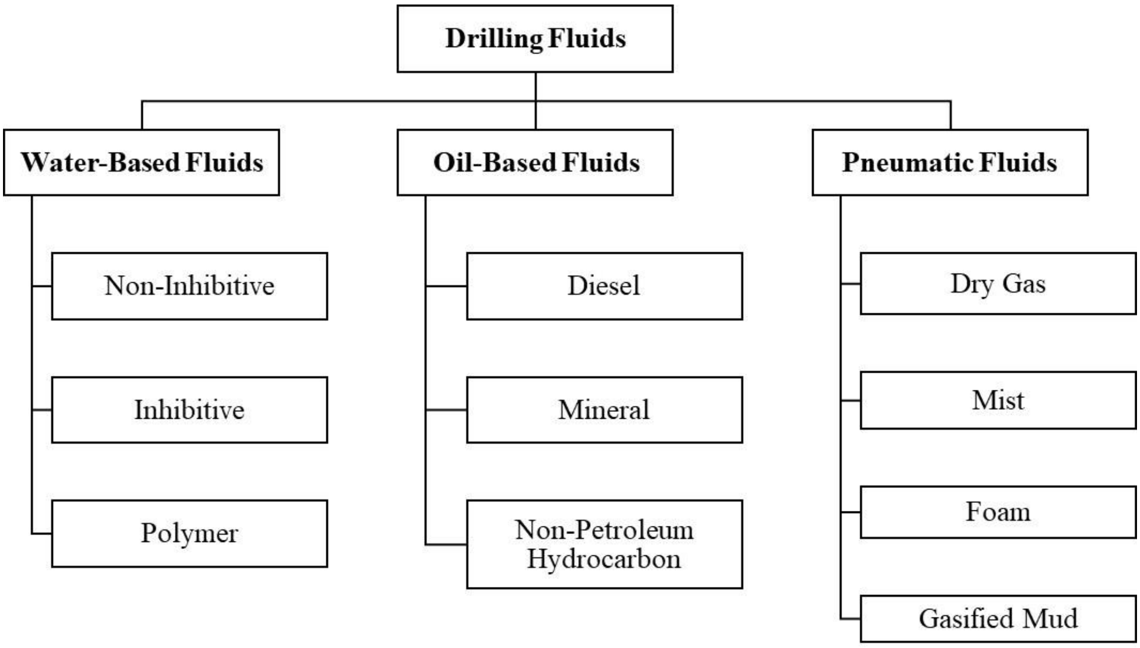

Figure 2.1: Drilling mud classification [24]

2.2.3. Water based drilling muds (WBMs)

The base fluid in this type of mud system can be fresh water, seawater, saturated brine, simple brine, or formate brine. Almost 80% of wells are drilled by water-based fluid (WBFs). Well condition, type of formation lithologies, cost and specific interval of the well being drilled determines the type of fluid [3]. For instance, sea water-based fluid is typically used to drill surface intervals which contain fewer additives. Hole cleaning and fluid loss control are usually done by addition of commercial bentonite. In deeper section, WBFs can be used depending upon the well condition or can be replaced by oil or synthetic based system [18]. WBMS are a composition of minerals, salts and organic compounds. The base fluid is water. There are different additives in water muds which includes, surfactants, organic polymers, barite, clay, salts and alkalis. WBMs may also contain some metal and the toxic metals found in WBMs include, copper, iron , mercury, zinc, barite, and nickel [25]. WBMs also contain organic matter such as biopolymers, which are very degradable but less toxic [26]. Although there are over 1,000 trade name or generic additives available for drilling mud formulation, most WBM contain no more than about 20 additives, with the majority being added in small amounts to change mud properties to solve specific down-hole problems. Other than water, the most common ingredients in most WBM are barite weighting material, salts (in various functional categories), and bentonite viscosifier. The composition of WBMs is shown in Figure 2.2 below.

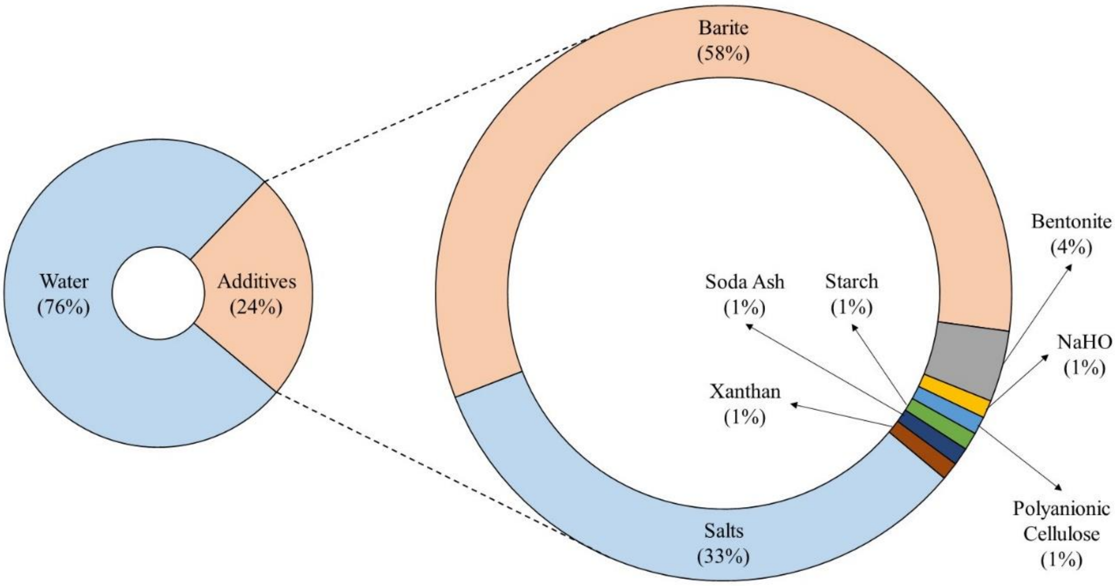

Figure 2.2: Composition of a typical WBM and additives [27]

2.2.3.1. Types of water-based muds

Water-based muds are classified into dispersed and non-dispersed muds. The main difference being the lack of dispersant.

- **Dispersed systems:** In dispersed systems, chemical dispersants are added to deflocculate clay particles so that rheology of high-density muds can be improved. Dispersants such as lignite and lignosulfonate are in use. Since the dispersants are acidic, they require an alkaline environment to function properly. pH level is maintained at 11.0 by adding caustic soda (NaOH). The mud weight of this type of system can be increased up to 20.0 ppg due to solid dispersion. lignosulphonate system is an example of dispersed mud system. The dispersants make it possible for the clay to deflocculate to control fluid losses. There is another class in WBFs termed as saltwater systems which are used to inhibit shale and to drill salt formation. Formation of ice-like hydrates can also be minimized by this fluid which can form around subsea equipment and well control equipment [18].

- **Non-dispersed systems:** In non-dispersed muds, dispersants are not added. Bentonite is one of the viscosifier and fluid loss agent used in WBMs. Example of non-dispersed system are polymer systems with low/no bentonite and simple gel-water system that are used to drill surface intervals. Dilution and flocculation are used to manage natural clays in non-dispersed system. Fine solids are removed from this type of system through a proper solid control system. In low solid non-dispersed polymer system, fluid rheology and fluid loss are managed by low and high molecular weight long chain polymer system. In HPHT applications specially designed polymer are used so that they can remain stable at high temperatures [18]. Non-dispersed drilling muds do not need high pH, dispersant is not needed but they are not tolerant of solids and contamination as the dispersed muds. Polymers are commonly used as loss of filtrate preventers and for viscosity. Polymer and other mud additives are likely to surfer contamination from produced gases and fluids. [19] classified water-based fluids as follows.

a) Polymers
b) Inhibitive
c) Non-inhibitive

Non-inhibitive fluids do not contain specific ions - sodium, calcium and potassium but inhibitive fluids have these ions [19]. Therefore, since non – inhibitive fluids contain none of these ions, they do not inhibit clay swelling. Non – inhibitive fluids are mixed up with the clay from the formation to be drilled or bentonite and caustic soda or lime. Other additives added to non – inhibitive fluids include deflocculants and dispersants. The common dispersants used in non- inhibitive fluids include, lignosulfonates, lignites or phosphates, which are usually spud muds that is muds used to drill a well from surface to a shallow depth [28]. Inhibited water-based systems reduce water wetting of the rock pores and do not contain chemical dispersants (thinners) neither ions. Clay swelling in inhibitive water-based mud is reduced by the presence of cations typically, Sodium (Na^+), Calcium (Ca^{2+}) and Potassium (K^+). Generally, K^+ or Ca^{2+}, or a combination of the two, provide the greatest inhibition to clay dispersion. This type of mud fluid is commonly used in drilling reactive shale formation and sandstone formations with reactive clays. Disposal amounts to higher cost and its one of the disadvantages of using inhibitive mud fluids since the source of the cation is usually a salt [28]. Polymers fluids provide mud properties relying on macromolecules either with or without clay interactions. Polymer are used to provide viscosity, control filtration properties and deflocculate solids. Polymer can thermally stay stable up to a temperature of 400 ° F despite of their many applications, polymer fluids have challenges because the presence of solids hinder running a successful cost effective polymer mud system [28]. Potassium chloride is used as brine for polymer mud systems to enhance shale inhibition.

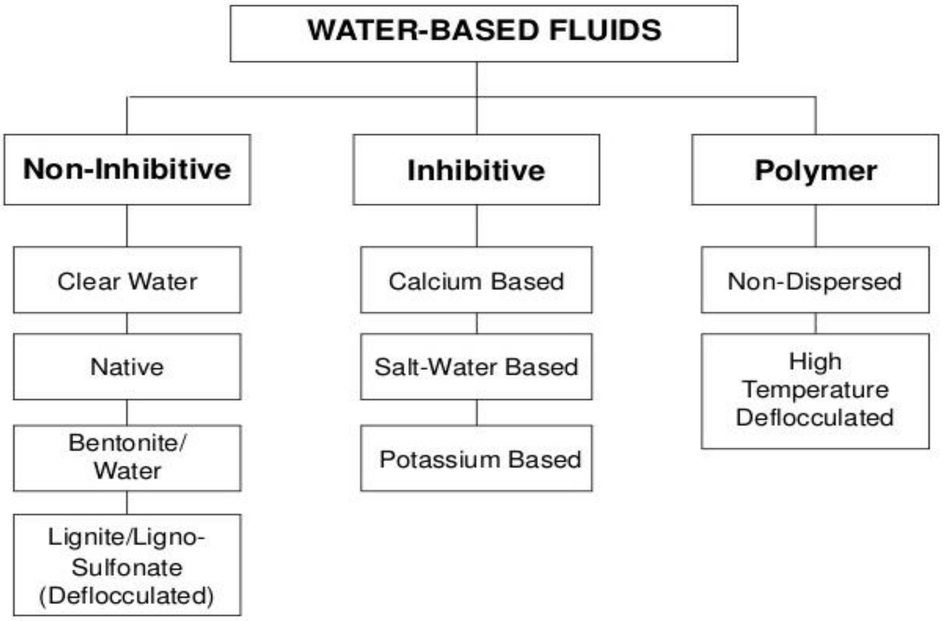

Figure 2.3: Water-based fluids classification [28]

2.2.3.2. Advantages and Disadvantages of WBMs

There are advantages and disadvantages of using water-based muds [3, 29]. These are:

- Advantages:
  - Environmentally friendly, low toxicity
  - Readily available
  - Easy to handle, prepare, inexpensive and cost effective
  - High rate of penetration
- Disadvantages:
  - Causes corrosion
  - Causes formation damage

  - Unwanted increase in density from salt in a formation
  - Causes clay disintegration and dispersion
  - Not effective in reactive shale formations

2.2.4. Oil based fluids (OBMs)

These systems were developed in 1960s to minimize several drilling problems such as swelling, high bottom hole temperature, high torque and drag, stuck pipe etc. The main constituent of OBMs is diesel, mineral oil or low-toxicity linear paraffin. The strength of emulsion is checked through monitoring of electrical stability of water phase. Oil based system utilizes barite as weighting agent and specially treated organophilic bentonite as viscosifier. Other chemicals are used to control fluid loss, to suspend the particulate, to elevate pH, to mitigate the effects of H_2S and CO_2 gases. Typically, 80/20 to 90/10 oil/water ratios is observed in field applications but in rare cases it can go to 95/5 as well [18].

One of the main benefits of oil-based system is to inhibit shale from swelling. This is accomplished by high salinity water phase. Mostly calcium chloride is used to attain inhibitive property in oil-based mud. The key issue with oil-based system is their environmental impact. Offshore drilling does not allow the whole drilling mud or cutting to be discharged without processing. Therefore, there is always a cost associated with OBMs to process and ship waste fluid and cuttings [18].

2.2.5. Synthetic-based drilling muds (SBMs)

These fluid systems are developed to minimize the environmental effect that OBMs usually make by keeping the cost effectiveness of OBMs. SBFs offer shale inhibition, wellbore stability and better lubricity in directional wells. Therefore, drilling performance of both OBMs and SBMs are quite similar. The performance benefits include minimal initiation pressure to break the gel; very low equivalent circulating densities (ECDs); and nominal mud losses while drilling, running casing, and cementing. Regulations for cuttings generated through the use of SBMs are not as strict as it is for OBMs [18].

2.2.6. All-oil fluids

High salinity water phase is normally used in invert-emulsion fluid to prevent swelling of reactive shales. Sometimes, long shale intervals are drilled with diesel or synthetic based oil with no water phase when there is a variation in formation water salinity [18].

2.2.7. Drill-in Fluids (DIFs)

Conventional fluid can severely damage the reservoir productivity due to undefined risks associated with it particularly in horizontal wells due to long term exposure. Drill-in fluid is a type of fluid that is designed to mitigate formation damage and to offer better hole cleaning with easy clean-up. It can be based on water, oil, or synthetic systems. It also has a compatibility with reservoir fluid so that production of emulsions and precipitation of salts can be avoided. A detailed study of pay zones cores can be helpful in designing drilling muds for reservoirs [18].

2.2.9. Pneumatic-Drilling fluids

Pneumatic fluids use air, gas, mist or foam to circulate cuttings out of the well. Specialized equipment is required when using this type of fluid to carry out operation in safe manner. Normally this type of fluid find its application in depleted or sub-normal pressure application and gives several benefits such as higher rate of penetrations (ROP) lost circulation prevention, hydrocarbon presence evaluation and many more [18].

2.2.10. Drilling mud additives

According to Schlumberger Oilfield Glossary, drilling mud additives are defined as a material that is added to a drilling mud system in order to perform one or more specific functions. They are always classified by names as its function to drilling mud such as viscosifier, loss circulation materials, polymers, weighting agents, surfactants, dispersants, thinners, inorganic chemicals and clays [27]. The additives listed are divided in different categories, viscosifiers, dispersants, thinners, weighting materials, pH-control additives, filtrate preventers, flocculants, foaming agents, loss of circulation materials, pipe-freeing agents, emulsifiers, defoamers, shale control inhibitors, surface-active agents, lubricants and temperature stability agents.

- **Clay minerals:** According to Moore and Reynolds [30], clay materials are found in the soils and sedimentary rock. They are made important by their surface properties, they are reactive hence making them applicable for industrial applications and environmental controls. The properties of clay like, high surface area, acidity and cation exchange capacity make clays play an important role of catalysts and adsorbents for toxic substances [31]. Clay in WBMs provides density, gel strength, viscosity, and yield point. Clay also provides fluid loss control abilities. The current used type of clay in this study is the montmorillonites (bentonite clay) but there are other types of clay like, kaolinites and illites.

- **Montmorillonites (Bentonite):** WBM fluids have conventionally relied on the use of clay-based viscosifiers, such as bentonite to provide an inexpensive means to impact adequate viscosity, suspension, and filtration control to the drilling mud. Even though bentonite readily hydrates to function as an efficient, inexpensive viscosifier for fresh-water muds, the increase in salinity leads to ineffective clay swelling and flocculation, hence reducing viscosity and high fluid loss [32]. The unique properties of bentonite clay is due to the structure, exchangeable ion type, chemical composition, and small crystal size of smectite [33]. Sodium bentonite swells while calcium bentonite is non swelling. Bentonite is one of the best filtration control agents there is. It is low cost and temperature stables hence it seems only natural that it should be the basis of filtration control in WBMs [34]. Bentonite is capable of solving most filtration problems if used properly. Its ability to control filtration is based on its naturally small, plate-like particles and high hydration degree. These characteristics depend on the chemical environment in which bentonite is placed. Calcium and magnesium cations displace par of sodium from the clay platelets in a bentonite mixture. Figure 2.4 shows the approximate dry bentonite requirements in various salinities [34].

  The performance of clays is influenced by calcium or magnesium ions which have a greater cation exchange replacing power than sodium. In drilling muds, changes are made when there is an increase in calcium or magnesium concentration. The clay in the drilling mud dehydrates and flocculates leading to a decline in plastic viscosity. The same also causes an increase in yield point, gel strength and fluid loss [34]. When selecting clay to use in drilling mud, the yield point, plastic viscosity, yield strength, thickness of mud cake, wall building properties, gel strength properties and suspension capacity in saltwater must be considered.

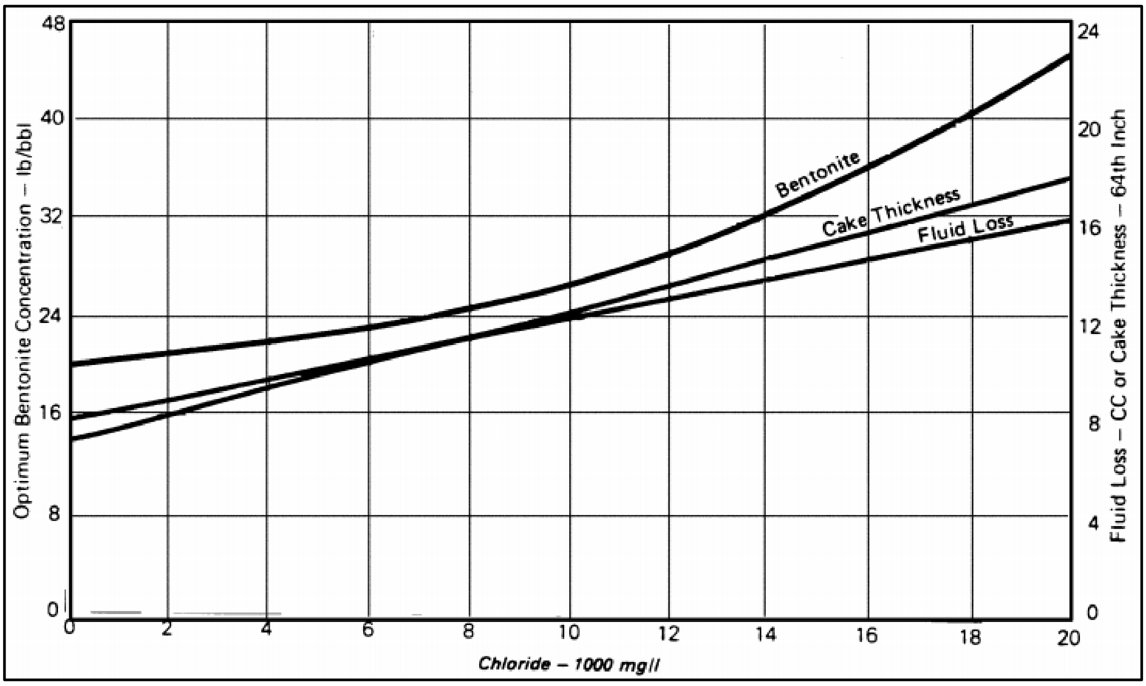

Figure 2.4: Approximate dry bentonite requirements in various salinities [35]

- **Polymer additives in drilling mud:** The use of polymers in the drilling mud system is to provide fluid loss control properties, viscosity, shale inhibition and prevent clay dispersion [32]. Polymers are very common in almost all WBM. According to Plank et al. [36] and Strickland et al. [37], synthetic polymers are stable at high temperatures.
- **Nanoparticles:** The use of nanoparticles in drilling mud serves a purpose of improving the electrical conductivity of the drilling muds. NP can enhance the drilling mud properties only by adding small amounts in the formulation hence, the drilling system could be a fluid of choice in drilling sensitive environments. The principal benefit of the NP as an additive for drilling mud in shale formations is the size. Additives used to control fluid loss have a particle size in micro or macro size Figure 2.5. This size particle is larger than the nanopore size of the shale formations. This difference in size would explain why these products cannot form a filter cake and control the filtrate invasion of the shale formation [38]. Nanoparticles can be added to the drilling mud to minimize shale permeability through physically plugging the nanometer-sized pores and shut off water loss. Hence, Nanoparticles can provide potential solution for environmentally sensitive areas where Oil-based muds used as a solution to shale instability problems. One conventional bridging theory is referred to as the one-third rule of filtration (Abrm’s theory) where the material used to plug a pore is required to be roughly one

third to one seventh of the size of the median pore opening. There are other theories with varying size requirements for the plugging material, however, none are perfect . an ideal pluging material will also accommodate the variability in pores within the formation [39]. More so, NP tend to create a thin filter cake in shale formation hence controlling the water influx avoiding further problems [40].

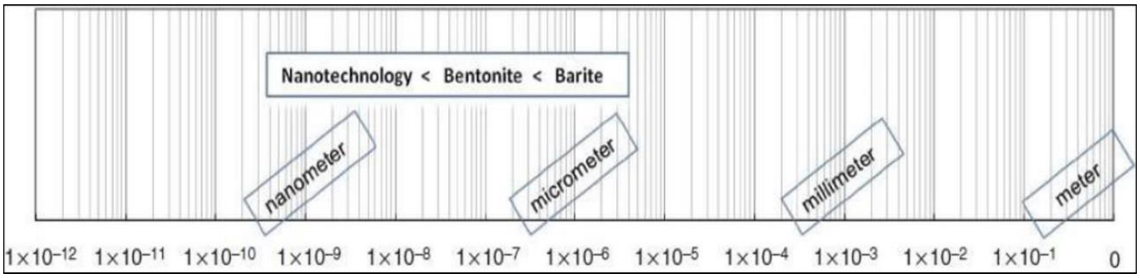

Figure 2.5: Particle-sized scale [38, 39]

- **Freshwater:** This acts as the continuous phase of any mud fluid. It provides the initial viscosity and acts as a base fluid, as a means of conditioning all additives used in formulating the drilling mud system. It also acts as a medium which facilitates heat transfer through the drilling mud, helps suspend solids in drilling muds, transfers the surface available hydraulic horsepower to the bit on the bottom of the wellbore. All the additives added in a drilling mud system are meant to improve the properties of the drilling mud [27].

2.2.11. Drilling mud properties

The physical and chemical properties of the drilling mud are maintained, controlled, and frequently observed for the mud system to function effectively in a drilling operation with the aim to avoid technical and economic losses. Drilling mud properties include density, rheology, and filtration properties. PH, lubricity, toxicity and electrical conductivity are also some of the properties the drilling mud system must have [22]. The physical properties prevent fluid loss, help in carrying the cuttings, suspend cuttings when drilling stops, stabilise the well-bore, and supply the hydraulic pressure to the bit. On the other side, the chemical properties may cause problems like damaging the formation, causing change in rheological properties, and cuttings transport problems [19]. The relevant properties of the drilling mud relating to this research are discussed and considered.

- **Drilling muds pH:** The pH of a solution is a measure of the hydrogen ion concentration hence the measure of the degree of acidity or alkalinity. pH of a drilling mud is vital for drilling mud control. pH can be measured either by a pH meter or a pH paper test strip. Clay interaction and effectiveness of additives depends on the pH. The corrosion of drilling and well equipment caused by acidic and sulphide contents in drilling mud can be controlled by monitoring the pH values. The pH also determines the solubility of components and contaminants in drilling muds [34]. When acid is added to water, the pH decreases on the scale from 7- 0 and the fluid is acidic. Fluids with pH values greater than 7 are alkaline and caustic is added. With pH equal to 7 is term neutral. The desired operating pH for drilling mud is generally 8.5 to 9.5 in order to reduce corrosion of the drill pipe and casing. Maintaining an adequate pH in a mud system is important for several reasons.

    - Corrosion rates are suppressed at a pH above 10
    - Calcium solubility is reduced as pH is increased.
    - The rate of thermal degradation of lignosulfonate is reduced at a pH above 10
    - Hydroxyl ions neutralize the H+ ions from H_2S and prevent hydrogen embrittlement.
    - A pH above 11 should be maintained if H_2S is anticipated.

- **Viscosity** of the fluid is the measure of the resistance to flow. It is an important drilling mud property especially in rotary drilling operations and must be controlled for better fluid performance [22]. The viscosity of a bentonite suspension at different shear rates is presented below.

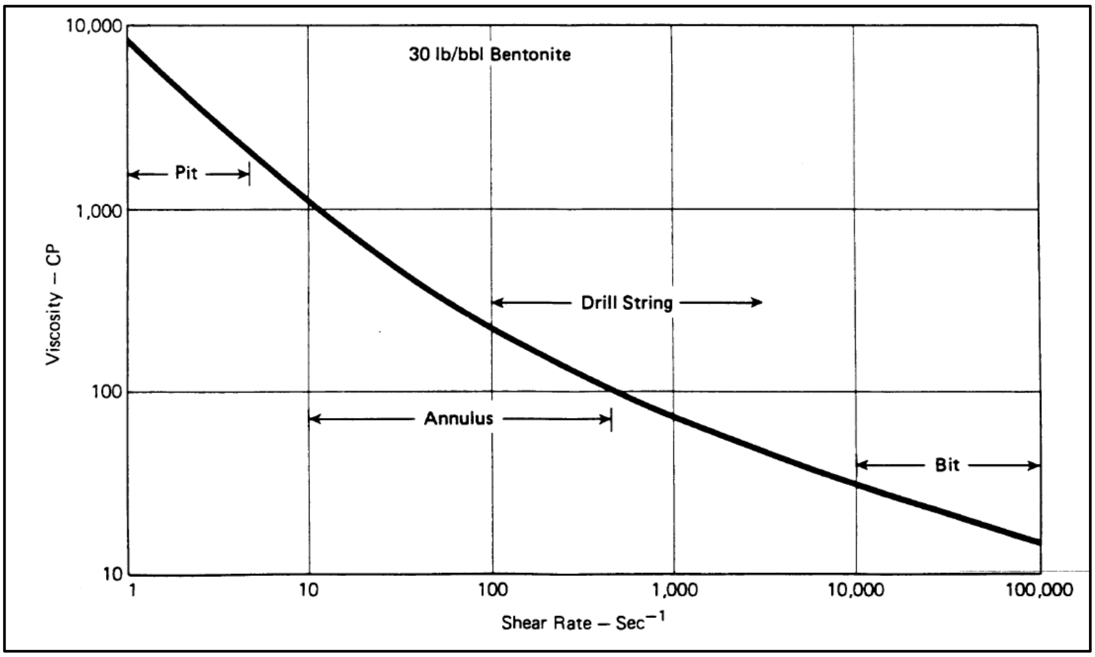

Figure 2.6: Viscosity of bentonite-water suspension at different shear rates [35]

Viscosity is represented and defined as the ratio of shear stress to shear rate of a drilling mud [19].

$$\mu = {}^{\tau}/_{\gamma} \tag{2.1}$$

Where, τ is the shear stress (Ib. /100ft^2), γ is the shear rate (sec^{-1}) and μ is the viscosity which is measured in centipoise (cP).

The viscosity of fluids varies with pressure and temperature. Most fluids viscosity is more affected by temperature rather than pressure. The effect of pressure on viscosity of liquids is always ignored in most experiments [41]. It was stated the concept that the pressure affects the material only above a particular value is valid only for the liquid-regime, in which the viscosity is not much affected for the case of 70 bar applied pressure [42]. On the other hand, it was stated that the rheological characteristics are affected for the solid -like regime even for the lowest pressure imposed on the fluid of 70 bar. One of the main concerns at high pressure conditions must be the drilling gel strength. It can be challenging to break up the material's structure and start flow under the conditions above hence extra care should be taken when starting the pumps [42].

For Newtonian fluid, the relationship between shear stress and shear rate is defined as effective viscosity. However, for Non-Newtonian fluid, the effective viscosity is not constant. Most drilling mud effective viscosity will be relatively high at low-shear rates and relatively low at high-shear rates [43]. It must be measured at a known shear rate to achieve a reliable value and at a specific temperature and pressure. The equipment for measuring viscosity of a mud fluid is viscometer. The viscosity of Newtonian fluid is independent of the shear rate while that of the Non-Newtonian fluid is dependent on shear rate. Most drilling muds are Non-Newtonian. Newtonian fluid's shear stress verse shear rate plot on a Cartesian graph (green lines) is linear but the plot of shear stress verses shear rate for non-Newtonian fluids shown on the graph is nonlinear as seen in Figure 2.8.

Furthermore, there are other rheological models that are used in drilling industry other than the Newtonian model described above. The non-Newtonian fluids viscosities vary with shear rate. Most drilling muds are non-Newtonian fluid, either viscosity changes with shear rate (i.e. Power Law model or Herschel-Bulkley Model), or a plastic yield must be overcome (i.e. Bingham plastic model). Fluids which increase in viscosity with increase in shear rate are called dilatants.

Temperature has different effects on the viscosity of liquids and gases. A temperature increases leads to a decrease in the viscosity of Newtonian liquids. The viscosity of Newtonian liquids can be defined by Arrhenius relationship. The essence of the Arrhenius equation is that the viscosity is proportional to the absolute temperature's reciprocal and governed by a single parameter, namely, the energy of activation [19, 44].

$$\mu = Ae^{-B/T} \tag{2.2}$$

Where T is the absolute temperature (Kelvin), and A (Arrhenius constant) and B (Activation energy) are liquid constants.

There are various types of non-Newtonian fluids with different characteristics: pseudoplastic fluids, dilatant fluids, thixotropic fluids, anti-thixotropic fluids and plastic fluids. The viscosity of pseudo plastic fluid depends on shear rate. Thixotropic fluids viscosity decreases with increasing time at a constant shear rate. Rheopetric fluids viscosity increases with increase in time Figure 2.7.

Most drilling muds exhibit thixotropic properties. In most drilling muds, increase in share rate leads to a decrease in viscosity. This occurrence is called shear thinning termed as temporary viscosity loss and pseudo plasticity [45].

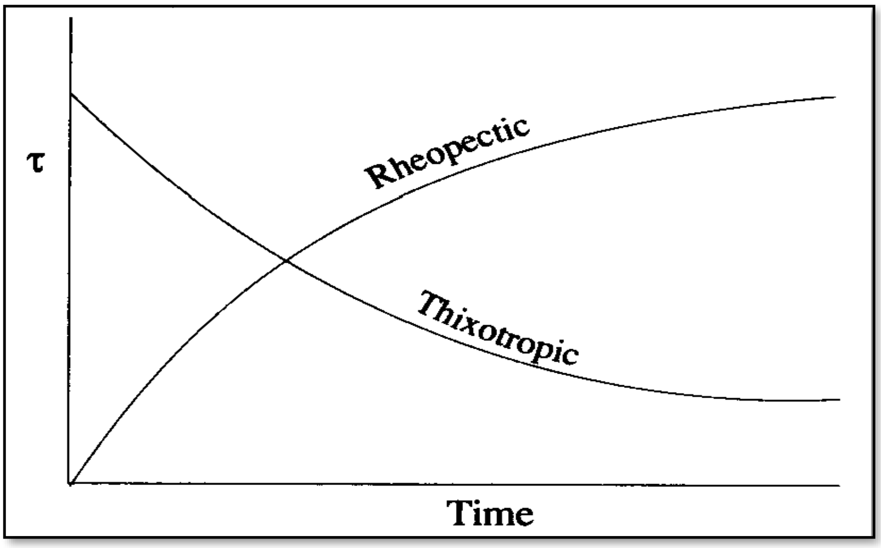

Figure 2.7: Relationship between shear stress and time [46]

2.2.12. Rheological models

There are many models used in analysing rheology of fluids and these include, Newtonian model, the Bingham plastic model, Herschel-Bulkley model and the Power-law model. These are used to approximate fluid behaviour [19]. Figure 2.8 below shows the rheological models used to analyse fluid behaviour [45].

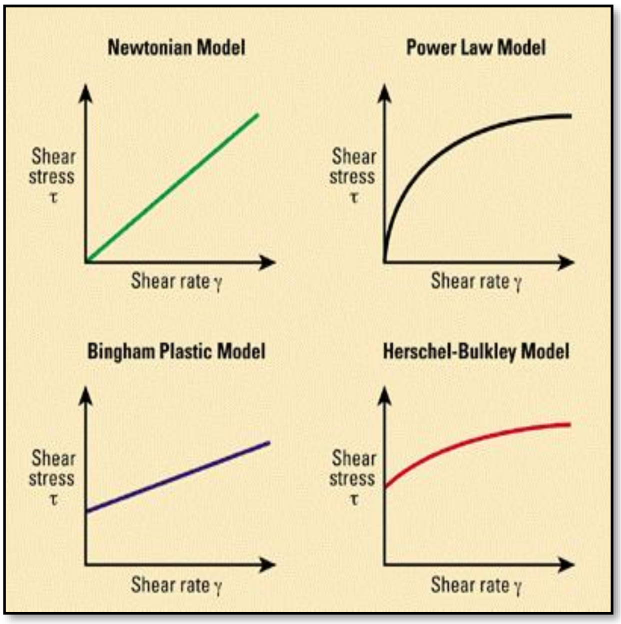

Figure 2.8: Four major rheological models [47]

2.2.12.1. Newtonian fluid model

Newtonian fluids viscosity is constant at all shear rates at a temperature and pressure and does not vary with time. Newtonian fluids exhibit a linear relationship between the shear stress and shear rate passing through the origin and the constant of proportionality being the viscosity as shown in Figure 2.8 [19]. The characterising of Newtonian fluid relationship can be expressed mathematically as shown in the equation below.

$$\tau = \mu\acute{y} \tag{2.3}$$

where,

τ = shear stress (Ib/100ft^2)
$\acute{y}$ = shear rate (sec^{-1})
μ = viscosity (cP)

2.2.12.2. The Power Law model

A power-Law model is described by two parameter rheological models of a pseudoplastic fluid or as a fluid whose viscosity decreases as shear rate increases [19].

$$T = K\gamma^{n} \tag{2.4}$$

Where K is the fluid consistency index, and the flow behaviour index is n. The viscosity at a shear rate of 1s^{-1} is K and is expressed in 1b/100ft^2, while the extent of shear thinning is shown by n. a smaller value of n represents a higher shear thinning behaviour. Most water-based polymer muds especially those containing xanthan gum can better be modelled by the power law equation better than any other two-parameter model including Bingham plastic model [48]. The power-law model is ineffective at high shear rates but effective at low-shear rate conditions [49].

2.2.12.3. Bingham plastic fluid model

The Bingham plastic model is like a Newtonian mode however it requires a plastic yield to be overcome before any shearing in the fluid will occur. The Bingham plastic model is widely used in the drilling muds industry to explain and describe flow characteristics for many mud types and it’s a two-parameter rheological model [19] mathematically described as;

$$\tau = \mu_p \gamma + \tau_y \tag{2.5}$$

Where,

$\mu_p = \theta_{600} - \theta_{300}$ and $\tau_y = \theta_{300} - \mu_p$

Where,

τ = Shear stress [lb/100 ft^2]

γ = Shear rate [sec-1]

τ_y = yield point [lb/100 ft^2]

μ_p = Plastic Viscosity [cp]

A Bingham plastic will not flow until the applied shear stress exceeds a certain minimum value τ_y known as the yield point. After the yield point has been exceeded, changes in the shear rate are proportional to changes in the shear stress and the constant of proportionality is called the plastic viscosity (μ_p). The value of τ_y must be high enough to be able to transport cuttings out of the hole, but not too large as a large yield point results in excessive pump pressure when starting mud flow. The yield point is a very important property of drilling mud. The functions of the mud associated with yield point are (1) to control pressure and (2) bore hole cleaning. The yield point improves the solid carrying abilities of the drilling mud [34].

2.2.12.4. The Herschel-Bulkley Model

The Herschel-Bulkley equation is preferred to power Law and Bingham plastic relationships because it results in more accurate models of rheological behaviour when adequate experimental data are available. The Herschel-Bulkley is a three parameter model [19, 49].

$$\tau = \tau_y + K\gamma^n \tag{2.6}$$

Where K is the fluid consistency index, the flow behaviour index is n. The Herschel-Bulkley model can represent:

- Yield-pseudo plastic fluid ($n < 1$)
- Dilatant fluid ($n > 1$)
- Pseudo-plastic fluid ($\tau_y = 0$, $n < 1$)
- Plastic fluid ($n = 1$), or
- Newtonian fluid ($\tau_y = 0$, $n = 1$) [19, 49].

This model gives the best fit of the viscometer measurement when compared with different rheological models [50].

2.2.12.5. Viscoplastic and viscoelastic models

Rheology has expanded to cover the constitutive theory of viscoelastic and viscoelastic characteristics in highly viscous fluids and solids.

- **Viscoplastic Model**

Viscoplastic fluid model, behave like a solid at low level of maximum shear stress and as a purely viscous fluid when the maximum shear stress (τ_{max}) of the fluid exceeds the yield shear stress (τ_y).

This model is frequently used to simulate drilling mud, which is utilised as a lubricant and a conveyance medium for drill chips. As a result, when $\tau_{max} \leq \tau_y$ shear rate magnitude ($\dot{\gamma}$) equals zero [51]. Figure 2.9 shows viscoplastic materials characteristic graph of the function $\tau(\dot{\gamma})$. When the shear stress is less than the yield shear stress τ_γ, the material models are solids, and the behaviour is elastic. Well as for $\tau \geq \tau_y$, the material models are fluids. When treating a material as a fluid, it is commonly assumed that the fluid is incompressible and that the material is rigid and free of deformations, when $\tau \leq \tau_y$ [51].

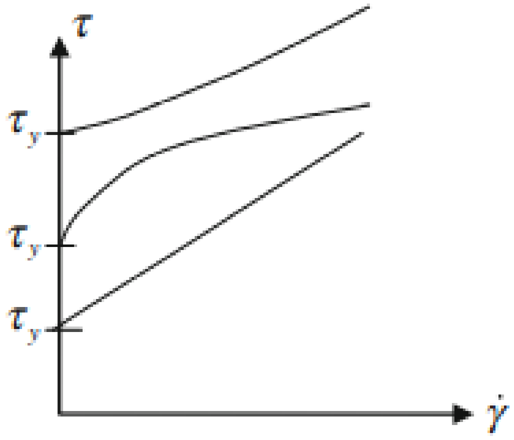

Figure 2.9: Viscoplastic model [52]

- **Viscoelastic Model**

Shear stress can be affected by both shear strain and shear strain rate in many real materials, both liquids and solids. These are known as viscoelastic materials. Materials that display both viscous and elastic qualities when deformed are known as viscoelasticity [53]. The relevant constitutive equation can be written as follows:

$$\tau = \tau(\gamma, \dot{\gamma}) \tag{2.7}$$

The property of materials that display both viscous and elastic qualities when deformed is known as viscoelasticity. Drilling muds have a time-dependent viscoelastic behaviour, which means they have both viscous and elastic responses when deformed. Drilling mud viscoelastic qualities are critical for evaluating gel structure, gel strength, barite sag, hydraulic modelling, and solid suspension. In general, the stresses in a viscoelastic fluid are determined by the deformation history of the fluid. Because the pressure p is always a function of the volumetric strain, all real fluids are viscoelastic. We can distinguish between viscoelastic and merely viscous models if we confine the debate to incompressible fluid models [51].

2.2.12.6. Plastic Viscosity

Plastic viscosity is the resistance to the fluid flow caused by mechanical friction within the fluid. Plastic viscosity is brought about by the solid phase and the liquid phase. The rate of penetration is directly affected by the plastic viscosity. A low plastic viscosity is an indication that the mud is capable of drilling rapidly because of the decrease in the viscosity exerted at the bit resulting in higher penetration rate [34]. Plastic viscosity is measured by a viscometer and calculated from the difference between the 600 rpm and 300 rpm dial readings in centipoise (cP) as shown in equation 2.8.

$$\mathrm{PV}\ (\mu_p) = \theta_{600} - \theta_{300} \tag{2.8}$$

Plastic viscosity is a function of the number of solid particles in a drilling mud. Figure 2.10 shows the suggested range of plastic viscosity ranges. If there is an increase in solid content in drilling mud, PV also increases. PV of the drilling mud also tends to decrease as temperature increases because the base fluid viscosity decreases (due to thinning of water). PV leads to an increase in pressure drop, hence reducing flow rate.

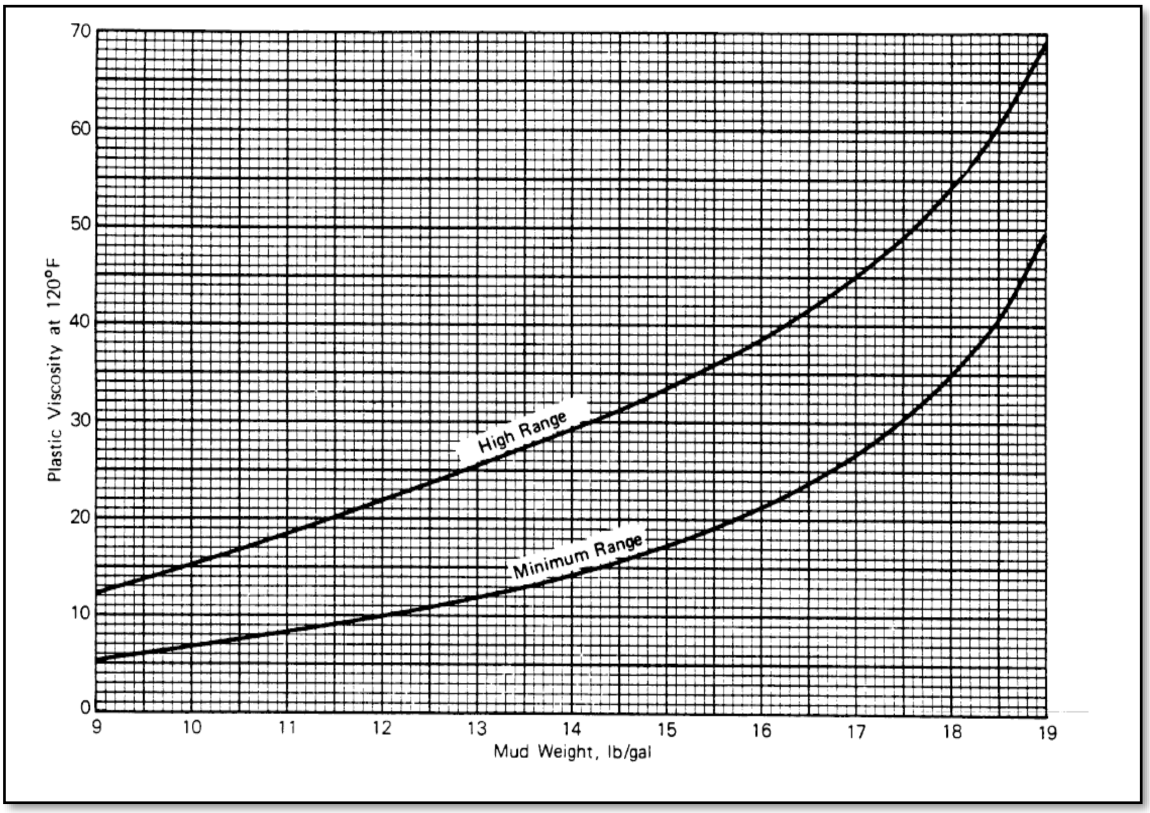

Figure 2.10: Suggested plastic viscosity ranges [54]

High plastic viscosity increase is not a desirable way of increasing the hole-cleaning ability of the mud therefore it should be maintained as low as practical. Minimum PV can be achieved only to a certain extent when the mud is kept free of drilled solids. Figure 2.11 shows the plastic viscosity of WBMs at various mud weights [34].

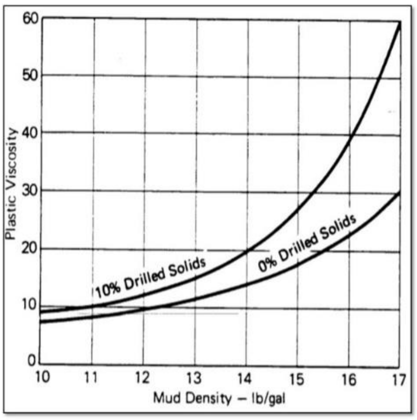

Figure 2.11: Effect of inert drilled solids on plastic viscosity [54]

Solids in a mud can be divided into two types, inert and active. Inert solids are those that have little tendency to react with each other or to a change in environment. They are non-swelling solids which are electrically uncharged and easily dispersed. Active solids have electrically charged surfaces and are reactive with their environment [34].

2.2.12.7. Yield point

Yield point is the measure of the electro-chemical attractive forces within a drilling mud in motion. Yield point is always a function of the solid concentration, the concentration and type of ions in a drilling mud and the surface properties of the mud solids. Yield point is measured by a viscometer. The yield point that is calculated from the Bingham equation is less than the true yield stress, which is needed to maintain flow but the value which is a bit higher [34]. For large molecules such as a polymer or colloidal particles colloidal particles collide with one another hence increasing the resistance of flow. The electrical interaction of solids is controlled by chemical treatment, and solids are used to adjust the mechanical interaction. Yield point's primary functions are two, hole cleaning capability and the pressure control characteristic of the mud [34]. Figure 2.12 shows suggested yield point range of different mud weights.

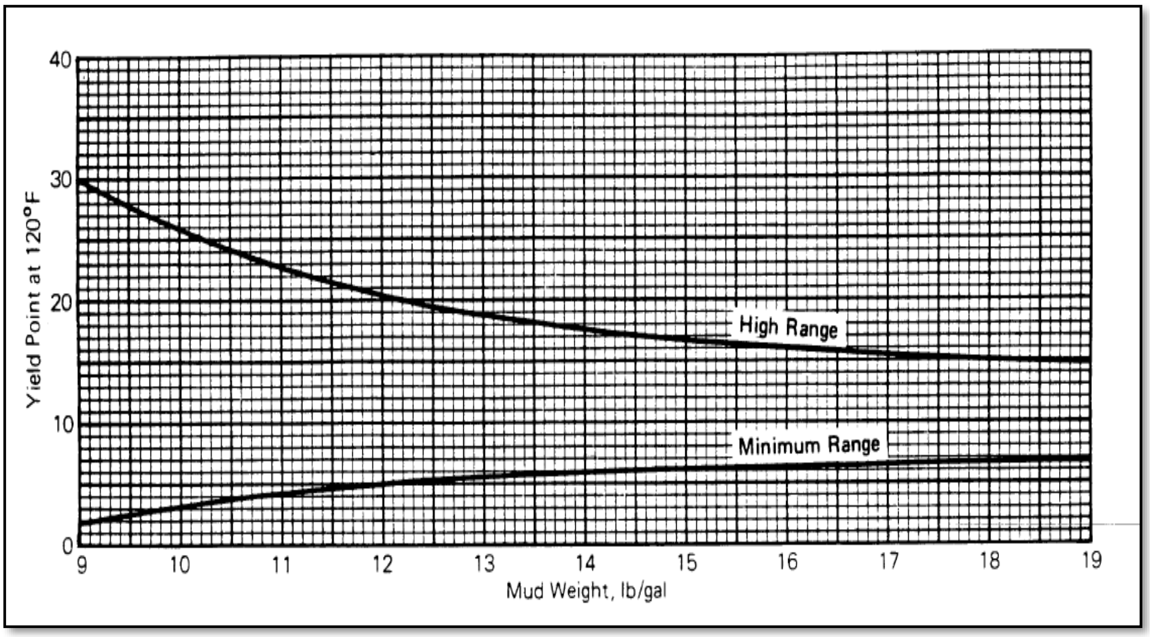

Figure 2.12: Suggested yield point range [54]

High concentrations of colloidal solids and the flocculation of clay solids causes high yield points. The lack of enough deflocculant, high temperature or contaminants such as salt, calcium, carbonates and bicarbonates cause flocculation. A high solid concentration will aggravate flocculation tendencies. More so, high yield point shows that a drilling mud is non-Newtonian and can transport cuttings better than any mud with a lower yield point.

2.2.12.8. Filtration

When a permeable formation is exposed to a mud fluid at a pressure higher than the formation pressure, filtration occurs. The pressure forces the filtrate to flow into the rock and solid particles of the mud fluid to be deposited on the formation wall forming a mud cake. When the formation permeability is lower, a thinner filter cake is formed which then reduces the volume of filtrate from the mud invading the formation. On the other hand, a thicker filter cake is unwanted in drilling mud operations as it reduces the hole diameter and allows excessive amount of filtrate to invade the formation hence leading to further problems. According to Annis et al. [34], filtration causes two different problems, those due to filtrate invasion and those due to filter cake deposition. Filtrate invasion problems are more related to formation evaluation and completion problems than drilling problems. High fluid loss causes flushing of the zone surrounding the wellbore to the extent that logging and formation test information is incorrect. Furthermore, filtrate invasion reduces formation permeability greatly as the solid particles in the mud fluid may plug the formation pores [34]. From the other side of drilling operation, the filter cake is of more concern than the filtrate. The filter cake causes problems like torque and drag, differential pressure sticking and poor primary cement jobs. Therefore, the best aim is to minimise the thickness and the mud cake permeability [34]. The two types of filtrations are dynamic and static. The difference is that dynamic occurs when the fluid is being circulated and static when the fluid is at rest.

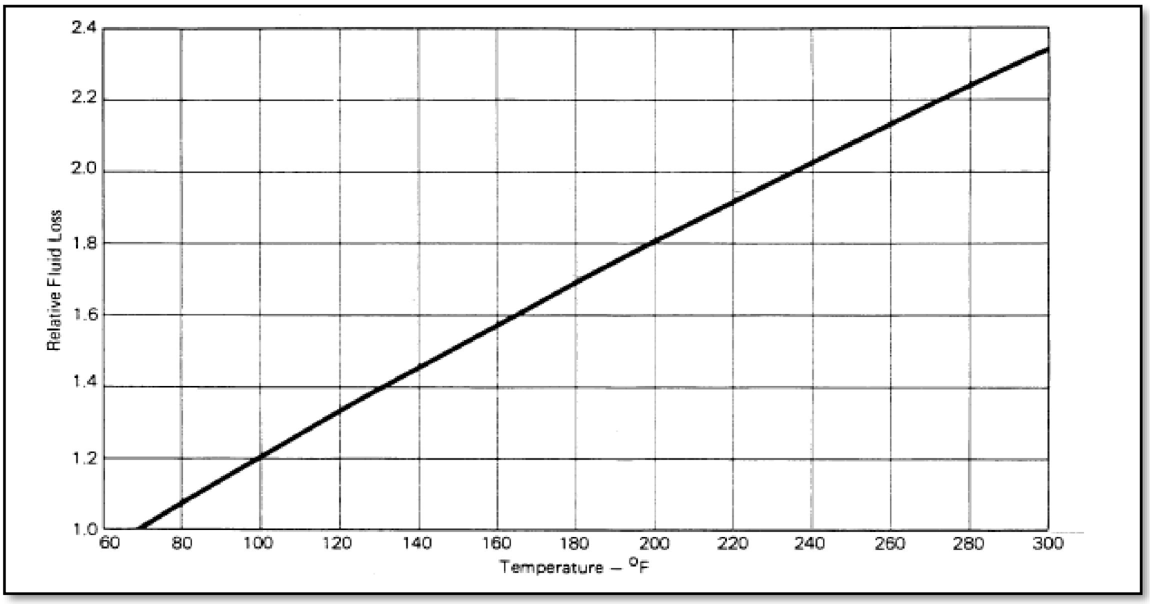

Figure 2.13: Temperature effect on fluid loss due to change in filtrate viscosity [34]

2.2.12.9. Gel strength

The measurement of the shear stress needed to initiate flow of a fluid that has been quiescent for a period of time is gel strength. Gel strength is caused by the electrically charged particles that link together to form a rigid structure in the fluid [34]. The unit is expressed in 1bs/100 ft^2. Gel strength is measured by a viscometer, and it represents the thixotropic properties of drilling mud. Gel strength is a function of the quality and kind of solids in solution, time, chemical environment, and temperature. Gel strength is increased by anything that promotes linking of particles in the suspension together and it decreases by anything that prevents linking of particles together [34]. Flocculation increases gel strength and deflocculation decreases gel strength in water-based muds. Dispersant like lignosulfonate is added to mud system to reduce gel strength. If a pilot test with addition of dispersant fails to reduce the gel strength, it means that the problem is due to colloidal solids or a chemical contamination problem. The issue can be solved temporarily with dilution with water which is expensive [34]. Gel strength is usually measured in two intervals on the 8-speed viscometer firstly at 10 seconds and then at 10 minutes, referred to as initial gel strength and final strength respectively. Gel strength is measured in 1b/100 ft^2.

Initial Gel strength refers to the shear stress measured at low shear rate after a mud has set quiescently for 10 seconds. The mud is stirred at 600 rpm from a viscometer, left in a static condition for 10 seconds and then the 3-rpm reading is recorded.

Final Gel strength refers to the shear stress measured at low shear rate after a mud staying quiescently for 10 minutes. Again, the mud is stirred at 600 rpm from the viscometer and the mud left in a static condition for 10 minutes and after, the 3-rpm reading is recorded.
Gel strength could be described as progressive, high and low-flat seen from Figure 2.14. This figure shows that a low-flat gel is most desirable while progressive and high-flat are both undesirable [52]. For a flat gel, the 10-second and 10-minute gels are similar.

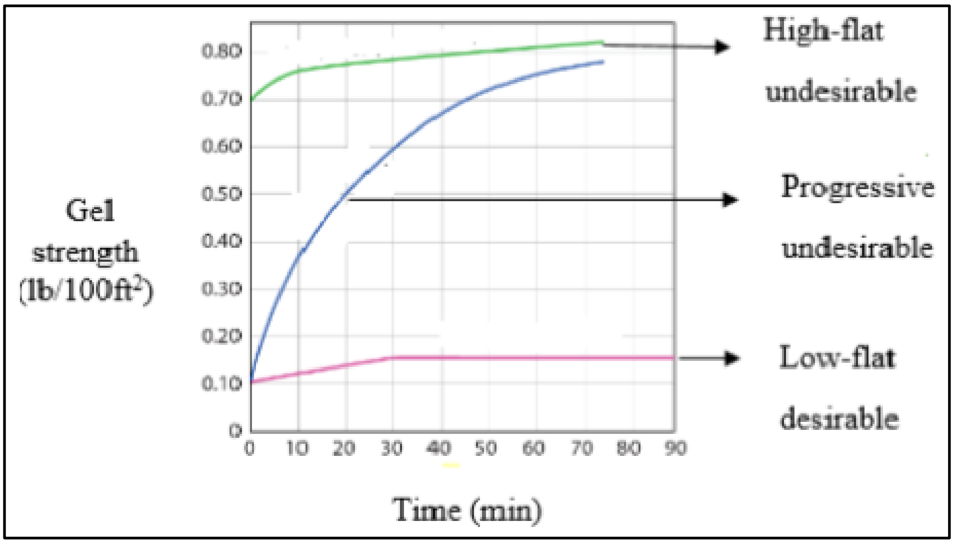

Figure 2.14: Variation of gel strength with time for drilling muds [52]

Flat gels show that the mud will remain pumpable with time in a static situation in the hole while on the other side, progressive gels situation will need extra excessive pump pressure to break to circulation. High -flat gel is unwanted because the situation will require high pump pressure to return to circulation.

2.2.12.10. Aging of drilling muds

Aging is the process where a freshly prepared mud system can fully develop its rheological and filtration properties. In this research study, some of the mud systems were aged statically and some dynamically in order to mimic and expose the mud to borehole conditions. The aging time may vary from 16 hours to several days. As mentioned earlier, there are two types of drilling muds aging, and these could be either at ambient or at raised temperatures: static and dynamic aging. The rheological properties like yield point, viscosity and gel strength of the drilling mud aged at a temperature increase as aging time increases, and the effects of aging diminishes as aging time increases. This is due to the fact that, as the particle number increases due to the aging of the mud, inter-particle forces increase leading to an increase in the yield point and gel strength [55].

2.2.12.11. Environmental impact

The environment is negatively impacted by the activities of hydrocarbon exploration and production. Today with the increasing environmental concerns most drilling muds with the potential to pollute the environment have been either prohibited or severely restricted in many countries. Environmental regulations and laws have restricted the use of drilling mud systems that have the potential to pollute the soil and ground water aquifers [56]. Drilling muds and drilling cuttings are the wastes generated during oil and gas drilling operation [57]. Some additives used in drilling muds are toxic and cannot be discharged off anyhow. The environment can be polluted by the heavy metals and hydrocarbon present in drilling wastes based on the type, nature and their concentrations [58]. There are different heavy metals and hydrocarbons in drilling muds. OBMs are formulated with saturated and unsaturated hydrocarbons. Darley et al. [22] explains that, the saturated and unsaturated hydrocarbons in OBM could be 60% and 45% respectively. Countries like USA, United Kingdom, Holland, Norway, Nigeria, European countries, Saudi Arabia and Qatar have prohibited the use of OBMs [56]. Based on the level of toxicity, OBMs are more toxic than WBMs. The cost of containment disposal can greatly increase the cost of using OBM fluids. Because WBMs are less harmful to the environment, it makes it a preferred option for drilling operation in many countries. WBMs with the same performance characteristics of OBMs are becoming available now which can be applicable in HPHT conditions boreholes. Synthetic polymer materials are environmentally friendly, and they are part of some high temperature WBM additives to act as stable dispersant and fluid loss control agents. Now, new Nano materials for HTHP conditions have been introduced in WBM fluid system by using a combination of clay and synthetic polymers to provide a stable rheology and fluid loss [56]. Therefore, this calls for designing a HPHT tolerant WBM which is eco-friendly. Most WBMs, synthetic based muds, and mineral -oil-types muds are non-toxic but may need enhancement to be able to perform in HPHT condition.

2.3. Water-based muds environmental considerations

Drilling muds represent 15 to 18 % of the total well drilling cost therefore, various techniques are needed for their formulation and characterisation [59]. WBMs originally for example spud muds, only contained water and clay but their effectiveness in regard to stability of the system, rheology and filtration properties were in general very poor. To increase the WBM performance in the current trend and most research is directed to this cause. Figure 2.15 shows the circulation system of the drilling mud. Despite the technical performance of oil-based drilling mud, there are many limitations.

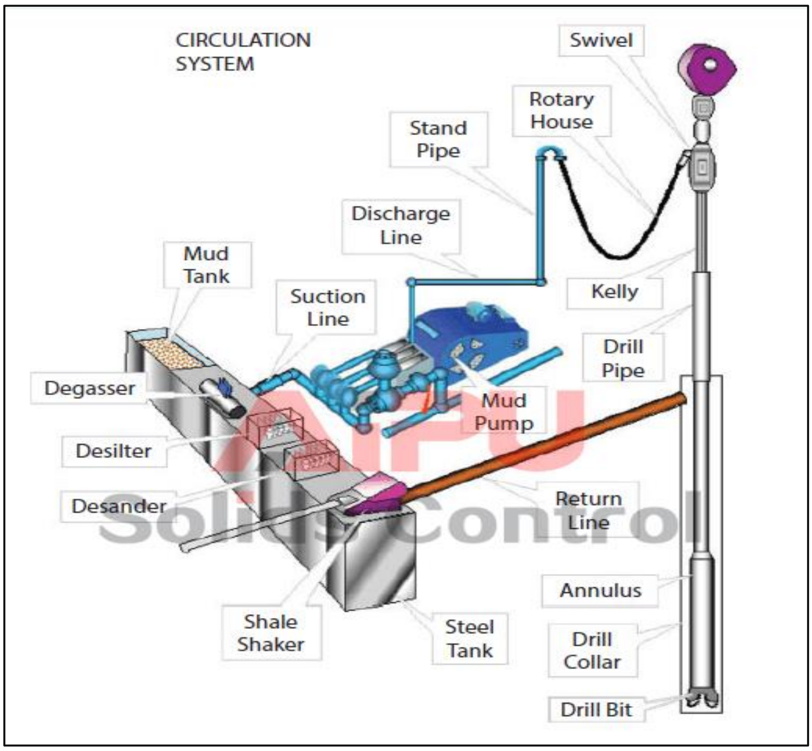

Figure 2.15: Mud circulation system [60]

OBM is likely to cause contamination, there are fire risks and there is a risk of environmental effect caused by OBM. The main objective of all drilling operations is to reduce safety and environmental risks while maintaining drilling performance [61]. Due to the pressure from environmental agencies and strict regulations, the trend and all efforts have been diverted to the development of environmentally friendly mud fluids that could replace OBM under HPHT but less toxic, efficient and less costly [3, 61]. Different studies have been ventured into to design high performance water-based fluids and one of the drilling additive able to make the performance of WBM get to OBMs are salts. Examples of salts that have been used include, potassium formate and sodium erythorbate. WBM based on Soluble silicates, which are salts have been developed and applied in the field. Silicate-based muds have been introduced as superior fluids in drilling troublesome formations. Furthermore, these fluid systems are environmentally friendly and inexpensive [62]. According to the experiment investigated by Van Oort et al. [62], the authors formulated a water-based with silicates. The authors presented the materials used in the silicate-based mud as shown in Table 2.1. They compared potassium chloride-based mud and silicate-based mud as shown in Table 2.2.

Table 2.1: Silicate mud formulation additives [62]

Additives	KCl / pol. / silicate	Sat.salt / silicate
Xanthan Gum	1.0 ppb	2.0 ppb
PAC R	1.5 ppb	-
PAC LV	1.0 ppb	1.0 ppb
Starch	4.0 ppb	4.0 ppb
Caustic	0.5 ppb	0-0.2 ppb
Soda Ash	0.25 ppb	-
KCl	5-35 ppb	-
NaCl sat. brine	-	0.9136 bbl
Barite	As requires	As required
Sodium Silicate	5% v/v	5% v/v

From findings by Oort et al. [62] the mud formulation with silicate performed better than the conventional WBMs, demonstrated excellent solid carrying abilities and well-bore stabilising capability. They discovered that OBMs and synthetics were to be replaced by improved HPWBM fluids. The temperature affected the rheological properties of the mud adversely. Using silicate-based mud could cause formation damage and is difficult to control the rheological properties of the drilling mud [63].

Table 2.2: KCL/Polymer and KCL/Polymer/Sodium silicate muds before and after aging at different temperatures [62]

	KCl / Polymer			KCl / Polymer / Silicate		
	BHR	AHR 200 °F	AHR 250 °F	BHR	AHR 200 °F	AHR 250 °F
Weight (ppg)	8.7	8.7	8.7	8.9	8.9	8.9
600 rpm	84	56	22	80	53	83
300 rpm	63	40	14	60	36	59
200 rpm	53	32	12	52	30	49
100 rpm	40	23	8	38	21	36
6 rpm	14	7	2	13	6	12
3 rpm	10	6	1	10	4	9
PV (cP)	21	16	8	20	17	24
YP (lbs/100ft^2)	42	24	6	40	19	35
Gels (lbs/100ft^2)	10/22	6/8	½	10/20	4/8	10/17
API	-	7.6	7.9	-	5.8	7.3
pH	11.06	10.05	9.13	12.75	12.65	12.55

The effects of cutting discharged in the Barents sea after drilling with water-based mud with potassium and sodium formate were considered and investigated by Zuvo et al. [64]. The sediments in the Barents Sea were surveyed on for physical, chemical and biological conditions. This was done to verify life cycle assessment (LCA) findings for formate brine. They found that the discharge of moderate amounts of formate brine had no adverse effect significantly on the marine environment. Potassium formate will be tried in the present study as an additive. The regulatory approaches for different regions and nations on environmental protection with respect to chemicals were compared by Gilbert et al. [65]. The authors used formate base drilling muds as an example in their research discussion. The findings agreed with the conclusions made by Zuvo et al. [64].

Ramirez et al. [66] investigated a formulated water-based mud which was to be used to drill through a troublesome shale section and to the top of the production reservoir without facing wellbore stability problems. The HPWBM was formulated with clay and shale stabilizers, a ROP enhancer, and sealing agents. It was found that the mud system was resistant to carbon and anhydrite contamination. It was also observed that gas kicks were controlled successfully without difficult, and the mud system exhibited excellent rheological properties. More so, it was noted that the mud system prevented bit balling and enhanced lubrication and the rate of penetration (ROP). It was concluded that a properly formulated water-based mud is an alternative to an oil-based mud especially in areas where environmental regulations and restrictions and formation evaluation problems are concerned. The conclusion drawn from

Ramirez et al. is in agreement with van Oort et al. [62] who also concluded that water-based muds are environmentally friendly. The mud system used in Ramirez et al. [66] is shown in Table 2.3 below.

Table 2.3: Mud formulation additives [66]

Component	Concentration (lb/bbl)
Bentonite	9.0
PHPA	1.5
Aluminium Complex	3.5
Amine	5.0
Low Vis PAC	1.0
Regular PAC	0.7
Blown Asphalt	4.0

The use of water-based mud has always been restricted to fields with temperatures less than 300 °F. This has been due to the limitations of the and challenges found in more aggressive environments. Water-based muds investigated by Oswald et al. [67] were used in formation with a temperature more than 300 °F. The Miano and Sawan fields in Pakistan had a temperature of up to 300 °F and due to the environmental effect and impact of the operation, water-based mud was suggested and used in this filed. From the conclusions, the findings agreed with those of Van Oort et al. [62] and Ramirez et al. [66] who recommended that WBMs can replace OMBs in drilling HPHT wells.

For the impacts on the environment by formate brine, Downs [68] exposed formate brines to hazard identification and procedure before it was applied in the field with regards to regulatory requirements. They observed that formate salts had a slight effect on the environment and users. They concluded that regulators will not restrict their use in drilling and completion operations both for onshore and offshore. These findings agree with the findings from Zuvo et al. [64] and Gilbert et al. [65].

2.4. The performance of high-performance water-based muds

The increasing environmental legislations in restricting OBM application in drilling operations have resulted to the use of water-based drilling muds as the most environmentally alternative. However, water-based systems in shale formations may cause many problems like wellbore instability and high torque and drag. For that reason, the alternative would be different kinds of inhibited water-based systems in which adverse effects of shale formation s can be controlled. Water-based drilling muds which imitate the performance of the oil-based drilling mud are commonly called high performance water-based fluids (HPWBF) [15]. Compared to conventional water-based mud systems, HPWBMs are more advantageous because they provide torque and drag reduction, cost effective, provide faster ROPs, shale inhibition and improved wellbore stability with minimised environmental effect compared to their counterparts [69]. More attention and discussion here will be given to the additives and procedure involved in the formulation of high-performance water-based muds. Knowing the compositions of HPWBMs is of great importance in their design. A lot of research and studies have been undertaken to develop HPWBM systems. Leaper et al. [70] and Al-Ansari et al [71] formulated a water-based mud with partially hydrolysed polyacrylamide and polyamide derivatives. They concluded that the mud formulation was successfully used to drill different wells and performed like OBM and it was environmentally friendly. But hydrolysed polyacrylamide and polyamide derivatives are synthetic polymers. Synthetic polymers stabilize at high temperature [36, 37] and generate high plastic viscosity [4]. Galindo et al, [32] developed a water-based high-performance mud which was thermally and rheologically stable at 400 °F and performed well in HPHT conditions. The fluid was hot rolled in the oven at 150 °F for 16 hours to get it ready for testing. The fluids were statically and dynamically aged at temperatures ranging from 300 to 400 °F. Mud fluid viscosity and pH values were measured with a viscometer and pH meter. The HP/HT filter press was used to the filtration properties of the mud fluid at 350 °F according to the API recommended practice. Figure 2.16 shows the effects of increasing temperature on viscosity of a drilling mud after 16 hours static aging.

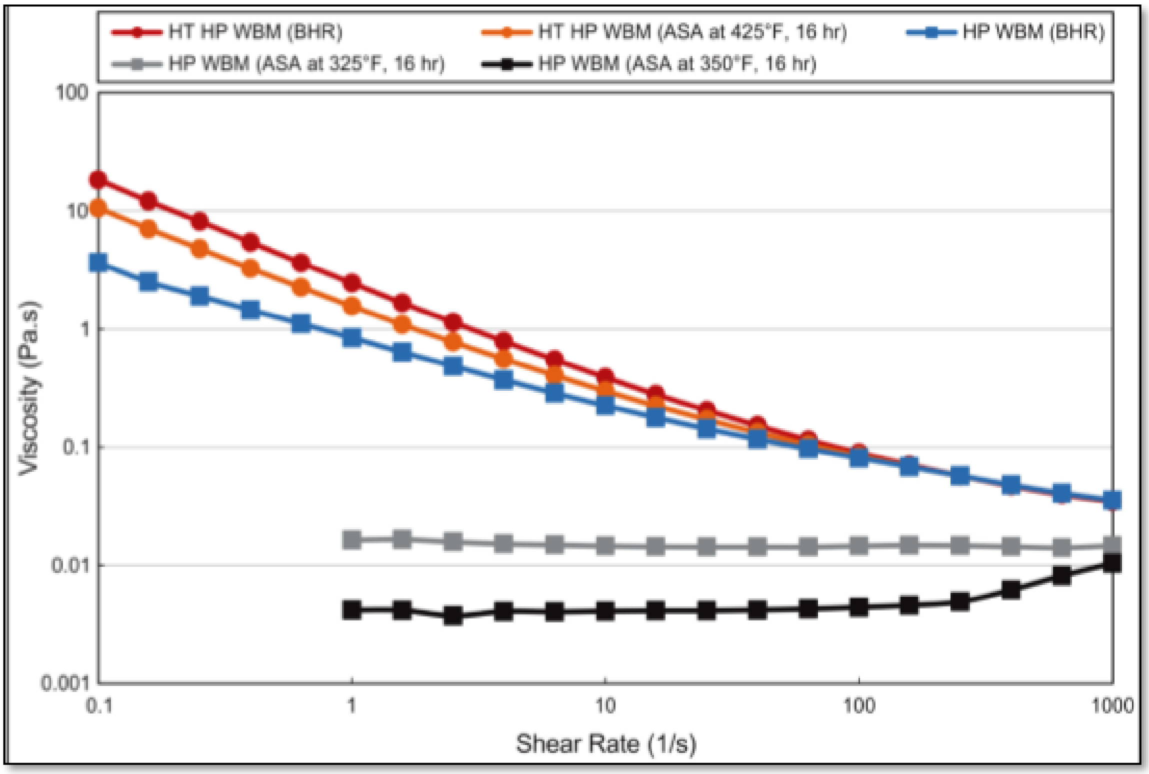

Figure 2.16: Temperature effect on viscosity after 16-hours static aging [32]

From the research, the authors concluded that the drilling mud properties were maintained up to 400 °F and the mud was resistant to contamination. More so, the mud formulation would be used in both onshore and offshore drilling without affecting the environment. The mud fluid composition is shown in Table 2.3. The authors concluded that the mud formulation would be used easily in extreme HPHT formations while maintaining the advantages of high-performance water-based drilling muds.

Table 2.4: Representative HTHP WBM formulation [32]

Sample	13.0 Ibm/gal
Water (bbl)	0.79
pH buffer (Ibm/bbl)	3.5
KCI (Ibm/bbI)	8.0
Rheology modifier (Ibm/bbI)	1.0
High temperature polymer (Ibm/bbI)	7.0
Thinner (Ibm/bbI)	30
Barite (Ibm/bbI)	311.0

Sawdon et al. [72] during their research formulated a WBM with the same performance as OBM in all applications except in HPHT conditions. This mud system was designed to work together with other additives. They also discovered that the mud formulation was environmentally friendly though the effects of HPHT were not considered. Abdon et al. [73] investigated a high solid deflocculated polymer (HSDP) mud with a density as high as 20.9 ppg (156 pcf) and used in a field with temperature of 300 °F.

The mud was formulated with polymer viscosifier, a polymer deflocculant and a polymer fluid loss agent. From field tests, the mud system was tolerant to contamination with monovalent and divalent cations (Na^{+}, Mg^{2+}, Ca^{2+}), carbonates (CO_3^{2-}, HCO_3^{-}), water, oil, gases and drilled solids. These observations by Abdon et. al. [73] agree with those of Al-Ansari et al. [71] and Gilindo et al. [74] who concluded that HPWBMs perform like OBMs. According to Luo et al. [75], they investigated the design and the field application of an amphoteric polymer mud system. The mud system was to solve the problems caused by conventional polymer when drilling high reactive shale formation. This mud system was used in oilfields of different geographic locations, formation lithologies and hostile environment such as high density, high salinity and temperature. They discovered that the mud system was effective in shale formation, stabilised borehole, improved rheological properties, high rates of penetration and protected the pay zone. The formed mud system was like that developed by Galindo et al. [32].

Wang et al. [76] formulated a water-based mud system. Magnesium aluminium silicate (MAS) was used as a high-performance rheological modifier in WBM to avoid sedimentation of suspended cuttings. After several rheological tests, it was observed that at low concentration, MAS showed better shear-thinning performance, higher gel strength and quicker recovery ability of gel structure which are the key factors for better cuttings carrying. After the tests, the authors concluded the mud system exhibited better shear-thinning performance, higher gel strength and quick recovery ability of gel structure at low-concentration. More so, after aging at 150 °C and 120 °C, the mud containing MAS maintained better rheological and filtration properties and enhanced thermal stability.

Mahrous et al. [77] investigated a water-based mud fluid to be used in drilling top holes and through the lower sections which would result in cost savings by reducing top hole fluid dilution as well as a reduction in waste disposal costs. The water-based mud system was to be used to drill in the Southern North Sea Basin and the HPWBM was expected to perform as an OBM. After field trial onshore, the HPWBM was to be used in more challenging offshore environments. After the test, it was reported that the well was drilled 11.6 days ahead of schedule and 20 % under the planned budge. More so, the time against depth curve was equally good as expected if an OBM system had been used. The authors also reported that the HPWBM lead to above 5% saving of the total well cost and it was 16% less expensive than conventional fluid systems. Furthermore, there was a further saving of 2.5% of the total well cost highlighted for -future onshore/offshore HPWBM applications. It was also realised that the water-based system would lead to reduction in waste disposal costs in offshore operations. It was concluded that the use of environmentally friendly HPWBM system in the Southern North Sea Basin would offer a huge cost saving with regards to waste management for both onshore and offshore well better than OBM and WBM systems.

Young et al. [78] water-based fluid formulation was meant to have the characteristics and perform like an invert emulsion fluid and exhibit environmentally friendly characteristics. The authors used different additives in their mud system which included, a dispersion suppressant, hydration suppressant, a viscosifier (Xanthan gum), a filtration controller and an accretion suppressant. They concluded that the mud system delivered like an invert emulsion -like mud fluid. different additives were used to formulate the mud systems which include the following shown in Tables 2.5 to 2.9.

Table 2.5: HPWMB composition

Seawater (ml)	292.0
NaCl (g)	80.4
Filtration controller (g)	3.0
Polymer viscosifier (g)	0.8
Dispersion suppressant (g)	2.0
Hydration suppressant (g)	10.5
Accretion suppressant (g)	7.5

Table 2.6: Silicate mud composition

Flash water (ml)	290.0
Sodium silicate (g)	42.0
Soda ash (g)	0.5
KCl (g)	30.0
Fluid loss agent (g)	5.0
Polymer viscosifier (g)	1.0

Table 2.7: NaCl/Polymer mud composition

Flash water (ml)	322.0
NaCl (g)	72.2
NaOH (g)	0.5
Bentonite (g)	2.0
Fluid loss agent (g)	2.0
PHPA (g)	1.0
Polymer viscosifier	0.5

Table 2.8 Oil based mud composition

Mineral oil (ml)	255.0
Primary emulsifier (ml)	10.0
Secondary emulsifier (ml)	2.0
Lime (g)	7.5
Polymer fluid loss agent (g)	2.0
Organoclay viscosifier (g)	6.0
25% $CaCl_2$ Brine (ml)	75.0

Table 2.9: Field mud composition of HPWBM

Product/Formulation	#1	#2	#3
Freshwater (ml)	42.0		320
Seawater (ml)	290	315	
NaCl (g)		20	
Filtration control (g)	3	4	3
Polymer viscosifier	1.25	1	1.25
Dispersion suppressant (g)	2	2	2
Hydration suppressant (g)	10	8	10
Accretion suppressant (g)	8	6	
#-Gulf of Mexico Deepwater well			
#-South China Sea shelf well			
#-Western USA land well			

Saki et al. [79] and Samaei et al. [80] formulated a water-based glycol mud. Both the rheological properties of water-based glycol mud and OBM were accessed and compared. The test was performed on cuttings from Maron oil field in Iran. In order to evaluate the performance of shale inhibition, a cutting integrity test was performed. The test shale samples were from Kazhdumi, Daryan and Asmari three problematic formations of Maroon oil field. It was found that the mud system reduced the dispersion of shale and hydration of cuttings. The system proved to be a good alternative to OBM fluid and other WBM systems. These finding agree with those from other authors like Lou et al. [75] and Young et al. [78] who said that WBM systems and perform like OBM systems. The properties of glycol-based mud were compared to OBM as shown in Figure 2.17 and 2.18. The effect of high temperature was not considered on the mud formulations.

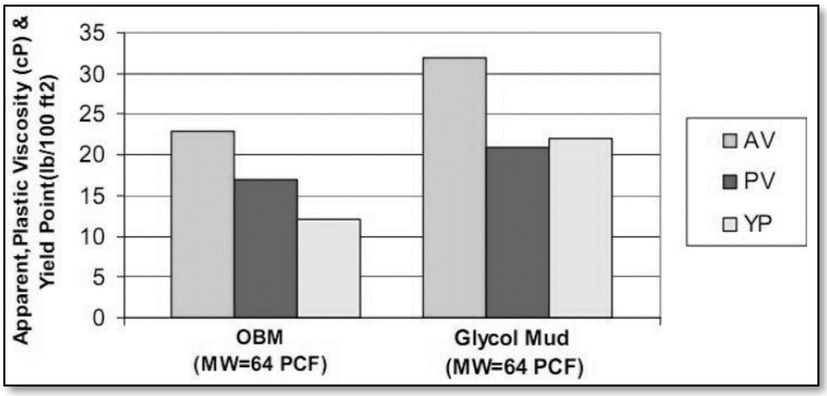

Figure 2.17: Rheological property comparison of OBM and glycol-based fluids [80]

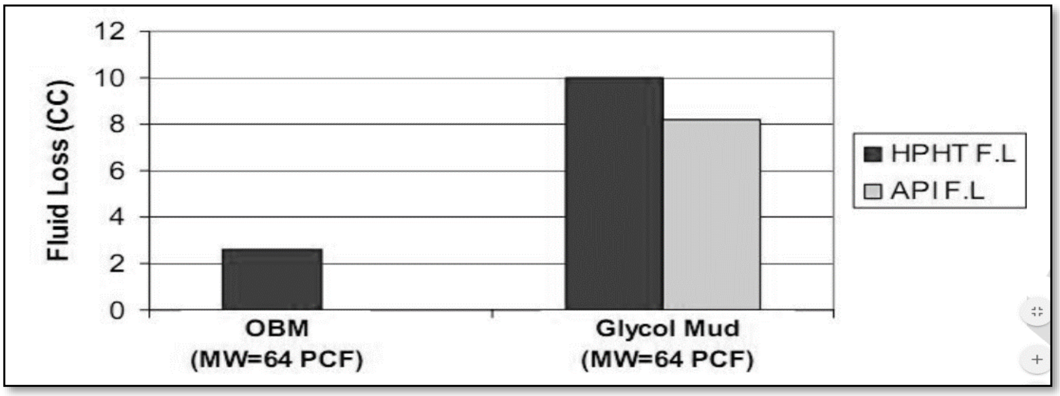

Figure 2.18: HPHT and API fluid loss comparison of OBM versus glycol mud [80]

Gholizadeh et al. [81] experimentally investigated a water-based mud system made up of a combination of am amine compound as the main inhibitor, PHPA as an encapsulator and a conventional shale inhibitor (KCl) which was used in lower concentration. This was compared to the conventional water-based inhibitor fluids and other shale inhibitor systems such as OBM and glycol mud. The mud system comprised of a unique poly-ethoxylated alkyl diamine compound for shale inhibition, an amphoteric/polymeric shale encapsulator, a high-performance lubricant/deflocculating agent and special fluid loss additive to be able to reach thermal stability of up to 200 °F. The findings from this work concluded that the water-based mud system showed optimum rheological properties and shale recovery that was close to that of OBM. More so, there was improvement in the thermal stability up to 200 °F. The formulation of the mud systems is presented in the Tables 2.10 and 2.11 and the comparisons are presented in Figures 2.19 and 2.20.

Table 2.10: Newly designed HPWBM components [81]

Materials	Amount needed per 1 m^3 of mud sample (kg)
Drill water	849.1
Hardness control additive	0.5
pH control agent	0.7
KCl	55.4
Filtration control agent	10
Viscosifier	2
PHP A	3
Amine-based inhibitor	50
Weighting agent	219.7
Defoamer	0.8

Table 2.11: Components of OBM [81]

Materials	Amount needed per 1 m^3 of mud sample (kg)
Primary emulsifier	23
Lime	23
Filtration control agent	20
Water	249.7
$CaCl_2$	86.8
Secondary emulsifier	6
Viscosifier	7.1
Barite	249.7

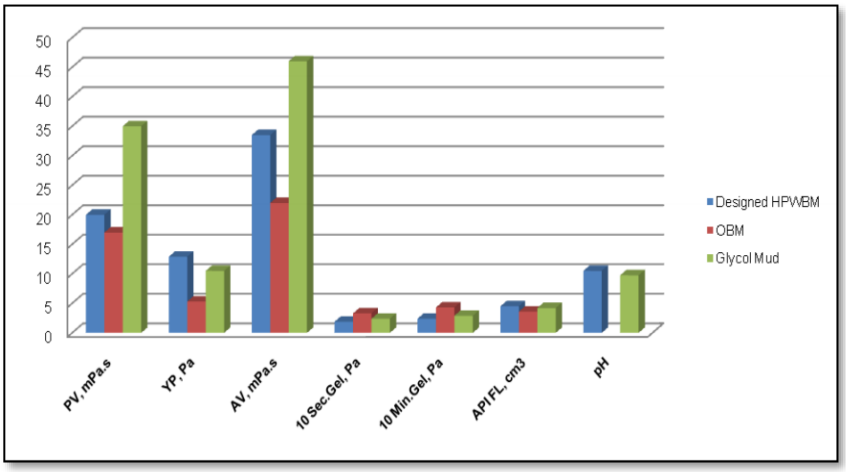

Figure 2.19: Rheological properties and filtration properties of designed HPWBM with amine additive, OBM and glycol mud [81]

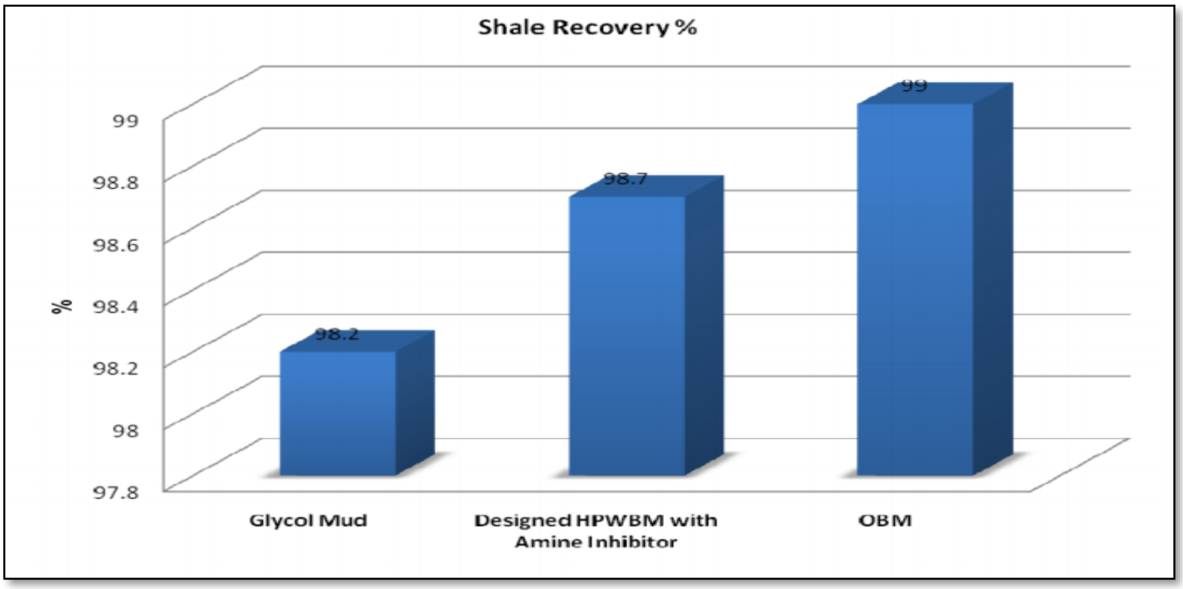

Figure 2.20: Comparison of quantitative shale recovery test results for three inhibitor mud systems, glycol mud, designed HPWMB and OBM [81]

2.5. Performance of water-based muds in HPHT environments

Little is known about the performance of drilling muds at extreme temperatures of 500 °F to 900 °F and at pressure of 25,000 to 40,000 psi. Due to the fact that, there is not a lot of equipment available to test the basic properties of density, rheology and filtration at such conditions, there is not much related research in the foreseeable future on such issues as effects on drilling mud, borehole stability and formation damage. Yet, all this is a necessity to effective development of drilling muds that can provide satisfactory performance, be economically feasible and be ecologically acceptable. According to Garrison et al. [82], little is known about the performances of drilling muds at temperatures in the range of 500 °F to 900 °F. Most high-performance water-based drilling muds mostly tolerate at operating temperatures up to 300 °F because they depend on biopolymer-based viscosifiers. Deeper exploration in extreme high temperature reservoirs (above 300 °F) requires new drilling mud technologies [32]. This chapter introduces the concept of high pressure and high temperature drilling and the problems associated with this kind of drilling.

2.5.1. High pressure and high temperature wells

In the past, it was believed that HPHT was a condition with pressure and temperature above the atmospheric conditions. Different service companies, operators, cement and drilling mud testing equipment companies and several pipe and tools manufacturers each slightly came up with a different definition for HPHT conditions [1]. Figure 2.21 shows the most common definitions for HPHT tier

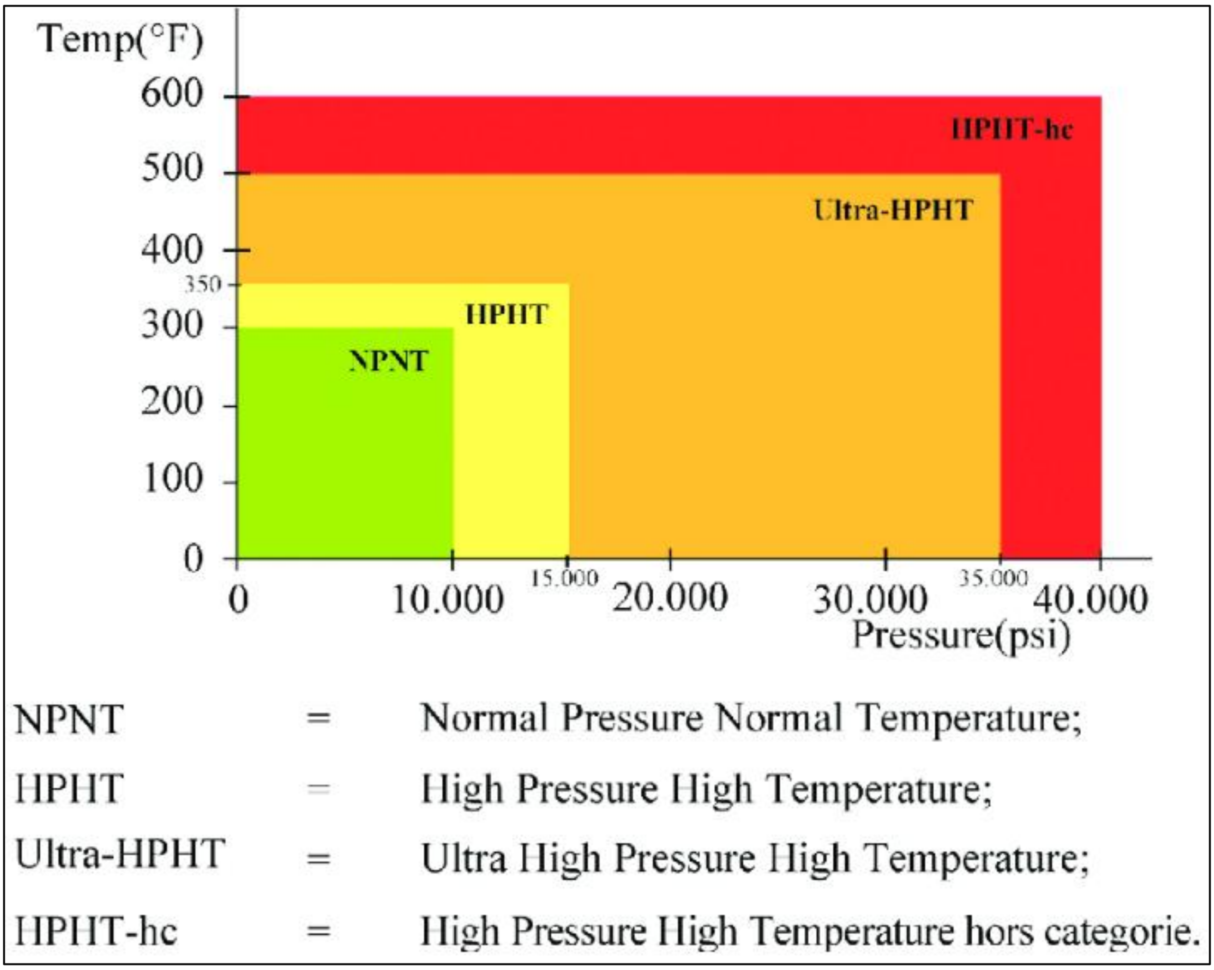

Figure 2.21: High pressure and high temperature tiers [1]

HPHT drilling process as defined by the USA Department of Energy is when a borehole passive temperature exceeds 350 ^{o}F and the pressure of 25,000 psi [83]. In more extreme drilling conditions, it may exceed 600 °F and 40,000 psi [84]. In such excessive settings, OBMs have been employed due to their superior stability [22, 85]. In HPHT environments, drilling muds are expected to motivate gelation and degradation of polymer additives whose role in the drilling mud system is to reduce fluid loss, act as surfactant and viscosifying agents [86]. The thermal degradation of additives due to drilling in HPHT environments results to the rheological and fluid loss property failure of the mud system leading to serious functional problems. Therefore, nanoparticles and microparticles have been used in the industry as thermal stability preservatives in drilling mud formulation as hydrophilic, amphiphilic and hydrophobic combination replacing polymer surfactants. Also, a multitude of very similar definitions for HPHT drilling project exist in the literature. According to Proehl et al. [83], a typical HPHT well is one whose bottom hole static temperature (BHST) is expected to reach 350 °F and the bottom hole static pressure (BHSP) to be in excess of 24,500 psi. In this project research, a third definition shall be assumed to hold whatever any reference to HPHT is made. HPHT was divided up as shown in Table 2.12. It must be noted that significant technology gaps still exist in drilling of such UHPHT wells and that is one of the main focus areas of the drilling mud industry today.

Table 2.12: High pressure and high temperature well classification [83]

Tier	**Classification**	**Bottom Hole Temperature Range (°F)**	**Max. Bottom Hole Pressure (psi)**	**Geographical Occurence**
I	Normal	300 – 350	15000	Common
II	Extreme	350 – 400	20000	North sea and Gulf of Mexico
III	Ultra	400 – 500	≥ 30000	Several deep gas reservoirs on North American Land and Gulf of Mexico Shelf

2.5.2. Challenges of HPHT drilling

Drilling muds are formulated to meet certain properties to be able to perform basic intended functions. The most common problems affecting drilling muds used in HPHT environment is the potential destruction of the mud properties under such elevated pressures and temperatures. In that case, proper balance of mud properties is vital to avoid oil and gas surge, kick, formation damage and other drilling problems associated with HPHT oil and gas wells. Operating in very extreme temperatures and pressure environments need extensive planning with special attention given to environmental regulations. Figure 2.22 describes the sources of safety concerns in HPHT drilling as published by the United Kingdom Health and safety Executive. The fact that such drilling operations may have to be undertaken with lesser knowledge of expected conditions for example pore and fracture pressures makes prior planning critical [87].

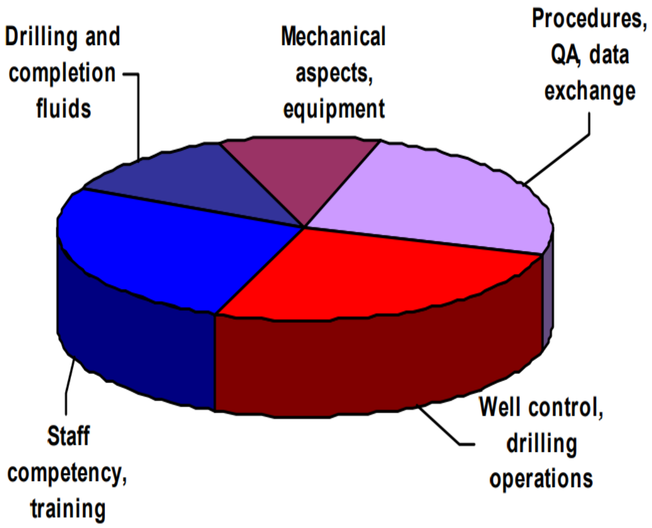

Figure 2.22: Safety concerns in HTHP drilling [87]

HPHT drilling problems involve different aspects and because of that, different factors have to be considered during the planning stage. Buchan [88] discussed the different factors related to HPHP environment that increase the likelihood of encountering non-productive time and below are;

- There is an increased likelihood of having a kick (unplanned influx of formation fluids into the annulus) due to very high reservoir pressure. Kick detection and prevention must be given special attention in HPHT drilling operations. Very narrow pore pressure/fracture pressure 'windows' are very common for HPHT well to have. Therefore, a small range of mud weights can be used to drill hole sections. Differential sticking issues may arise when drilling elongated sections at high mud weights [89]. Figure 2.23 shows a typical pore fracture pressure profile for HPHT wells.
- Will led to heavy casing strings due to the depth at which many HPHT wells are drilled at. Therefore, a detailed analysis of torque and drag to avoid drill string and casing failure is necessary. Also, because the increase of temperature lowers the strength of the material, this must be analyzed and accounted for.
- HPHT conditions may lead to drilling and completion equipment being operated at the limits of their design. Most current logging while drilling (LWD) and measurement while drilling (MWD) tools have a maximum performance temperature of 350 ^{o} F. Meaning, there will be a need for a better rated equipment to avoid unnecessary wastage

of drilling time when drilling ultra-high temperature wells. Also, though they are meant to work in HPHT conditions, the risk of failure will increase with time of usage which will affect attempts to drill for long periods of time without breaking.

- Also, due to differential sticking caused by excessive overbalance drilling, drilling mud related issues may result in loss of circulation, well control concerns and kick.

Figure 2.24 gives an insight into the different factors that need to be addressed when starting on a HPHT operation. It is evident that a HPHT field possesses challenges that need to be solved and provides a rich ground for engineering improvement.

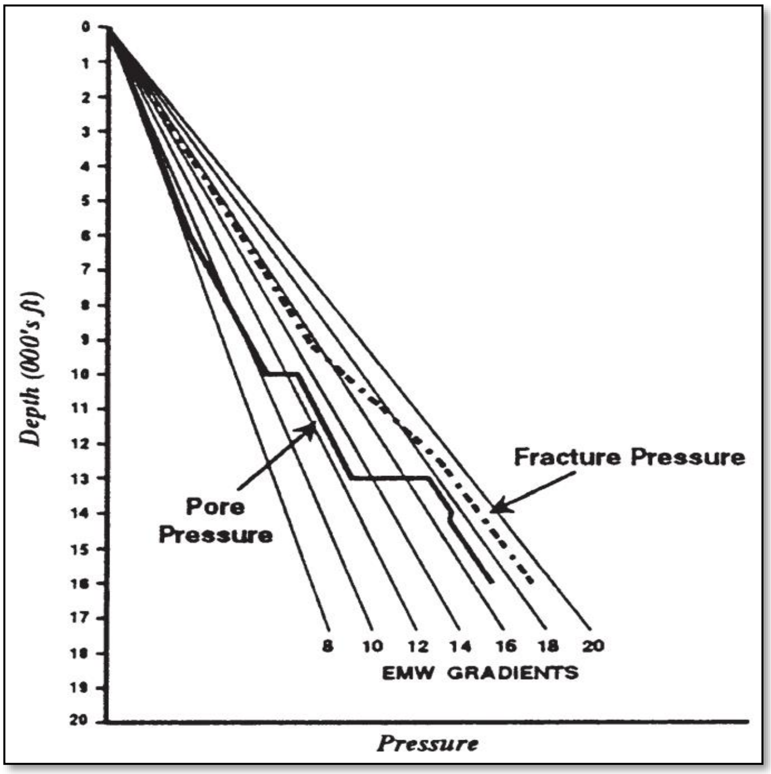

Figure 2.23: Typical drilling window for a HPHT well [88]

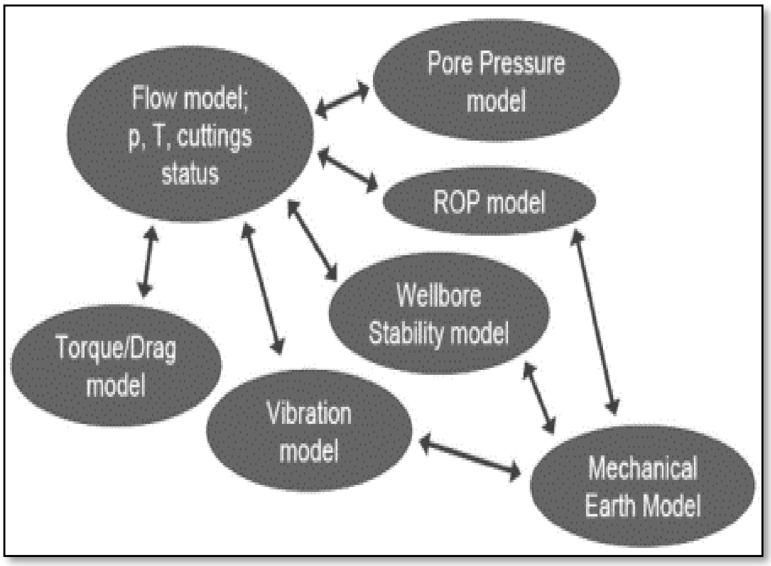

Figure 2.24: Factors in a HPHT project to consider [88]

2.5.3. Existing research and laboratory studies on HPHT properties of water-based muds

In this sub-section, the existing literature on HPHT variations on WBMs as well as the different aging times from some of the experiments that have been conducted by others in the past which are a vital subject to talk about in this project are provided and reviewed. This will shade some light on the foundation of the experiments that make part of the bulk of this research and also provide a summary of experimental techniques used before that will be adopted as part of this work. More so, viscosity dependence on different factors including, temperature, pressure and effect of time will be studied. The variables mentioned will be studied in regard to their effect on viscosity and tested in the laboratory and presented in this report later.

Davison et al. [90] explained the effect of yield stress in WBM fluids formulated with Bentonite. The fluid was exposed to offshore drilling conditions by heating it to 195 °F and then cooled down to 30 °F where subzero temperatures in the riser section may be experienced. From the observation, the yield point increased during the heating process but did not reduce during the cooling process, it continued to increase. The authors concluded that, it was a strong indication that the mud had flocculated at high temperatures.

Guven et al. [91] experimentally investigated various clays used in drilling industry by comparing the rheology. They concluded on the effect of hot rolling on the structure and rheological behaviour of bentonite suspensions at high temperature. It was observed that hot rolling at 400 °F to 600 °F completely remove the viscosity enhancement that was typically seen. The authors believed that this was due to dissolution of smectite platelets in water during the high temperatures hot rolling. The authors also concluded that flocculation increased fluid loss properties due to increased permeability of the mud cake. The viscosity profile of a 6 % bentonite mud fluid that was hot rolled at different temperatures is presented in Figure 2.25 below.

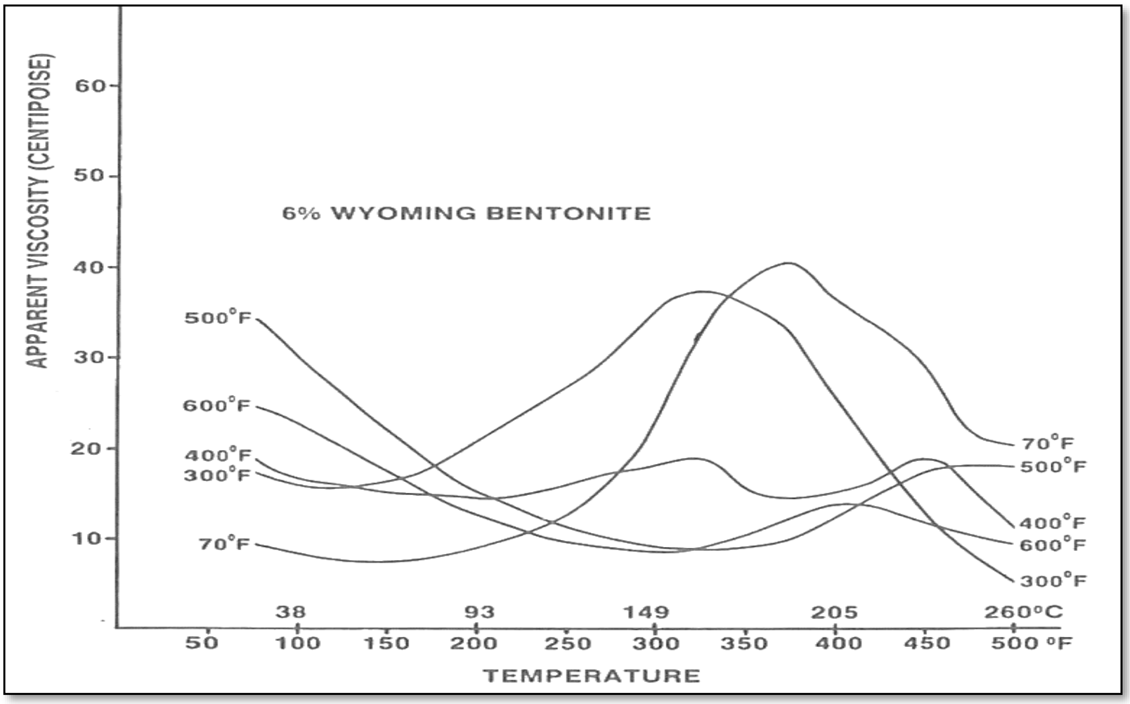

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Figure 2.25: Hot rolling effects on bentonite suspensions [91]

An investigation was conducted by Sinha [92] on the rheological measurement to quantify the effect of pressure and temperature on various WBM and OBM fluids formulations. Figure 2.26 shows the equivalent viscosity of 18.4 ppg WBM used in the filed as a function of depth under simulated geothermal gradient and pressure gradient. After a certain depth, the authors noticed a spike in viscosity that corresponded to high temperature gelation of the fluid.

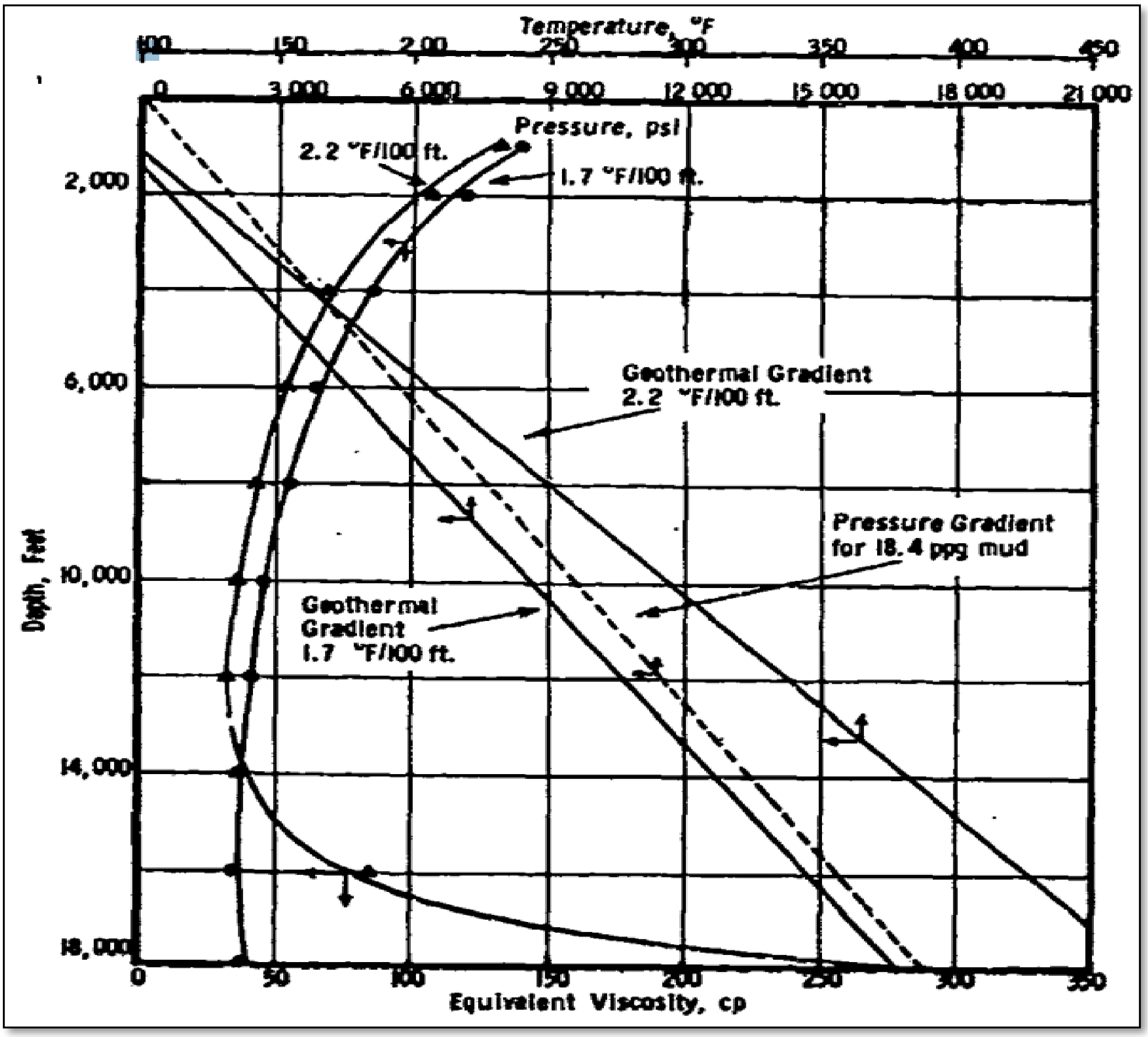


Figure 2.26: Viscosity of WBM as a function of depth [92]

Ali et al. [55] experimentally investigated the effect of HPHT and aging on WBMs. From the study, the results were evaluated taking into consideration the effective viscosity, plastic viscosity, shear stress vs shear rate relationship, yield point and gel strength.

Effects of temperature

From the results, it was observed that the effect of high temperature on the rheological properties of the drilling mud was due to the complicated interplay of several factors such as: changes in the electrical double-layer thickness, reduction of the degree of hydration of the counterions, increased thermal energy of the clay micelles, reduction of the viscosity of the suspending medium and increase dispersion of associated clay micelles. Figure 2.27 - 2.31 shows that the rheological properties reduced gradually with the increase in temperature for all values of aging time. This change in rheological properties was explain better by Al-Marhoun et al. [93]. From their conclusion, difference in the rheological properties was due to the effect of gypsum and lime added to the solution of which the two released a large amount of calcium ions in aqueous solution when heat was applied. Both results from Ali et al. [55] and Al-Marhoun et al. [93] agreement and from their conclusions both stated that, a) for a particular temperature, shear stress increases with shear rate, b) that for the same shear rate, shear stress decreases with increasing temperature and temperature effects are diminishing as temperature increases. This was due to the copolymers and bentonite undergoing degradation due to heat and mechanical shearing. The results of test data at different temperature showed that the temperature effect decreased as temperature increased and the effect on shear rate vs shear stress was very small for temperatures over 392 °F.

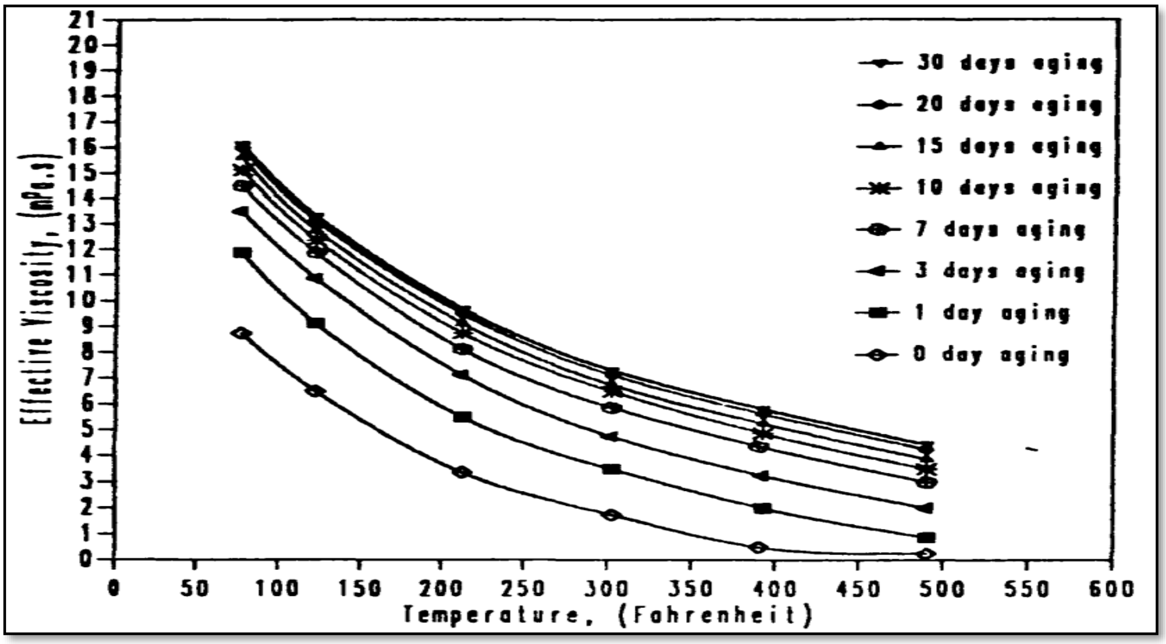


Figure 2.27: Effective viscosity versus temperature for different aging time at 3000 psig [55]

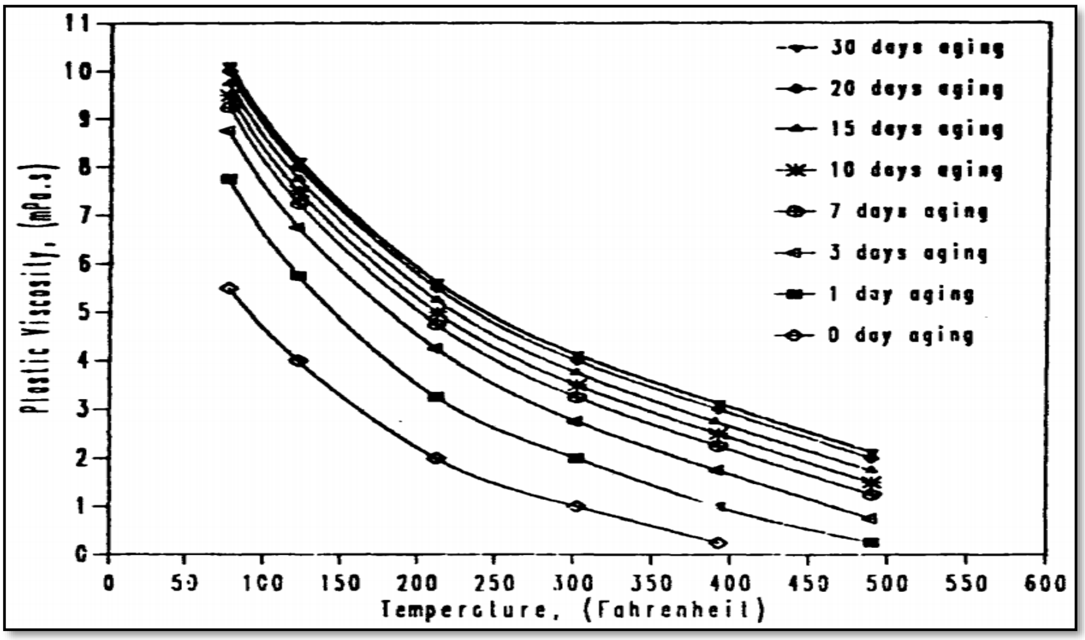


Figure 2.28: Plastic viscosity versus temperature for different aging time at 3000 pisg [55]

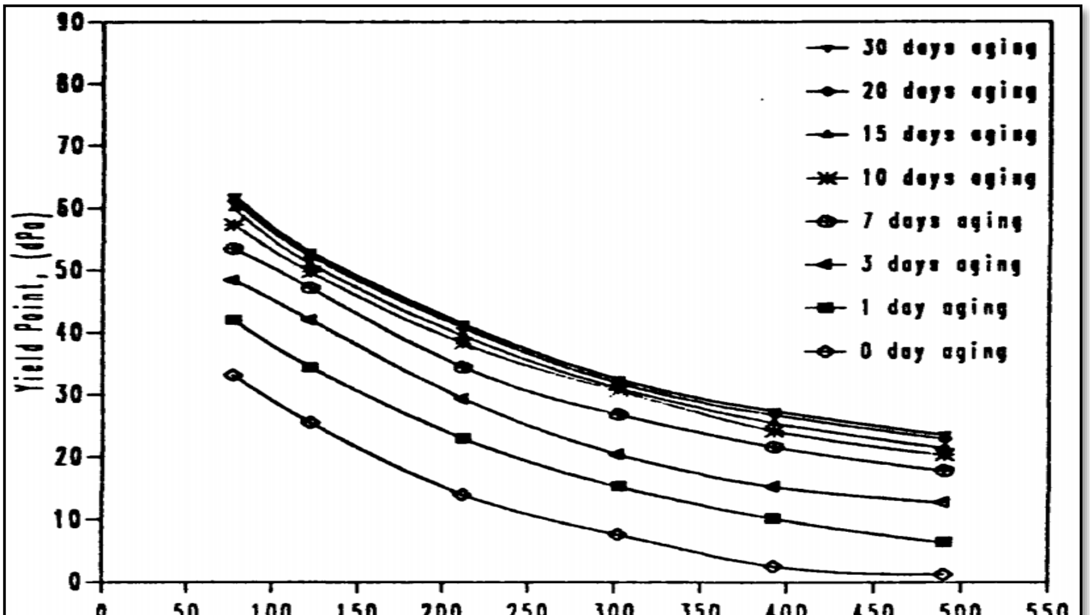


Figure 2.29: Yield point versus temperature of different aging time at 3000 psig [55]

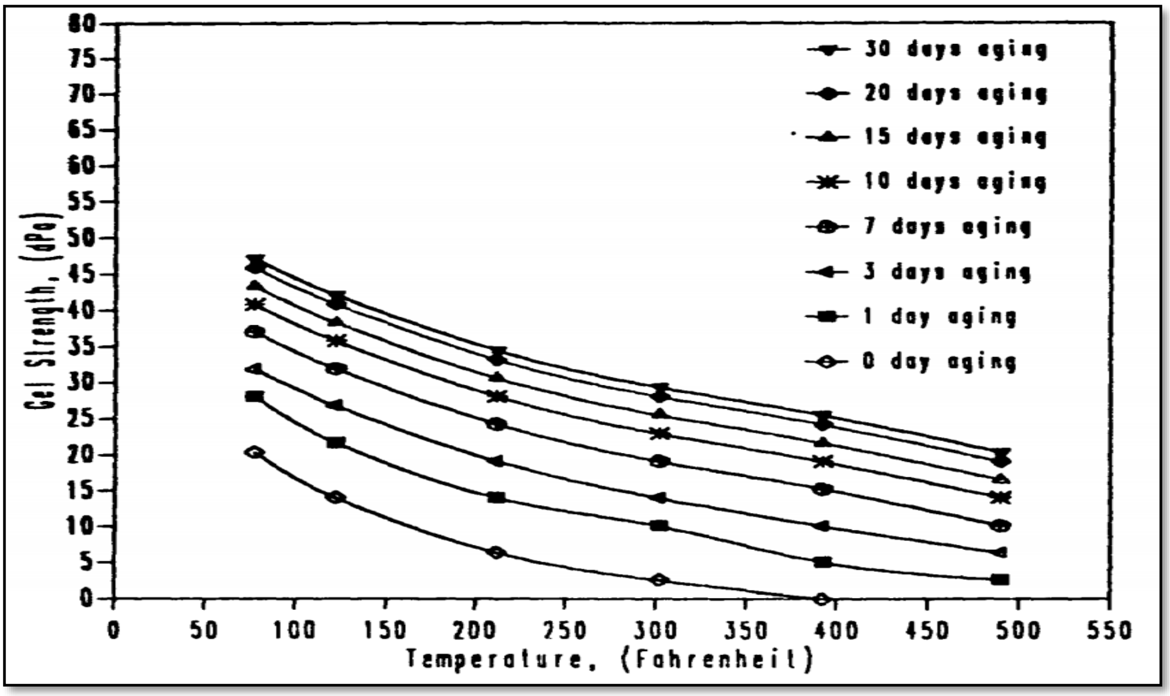


Figure 2.30: Initial gel strength (10 sec) versus temperature for different aging time at 3000 psig [55]

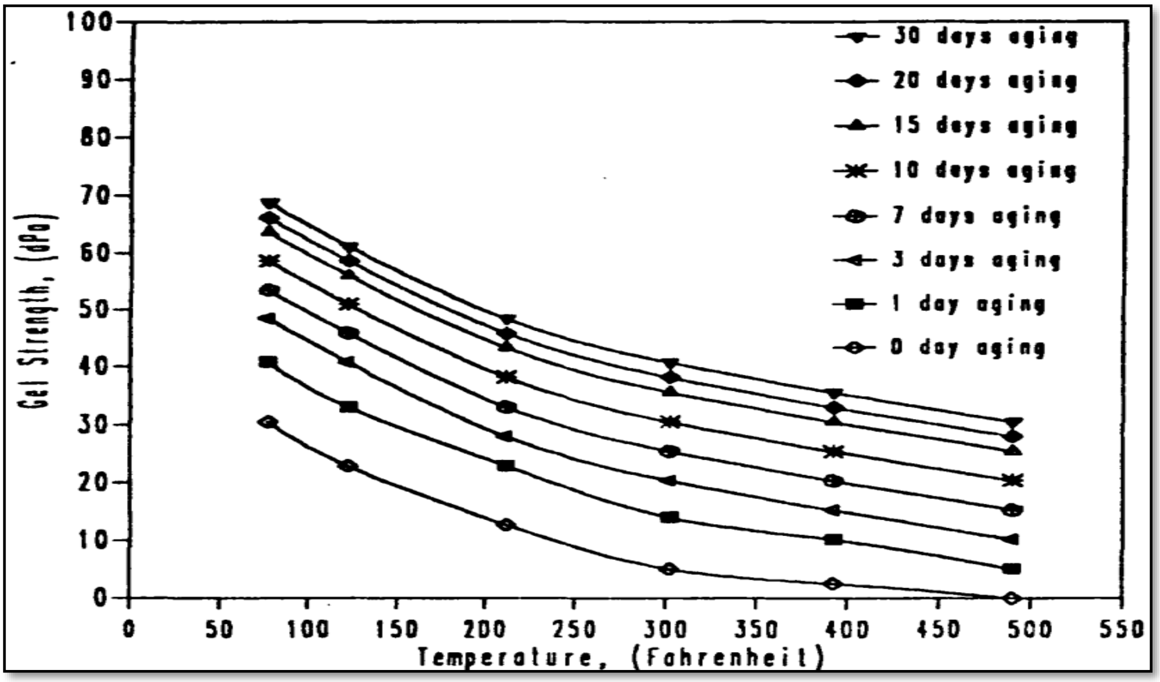


Figure 2.31: Gel strength (10 minutes) versus temperature for different aging time at 10,000 psig [55]

In addition to the effects of temperature, Ali et al. [55] also studied the effect of aging on the properties of drilling muds. They observed that viscosity at a particular temperature increased with the increase in aging time and aging effects were reducing with the increase in time. The authors concluded that this was due to the degree of dispersion and flocculation increase when muds are aged dynamically. It was also observed that the viscosity and shear stress increased with the increase in pressure at a given shear rate. The authors explained that this was due to the fact that as pressure increased, the density of the liquid phase increased and therefore the rheological properties of the fluid increased.

Salimi et al. [94] experimentally investigated the rheological behaviour of polymer-extended water-based drilling muds at high pressures and temperatures simulating their real working conditions in a deep oil well. It was observed that at any given pressure and temperature, the shear stress increased nonlinearly with shear rate for all test fluids. But also, it was realised that at a given shear rate, only for base muds that an increase in pressure and temperature was accompanied with an increase in shear stress when flow curves at different pressure and temperature were compared with each other. The increase was found to be more noticeable at higher shear rates.

On the other hand, there was a diversion of the trend as for all the nine polymer extended muds, increase in pressure or temperature resulted in a decrease in shear stress. It was concluded that the effect of temperature on the flow curve was more extreme compared to the effect of pressure [94].

2.6. Introduction to nanotechnology

Nanotechnology over the decade has become and brought excitement in many industries. The accurate manipulation and control of matter at sizes of 1-100 nanometres has completely changed many industries oil and gas included. Nanotechnology is the use of very small pieces of material at a dimension between approximately 1 - 100 nanometres, by themselves or their manipulation to create new larger scale materials with unique qualities that enable novel applications [6, 95]. Nanotechnology is becoming of interest to the parties concerned due to its broad impact on more than one discipline. The applications of nanotechnology have widened through different petroleum disciplines from reservoir to exploration, drilling, completion, production and processing and refinery. For example, nanoparticles have widely been used in formulation of drilling mud systems in order to improve their filtration and rheological properties. Also, nano-sensors have been developed to improve the resolution of subsurface imaging leading to advanced field characterisation techniques. Nanotechnology has also been applied in oil and gas production to improve oil recovery via molecular modification and manipulation of the interfacial characteristics. Furthermore, in a similar way, it provides new techniques to improve post production processes [6]. The size of nanoparticles gives them some useful characteristics such as an increased surface area to which other materials can bond in ways that make them stronger or lightweight materials. Size does matter at nanoscale when it comes to how molecules react to and bond with each other [6].

2.6.1. Nanotechnology in oil and gas industry

The unending effort to understand nanoparticles properties, their behaviour, characteristics and advantages has led to many applications in different industries like medical, cosmetics electronics, food, fabric, paining and coating industry. The oil and gas industries have not been left behind in regard to this research topic and very many different research and investigations have been performed on nanoparticles application in exploration, reservoir, production, completion, drilling and refinery over the years. Many industries have invested heavily in their research and development R/D departments regarding it this topic.

Nanotechnology has been massively successfully in the construction and completion devices like fracturing balls used in the fracture stage. The introduction of controlled electrolytic metallic (CEM) nanostructures gave way to the use of fracturing balls that will disintegrate in the presence of the appropriate fluid [6].

Nanoparticles have been used in oil and gas exploration to design sensors that enhance the formation of image contrast agents. Such nanomaterials when combined with smart fluids can be applied as extremely sensitive sensors for HPHT conditions. The use of nanoparticles as opposed to macro for imaging is vital considering the size of the pores, the increased surface area of the NP and the mobility associated with them [96]. Several researchers used NP’s capabilities to resist HPHT conditions in deep wells, gather reservoir characterization data, recognise types of fluids and flow monitoring behaviour [97]. NP’s have been used to improve polycrystalline diamond compact (PDC) bit technology. They have been applied to PDC cutter to obtain unique surface which is completely homogeneously with the PDC matrix [98].

Other researchers have investigated the application of nano-emulsion to improve hole cleaning and reverse formation wettability to achieve a better adhesion with cement slurry in a cementing operations [99]. Also, Nickel iron Ni-Fe NP’s (50nm) have been suggested to use in the production and recovery of gas hydrated based on the particle size and the capability to increase temperature needed to disturb the thermodynamic equilibrium inside the formation of the unconventional reservoir and allow associated gas recovery [100]. Other researchers have experimentally studied a variety of NP’s in drilling muds at the lab scale for many different reasons. CuO and ZnO NPs to improve the thermal stability and electrical behaviour of WBM [101]. Silica NP investigated as fluid loss additive in shale formation [38, 102].

The advantages nanoparticles present is their size that can fit and efficiently plug the shale nanopores hence providing a solution to improve the development of unconventional shale plays without the risk of dealing with irreversible plug techniques offered by the conventional WBM. Nanoparticle WBM can be used instead of OBM in sensitive areas to improve drilling mud inhabitation capabilities and increase the thermal resistance of conventional drilling muds additives, hence presenting a WBM eco-friendly alternatively to drill unconventional shale plays. Nanoparticles of mixed metal hydroxides (MMH) have been used to replace polymers as viscosity modifying agents [103]. Nanoparticles of MMH promote aggregation between the platelets of bentonite/montmorillonite clay to form a gel structure by working as a bridging material.

2.6.2. Performance of nanoparticles in water-based muds

Drilling muds are very vital in the entire drilling operation in every well from spud mud to the completion fluid used in the final displacement nearing to continuing with further operations. The challenge of drilling shale formations and the need to create eco-friendly drilling systems is where nanotechnology can be of great importance. Advantages such as the creation of thin filter-cake, reduction of formation damage, control of fluid invasion of filtrate, reducing cutting dispersion, improving rheological and thermal properties as well as strengthening of wellbore walls are among the benefits that have proved their potential in the drilling industry. Therefore, the current literature has the aim to provide a wide knowledge on nanoparticles as the main additives in drilling mud systems while also providing information on previous projects and why they led to excellent results that support nanoparticles as effective additives.

One of the sources of solid particle and particulate invasion into the formation is the spurt loss. Beeson et al. [104] explained that spurt losses ranging from 2.3 to 7 ml can take place in the formation with a permeability in the range of 7 to 469 md. Formation damage is more likely to be increased by muds that produce soft and thick cakes. This therefore shows why it is important for a mud design to produce a clear filtrate with no spurt, well-dispersed and tightly packed thin mud cake and low filtrate volume. It is always very hard to fulfill certain functional task using conventional macro and micro type mud additives. Most recent research has shown that nano muds have the required properties for applications in drag reduction, gel formation, heat transfer, binding ability for sand consolidation, wettability alteration and corrosive control

[96, 105]. According to Smalley et al. [106], the laws that govern nanoscale material behaviour differ from the laws governing the micro and macro-scale behaviour. Nanoparticles have a very large surface area per volume. They are smaller compared to micro particles and therefore they require very low additive concentration to provide superior fluid properties at low concentration [107].

The large surface area to volume massively increase the interaction of the NPs with the surrounding fluid [108]. This special property of NPs provides increased interaction with reactive shale to eliminate shale-drilling mud interactions and other borehole problems [109]. The large surface area per volume allows the use of less proportions of nanoparticles to be applied compared to micro-size additives usually used to achieve similar effects. The use of small volumes of nanoparticles in drilling muds decreases drilling time and increases the productivity index of the drilling operation by increasing the rate of penetration (ROP). The main advantage of NPs would be to control spurt and fluid loss into the formation that would have led to formation damage [110]. NPs have the capability of forming a thin and impermeable filter cake and due to their large surface area to volume ratio, the mud cake particles can therefore be removed by traditional cleaning techniques during the completion stage. Hence, NPs can perform as rheology modifiers, fluid loss additives and shale inhibitors at very small concentration [102].

2.6.2.1. Effect of NP in the reduction of fluid invasion in shale formations

The main advantage of the nanoparticle as additives in drilling muds in shale formations is the NP size. The additives that were used to control filtration have a particle size distribution at a micro or macro size scale and these particles are larger than the pore structure of the shale formations which is at nano size. The difference in the size of micro particles and nanopores clearly explains the reason why these products cannot build a filter cake and control fluid filtrate invasion to the wellbore to the shale formation in the near-wellbore region [38]. Nanoparticles present a solution to this problem as their size fits properly to the nanopore structure of shales according to Abram’s plugging theory which stated that the median particle size of the bridging material should be between 1/7 to 1/3 or slightly more than the median pore throat size of the formation to protect [39]. Nanoparticles can create a thin filter cake in the shale wellbore walls that stops the influx of water hence avoiding further drilling problems [40]. From previous studies, research found that NP are able to create an external mud cake instead of an internal cake that may cause formation damage and is impossible to remove before cementing. NP have the ability to create a filter cake with less % of solids which helps to remove them easily with pre-flush fluid before cementing begins [109].

Formation damage prevention is more desired than reduced production as it increases operational costs relating to remediation operation especially for low reservoirs such as shale formations. On the other hand, NP filter cake has proved to be strong and thin enough to reduce the spurt filtrate and avoid solid phase invading the formation and damaging it. Spurt loss relates to the volume of filtrate that is lost to the formation before the formation of a mud cake [102]. Therefore, the advantage of NP to control spurt losses, reduce the concentration of solids in drilling mud, reduce the filtrate volume and build a thinner and non-erodible mud cake make them useful in drilling muds needed for shale formations.

Al-bazail et al. [111] and Sensoy [112] experimentally investigated silica NP in a drilling mud system of size 20 nm with concentration of 10 wt.% as the main additive and the aim was to reduce filtrate loss into Atoka shales which led to 98 % reduction. From the results presented by the authors, it showed that the use of NP in WBM successfully protected the shale formation. The authors observed that there was a reduction in the permeability by a factor between 5 to 50. However, the research study raised concerns as the authors concluded that at least 10 wt. % of functionalized NPs is needed to achieve the required results in which this would increase the cost of NP-WBM.

The results achieved with silica NP as a plugging agent on the evaluation done on Atoka shale, lead to various research by many other researchers who extended the technique to other shale formations [112]. In order to bring down the cost of functionalized NP, researchers evaluated the ability of non-modified SiO_2 NP to reduce the permeability in Atoka shales. Still from the results, the minimum NP concentration to effectively plug the shale nanopores was close to 10 % by weight showing no difference to the previous work with functionalised NPs [38]. In spite of that, 10 % wt. concentration of NP both modified or not was deemed too much to consider viable for an oil and gas application. Other researchers have reduced the concentration up to 3 % and have acquired good results in the transition pressure test [113, 114].

It should be noted that despite the good results, nanoparticles surface modification still increases the cost associated with the NP-WBM which affects the goal of an affordable replacement to the preferred OBM system. Beg et al. [115] investigated the rheological characteristics of water-based fluids using nanoparticles. Different samples containing titania and silica nanoparticles were analysed. The properties of the mud were studied before and after statically aging the mud samples at 80 ° C for 16 hours. The authors observed that titanium nano particles at a concentration of 0.60% (w/w) before aging exhibited better results.

Aramendiz et al. [116] investigated silica (SiO_2), and graphene oxide NP in WMB with the aim of studying and analysing NPs inhibiting effect on Woodford shale with conventional KCl/Partially hydrolysed polyacrylamide mud (PHPA). Silica size used was of 15 nm to 20 nm and graphene oxide size ranged from 1.3 μm to 2.3 μm.

The methodology followed was classified in two main tasks:

a) shale rock and NP characterization,
b) drilling mud characterization.

The mud samples were tested at temperatures of 77 °F and 100 psi for LTLP filter test and 250 °F and 500 psi for HPHT filter test. The muds were aged at 150 °F, 200 °F, and 250 °F. The nanoparticles were tested in concentrations of 0.25 wt.%, 0.4 wt.%, 0.5 wt.% and 2 wt.%. The authors observed that NPs reduced Woodford shale cutting erosion to 23.48% compared to the conventional KCl/PHPA fluid. These results suggested according to the authors that NPs efficiently controlled the formation fluid interaction hence improving the inhibition capabilities of the WBM. Furthermore, the NP mud had a lower spurt-loss which suggested a more impermeable and compacted filter cake because of their well-dispersion along the surface of the filter cake. From the aging results, nanoparticles preserved more than 42.97% of the initial carrying capacity (YP) of the WBM at elevated temperature of 250 °F while the KCl/PHPA mud showed a severe reduction of 95.25%. Nanoparticles in WBM were able to form a non-progressive gel structure no matter the temperature.

The authors also observed that NP-WBM improved the filtration properties. There was a reduction in the LTLP and HPHT filtrate of 20.93 % and 27.21% respectively. Also, Zakaria et al. [102] evaluated an in-house NP in a WBM system which showed the same ability to reduce both spurt and filtrate loss when compared with a conventional loss of circulation materials (LCMs). Under different conditions, the reduction was nearly 40 % showing a superior plugging property compared to conventional LCM products. From the study of Muili et al. [117], the authors investigated the effects of nanotechnology on the apparent viscosity, viscoelastic properties, filtration performance of surfactant-based fluids (SBFs) or viscoelastic surfactants (VESs), polymeric fluids, and SBF/polymeric-fluid blends were presented. Nanoparticle fluids were prepared by adding 20-nm silica at concentrations of 0.058, 0.24, and 0.4 wt.%, to the clean mud. The apparent viscosity and viscoelastic data were collected within a temperature range of 75 °F to 175 °F. Results showed an improvement in the apparent viscosity and viscoelastic properties of surfactant-based and polymeric nanofluids up to a nanoparticle concentration of 0.24 and 0.4 wt.% respectively.

2.6.2.2. Nanoparticle stability in drilling muds

The main concern of NP muds is the maintenance of stability. That is to say, avoiding NP aggregate formation that might form solids and lead to rheological problems. While drilling shale formations or in the drilling mud systems, NPs are likely to face stability issues at high temperatures and salty environments [118, 119]. NP plugging mechanism in shale formation nanopore goes beyond than just a physical seal. The particle size of NP that allows the plugging of the shales nanopores is not the only consideration for NP application stability in WBM. There are other factors like surface charge density, zeta-potential, NP shape and concentration, salt content and pH among others [120].

Studies recently have suggested that the surface of NPs can change its surface charge based on the medium conditions like pH. The adhesion behaviour of NPs to the shale pores will increase as well as the rate of deposition and the bond strength if the Van der Waals attraction forces between the shale surface and the NPs surface are higher than the repulsion forces. Meaning that the plugging ability of the NP will improve. The Van der Waals force is an attractive type interaction and is inversely proportional to the sixth power of the distance between the surface of the particles [121, 122]. On the other hand, if the repulsive forces between NP are weak, the more likely for the solution to start to form aggregates affecting the stability of the NP-WBM hence reducing its ability to seal the nanopores [123, 124].

To know the stability of a NP solution, Zeta-potential (ζ) measurements highlight the degree of the solution dispersion. Zeta-potential between -30 mv to +30 mv shows that the attractive forces in the mud system are greater than the repulsive forces which may result to aggregation on NP and after flocculation. According to Mahmoud et al. [125], a mud is a stable colloidal system with a Zeta-potential value above 30 mV. The Zeta potential values of both nanoparticles and shales can be modified by altering the pH of the solution. If the mud system with NPs having a negative surface charge pH is reduced, aggregation happens, and the surface charge turns to neutral. On contrary, if the pH of the same mud system is increased, the repulsive forces will increase hence improving the dispersion ability of the solution and ability to reach the shale surface at the same time because the shale has a negative charge.

The defining factor in this is reaching a balance between the NP-NP repulsion and NP-shale surface attraction. As for NPs, they are very sensitive to pH concentration but looking on previous studies, SiO_2 NP proved that nanoparticles can be stable and can improve the rheological and filtration properties in low pH (9.4) and high pH (11.5) at the same time maintaining a good shear thinning capacity better than the mud system without NPs at different pH [126]. The impact of silicon oxide (SiO_2) NPs on improving the performance of heat transfer behaviour and specific heat capacity of WBM was experimentally investigated also by Ahmadi et al. [127].

SiO_2 in concentrations of 0.1, 0.3, 0.8, 1, 1.5, 3, 5 % wt. and in nanosized of 10-20 nm were tested at temperatures ranging from 0-76 °C. SiO_2 was found to have improved the stability of the drilling systems tested. In both systems, the specific heat coefficient improved. Increasing the heat transfer coefficient improved the heat transfer in the mud system. William et al. [128] investigated the effect of CuO and ZnO NPs in sizes of <50 nm in WBM. The NPs were tested in concentrations of 0.1 wt. %, 0.3 wt. %, and 0.5 wt.% at temperatures of 25 °C, 70 °C, 90 and 110 °C. The pressures were kept at 0.1 and 10 MPa. The authors observed that the WBM with NPs showed improved thermal and electrical properties by about 35 % compared to WMB with no NPs. Also, it was noted that the WBM with CuO NP exhibited improved thermal properties and was more resistant to HPHT conditions than ZnO WBM.

There is still more research done on NP by evaluating different methods to stabilise NPs in WBMs. Methods used have been using coated or functionalized NP, others reducing the concentration in the liquid medium, and others analysing the factors affecting the non-modified NP to enhance their stability [129]. The stability of NP solution is affected by salt. The NP double layer is affected as the salt concentration increase and the repulsive forces decrease allowing aggregation to occur [119]. Another technique to protect the NPs is surface change. NP which are functionalized (modified surface, coated, nanocomposites) suffer less from aggregation. Each functionalized NP will have a shield in its own surface that increases the repulsive force hence stabilising the solution [9, 130]. Modifying NPs can be expensive affecting the overall cost of the drilling mud in a drilling operation. If correctly tested against potential instability factors like (salt and pH) non-modified NPs can decrease the economic factor related to the design of a NP-WBM.

2.6.2.3. Nanoparticle effect on the drilling mud rheology

Low viscosity at high shear rates and higher viscosities at low shear rates are exhibited by drilling muds with good pumpability. This condition provides safer trips in and out of the borehole due to the ability of the drilling mud to support cuttings at static conditions, while at higher shear rates help to reduce friction losses and control the formation of cutting beds and improve drilling mud hydraulic and hole cleaning. From the literature, SiO_2 NPs have positively influenced the drilling mud rheology and carrying capacity with very few exceptions among experimental researches that experienced a decrease in YP [131, 132].

The reason for the results was due to the inhibition effects of NPs on the bentonite hydration process or flocculation due to the NP poor zeta-potential values. The key is to find an optimum range of the YP value at the same time not to affect the cutting transport to surface as low YP helps to avoid high pump pressures. More so, some studies showed evidence that there was long term stability to drilling mud in terms of gel strength at fresh conditions and at aged conditions with no progressive behaviour when SiO_2 NPs were applied which is a desirable condition in WBM at HPHT conditions were conventional additives tend to degrade rapidly.

With non-progressive gel strength, it indicates that NPs can decrease the flocculation of bentonite at high temperature thus providing a more stable system when compared with conventional WBM with no NP. Changes in drilling mud rheology due to addition of NP shows how important it is to maintain the correct dispersion of NPs in a drilling mud to avoid aggregation that might precipitate at downhole conditions and lead to wellbore problems. Therefore, evaluation of NP stability against concentration might avoid any aggregation problems that can lead to increased YP. A higher YP can affect the cutting carrying ability of the NP-WBM and reduce the ROP. ROP is increased in hard formations with low solids in a WBM and formation damage is prevented in the productive zones. The surface of NPs compared to its volume ratio plays a big role in reducing the solid concentration in the drilling mud and therefore, less materials will be required, the interaction between the formation drilling muds will be reduced and the effects of high % of low gravity solids (LGS) in the drilling mud will be achieved.

According to Ponmani et al. [101] several researchers have already tested a low NP concentration of between 0.1 % to 0.5% by wt. From the observations was the ability of the NPs to improve the thermal and electrical conductivity of the drilling mud systems. Due to the large surface area per unit volume, it was discovered that NP can absorb and dissipate heat while drilling and cooled the down hole tools plus the bit. Furthermore, the high thermal conductivity of NP prevents hydration that would have been caused by temperature on the conventional additives hence maintaining the rheological properties of the drilling mud making the mud system more stable while serving as a shield to polymers that might have suffered from high degradation rate at HTHP conditions.

Bayat et al. [133] investigated the rheological properties of a bentonite WBM in the presence of various metal oxide NPs while also establishing the optimum concentration of NPs in WBM.

The NPs were tested in concentrations of 0.01 wt. %, 0.05 wt. %, 0.1 wt. % and 1 wt. %. The different NP sizes were of 40 nm. From the research the authors concluded that SiO_2 revealed a good improvement of WBM rheology and acceptable enhancement in the characteristics of the final mud system in regard to filtrate loss and filter cake. The use of Al_2O_3 NPs in improving the WBM rheological properties was not recommended but TiO2 and CuO NPs at a concentration of 0.5 wt. % exhibited good rheological properties in bentonite WBM.

Also, Dejtaradon et al. [134] experimentally investigated the impact of ZnO and CuO NPs on the rheological and filtration properties of WBM fluids. The NPs in the sizes of 50 nm were added in the WBM formulations in concentrations of 0.1 wt. %, 0.3 wt. %, 0.5 wt. % 0.8 and 2 wt. %. The HPHT filter test was conducted at 500 psi and at 100 ^{o} C. The rheological properties were conducted at temperatures of 25 °C, 50 °C, and 80 °C). The authors observed that with a small quantity of NPs, there was a reduction of shear stress and improvement in the rheological properties of the mud fluids. But when the concentration of NPs was increased, shear stress increased gradually and both mud system's rheological properties decreased though ZnO NPs produced better rheological properties than CuO NPs. At HPHT conditions, both mud systems exhibited shear thinning behaviour, showed a decrease in shear stress and an improvement in rheological properties. There was a reduction of filtrate loss for both NP systems for 18.6 % ZnO and 30.2 % CuO compared to the base fluid. Furthermore, it was observed that there was an increase in filtrate loss as 1 wt.% concentration. Also, there was a mud cake reduction of 23.6 % and 27.6 % for ZnO and CuO respectively compared to the base fluid. The authors concluded that ZnO NPs showed a better ability to improve the rheological properties while CuO NP exhibited superior filtration loss reduction. However, CuO NPs were deemed and considered environmentally friendly drilling mud additives.

Medhi et al. [135] examined the effect of NPs in conventional bentonite-based mud fluid and a non-damaging drilling mud (NDDF). The effects of silica and copper oxide NPs on the rheological and fluid loss properties of drilling muds was investigated. NPs were tested in concentrations of 0.5 %, 0.8 % and 1 %. Silica NP in non-damaging drilling mud (NDDF) enhanced the rheological properties and also gave better fluid loss control compared to bentonite-based mud. It was observed that at 0.5 % concentration, silica NPs emerged as an excellent fluid loss control agent. CuO showed greater thinning behaviour in bentonite fluid, viscosity decreased with increase in concentration of CuO. However, the fluid loss decreased with increase of CuO except for 0.5 %.

Kosynkin et al. [136] investigated and showed that graphene oxide (GO) with a concentration of 0.2 % (w/w) by carbon content exhibited 15.27 % fluid loss reduction in water-based drilling mud compared to WBM control drilling mud sample. Investigations by Mahmoud et al. [137] on the effect of ferric oxide concluded that ferric oxide nanoparticle application at concentrations of 0.3, 0.5 and 1.0 wt.% decreased the mud cake thickness by 8.8, 21.9 and 38.7%, respectively as compared to the mud cake thickness of the base fluid. Cumulative fluid loss volume of 16.9 % and 3.9% decrease was observed for mud fluids with 0.3 and 0.5 wt.% of ferric oxide concentration but there was an increase of 15.6% when the concentration of ferric oxide was increased to 1.0 wt.%.

Hassani et al. [138] investigated carbon-nanotubes, SiO_2 and ZnO nanoparticles in WBMs under elevated temperature of 104 °F. They targeted the thermal conductivity, PV and YP. From the observation, SiO_2, carbon-nanotubes and ZnO nanoparticles tested in concentration of 2.0 wt.% resulted in rheological improvement with the highest improvement achieved from silica nanoparticles. Silica nanoparticle muds were first studied by Sharma et al. [139] using nanomaterials of size 20 nm in drilling mud. The researchers investigated the impact of silica NPs on the rheology of drilling mud and observed that YP and gel strength decreased more with 1.0 wt.% silica well as a small decrease at 3 wt.% silica was observed. Srivatsa et al. [140] concluded that addition of silica NPs resulted to 30% viscosity increase by one sample more than the base mud. This agrees with the work of Mao el al. [141] who concluded that silica NP of size 12 nm addition in drilling mud resulted to increase in viscosity at HPHT conditions.

Similar results by Taraghikhah el al. [123] were demonstrated at up to 1.0 wt.% silica concentration and Hassani el al. [138] also studied SiO_2 nanomaterials and a hybrid NP mud containing silica and carbon nanotubes. The author and the co-authors stated that both NP types increased viscosity of the mud greatly with silica NPs showing great behaviour compared to hybrid NP mud. On the other hand, Salih et al. [126] evaluated the effect of silica nanoparticles of 5.7 nm on drilling mud and addressed the negative implications of silica nanoparticles on the mud rheology such as, gel strength and yield point (YP). It was observed that nano silica in concentrations of 0.1 wt.% - 0.3 wt.%. had an impact on the properties of the mud with high sensitivity to pH changes.

Some attempts were also made to enhance the cutting carrying property of WBMs using silica nanoparticles in another study by Elochukwu et al. [142]. It was observed that additions of silica NPs reduces the WBM’s yield point (YP) which affects the cutting carrying effect of the mud. However, change of the surface charge of the nano silica using alkylbenzyldimethylammonium chloride (ABDACI) resulted in improvement of YP and PV of the mud system. An interesting observation after nano silica modification was the reduction of the filtration loss and a smaller mud cake. Mahmoud et al. [125] investigated ferric oxide NPs and silica NPs of size 12 nm under HPHT conditions. They concluded that ferric oxide NPs improved the rheology of the bentonite mud however, silica NPs adversely affected the rheology of the mud fluid. Increase in silica NPs resulted in more agglomeration which increased porosity and permeability of the filter cake. These findings agree with the experimental research by Vryzas et al. [143]. They studied the effect of 12 nm iron oxide NPs and silica nanoparticles in drilling mud. From the conclusion, filtrate loss was reduced by 42.5% with a maximum amount of nanoparticles in concentration of 5 w/w % compared to the base fluid. Surprisingly, application of silica NPs substantially increased the filtration loss at nanoparticle concentrations of 0.5% and 1.5% (w/w) resulting to 54.1% and 46.8% increase respectively. At both LPLT and HPHT conditions, silica nanoparticle adversely affected the mud fluid filtration properties.

Nano fluids are also prepared using metal oxides additives in drilling mud. However, Sadeghalvaad et al., [144] prepared nanocomposite after polymerization of acrylamide monomer with TiO_2 nanoparticle presence. In the study, the authors added 14 grams of nanocomposite to 350 mL distilled water followed by 10 grams of bentonite. The tests showed improved fluid loss up to 64% and less mud cake relative to conventional drilling muds. NP selection of optimum concentration is a key parameter to avoid further rheology issues (excessive PV/YP/Gels). Previously, researchers found that once the NP concentration exceeds the optimum value, agglomeration occurs which not only affects the rheological properties negatively but also increases filtration into the shale formation [109, 145]. Therefore, to design a stable NP-WBM, avoiding aggregation and flocculation tendencies of NPs is one of the most important points to correct.

2.6.2.4. Effect of NP in wellbore strengthening

Nanoparticles can prevent pore pressure build up by controlling the loss of drilling mud into the formation showed by previous research on pressure transient tests [38]. NPs in other words maintain the overbalance of the drilling column in the safe mud widow by preventing drilling mud invasion into the formation that can increase the pore pressure and lead to wellbore collapse. The lighter weight of NP-WBM also minimises the chances of experiencing fractures due to excessive overbalance shown in Figure 2.32.

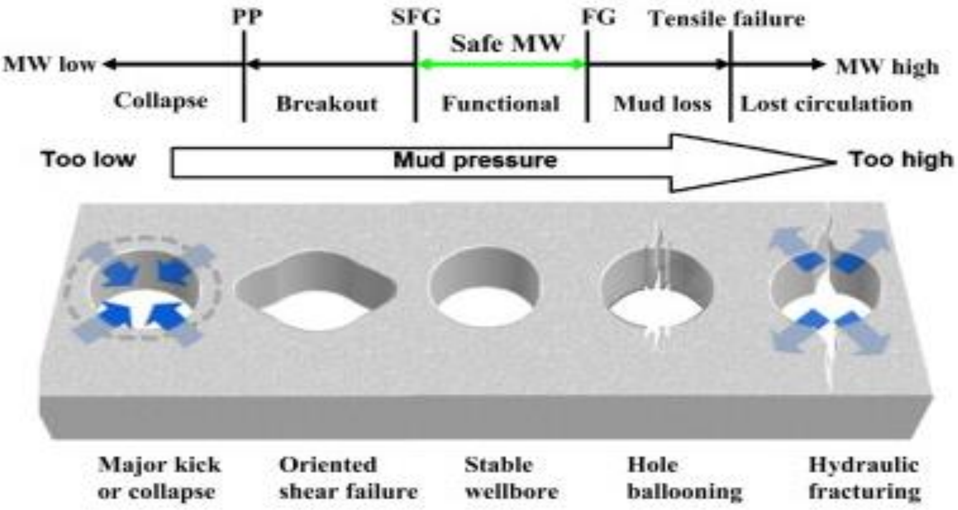


Figure 2.32: Relationship between mud pressure (mud weight, MW) and borehole failures [146]

Nanoparticles can increase the wellbore strengthening in shales and also reduced torque and drag (T&D). While drilling shale formations, NPs ability to form a thin, flexible and no-erodible mud cake indicates it's potential to reduce drilling problems such as excessive T & D or potential stuck pipe in the long lateral sections. The thin external homogeneous filter cake in the horizontal section reduces the drill string area that is in contact with the low side of the well hence decreasing the risk of stuck pipe Figure 2.33. The formed thin filter cake and the NP itself facilitates the reduction of friction resistance, generating less tortuosity of the wellbore while increasing the ROP, which is desirable in extended reach wells or multilateral sections [109, 123].

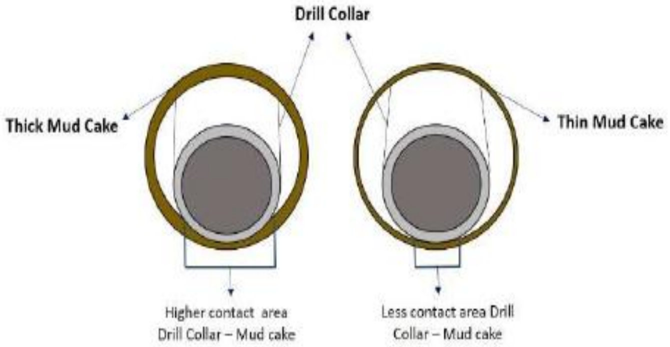


Figure 2.33: Contact area between mud cake and drill string [147]

Several types of research on the advantages of NPs have been done using modified and non-modified nanoparticles. Boul et al [9] and Sensoy et al. [112] investigated the modified NPs while researchers like Cai et al., [38], Srivatsa et al. [140] and Ziaja et al. [145] investigated non-modified NPs. The analysis of spurt and filtrate loss volumes of the static filtration test as well as the HPHT was included and related to the increase of rock samples fracture pressure [10]. OBM with NP exhibited an increase in the range of 20% to 30% in the fracture pressure [10]. Nanoparticle concentration of 0.5 % to 2 % by wt. showed an important reduction which meant that a positive impact in terms of cost and stability for NP drilling muds. Afterall, the base fluid for the tests was OBM which reduced interaction with the shale matrix due to the capillary therefore hiding the real effect of the NP. But similar studies had to be addressed with WBM to prove their capabilities and support the intention of an environmentally friendly drilling mud system.

The assumption that Darcy flow can be applied to shales was not to be assumed but transient pressure test could give a good analysis of the ability of NP to decrease permeability and increase stability of the wellbore while drilling. The literature has already showed that NP has the ability to improve the strength of shales. On the other hand, wellbore strengthening using of NP-WBM not only depends on the presence of NP. NP solution stability is very important to keep them dispersed while maintaining their original shape as well as reduce the aggregation tendency. This will ensure that the original NP structure is kept as much as possible and led to plugging of the nanopores hence increasing the wellbore strengthening [120].

According to Sharma et al. [139], they stated that there is still some specific doubts about NP’s ability to seal micro or Nano fractures and the results indicated a poor performance, but if concentration and shape of NPs is optimum, by combining conventional LCM additives like graphite can enhance the NP-WBM system when trying to provide wellbore strengthening to shale formations with natural micro fractures. There cannot be an increase in wellbore strengthening (WS) with a high fluid loss of the NP-WBM. Stability in rheology and improved inhibition properties work together to avoid cuttings dispersion hence reducing the risk of density increments. Therefore, understanding the formulation and selecting materials that are stable enough under different conditions is the key.

Nanofluids are colloidal liquid suspensions of nanoparticles with concentrations ranging from 0.01 - 5 % [148-150]. Nanoparticles can be used in a powder of ceramics Shin et al. [151] and Chung et al. [152], metal oxides [152-154], carbides [155], nitrides [156, 157], carbon nanotubes [158] and metals [150] which might be suspended in organic, aqueous or ionic liquid media. As mentioned early, one area in which nanofluids have attracted attention is in the formulation of oil and gas drilling mud systems and specially in this work, silica nanoparticles will be investigated in detail.

2.6.2.5. Hybrid nanofluids

In recent years, many experimental and analytical studies of hybrid nanofluids have been conducted. A new form of nanoparticle mud fluids has been brought into the market to address the issues of well instability in the oil and gas industry. Hybrid mud fluids have been introduced and different researchers have concluded that they have exhibited excellent performances in drilling operations. Hybrid nanofluids are a novel type of nanoscale fluid in which metallic nanoparticles of varying size and material are integrated in a base fluid to obtain excellent thermal performance and synergy [159]. They are a modified version of conventional nanofluids. Hybrid nanofluids are growingly being used in fields such as petroleum industry, medicine, smart pumping systems, coatings, fuels, adhesives, and lubricants. Hybrid mud fluid consists of two nanoparticles which are combined together to achieve enhanced rheological properties. Unitary nanoparticles have been combined to get hybrid nanoparticle mud fluids which have been found to be stable under HPHT elevated conditions.

A study by Beg et al. [160] recently proposed the use of different nanoparticles. The use of titanium and silica NPs in conjunction with WBM was studied in their research for the production of NPs drilling mud mixtures. Conventional standardise tests were used to assess lubricity and rheology. Their experimental results showed that 0.60 weight percent TiO2 NPs enhanced formulation stability, lubricity, and mechanical properties of drilling mud [160].

Barry et al. [161] used clay hybrid NPs to study the filtration and rheological properties of muds under various HPHT conditions. From the results, clay hybrids (Al_2O_3-SiO_2 and iron oxide clay hybrid) NPs with interaction of surface charge and modification reduced drilling mud filtration loss volume [161]. Using different NP groups was also proposed in Husin et al. work. The usage of silver nanoparticles (nanosilver) and graphene nanoplatelets in combination with WBM for creating NPs drilling mud mixes was studied in this study. Conventional standardised tests were used to analyse density, rheology, and filtration studies. They found that silver nanoparticles and graphene nanoplatelets enhanced plastic viscosity by 64% and 89%, respectively. Furthermore, both the fluid loss and yield point values were reduced [162].

Wang et al. [76] looked at the feasibility of introducing aluminium, magnesium, and silicate NPs into water-based drilling mud. The rheological, filtration, and thermal stability of the water-based mixture improved. Furthermore, using magnesium aluminium silicate NPs in water-based drilling could significantly reduce the use of conventional ones, which is environmentally friendly [76]. Gurluk et al. [163, 164] investigated the benefits of ZnO and MgO NPs in Calcium chloride and Calcium bromide solutions as drilling muds using a unique surfactant (amidoamine oxide). They came to the conclusion that adding NPs to surfactant viscoelastic solutions improve thermal stability. Furthermore, they discovered that at 135 ^{o}C, drilling muds containing ZnO NPs became the major factor in the elastic modulus system.

Drilling muds have also been modified with iron NPs. In HPHT conditions (121 ^{o}C and 500 psi), Contreras et al. [165] investigated the performance of drilling muds with high and low concentrations of iron-based and calcium-based NPs. According to the findings, adding metal NPs reduced fluid loss by 76%. They also discovered that by combining graphite with both nanoparticles, fluid loss could be reduced to zero. Alvi et al. [166] used iron nanoparticles in drilling muds in another study. The results showed that adding boron nitride and iron NPs to drilling mud lowered the mechanical friction coefficients. Iron nanoparticles lowered API static filtrate loss. Nanoparticles have also been shown to have an effect on the viscosity parameters of drilling mud [166]. The new trend of nanoparticle drilling mud has been reported as an efficient system which has improved drilling mud system’s rheology, filtration properties and has proved to be thermally stable under elevated conditions.

2.6.2.6. Challenges

Although the use of nanomaterials can provide significant technical advantages, the drawbacks of nanomaterials in drilling muds cannot be overlooked. The cost of nanomaterials is a major issue that should be considered before beginning a project. In general, the synthesis, services, and production process of nanomaterials can be extremely expensive, not forgetting that a large volume of nanoparticles is always used in the drilling operation. The conditions and properties of each oil filed and well, and the compatibility of nano fluids, posses another challenge. High temperature, chemical alterations and salinity in some formations can be the destructive agent to nanomaterial structure. Another concern is the unknown safety hazards and health effects of nanomaterials [167, 168]. As a result, standard industrial hygiene practises may significantly improve the safety hazards protection in nanomaterial drilling operations. Because nanotechnology is a relatively new technology for producing new drilling muds, there are few experimental and field tests, analyses, knowledge, and experience on its long-term performance.

2.7. Introduction to Colloid system

The dispersion of small solid particles, gas bubbles and liquid droplets in another liquid or solid in a size range of 1 nanometre to 10 micrometres is a colloid. The term "model colloids" implies to colloids of well-defined sizes, shapes and surface properties which are formed under controlled conditions such that the particles are nearly identical in the dispersion or at least in almost all aspects. Monodisperse particles are contained in a dispersion when all the particles are of identical size as shown in Figure 2.34(a). A stable colloidal dispersion is one that is resistant to physical changes over a period of time, and it is destabilised by undergoing mechanisms such as flocculation, sedimentation and coagulation. Nanofluids are a type of colloid in which the dispersed medium is a nanoparticulate. The large surface area of nanoparticles is unstable. Aggregation is a method by which the surface area can be decreased hence the absence of a stabilising force, particles in the dispersion tend to form large aggregates. Stability is achieved by the increase in repulsive forces between particles to prevent them from aggregation hence allowing them to remain dispersed as single particles [169].

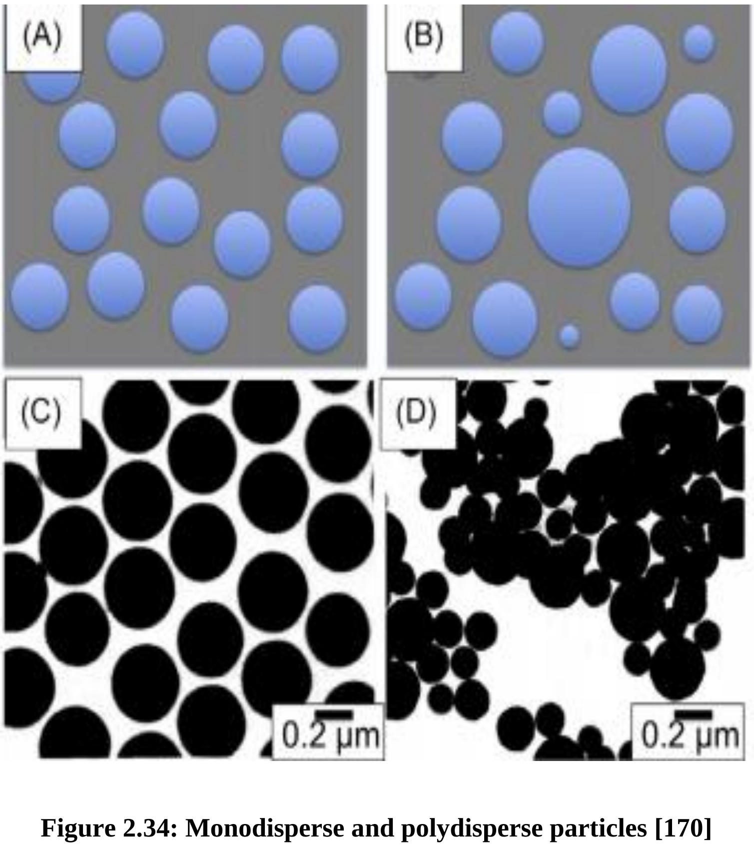


Figure 2.34: Monodisperse and polydisperse particles [170]

The synthesis conditions can be altered to obtain particles of varying size, or polydisperse particles such as those shown in Figure 2.34 (b) and (d) respectively. The electron microscopy of monodispersed and polydisperse spherical silica particles prepared by a well-established Stober method [171, 172] as shown in Figure 2.34 (c) and (d). In Figure 2.34 (c), it appears that the silica colloids are monodispersed. As seen from Figure 2.34 (c), silica colloid particle population displays a very narrow size distribution. Therefore, there are no true monodisperse particles in that sense. In other words, the size distribution can be either narrow or broad according to Chhabra et al. [170] but both monodisperse and polydisperse particles can be taken to be model colloids depending on the colloid phenomena under investigation.

2.8. Synthesis of Colloids

Several methods can be used to prepare colloidal scale particles and they can be classified into top-down and bottom-up approaches. The top-down approach includes a bulk solid converted into smaller particles by high energy ball milling, lithography, etching, and the electric synthesis route and many more. Contrary to that, in the bottom-up approach, the constituent molecules or atoms are assembled by processes like nucleation and growth to give rise to particles that are one or more orders larger in size than the atomic length scale.

Monodispersed colloidal silica is of fundamental interest and of great practical use as well in many industries. It’s method of preparation has attracted great attention in the past [171, 173]. A common method has been the catalysed hydrolysis of silicon alkoxides. The Stöber method has been widely used in synthesis of silica nanoparticles. Using ammonia and tetraethyl orthosilicate (TEOS) has been widely used for the preparation on monodisperse silica particles in different ranges of 20-1000 nm [174]. Different researchers have addressed and described the chemical synthesis involving hydrolysis and condensation of TEOS. Both stages take place in alcohol solutions in the presence of ammonia. There are different conditions such as temperature, pH, reagent concentrations and many more on which the polydispersity and the size of silica depend.

2.9. Stöber approach for silica (SiO_2) colloids

In 1968, Stöber et al. [171] completely changed the silicon oxide world by the introduction of sol-gel process to generate monodisperse particles of silica. The chemical reagents used for the Stöber synthesis of silica colloids are ethyl alcohol C_2H_5OH), tetraethyl orthosilicate (TEOS), water (H_2O), and ammonia (NH_3) [171, 172]. This process first involves the reaction of TEOS with H_2O in ethanolic aqueous mixture, which is a hydrolysis reaction catalysed by NH_3 [169]. The polymerization of TEOS into silica particles goes through hydrolysis and condensation reactions written as follows [175-178]:

$$\mathrm{Si(OR)_4 + xH_2O \xrightarrow{hydrolysis} (OH)_xSi(OR)_4 + xROH} \tag{2.9}$$

$$\mathrm{Si(OH)_4 \xrightarrow{condensation} SiO_2 + 2H_2O} \tag{2.10}$$

The mechanism involved in silica formation still remains unclear though up to now, it is generally accepted that silica polymerization and particle formation follows a 3-stage process as proposed by Iler et al. [179] in 1979 and illustrated in Figure 2.35.

a) Oligomerization of monomers through hydrolysis and condensation reactions to form stable primary particles of a critical size
b) Growth of the nuclei to form spherical particles
c) Aggregation of nuclei or particles into branched chains that extend to networks within the liquid medium, thickening it to a gel.

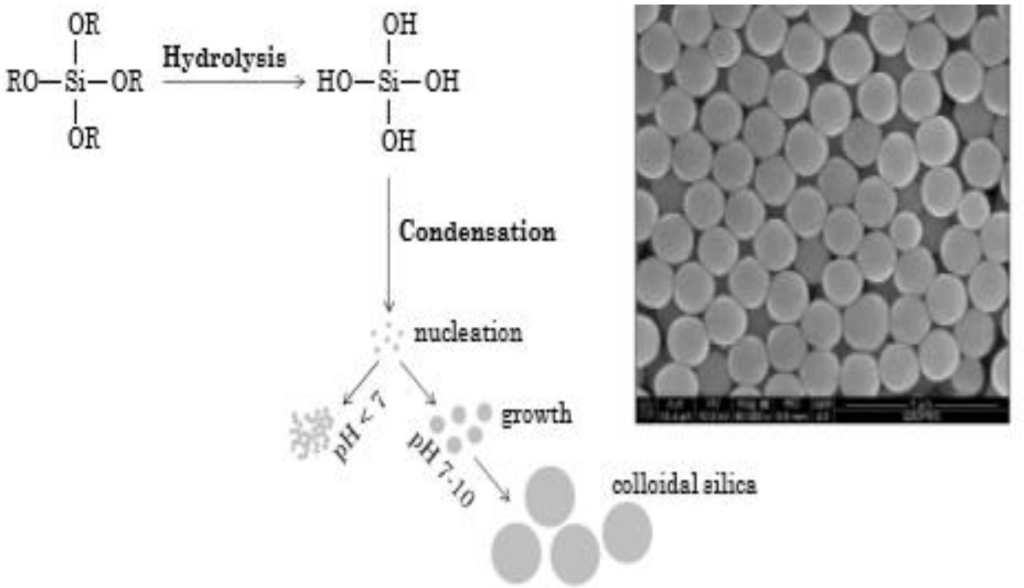


Figure 2.35: Schematic of colloidal silica synthesis as proposed by IIer and Scanning Electron Microscope (SEM) image of 280 nm diameter particles [179]

Though there are uncertainty over the formation mechanisms of the particles, it is clear that hydrolysis and condensation reactions control the final size and morphology of the synthesized silica particles. Both reactions occur hand in hand showing a competition between hydrolysis of alkoxy groups from the organosilanes and condensation reactions.

A condensation reaction will occur leading to the conversion of the silanol molecules to monodisperse silica (SiO_2) colloids [169]. The size of the silica particles like any other colloidal synthesis from Stöber method is mainly controlled by the contribution from nucleation and growth of the particles and these phenomena are also dependant on the hydrolysis and condensation of TEOS, controlled by the reaction conditions like temperature, solvents, pH and so forth [180]. Many researchers have widely investigated the Stöber process and the influence of different synthetic parameters like concentration of reactants, nature of solvents on the size of the prepared particles. From different research, it has been noticed and concluded that particle size is determined by the complexity of the interplay between all these factors.

The reaction temperature is an important parameter to consider when addressing the size of the particle. From the literature by [172, 181-183], they reported that the diameter of the particles reduces with an increase in the reaction temperature. Increased reaction temperature results to increased hydrolysis and condensation reaction rates, which result to increased nucleation rate. A high number of nuclei are formed from a high nucleation rate hence the final size of the particles will decrease. More so, Tan et al. [184]. and Zhang et al. [185] reported that the linear growth and formation of the structure of silica particles occurs simultaneously though the latter occurs more rapidly at increased temperature, which verifies the formation of smaller spherical particles at higher temperature.

The concentration of ammonia used in the method as a catalyst is also a defining factor in the final size of the silica particles. The hydrolysis and condensation reactions of TEOS are facilitated by ammonia as a catalyst through the increase of the concentration of hydroxide ions (OH) [186]. Similarly, as discussed earlier, there will be formation of numerous nuclei, which leads to smaller particles due to increase in the initial concentration of ammonia. However, another vital parameter has to be taken into consideration while considering ammonia concentration. There will be an increase in the ionic strength of the suspension together with the ammonia concentration which will lead to a decrease of the double layer thickness of the particles [187]. The static repulsive force between the particles as a result is thought to be dominated by the van der Waals attractive forces leading to a formation of larger particles. Therefore, the balance between both contributions that is, the ionic strength caused by ammonia concentration and its catalytic effect on the hydrolysis of TEOS is dependent on the water content of the suspension. Bogush et al. [172] reported that the size of the particles increases with the concentration of ammonia and water until maximum size is achieved and after which, the particles become smaller. Same effects of ammonia concentration due to low or high-water content have been reported in the literature by Sadasivan et al [188], Yokoi et al [189] and Byers et al. [190] .

The solvent choice is also a vital parameter to consider when preparing silica nanoparticles namely using a low molar-mass alcohol. The two factors that will play an important role here include the diffusivity of TEOS in the chosen solvent and its polarity. TEOS diffusivity in the solvent; related to its viscosity, will decrease with increasing molecular weight of the solvent; in the media with higher viscosity, the diffusion of TEOS, hence the reaction rate is reduced [188]. The particle size in the growth process is also affected by alcohol solvents like (ethanol: 23.3, methanol: 32.6, propanol: 20.1) which have different relative dielectric constants [178]. A solvent with a lower dielectric constant result to a situation where the repulsive force between particles decreases as compared with the van der Waals attractive force hence the growth of the particle will be facilitated. Therefore, the lower the dielectric constant of the solvent, the bigger the particles formed. As a result, and from the investigations done by Wang et al. [181], Deák et al. [191] and Green et al. [192] silica particles prepared in methanol are smaller than the ones prepared in ethanol or propanol.

From the literature overview, the size control of the particles appears to be strongly determined by the influence of a few factors; altering the parameters seems to be sufficient to vary the size of the prepared particles to a certain extent.

2.10. Stability of particles dispersion

For colloid dispersion, stability is when the particles in the dispersion continue to exist as individual units without clustering together or forming aggregates Figure 2.36. Stabilisation of colloids is mostly about how to prevent particles from aggregating or flocculating. Stabilisation method includes repulsive forces between particles preventing their aggregation and allowing them to remain dispersed as single particles [193]. Classical Derjaguin-Landau-Verwey-Overbeek (DLVO) is the commonly applied theory in colloidal science for estimating the interaction potential between particles [193, 194]. The theory represents the total interparticle interaction as a sum of the of the attractive van der Waals interactions and repulsive electrostatic interactions (Equation 2.11). The particles will aggregate, and the colloid will be unstable if the electrostatic repulsion is less than the van der Waals attraction [193].

$$V_T = V_A + V_R \tag{2.11}$$

Where:

V_T = total interaction potential
V_A = attractive van der Waals interaction potential
V_R = repulsive electrostatic interaction potential

Colloidal stability can either be thermodynamically or kinetically. Thermodynamically stable colloids exhibit extraordinary long-term stability. In many cases, colloidal particles in a well-dispersed state is not thermodynamically favoured according to Chhabra et al. [169] for example, because of the high surface area and attractive interactions, metallic colloids always cluster together and precipitate out of the solution. The most common method used for stabilizing colloids against aggregation is to impart kinetic stability, such that a large energy barrier for the processes that lead to destabilisation of colloids are present or to completely remove the attractive forces between the particles. If the gravity effects are negligible and the particles are so small, and if not thermodynamically stable, the aggregation of particles can be avoided by means of refractive index matching, electrostatic stabilisation, steric stabilisation, and depletion stabilisation [195-197].

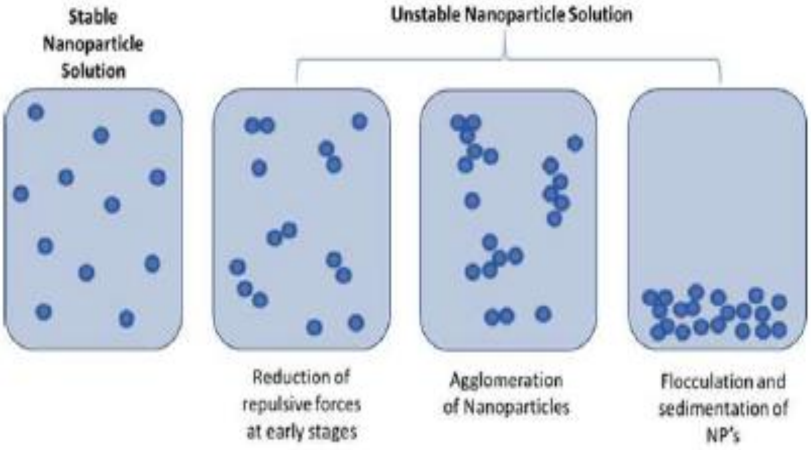


Figure 2.36: Nanoparticle unstable process [198]

2.10.1. Steric Stabilisation

In steric stabilisation of colloids, long chain molecules are attached on the surface of the particles such that each particle is with a thin shell of envelop of long-chain molecules as seen in Figure 2.37. The attaching of long-chain molecules can be achieved by chemical synthesis also referred to as chemical grafting seen in Figure 2.37 (a) or by adsorption. Figure 2.37 (b) and (c) presents the steric stabilisation of colloids due to the adsorbed polymer molecules and surfactant molecules respectively [169, 199]. Particles such as that when dispersed in a solvent, a brush-like formation formed may assume an extended conformation or a collapse configuration [169]. The attractive van der Waals forces are completely masked and hence provide stability to the colloids when the dimensions of the brush -like layers exceed a few nanometres [169].

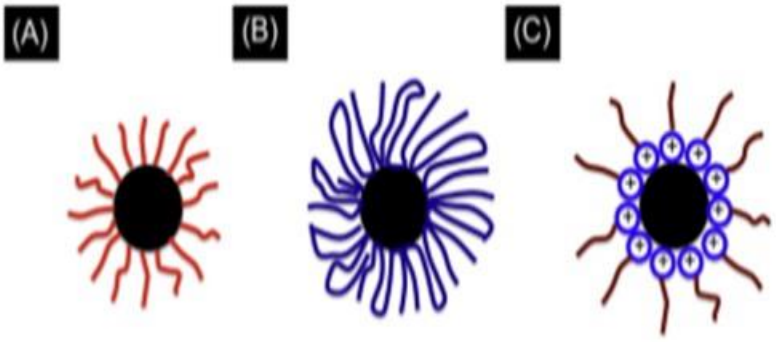


Figure 2.37: Presentation of particles with brushes on their surface

(A) covalently attached long-chain molecules, (B) adsorption of long chain molecules such as polymers, and (C) adsorption of surfactant molecules such that the tail group is exposed to continuous medium in which the particles are dispersed [169].

2.10.2. Electronic stabilisation

In electrostatic stabilisation, an energy barrier that is much larger than the thermal energy is achieved by imparting interparticle repulsion as a consequence of charges on the particle surface [169]. In electronic stabilisation mechanism is when the van der Waals forces are counterbalanced by the repulsive forces acting between the charged colloidal particles, a negatively charged particle is shown in Figure 2.38 [200]. When a colloidal particle moves in the dispersion medium, a layer of the surrounding liquid remains stuck to the particle; the boundary of this is the slipping plane. Zeta potential is the electric potential at the slipping plane. The zeta potential is an important parameter that needs to be measured as it assesses the instability of charge-stabilised colloids. The zeta potential is positive if the particle is positively charged and negative if the particles are negatively charged [169]. The higher the zeta potential, the higher the surface charge and the more stable is the dispersion. A zero-zeta potential is called the isoelectric point also called the point of zero charge which indicates total aggregation

[169]. For example, large positive (+30 mV) or negative potential (-30 mV) results typically in stable dispersion because of electrostatic repulsion and vice versa [169, 201].

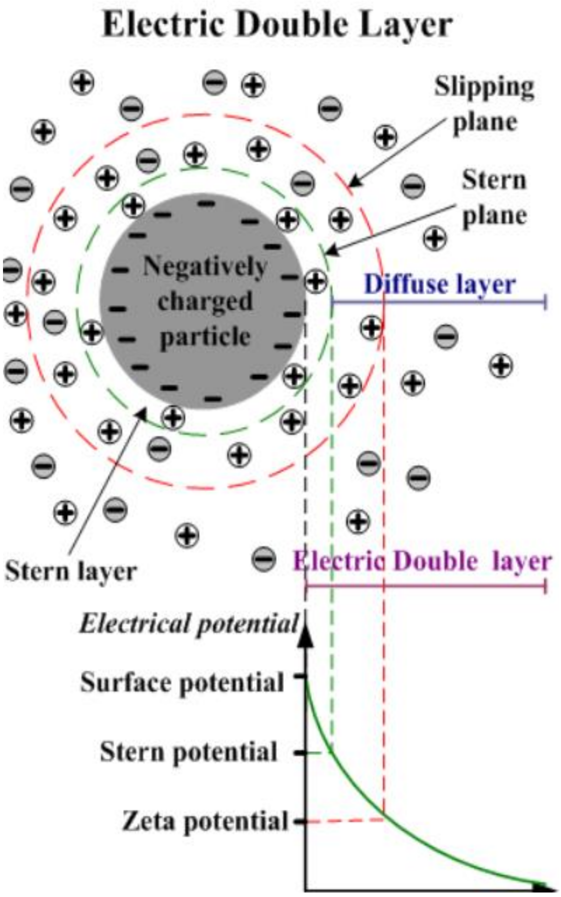


Figure 2.38: Electric double layer [201]

Charged molecules added to a dispersion of colloidal always adsorb on the particle surface leading to improved stability. In Figure 2.39 E -H, there is acquisition of charge by the colloidal particles as a result of adsorption of charged surfactant molecules and charged polymers [169]. Regardless of the mechanism that results to charge on colloidal particles, any charge stabilised colloidal dispersion must have (1) charged particles and charges that, for all purposes of practical can be assumed to be attached to the particles, and (2) counter ions, which are the ions that are released into the solution when the particle acquires surface charge.

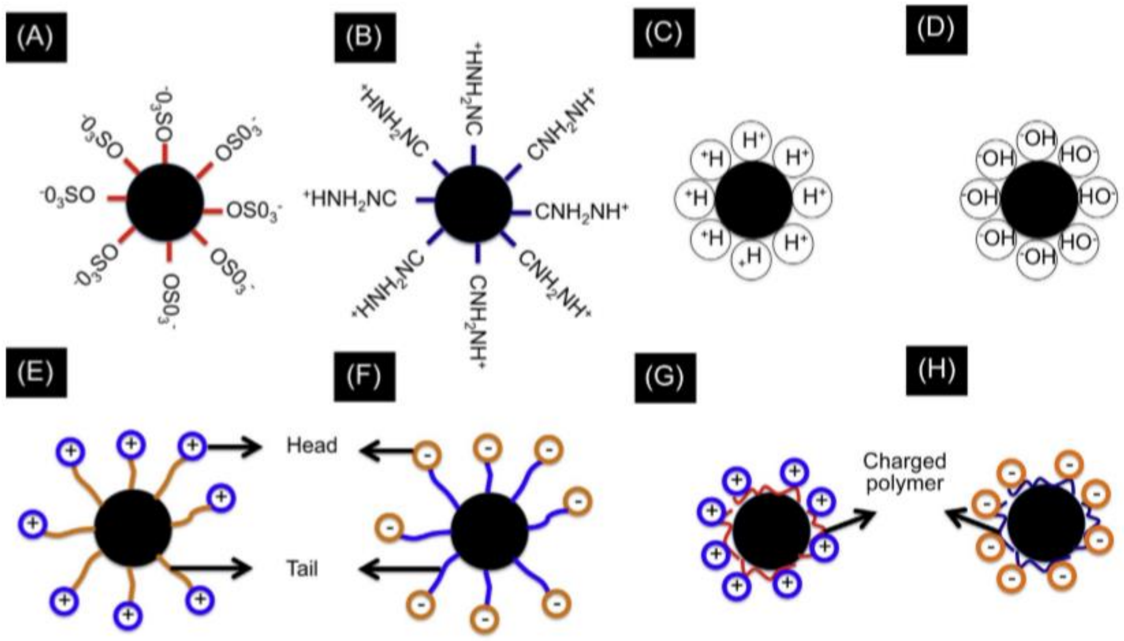


Figure 2.39: Representation of different mechanisms that result in charge on particle surface

dissociation of covalently attached chemical species on particle surface (A, B),
adsorption of ions (C, D),
surfactant molecules (E, F), and
charged polymers or polyelectrolytes (G, H) *[169]*.

The total charge on all the colloidal particles in the dispersion must be equal but opposite in magnitude to the total charge of all the counter ions in the dispersion so that the dispersion is electroneutral [169].

2.10.3. Refractive index Matching

This method of stabilisation of colloids involves the dispersion of particles in a solvent whose refractive index is same as that of the particles [169]. This will ensure that the widely present van der Waals forces of attraction between the particles become negligible. Silica particles dispersed in ethoxylated trimethylolpropane triacrylate is one example of index matched colloidal dispersion [202].

2.10.4. Depletion stabilisation

The depletion stabilisation involves the addition of nonionic polymers to colloidal dispersion. Unlike steric stabilisation of particles, in depletion stabilisation, polymer molecules that are added to a colloidal dispersion are not adsorbed onto the particle surface and are free to move

[203]. When particles that are in a pool of polymer solution approach each other, in general, the polymer molecules between the particles are expected to leave the gap i.e., the region between the particles. That is, the polymer is supposed to deplete from the region between the particles. However, when the interaction between the polymer and the solvent is preferred, i.e., when the polymer is in a good solvent, polymer remains in the region between the particles, as this is energetically more favoured. In such cases, the polymer molecules continue to exist between the particles and this provides excellent stability to colloidal dispersions via what is called the depletion stabilisation [204-206].

2.11. Colloidal interaction

It is important to tune the interaction forces or the energy of interaction between colloidal particles in a dispersion when designing optimal solution processing routes for the fabrication of novel materials. The structural and functional properties of the final materials derived following solution processing can be modulated by a precise control of the colloidal interactions [170]. The control of colloidal interactions can be used to create a wide assembly of colloids and nanoparticles that can be used in many applications in different industries. A good understanding of the colloidal interaction can be used to predict stability, induce de-stabilisation of particles in the dispersion and also improve transport properties of the dispersion [169]. For example, many operations such as slurry transport , demand that single particles in a colloidal dispersion are well dispersed so that there is no aggregation on the other side, certain operations like water treatment rely on the aggregation of particles of flocs so that unwanted particles are effectively and efficiently removed by gravity sedimentation [169].

When more than two particles in a dispersion are very close, they tend to interact with each other and feel the presence of the other. The interaction may be attractive or purely repulsive or a combination of both between the colloidal particles, analogous to atomic and or molecular interaction [169].

2.12. Silica Nanoparticles

In this work, silica nanoparticles were selected to produce the nanofluids. Because silica nanoparticles (SiNPs) have a well-known and controllable surface chemistry, they were always used conventionally. Silica NPs can be made easily in defined sizes with low size dispersity and they can be prepared in large amounts without altering the desired particle properties [171]. As mentioned earlier, the Stöber method was used to prepare the SiNPs. In this method involves the hydrolysis of TEOS [$Si\ (OEt)_4$] into silanol monomers [Si- (OEt)4−x(OH)x], and the condensation of the silanol monomers into a siloxane network where x and 4 – x represent the number of silanol and ethoxy groups , respectively (x = 1 – 4) [207] to produce SiNPs of well-defined sizes, terminated by hydroxyl groups. The particles can then be functionalised by condensing a functional group bearing a silane on the surface producing particles of known surface functionality [208-211]. A simple method which could act as an alternative was created by Nakayama and Ishimura in which a single silane bearing precursor, with a functional group attached is reacted in a single reaction to produce particles of the desired size and functionality [212]. However, Mangos et al. [213] modified the method hence producing on a large scale particles of controlled size and functionality.

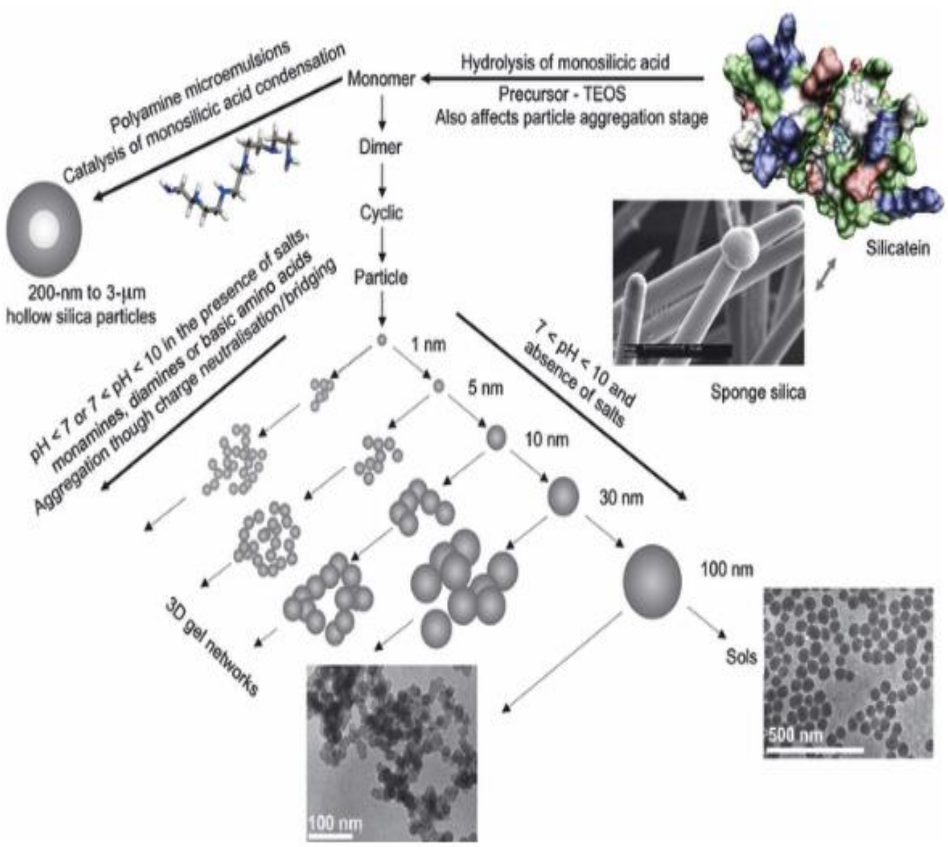


Figure 2.40: Pathways to silica formation orthosilicic acid through oligomers to particles and aggregated structures [214]

2.12.1. Growth Mechanism

Organosilane monomers growth into larger structures is influenced by the pH, temperature, alkoxide concentration and the solvent effect [207]. If the silica structure is formed below a pH of 7, it results is a porous 3D gel shown in Figure 2.40. On the other hand, above acidic conditions, the oligomers of the particles are largely unchanged, facilitating their contact and allowing greater connectivity to occur [207]. The intermediate silanol group will be highly charged under basic conditions hence stabilising the particles as they are formed and allowing them to remain separate and discrete [215]. The specific conditions of formation determine the size and uniformity of the particles. As seen from Figure 2.41 solution pH affects the structure produced.

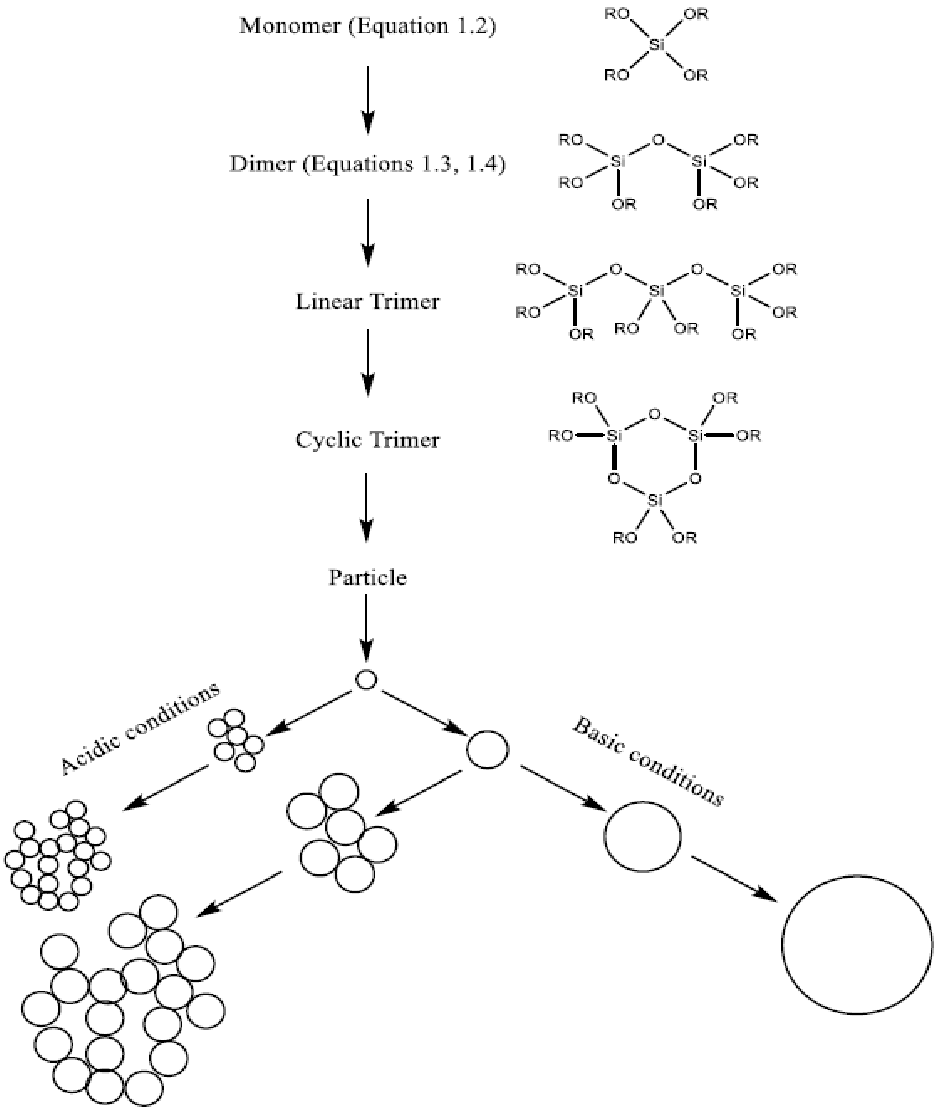


Figure 2.41: Structure of silica formation pathways from silane precursors [214]

No matter the silane precursor used, the reaction can be expected to proceed as shown in Equation 2.13 - Equation 2.15.

$$\mathrm{Si(OR)_4} \xrightarrow{\text{hydrolysis}} \mathrm{Si(OR)_3OH + ROH} \xrightarrow{\text{condensation}} \mathrm{Si(OR)_4} \tag{2.13}$$

$$2(\mathrm{Si(OR)_3OH}) \xrightarrow{\text{condensation}} \mathrm{(OR)_3SiO(Si(OR)_3) + 2H_2O} \xrightarrow{\text{hydrolysis}} 2(\mathrm{Si(OR)_3OH}) \tag{2.14}$$

$$\mathrm{Si(OR)_3OH + Si(OR)_4} \xrightarrow{\text{condensation}} \mathrm{(OR)_3SiO(Si(OR)_3) + ROH} \xrightarrow{\text{alcoholysis}} \mathrm{Si(OR)_3OH + Si(OR)_4} \tag{2.15}$$

Linear are formed from dimer, then cyclic trimers, forming the particle precursors through repeated hydrolysis and condensation reaction [214]. Under basic conditions, the condensation reaction is always assumed to progress through the nucleophilic attack of the deprotonated silanol group on an unchanged silanol. Further condensation reactions can occur following the condensation hence increasing the size of the particle [216]. Since OSi is a better electron withdrawing group than OH, which in turn is better than OR, this means the more substituted silicon centres are favoured for reaction compared to monomers or dimers thus resulting to particle growth [216]. A clear mechanism of this particle growth is well studied in the literature with three major proposed mechanisms: a nucleation growth model such as the LaMer model, a controlled aggregation model, or a combination of the methods as shown in Figure 2.42.

LaMer model of particle growth suggests that the monomer concentration in solution increases to a critical level at which point, nucleation sites form [217]. Immediately the concentration is reduced below the critical value thus preventing the formation of additional nucleation sites. The sites are charge stabilised in solution under basic conditions preventing their aggregation. Larger particles will then result from particles growing through the addition of monomer units to the growing sites [207, 215].

According to controlled aggregation mechanism, nucleation continues throughout the reaction forming small primary particle units [218]. The primary particles will be small, showing poor colloidal stability and a tendency to aggregate. The formed aggregation form into large stable particles throughout the reaction. In mixed models, it suggests both reactions occurring with the formation of primary aggregating units as the first stage of the reaction [207]. The aggregates will be formed by the primary particles until the monomers concentration in solution falls below the critical nucleation concentration preventing the formation of new primary particles [219]. There is precise research into growth mechanism of Stöber silica particles which has been undertaken by many researchers across a broad timeframe considering a wide range of conditions as well as requirements for the formed particles.

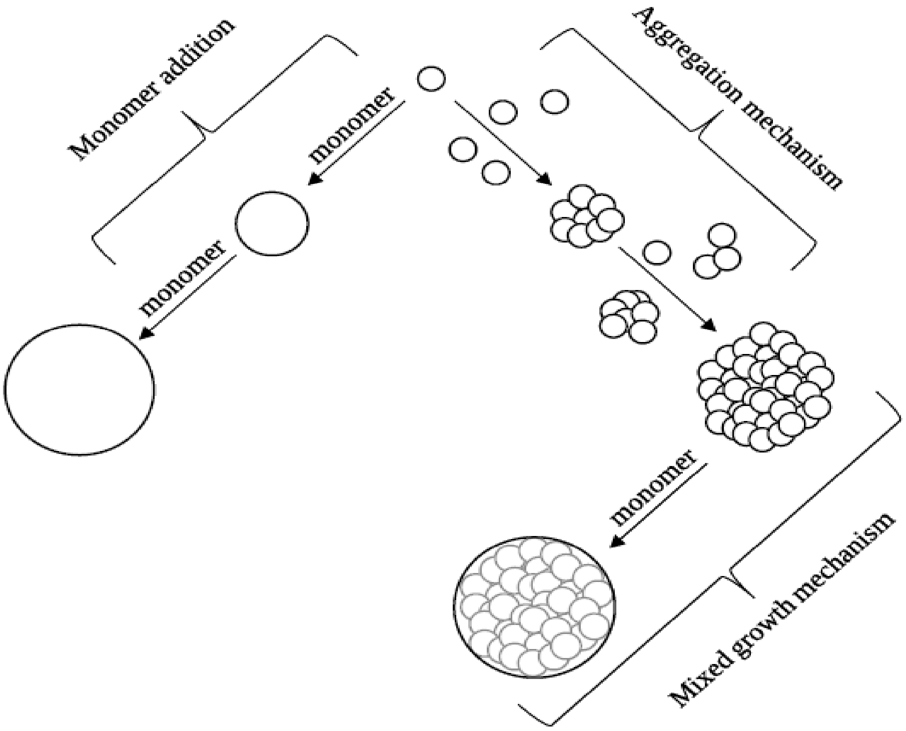


Figure 2.42: Representation of stober silica particle growth by monomer addition, aggregation, or mixed mechanisms [219]

2.13. Silica Nanoparticles Synthesis and Characterisation

2.13.1. Silica Synthesis by Stöber method

Nanoparticles were prepared by the sol-gel process on the basis of the Stöber well know method. The synthesis of nanoparticles was facilitated by the hydrolysis and condensation of tetraethyl orthosilicate as a silica precursor in a mixture of ethanol/methanol and water with ammonia solution as a catalyst to start the reaction [171]. Ethanal/methanol and water acted as solvents. Silica preparation followed the following process and conditions were altered to acquire the required sizes. This study also involved preparing silica using different synthesis methods to compare the sizes under different synthesis conditions such as different catalyst or solvent.

In brief, initially 2.35ml (0.015 mol) of tetraethyl orthosilicate (TEOS) was mixed with 13.5 mL (0.5 mol) of absolute ethanol. The mixture was stirred at room temperature. After 5 minutes, 0.5 mL (0.03 mol) of pure water (Milli-Q water), 2.27 mL (0.12 mol) of ammonium hydroxide and 13.0 mL of absolute ethanol was added into the solution which yields a total volume of ~35.0 ml. The reaction was allowed to continue for 6 hours under magnetic stirring for completion at room temperature. The resultant solution was directly evaporated at 45 ° C. As mentioned earlier, the precursors (TEOS, ammonia and water content) were varied to figure out the changes in size of the Silica nanoparticles. The effects of altering these parameters were observed from the DLS (Dynamic Light Scattering) technique and DCS (Differential Centrifugal Sedimentation) also known as (CPS Disc Centrifuge System). Figure 2.43 illustrates the procedure for the preparation of silica nanoparticles. Some of the tried parameters are tabulated in Table 2.12. it should be noted that all concentrations were calculated based on the final reaction mixture concentration.

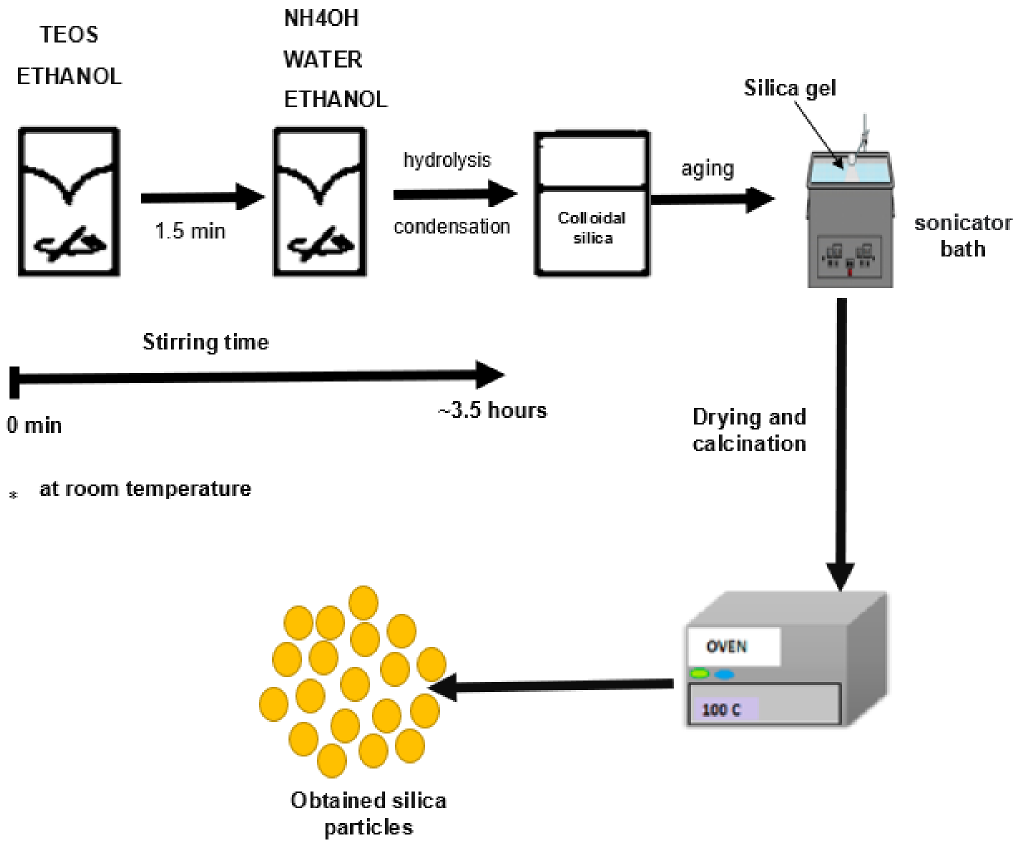


Figure 2.43: Silica nanoparticle preparation procedure [220]

The appearance of the resulting mixture can give a rough estimate on whether the particle size is small or large. The size from small to large results in a transparent mixture that turns into a white cloudy suspension. More to the above, the drying step that includes the centrifuge process and evaporation processes according to particle size can be determined. Both centrifuge and evaporation processes can be applied to obtain the solid powder if the size of the particles is larger than ~20nm. However, if the size of the particles is smaller than ~20nm, the evaporation process should be applied to get the solid powder [169].

In 1968, Stober et al. [171] reported a pioneering method for the synthesis of monodispersed spherical silicon dioxide nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of a catalyst ammonia. Different sizes of nanoparticles ranging from 50nm to 1μm were prepared with a narrow size distribution [171]. The sizes depended on the type of silicon alkoxide and alcohol [221]. In this method, the hydrolysis of Tetraethyl orthosilicate (TEOS) using ammonia as a catalyst and ethanol as a solvent was involved. TEOS, water, pentanol and ammonia were used as precursors [222]. Under ammonia catalysis, TEOS was mixed and stirred vigorously with water and glyceryl alcohol at room temperature.

The preparation of an aerogel was discussed by Peri [223] where TEOS was being hydrolyzed in the presence of hydrochloric acid (HCI), the gel was altered in water at 100 °C, and the water was replaced by methanol and the gel was dried. The same method was studied further by Stolarski et al. [224], different tetrafuntional siliconalkoxide precursors were used to synthesize the silica gels which was denoted as $Si(OR)_3$. There are five stages involved in the process of silicon alkoxides and they include: production of monomers by hydrolysis of precursors; formation of siloxane bonds and oligomers through the condensation and polymerization; growth of particles and clusters; gelation; and aging [192, 224]. As mentioned earlier, spherical silica nanoparticles that range in 5-2000 nm can be synthesized by using this method. The hydrolysis reaction in general is as follows:

$$\mathrm{Si(OR)_4 + H_2O \quad \rightarrow \quad (OR)_3SiOH + ROH} \tag{2.16}$$

Singly hydrolysed TEOS monomer [(OR3) Si (OH)] are produced by the hydrolysis reaction. Eventually, this intermediate reaction produced condenses to lastly form silica [192].

$$\mathrm{(RO)_3Si(OH) + H_2O \quad \rightarrow \quad SiO_2 + 3ROH} \tag{2.17}$$

The hydrolysis of the silicone alkoxides $Si(OR)_4$ and subsequent polycondensation is due to the gelation of silicon alkoxide solutions which leads to the formation of polymers and particles with siloxane bonds [225].

2.14. Sol-gel previous studies

From previous research, Rao et al. [226] used tetraethyl orthosilicate (TEOS) as a precursor material. Several reports have also reported the production of silicon dioxide aerogels using Tetraethoxysilane (TMOS) precursor, but TMOS is five times costlier compared to TEOS and also toxic which can cause blindness [226]. The authors presented the use of two step sol-gel process for production of silicon dioxide aerogel using low cost and environmentally friendly metal alkoxide precursor, TEOS.

The influence of TEOS as a precursor, concentration of acid and NH4OH, temperature and hydrolysis time on the rate of gelation were studied by Boonstra et al. [227]. The author observed that the gelation time increased as the hydrolysis time increased and higher ethanol concentration would increase the gelation time. Some important parameter for controlling synthesis conditions include water content, the solvent, concentration and type of catalyst used [227]. The influence of solvent nature on the rate of synthesis has been classified into either polar or nonpolar and as protic or aprotic. Aprotic solvent is unable to be deprotonated to form enough strong nucleophiles which are necessary for the hydrolysis process [228]. Table 2.13 below shows the classification of solvents.

Table 2.13: Solvents classifications [228]

Protic Polar Solvent	Aprotic Polar Solvent	Nonpolar
Methanol	Dimethylsulfoxide (DMSO)	Dioxane
Ethanol	Dimethylformamide (DMF)	Benzene
Formamide	Acetonitril	Hexane
Water	Acetone	Chloroform

The acidic synthesis route of mesoporous silica (pH < 2.0) could usually lead to many topological constructions [229]. Stucky et al. [229] also reported that silicon dioxide can be synthesized in either the alkaline route or the acid route both using amphiphiles as templates. The precursor of silicon dioxide while taking the acid route could be silicon alkoxides. The acid catalysis speeds the hydrolysis versus the condensation rate and condensation is promoted at the ends of silicon dioxide polymers to form linear silicate ions. The alkaline route results to highly condensed and compact structure and the acid route leads to a more fuzzy and soft network [230]. More so, the important parameters that affect the structure are precursor type, nature of catalyst, aging time, aging temperature, drying time and drying temperature [231].

According to Yin et al. [232] nanoparticles were of silicon dioxide films prepared from hydrolysis of tetraethyl orthosilicate (TEOS) catalysed by R_4NOH in water medium using the sol gel process. The formation of silicon dioxide gel was after annealing at high temperature.

2.15. Summary of the literature

The literature has shown that the challenges of drilling in HPHT conditions are far from being solved completely regarding to degradation. The industry is gearing in the direction of using drilling mud additives which are environmentally friendly, cheap and can at the same time similarly perform as OBMs in HPHT environments. Even though different vegetable oils have been used as a replacement of diesel oil, the stability of these muds has always been questioned and found short under HPHT conditions. These muds have not solved the issue. The current trend has led oil and gas companies to focus on nanoparticles due to their size, stability surface area to volume ratio and ease to modify. The gap in the industry is that even though nanoparticles have been widely received, they are very expensive and often have led to increased cost of drilling operations. In addition to that, NPs have not been able to single handily offer the needed drilling mud properties therefore, other additives have to be added to supplement their performance. Therefore, a cheap NP is needed to reduce drilling costs.

No.	Author/ Date/Study	Study purpose	Methodology	Equipment used	Pressure/ Temperature	Nanoparticle characteristics	Concentration	Targeted rheological properties	Main finding
1	Al Ruqeishi, M.S. Al Salmi, Y. Mohiuddin, T. 2018 Nanoparticles as Drilling muds Rheological Properties Modifiers.	To investigate the fluid loss, density and viscosity on the water-based fluid from Wadi Laithm oil filed located in southern Sultanate of Oman. Evaluate the rheological properties of the drilling mud.	The mud fluids were prepared and investigated before and after adding carbon nanoparticles and ZnO nanoparticles.	Filter Press API (LPLT) from Fan. Dynamic viscometer expert series from fungi lab. Anton Paar DMA 5000 – Fluid density. Scanning electron microscopy (SEM)	100 pa Temperature: 25 °C, 35 °C, 65 °C, 85 °C	Carbon nanoparticles (CNp)(Diameter 50-250nm, lengths between 0.5- 5µm, purity>99%, Shape-Semi-spherical) ZnO Nanowires (Diameter 74±16 nm, Length 1.3±0.10µm)	1, 2 and 3 grams	Density Filtrate loss Borehole cleaning properties	A carbon nanoparticle additive succeeded in hindering the drilling mud from the sagging effect for more than three weeks in time. Drilling mud densities and viscosities were increased by the addition of 1-3wt. % from carbon nanoparticles and/ or ZnO nanowires. Nanowires additives increased the drilling mud densities two times more than the spherical carbon nanoparticles. The drilling mud water loss was reduced significantly after the addition of a small fraction of carbon nanoparticles, which is important in lubricating the drilling bit and controlling the fluid viscosity.
2	Guan, O.S. Gholami, R. Raza, A. Rabiei, M. Fakhari, N. Rasouli, V. Nabinezhad, O. 2018 A nanoparticle-based approach to improve filtration control of water-based muds under high pressure high temperature conditions. *Petroleum*.	To design a nano base fluid using Nano Glass Flakes (NGFs) as a cheap but efficient to improve the filtration control of WBM.	A series of rheological, filtration loss and conductivity test were carried out on NGFs.	FANN Multimixer 9B FANN Model 35 Viscometer FANN Series 300 LPLT Filter ANN Model 175CT HPHT Filter Press	LPLT- 77 °F & 100 psi HPHT- (600 psi & 100 psi back pressure at 50 ° F	Nano Glass Flakes 100 nm	0.5 wt.%, and 1.0 wt.%	Plastic viscosity (PV) Yield point (YP) Gel strength	The results obtained indicated that by adding NGF, without modification increased the yield point, plastic viscosity and the gel strength of the drilling muds which may not be desired. Alternatively, the yield point, plastic viscosity and gel strength decreased once modified NGFs were used. Filtration loss tests indicated that the modification of NGFs using surfactant Hexadecyltrimethylammonium bromide (CTAB) helped to create a strong and rigid structure network formed by the ionic interaction hence reducing filtrate loss of the muds under LPLT and HPHT conditions. The mud cake thickness and permeability were also decreased upon adding the modified NGFs. The good thermal properties of NGFs and improvement of mud conductivity was another good characteristic which improved the electrical conductivity and drilling efficiency.
3	Bayat, A.E. Moghanloo, P.J. Piroozian, A. Rafati, R. 2018 Experimental investigation of rheological and filtration properties of water-based drilling muds in presence of various nanoparticles.	To determine the rheological properties of a bentonite -WBM in presence of various metal oxide NPs. Finding the optimum concentration of the NPs	The NPs were dispersed in the bentonite drilling mud with concentrations of 0.01, 0.05, 0.1 and 1 wt%. Thereafter, plastic viscosity, yield point, gel strength, filtration loss and filter cake thickness were evaluated, and the results were compared to each other.	X-ray diffraction (XRD, model D5000, SIMENS). Transmission electron microscopy (TEM, model JEM-2100/HR, JEOL, Acc.200.00 kV) Mixer V-G meter viscometer Filter press (Series 300 A	LPLT- 27 °C & 100 psi	Al_2O_3 (40 nm, purity 99% and specific surface area 60 m^2 /g). TiO_2 2 (40 nm, purity 99.5%, specific surface area 50–100 m^2 /g) CuO (40 nm, purity 99% and specific surface area 50 m^2 /g). SiO_2 2 (40 nm, purity 99.5% and specific surface area 160 m^2 /g).	0.05,0.1, 0.5 and 1 wt.%	Plastic viscosity (PV) Yield Point (YP) Gel strength Filtration loss Filter cake thickness	Plastic viscosity, yield point and gel strength of the Bentonite-WBM were increased by adding Al_2O_3 NPs that are favourable. Al_2O_3 NPs also increased the Bentonite-WBM fluid loss which was undesirable Utilizing Al_2O_3 NPs to improve the Bentonite-WBM rheology was not recommended TiO2 and CuO NPs resulted in decreasing of plastic viscosity, yield point and gel strength. These two NPs at concentrations below 0.5 wt% are recommended additives to improve the Bentonite-WBM rheology SiO_2 NPs revealed a good improvement in the bentonite-WBM rheology and acceptable enhancement in the characteristics of the final mud product in terms of filtrate loss and filter cake.
4	Smith, S.R. Rafati, R. Haddad, A.S. Cooper, A. Hamidi, H. 2018 Application of aluminium oxide nanoparticles to enhance rheological and filtration properties of water-based muds at HPHT conditions.	To evaluate the apparent viscosity (AV), Plastic viscosity (AV), yield point (YP), gel strength after 10 sec and 10 min and filtration properties of water-based fluids (WBFs) with added aluminium oxide NPs ate LPLT and HPHT conditions.	Rheological properties and filtration properties both at LPLT and HPHT conditions measure both for a WBM with added aluminium oxide NPs compared against base sample with no NPs and comparisons were made of fluids with aluminium oxide and samples of silica NPs with same concentrations Shear stress versus shear rate was evaluated. Filtration test was performed base on the standard API filter press test	OFITE-800 viscometer at normal pressure normal temperature (NPNT) Fann 35SA viscometer higher temperatures OFITE filter press (NPNT) Fann HPHT 175 ml filter press (HPHT)	Filtration test of Base WBF & NPFs at NPNT (23 °C and 14.7 psi) At HPHT (up to 120 °C and 500 psi) Enhanced NPFs Rheology At 50 °C and 80 °C HPHT filtration test 120 °C and 500 psi for 30-min Aging done 16 h at 120 °C and 100 psi.	Aluminium oxide NPs, (thermal conductivity, around 30 Wm−1 K−1, and surface area of 40 m2/g, small balls) Silica NPs (thermal conductivity of 1.4 Wm−1 K−1 and surface area of 175–225 m2/g, powdery texture).	0.1, 0.2, 0.5, 1 wt.%	Plastic viscosity Yield point Gel strength Apparent viscosity	The dispersion of aluminium oxide nanoparticles increased the thermal stability of the fluid, considerably more than the base sample and the sample with silica NPs Overall aluminium oxide NPs in low concentrations enhanced the thermal stability of the WBF and provided lower degradations compared to the base sample and the samples with silica NPs. The HPHT filtration for the sample with aluminium oxide NPs had lower increase in filtrate volume than the base sample, and the sample with silica NPs. Lower increase in shear stress for the sample with aluminium oxide NPs compared to the base sample and the sample with silica NPs.

5	Katende, A. Boyou, N.V. Ismail, I. Chung, D.Z. Sagala, F. Hussein, N. Ismail, M.S. 2019 Improving the Performance of Oil Based Mud and Water Based Mud in a High Temperature Hole using Nanosilica Nanoparticles	To design a water-based and oil-based nano muds in order to achieve their functionalities from the commencement of drilling process to its cessation using Nano silica as an enhancing nanosized additive.	The methodologies in this study were based solely on laboratory experimental work. The rheological property tests were conducted according to the recommended practice of API RP 13B-1 for examining a drilling mud.	FANN Viscometer. Electronic balance Transmission Electron Microscope (TEM) Multi-mixer LPLT & HPHT filter press OFITE Lubricity Tester	100 psi Temperature range of 77 °F - 300 °F.	Nano silica 14 nm	0.5, 1.0, and 1.5 wt.%	Plastic viscosity Yield point Gel strength (10 sec & 10 min) Lubricity	Nano silica effectively dispersed without using an ultrasonicator by only altering the pH of the mud, Nano silica effectively improved most of the rheological properties of both WBM and OBM even though the API and HPHT fluid losses had to be improved. The optimum concentration of nano silica in OBM in improving rheology was 0.5 ppb. The optimum concentration of nano silica that effectively enhanced the rheological properties of WBM was 1.0 ppb.
6	Anoop, K. Sadr, R. Yrac, R. Amani, M. 2019 Rheology of a colloidal suspension of carbon nanotube particles in a water-based drilling mud	Aim was to study the rheological properties of WBM with Multi-walled carbon nanotubes (CNT) nanoparticles at HPHT. To Study the effect of temperature and pressure for the various particle loadings of nanoparticles at different shear rate.	HPHT experiments were conducted to study the rheological characteristics of the base mud and CNT-Nano mud suspensions.	HPHT viscometer Chandler Viscometer 7600 Hamilton Beach single spindle mixer	Pressure: 170 MPa Temperature ambient to 180 ^{0}C	MWCNT (≥98% carbon basis, O.D. x I.D. x L-10 nm ± 1 nm x 4.5 nm ± 0.5 nm x 3 – 6 μm)	0.027%, 0.056%, 0.11%, 0.22%	Plastic Viscosity	Both WBM and CNT mud showed shear thinning behaviours at all experimental conditions. Addition of CNT particles increased the viscosity of the drilling mud. Addition of 0.22 wt.% CNT lead to increase in viscosity five folds compared to that a base mud at ambient condition. The viscosity of the base mud increased with an increase in pressure. Similar observation was seen for the nano mud at low concentration, however at higher concentration, CNT mud viscosity values decreased with an increase in pressure. Viscosity of base mud as well as nano mud at low concentration increased at first with increase in temperature but after 100 ^{0}C the trend reversed with increase in temperature. Further increase in CNT concentration lead to viscosity decrease with increase in temperature similar to that of WBM.
7	Cheraghian, G. Wu, Q. Mostofi, M. Li, M.C. Afrand, M. Sangwai, J.S. 2018 Effect of a novel clay/silica nanocomposite on water-based drilling muds: Improvements in rheological and filtration properties.	The objectives of this study were as follows: To develop an effective solution to improve rheological properties and reduce the filter cake created by drilling muds with addition of NPs. To compare the performance of nanoparticle impregnated WBs (nano-WBs) with conventional base WBs.	Clay and silica were used to synthesize a nanocomposite as a fluid loss additive. The rheological and filtration loss properties of WB were investigated with the addition of Clay/SiO2 and SiO2 nanoparticles in varying concentrations.	Rheometer Model35 Viscometer HPHT filter press	Rheological tests at 25 and 90 ° C. Filtrate test at 25 °C. 100 psi.	Fumed silica Sodium bentonite clay	0.1, 0.5, 1 and 1.5 wt.%	Apparent viscosity Yield point (YP), Plastic viscosity (PV)	It was found that the CS NPs have improved the rheological stability of drilling mud at higher temperature. The improvement in the rheological stability increases at higher concentrations. NPs also found to improve the filtration loss properties significantly The NPs at higher concentrations yielded thin and compact filter cakes. The results of the tests showed that CS and SiO2 NPs can improve the filtration by an average of 60 and 45% at low temperature, and 65 and 10% at higher temperature, respectively
8	Ahmadi, A. Monjazi, M. Pirbaloti, B.A. 2018 Investigation of the effect of nono-silica particles on heat specific properties of water-based drilling muds and rheological properties.	In this study, the impact of silicon oxide nanoparticles on improving the performance of heat transfer behaviour and specific heat capacity of drilling mud was examined.	At first, a base drilling mud sample is used as the basis for measuring other samples. Then, various other samples were prepared by adding nanoparticles at different concentrations. After that, the specific heat capacity was measured for two types of nanoparticles with different hydrophilic and hydrophobic	Viscometer Fann. PH meter.	0 -76 °C	silicon oxide (SiO_2) 10 – 20 nm	0.1, 0.3, 0.8, 1, 1.5, 3, 5 wt.%	Plastic viscosity (PV) Yield point (YP) Gel strength Apparent viscosity Thermal stability	Increasing the concentration of nanoparticles increases the rheological properties of bentonite-based and smectite-based drilling muds. By increasing the concentration of nanoparticles to a certain extent, the amount of gelatinization properties of the drilling mud decreases and again become incremental from a specific concentration onwards. Changes in the amount of gelatinization in the drilling mud are because of changes in the cation exchange

			properties at different concentrations and compared with the base mud. Then, the rheological properties of drilling mud are measured as other parameters affecting heat transfer. Rheology changes are measured with Viscometer Fann.						capacity due to the negative charge saturation of nanoparticles in the clay plates. Increasing nanoparticles to the bentonite-based mud system increases the specific heat coefficient of the fluid up to 4960 j/kgc, which is remarkable per se. Increasing nanoparticles to the smectite-based mud system has increased the heat transfer coefficient by 5370. Increasing specific heat coefficient itself will increase the heat transfer coefficient and thus improve heat transfer around the drill.
9	Medhi, S. Chowdhury, S. Gupta, D.K. Mazumdar, A. 2019 An investigation on the effects of silica and copper oxide nanoparticles on rheological and fluid loss property of drilling muds.	To study the effects of NPs in conventional bentonite-based drilling muds (BDF) and non-damaging drilling muds (NDDF).	Characterizing the mud fluids rheological properties Comparing the performance of NPs-based BDF and NDDF with base fluid without NPs. Performances were evaluated by characterizing the mud in ambient as well as after exposing it to bottom- hole temperature (80 °C) for 16 h.	OFITE API filtrate loss equipment Fann viscometer Hot roller oven OFITE mud balance.	200 psi and 80 °C Hot roller oven for 16 h at 80 ° C	Silica (SiO_2), 22–48 nm Copper oxide (CuO), 27–53 nm	0.5%, 0.8% and 1%	Plastic viscosity (PV) Yield point (YP) Gel strength Apparent viscosity	Silica NPs in NDDF enhanced the rheological properties and also gave better fluid loss control in comparison with its effect when used with BDF. Silica NPs emerged as an excellent fluid loss control agent when used in concentrations of 0.5% by weight as it yielded the minimum filtrate loss in the bottom-hole and surface conditions. There was least effect on rheological properties at 0.5% concentration while the performance of 1% by weight of silica NPs in NDDF has showed mud thickening properties. Silica reduced the rheology when used with conventional BDF. But at 0.5%, silica reduced fluid loss in BDF. 1% of CuO in NDDF showed thinning behaviour while 0.5% showed good fluid loss control. When used in BDF, CuO showed greater thinning behaviour, Viscosity decreased with increased in concentration of CuO. However, the fluid loss decreased with increase CuO except for 0.5%.
10	William, J.K.M. Ponmani, S. Samuel, R. Nagarajan, R. Sangwai, J.S. 2014 Effect of CuO and ZnO nanofluids in xanthan gum on thermal, electrical and high-pressure rheology of water-based drilling muds.	Aim was to study the enhancement in thermal and electrical properties of Nanofluid-enhanced WBM (NWBM) prepared using the nanofluids of CuO and ZnO (size <50 nm) in a xanthan gum aqueous solution as a base fluid and used as an additive in WBM.	The nanofluids are prepared using 0.1, 0.3 and 0.5 wt.% concentrations of CuO and ZnO. The prepared nanofluids are added as an additive of 1% (by volume) to WBM. The effect of nanofluids on the thermal and electrical properties of WBM is studied	Rheometer Mixer KD2 pro with KS-1 sensor. PC 700 Eutech Instrument.	Pressures (0.1 MPa and 10 MPa Temperatures 25, 70, 90 and 110 ^{0}C	CuO and ZnO (size < 50 nm	0.1, 0.3 and 0.5 wt.%	Rheological, thermal and electrical properties	The NWBM shows improved thermal and electrical properties by about 35% compared to WBM. An increased concentration of nanoparticles further enhances electrical and thermal properties of drilling muds. The NWBM based on CuO nanofluid show improved thermal properties and are more resistant to HPHT condition than ZnO-based NWBM. The effect of pressure on the rheology of NWBM was more significant at higher temperatures, resulted in better rheological stability in case of NWBM.
11	Bég, O.A. Espinoza, D.S. Kadir, A. Shamshuddin, M.D. Sohail, A. 2018 Experimental study of improved rheology and lubricity of drilling muds enhanced with nano-particles.	Aim was to evaluate the rheological characteristics and lubricity of different nano-particles in water-based mud, with the potential to reduce costs via a decrease in drag and torque during the construction of highly deviated and ERD wells.	The nanoparticle muds were prepared using 0.2 and 0.6 wt.% concentrations of titanium oxide (TiO_2) and silicon dioxide (SiO_2). Analysis of rheology, density and lubricity before and after aging was done to study the effect of nanoparticles.	Lubricity tester Aging cells and oven Viscometer-Model 800 OFITE	Temperatures 26 °C 40 °C 60 °C and 80 °C	TiO2, (Average particle size 30 nm), SiO2 (Average particle size 20–30 nm)	0.2 and 0.6 wt.%	Rheology Lubricity Density	Before aging, silica nano-particles generally result in a decrease in the yield point and apparent viscosity of the drilling mud, which may be related to superhydrophilic characteristics. After aging, and before stirring, greater plastic and apparent viscosity is achieved for silica nano-particles and lower viscosities with the titania nano-particles. Before aging, titania nano-particles achieve the highest efficiency (low plastic viscosity and a high yield point), whereas silica nano-particles showed the lowest efficiency.

									After aging, and before stirring, greater plastic and apparent viscosity is achieved for silica nano-particles and lower viscosities with the titania nano-particles. After aging and before stirring, titania nano-particles cause a reduction in the drilling mud yield point, whereas silica nano-particles cause the opposite effect.

Chapter 3: Materials and Experimental Methodology

3.1. Overview

This chapter presents four (4) distinct methodological approach for developing this study. It provides information about the experimental methodologies including the chemicals used in the experimental work, and the experimental apparatus details. The procedures used in the research work will be detailed starting with nanoparticle synthesis, and lastly preparation of nanoparticle drilling muds.

- **Phase 1 (NP Synthesis):** During this phase, silica nanoparticle synthesis and analytical characterisation techniques will be developed. The experimental conditions will be defined, and the methods for producing powdered silica from colloidal mixture will be described in detail. The process of silica synthesis will be described, as well as the reaction conditions that were changed to achieve different sizes and surface modifications.

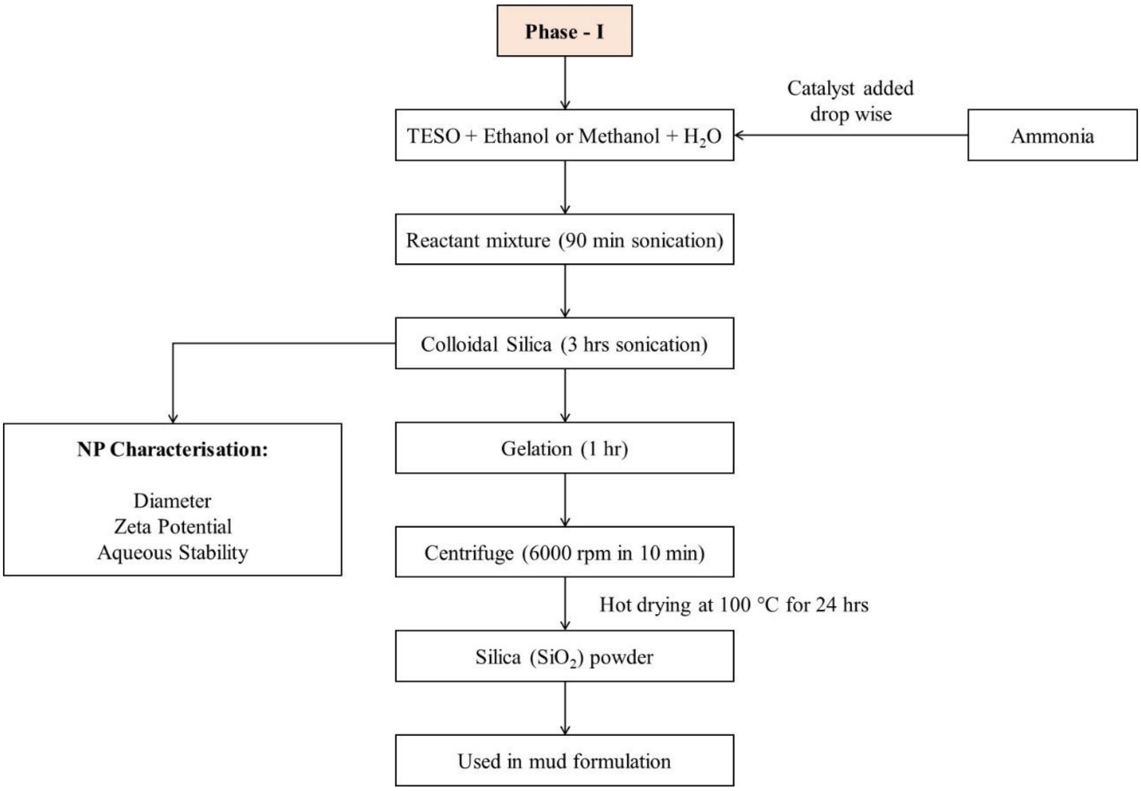


Figure 3.1: Structure and sequence of experimental investigation Phase-I

- **Phase II (Mud Formulation):** The mode of operation used for mud formulation and testing will be detailed, plus the equipment used for mud fluid analysis explained. This phase will also explain the experimental materials involved in this research work. The procedure for testing the rheological properties of the mud formulations will be detailed in this phase. In oil and gas industry, mud formulations are tested to determine their rheological, filtration and other properties. If the mud properties measured are not suitable for a drilling operation, the properties of the mud are varied until the desired values of mud properties are achieved. Therefore. The optimum concentration of nanoparticles in the colloidal mixture will be established. The mud fluid properties obtained will then be used to foresee and predict the design and characteristics of drilling mud systems. The Model 1100 viscometer will be used to investigate the rheological properties of the mud fluids.

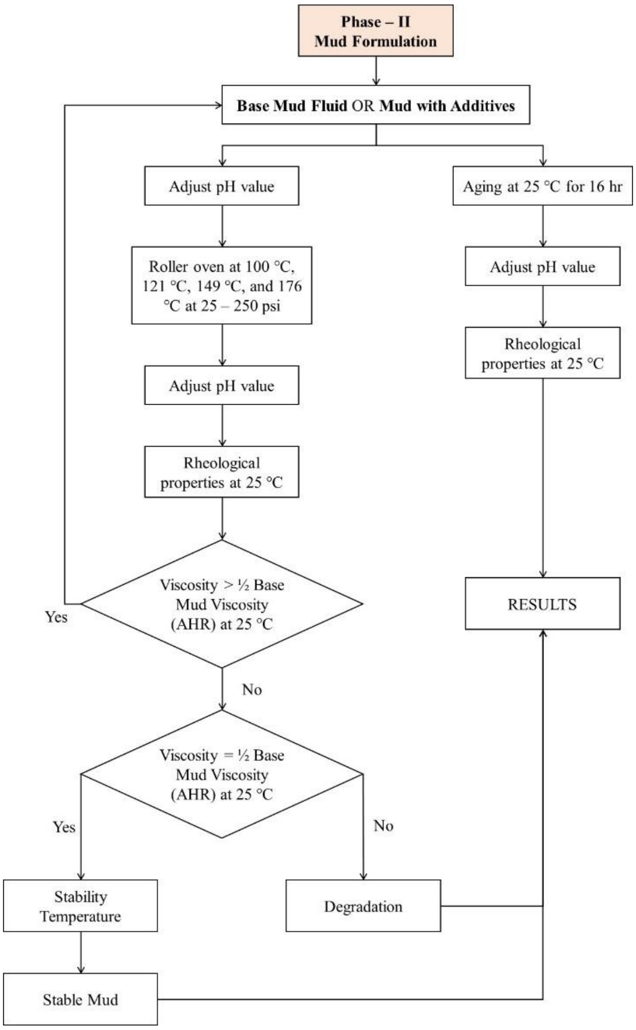


Figure 3.2: Structure and sequence of experimental investigation Phase-II

- **Phase III (NP Surface Modification):** This phase will explain the process of surface functionalisation/modification of silica nanoparticles and the materials used for this purpose. The cationic surfactant grafted on the surface of nanoparticles in order to alter the surface charge of the nanoparticles will be specified.

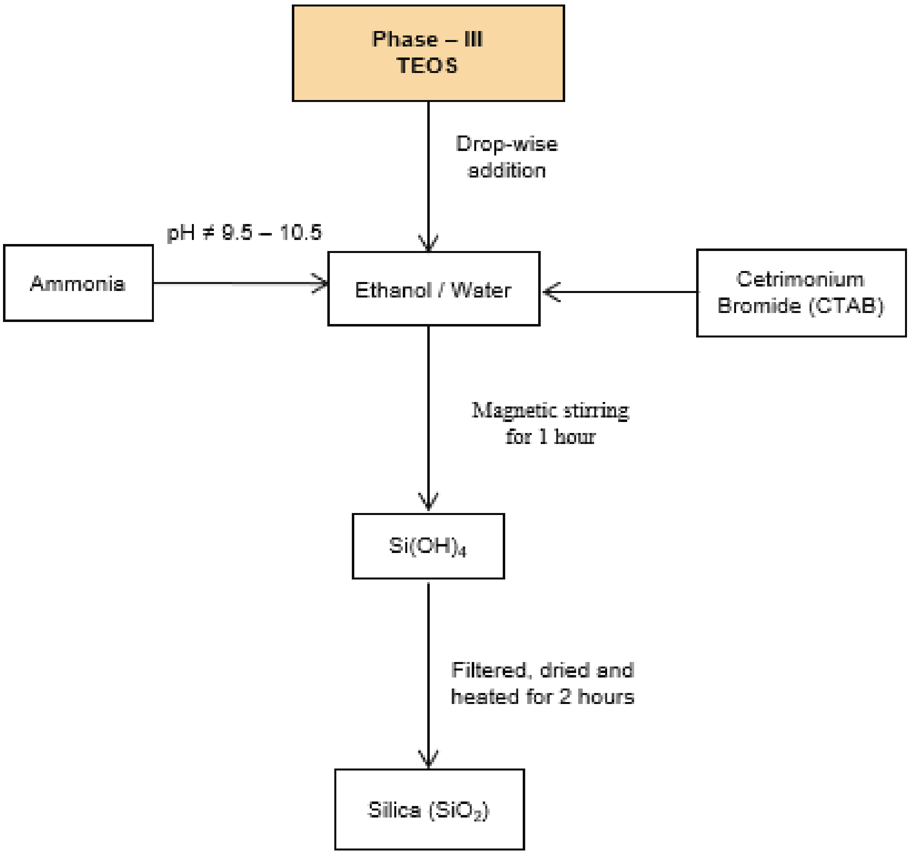


Figure 3.3: Structure and sequence of experimental investigation Phase-III

- **Phase IV (Filter Cake Analysis):** This phase will describe the characteristics of the filter cake produced by the new mud fluid system at high pressure and temperature.

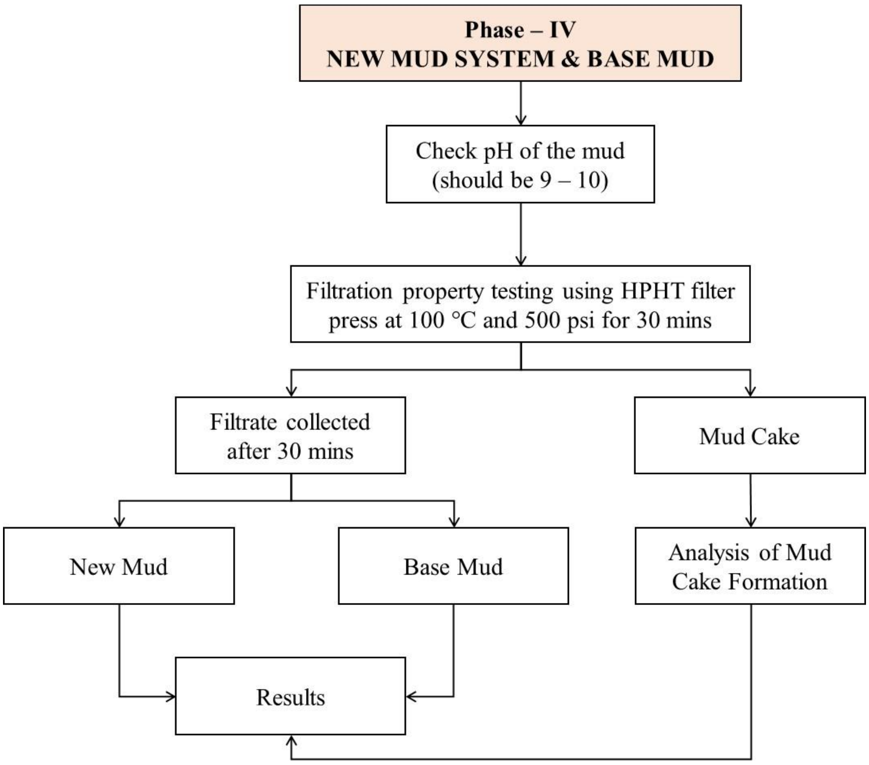


Figure 3.4: Structure and sequence of experimental investigation Phase-IV

3.2. Materials and Equipment

This sub-section presents the materials used in the formulation of silica nanoparticles and the materials use in the formulation of the drilling mud systems.

Fresh water was used as a base fluid, and it also served the purpose of conditioning bentonite and other additives that were used for drilling mud preparation. Sodium bentonite provides the initial viscosity, fluid loss control and cutting suspension abilities. Pipe sticking problems could be controlled by keeping the bentonite clay concentration very low as high solid contents in drilling muds could result to problems like pipe sticking [22]. Barite will be used as a weighting material. These materials were used as a benchmark for designing a control mud system. Chemicals and other materials were used in the synthesis and surface modification of nanoparticles.

Table 3.1: Chemicals and material list

Components	Purity	Molecular weight (g/mol)	Density (kg/m^3)	Purpose
Bentonite	80-90%	180.1	600 – 1100	Filtrate loss preventer, Viscosifier
Barite	98%	233.4	4500	weight material
Sand	99%	60.08		Filtrate loss preventer
polyanionic cellulose	> 98%	1.146	0.7 – 2.85	Filtrate loss preventer,
Hydrochloric acid (HCl)	37%	36.46	1200	pH modifier
Sodium Hydroxide (NaOH)	99%	39.997	2130	pH modifier
Flash water	- 99.96%	18.015	1000	Base fluid for mud preparation
Tetraethyl orthosilicate (TEOS)	≥ 99.0%	208.33	940	Silica precursor
Hexadecyltrimethylammonium bromide (CTAB)	> 95%	364.45	500	Surface charge modifier
Ethanol	> 99.8%	46.069	780	Solvent
Ammonia 28%	28%	35.05	900	Catalyst in the silica synthesis
Milli-Q water	18.2 Megaohm (MΩ-cm)	18.02	1000	Solvent

The equipment used in this study are as follows. This section explains their operating procedures, calibration, sources of error, accuracy and safety measures of operation as described below.

Magnetic stirrer
Dynamic Light Scattering (DLS)/Zetasizer
Differential Centrifugal Sedimentation (DCS)
Scanning Electron Microscopy (SEM)
Centrifuge
Hamilton beach mixer
Model 1100 viscometer
Model 800 viscometer
pH meter
Roller Oven
Aging Cells
Sonicator

3.2.1. Magnetic plate Stirrer

The magnetic plate stirrer (Figure 3.5) was used in this study during the mixing and synthesis of nanoparticles. It was used to shear and mix different solvents and additives that were used in making nanoparticles. This type of stirrer has a temperature range of up to 300 °C. The speed would be adjusted up to 2000 rpm.

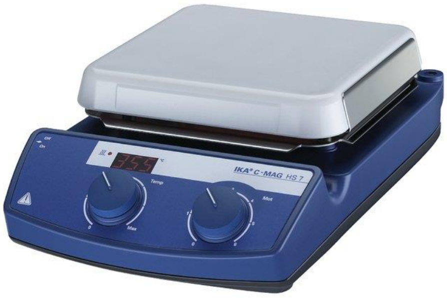


Figure 3.5: Magnetic plate stirrer

<u>Safety</u>

- Has a fixed safety circuit of 550 ^{o}C.
- It has a powerful motor for stirring quantities of up to 5 litres (H_2O).
- It has a Top indicator, hot surface warning to prevent burns
- Exact temperature setting via digital display (LED)
- It pocesses a digital error display
- It has an elevated control panel to protect against leaking fluids.

<u>Procedure</u>

The magnetic plate stirrer device employs a rotating magnetic field to cause a stir bar (or flea) immersed in a liquid to spin according to the set speed thus stirring it. The magnetic stirrer was placed on a stable well levelled surface and a stir bar placed at the bottom of the glass container and then placed on the centre of the magnetic stirrer plate. The liquid to be stirred was filled into the glass container and the on/off switch turned on. The speed was adjusted starting with a low stir rate then the knob was adjusted until the required stirring speed was achieved. After the expected stir time had finished, the stirrer was switched off, and the stir bar removed from the glass container. The stir bar was washed thoroughly with mill-Q water and the glass wares were washed to. They were then placed in the oven to dry and after stored.

3.2.2. Dynamic Light Scattering (DLS)/Zetasizer

The DLS combined with zeta potential applied by Particle Analytical (Malvern Nano Zetasizer) was used to measure the particle size distribution using laser dynamic light scattering and analysis of the Brownian motions of particles in the media. It will measure the particle and molecular size. The diffusion of particles moving under Brownian motion is measured by this technique and converted into size and a size distribution using the Stocks-Einstein relationship Equation 3.1. Therefore, the measured hydrodynamic diameter refers to how a particle diffuses within a fluid. This equipment was used to measure both particle size and zeta-potential. The working range of a DLS is between 1nm to approximately 5 μm [233, 234]. It works on the principle that it analyses dynamic properties and size distribution of a broad variety of physical chemical and biological systems containing different suspended constituents [235]. It is based on extracting of information from time - dependent fluctuations of the light scattered from a spatially limited volume within the sample. When a suspension of particle is hit by a monochromatic coherent beam of light, generated scattered light waves spread out in all direction. The suspended particles of the colloidal dispersion under investigation undergo Brownian motion. This motion results in fluctuation in the distances between the particles and hence also in fluctuation of the phase relations of the scattered light [235]. Laser Doppler Micro-electrophoresis is used to measure zeta potential. An electric field is applied to a solution of molecules or a dispersion of particles which then move with a velocity related to their zeta potential.

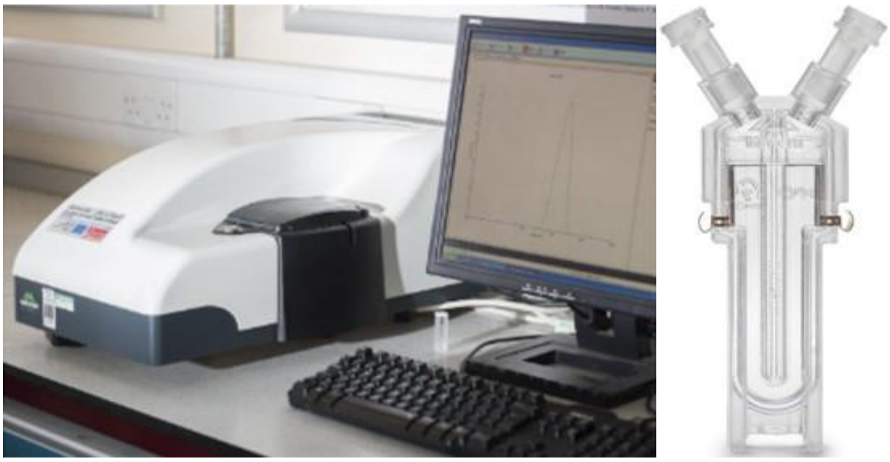


Figure 3.6: Dynamic Light Scattering (DLS)/Zetasizer and Folded capillary cells

Safety

- Minimise Particulate Contaminants as will affect the measurements
- Filter the sample before analysis
- Make sure the sample is concentrated and not dilute
- The folded capillary cells must be clean

Procedure

As mentioned earlier, the DLS measures the hydrodynamic diameter of nanoparticles in solution and provides information on the aggregation state of the nanoparticles in solution. The sample is suspended in a solution to give slight cloudy. A laser is then fired through the sample and the particles in the sample scatter the light in all direction by Rayleigh scattering [236]. The changing distance of the particles due to Brownian motion causes interferences of the light scattered by the neighbouring particles.

By monitoring the intensity of the scatted light time at a fixed angle, this data is mathematically converted into nanoparticle size and distribution within the sample. In other words, the analysis of these occurred time -dependant fluctuations in the scattering intensity gives information about the speed of the particles in the solution. Only a small sample is filled into the folded capillary cell (only 0.1 ml) and the equipment will deal with a range of active concentrations with measurement time only requiring a few minutes (10 minutes). Using a diffusion coefficient, the hydrodynamic diameter of a nanoparticle could be determined [237]. After measurement, the measured data will be Stored in the folder created which then can be exported into excel.

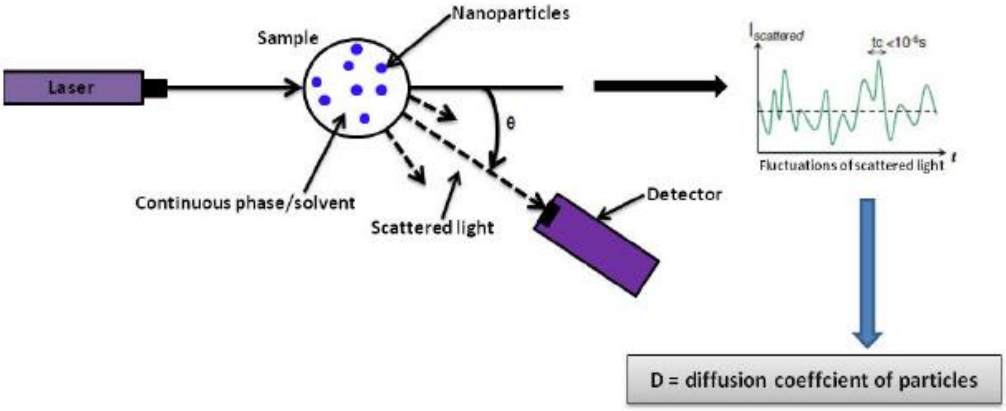


Figure 3.7: Dynamic scattering principle illustration [238, 239]

$$R_h = \frac{k_B T}{6\pi\eta D} \tag{3.1}$$

Where D is the diffusion coefficient of the particles, k_B the Boltzmann constant, T the temperature, η the dynamic viscosity of the continuous phase and R_h is the hydrodynamic radius [239].

3.2.3. Differential Centrifugal Sedimentation (DCS)

The DCS is a new and innovative but simple particle size characterisation technique which has become vital and common in recent years. The recent advances in technology have overcome previous limitations and difficulties of sedimentation and disc design with this technique. The DCS now is a powerful tool in the measuring nanoparticles size distribution down to 2 nm. It has the ability to resolve very close multi -modal particle distributions and to distinguish extremely small shifts and changes in particle size. The particle range for the DCS is from around 2 nm up to 80 microns [240] (exact range will base on density) but the real benefits over other traditional nanoparticle techniques like the DLS are noticed below around 300 nm [240]. The DCS has distinct benefits which include the following.

- Ultra-high resolution capability able to detect, measure and resolve peaks which differ in size by as little as 2%.

- Results are comparable to SEM/Microscopy analysis.
- High sensitivity able to detect and measure extremely small and subtle changes in size distributions for example small additional peaks.
- Quantitative analysis to give weight and number distribution.

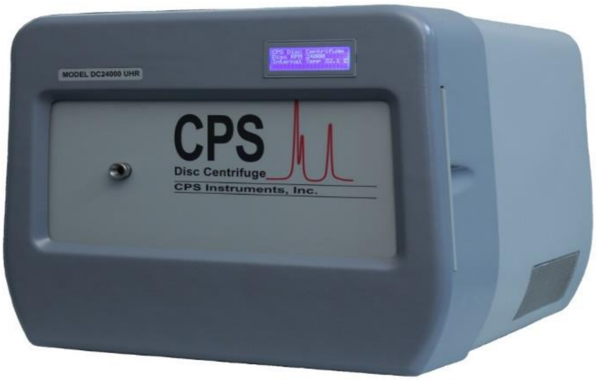


Figure 3.8: Differential Centrifugal Sedimentation

Safety

- Before measure, the disc should be clean and free from any previous samples
- Calibrate prior to each measurement
- Clean the disc housing in case a few drops of the liquid splash off the rotating disc
- Air filters should be cleaned each several months
- Close the door when in operation and during injection, inject in the right position.

Procedure

A typical routine operation of a DCS system is simple and the equipment is easy to use though very delicate if not handled with care. First, the equipment before everything needs to be checked if the disk is clean. Then it is switched on and the centrifuge is set to a correct speed, based on particle size and particle density (usually by retrieving an existing preset methodology from the software. The centrifuge chamber is then filled with the appropriate density gradient fluid. The instrument is calibrated by running a calibration standard making sure that you inject a PVC fluid before every injection. After the calibration is completed, samples are run.

3.2.4. Scanning Electron Microscopy (SEM)

Due to the continuous shrinking of size and dimension of material used in different applications, the SEM has become a powerful and vital tool for characterization of materials. It uses electrons for imaging the same way that light microscopes use visible light [241]. Electrons are created and fired using an electron gun which accelerates down the microscope passing through a series of lenses and aperture hence creating a focus beam which then interacts with the surface of the sample.

Figure 3.9: Scanning Electron Microscopy

Procedure

The sample is placed on the stage in the chamber of the microscope before a vacuum is created in the chamber via a series of pumps. Scan coils control the position of the electron beam above the objective lens. The coils allow for the beam to scan across the surface of the sample, enabling information about a defined area to be collected. The interaction between the sample and the electron creates a number of signals in the form of secondary electrons, backscattered electrons and characteristic x-rays detected by detectors. The images are created by detectors and displayed on the computer screen [241].

3.2.5. MISTRAL 1000 centrifuge

The centrifuge is used to separate particles suspended in a liquid. They work on the principle of separating particles suspended in a liquid according to particle size and density, viscosity of the medium and rotor speed [242]. Within a solution, particles of higher density than the solvent are caused to sink by the gravitational force and those less dense than the solvent are caused to float on the top. Centrifugation takes advantage of small differences in density to separate particles within the solution. As the rotor spins around a central axis, it generates a centrifugal force acting to move particles away from the rotational axis. If the centrifugal force exceeds the buoyant forces of liquid media and the frictional force created by the particle, the particles will sediment.

Figure 3.10: Centrifuge

Safety

- Ensuring the centrifuge is on an appropriate surface level worksurface before operation
- Switch off after use
- Following manufacturer instructions
- Balancing the tubes correctly
- Leave the lid closed when in operation
- Balancing the masses to the nearest 0.1 gram

Procedure

The centrifuge should be on a levelled surface and then switched on. The tubes in the rotor are then balanced by mass to counter the opposite mass. The tubes are covered and then locked tightly. After, the door locked. The speed and time are set and in so doing all this, making sure that the face shield and safety goggles are worn. After setting, press “Start”, and the centrifuge will run.

3.2.6. Hamilton beach mixer

This Hamilton beach mixer Figure 3.11 was used for mixing drilling muds during lab preparations. It was used to shear water and other drilling mud additives to produce a consistent drilling mud mechanically. In this study, the three-speed model was used. The low speed is equivalent to 10, 000 rpm while the medium and high speed are 14,000 and 17,000 rpm respectively.

Figure 3.11: Hamilton beach mixer

Safety

- Personal protective equipment worn during use
- Its cord was unplugged from electric supply after use
- Manufacturer’s operating instructions on electrical shock was followed
- The mixing spindle was not touched while stirring

Procedure

The weighing balance was used to measure the specific amount of solid and powdered additives. A specific volume of Water was measured by a graduated cylinder. The drilling mud additives were added to 350 ml (one lab barrel) of freshwater in the mud mixing cup. The mud mixing cup was placed under the spindle of the Hamilton beach mixer and stirred at room temperature for 30 minutes. Lump materials adhering to the mud mixing cup were scraped off the cup sides after 25 minutes and stirring continued for 5 minutes to complete the 30 minutes.

3.2.7. The Model 1100 viscometer

The viscometer Model 1100 viscometer, which is fully automated, was used to measure the shear stress, shear rate, apparent viscometer, low shear viscosity, yield point (YP), plastic viscometer (PV) and gel strength of drilling muds at 25 °C. The fully automated Model 1100 pressurised viscometer Figure 3.12 is operated with ORCADA software. It is speed (ROM) accuracy is 0.001 and shear rate range (s^{-1}) is 0.01 – 1.002. The accuracy of instrument calibration is the r^2C value equal to or greater than 0.9990 (OFT Testing Equipment, 2015).

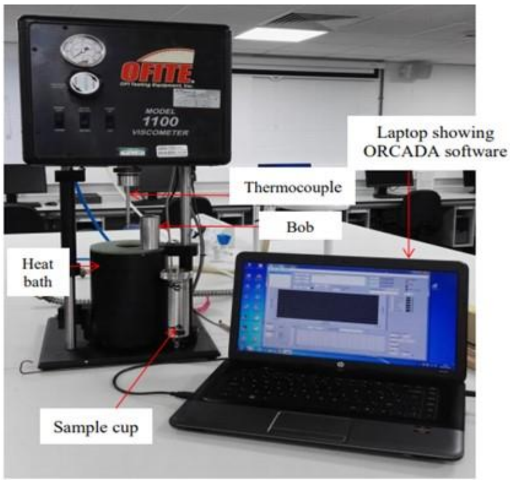


Figure 3.12: Set up for rheological measurement

The back of the instrument is located A three ¼” (6.35mm) NPT fittings. A water source drain horse and nitrogen source are connected to the appropriate fitting. To pressurize the drilling mud sample above temperature of 100 ^{o} C, nitrogen is used to prevent the sample from boiling while water is used to raise and lower the heater. The 9-pi RS232 cable is used to connect the computer to the viscometer, a Local Area Network connection with an Ethernet cable, or Bluetooth (OFI Testing Equipment, 2015).

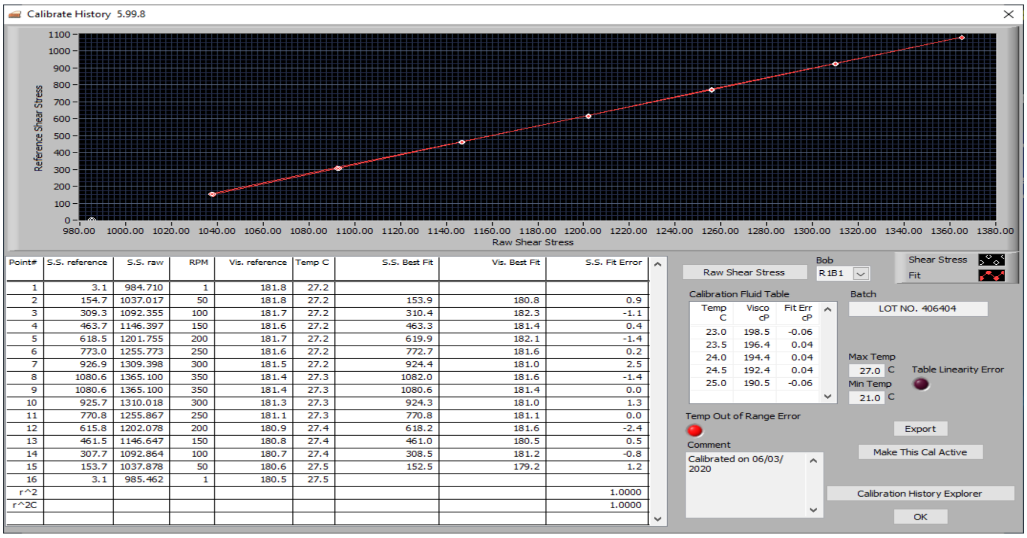
<u>Calibration (OFI Testing Equipment)</u>

The ORCADA calibration program is calibrated before performing any test. Calibration must be done due to following reason:

- The instrument is not used for many days

- The bob is changed
- If operated for two weeks
- The instrument has been serviced
- The r^2 value below 0.99 during a sweep
- Monthly checks must be done when testing drilling muds.

The calibration process started by opening ORCADA software on the computer. Utilities chosen on the menu bar and after “Calibration Shear Stress” was selected. “Shear Stress Raw” value was observed and recorded while the unit was at 0 RPM. The calibrated fluid was used with in the accepted range. The B5 bob was used and the 200cp calibration fluid was used. The speed for calibration were set greater than 0 and les s than 300 and after, the STAR Calibration is pressed. The values of r^2C” was noted and when it is below 0.999, recalibration was done. Below is Figure 3.13 showing a completer calibration of the unite before use.



Point#	S.S. reference	S.S. raw	RPM	Vis. reference	Temp C	S.S. Best Fit	Vis. Best Fit	S.S. Fit Error
1	3.1	984.710	1	181.8	27.2			
2	154.7	1037.017	50	181.8	27.2	153.9	180.8	0.9
3	309.3	1092.355	100	181.7	27.2	310.4	182.3	-1.1
4	463.7	1146.397	150	181.6	27.2	463.3	181.4	0.4
5	618.5	1201.755	200	181.7	27.2	619.9	182.1	-1.4
6	773.0	1255.773	250	181.6	27.2	772.7	181.6	0.2
7	926.9	1309.398	300	181.5	27.2	924.4	181.0	2.5
8	1080.6	1365.100	350	181.4	27.3	1082.0	181.6	-1.4
9	1080.6	1365.100	350	181.4	27.3	1080.6	181.4	0.0
10	925.7	1310.018	300	181.3	27.3	924.3	181.0	1.3
11	770.8	1255.867	250	181.1	27.3	770.8	181.1	0.0
12	615.8	1202.078	200	180.9	27.4	618.2	181.6	-2.4
13	461.5	1146.647	150	180.8	27.4	461.0	180.5	0.5
14	307.7	1092.864	100	180.7	27.4	308.5	181.2	-0.8
15	153.7	1037.878	50	180.6	27.5	152.5	179.2	1.2
16	3.1	985.462	1	180.5	27.5			
r^2								1.0000
r^2C								1.0000

Bob: R1B1

Calibration Fluid Table

Temp C	Visco cP	Fit Err cP
23.0	198.5	-0.06
23.5	196.4	0.04
24.0	194.4	0.04
24.5	192.4	0.04
25.0	190.5	-0.06

Batch: LOT NO. 406404

Max Temp: 27.0 C

Min Temp: 21.0 C

Comment: Calibrated on 06/03/2020

Figure 3.13: Calibration of ORCARDA software

Accuracy

- Calibration: $r^2C \geq 0.999$
- The speed (RPM) is 0.001

Source of Error

- Bent thermocouple
- Test carried out at wrong temperature range

- Unite not calibrated before use
- Using expired calibration fluid
- Carrying out tests with “Shear Stress Raw” value reading more than 2 or 3 units

Safety

- Removing the mud cup when the pressure is 0
- Following the manufacturer operating instructions
- Pressure reduced when the sample temperature is below 49 ^{0} C
- Cleaning the bob after use

3.2.8. Aging cells

These cells are used in the hot roller oven to expose the drilling mud to temperatures above the boiling point of water and maintain the mud still in liquid state. These cells can be used during static and dynamic aging of the mud and below, the 260-mL and 500-mL cells Figure 3.14 were used in this experimental research. The table below specifies the mud volumes, pressurising pressure and the temperatures recommended for aging.

Table 3.2: Mud volume and pressure for aging at high temperature [243]

Aging Temp (°F/°C)	Water Vapour Pressure (psi)	Coefficient of expansion of Water	Suggested Applied Pressure (psi/kPa)	Mud Volume in 260 ml cell (ml)	Volume with Teflon Liner	Mud Volume in 500ml cell(ml)	Volume with Teflon Liner
212/100	13.7	1.04	25/172	225	130	450	326
250/121	30	1.06	50/345	225	130	450	326
300/149	67	1.09	100/690	200	166	425	308
350/176	135	1.12	150/1,034	200	166	400	289
400/204	247	1.16	250/1,724	-	-	375	271
450/232	423	1.20	300/2,069	-	-	375	253
500/260	680	1.27	375/2,586	-	-	325	235

Figure 3.14: Aging cells, (LEFT) 500 ml, and (RIGHT) 260 ml [244]

Source of Errors

- Overfilling the cell
- Leaking of valve
- Not pressurising the mud at the right pressure
- Damaged O-ring

Safety

- Following manufacturer operating instructions
- Wearing eye protection
- Tightening the set screws properly
- Cooling the aging cells at room temperature and releasing the pressure before opening.

Procedure

- First, the O-ring was carefully inspected for defects and placed in the groove in the cell body. If found with cuts and nicks, they were replaced. The valve stem was blown through with air to make sure it was not plugged.

- The test appropriate volume and safe initial pressure for the temperature at which the sample was to be tested selected from the Table 3.2 above was determined. The correct volume of the fluid was placed in the cell making sure not to get fluid in the O-ring groove.
- Spilled fluid was cleaned from the edged of the cell and the inner cap was placed on the top of the cell body O-ring so that it seats in place. The outer cup was hand tightened in place. The screws were tightened by the Allen wrench in the outer cap. The valve stem was inserted with the O-ring in place into the inner cap and tightened completely. The valve stem was loosened approximately one half turn before pressurising.
- The valve stem was closed when the desired pressure was reached by tightening it with a wrench. The cell was then immersed in water to ensure there was no leaks and checked for any bubbles coming from the valve stem or cell cap.
- The aging cell was then placed in the oven and the test temperature set.
- After the desired aging time had elapsed, the cell was removed from the oven and allowed to cool until the sample temperature was (149 °C) or less, then the cell was water cooled.
- When the cell temperature reached room temperature, the cell pressure was released, and the screws loosened, and the cell was opened and cleaned after.

3.2.9. High Pressure – High Temperature Filter Press

This equipment was used to investigate the filtration properties of drilling muds. The filtration properties of a mud fluid are affected by the quantity, type and particle sizes as well as temperature and pressure. It is very important to evaluate the filtration properties and investigate the filtrate and filter cake characteristics for the purposes of treatment and control [245]. Below is the complete assembly of the filter press Figure 3.15 consisting of the controlled pressure source (CO_2), high pressure test cell, heating jacket and stand.

- **High pressure test cell:** The test cell holds the mud sample. The filter press handles standard filtration tests at raised temperatures and pressure. It operates at the maximum pressure of 2000 psi and maximum temperature of 400 °F (240 °C).

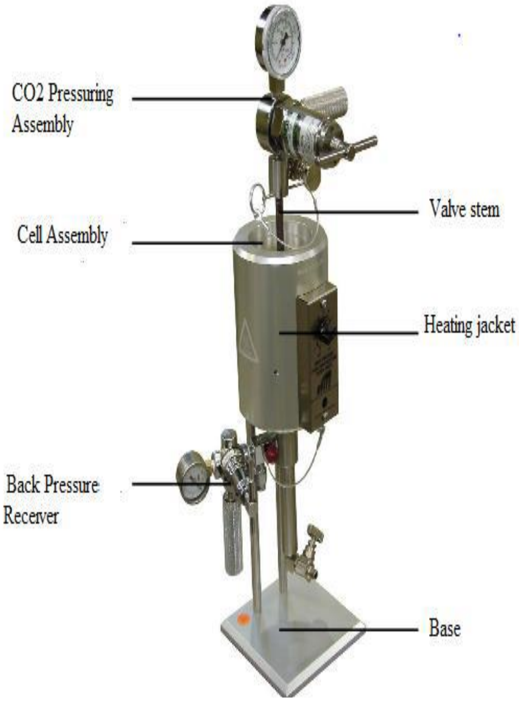


Figure 3.15: HPHT Filter press

- **Controlled pressure source carbon dioxide:** Carbon dioxide cartridges were used to pressurize. They contain enough gas to run a complete 30-minutes filtration test and for the standard API, 500 psi differential test and 600 psi on the top manifold and 100 psi on the bottom back pressure is set.
- **Suitable stand:** This stand offers the stability on the surface being worked on. It also has a heating jacket used for heating and maintaining the temperature of the cell throughout the test.

3.3.9.1: High Pressure -High Temperature Filter Press operation

The filter press simulates filtration against a permeable formation at HPHTs. At the targeted temperature, the sample is filtered across the filter media as the pressure is applied to the top of the cell. The carbon dioxide cartridges were used as the pressurization source.

- Preheat the jacket by connecting the power and turning the thermostat to obtain the required temperature.
- The filtrate cell is filled with the mud sample, the filter paper is applied, and the cell cover is inserted in the right position. The valves are tightened, and the cell put in the heating jacket.

- The pressure unit both on the inlet (top) valve stem and outlet bottom stem was attached, and the locking pins inserted.
- On reaching the targeted temperature, the mud was pressurized by screwing in the nitrogen cartridges. The stems were open, and the backpressure set. The timer was set, and the test started.
- All safety precautions were adhered to, and the test was according to the API standard.
- After 30 minutes, the test was stopped, and the pressure was released by closing the upper valve stem and backpressure valve stem lower.
- The bleed valve both on the cell manifold and backpressure receiver were opened to de-pressurize the system. Finally, every part was disabled.

Safety

- Follow safety precautions
- Check all parts for damages and if any replace parts
- Wear protective googles
- Reduce cell temperature before opening the cell

3.2.10. Roller oven

The effects of temperature and pressure on drilling mud when under borehole conditions were determined by the roller oven. This was used to mimic real borehole conditions to be able to evaluate the effect of the different temperatures and pressure have on the mud fluid systems under evaluation. All the drilling mud systems were aged dynamically for 16 hours to ascertain the interaction between a drilling mud and wellbore annulus. Figure 3.16 shows the roller oven used for the experimental research.

Figure 3. 16: Aging roller oven [244]

Procedure

The test can be run with a timer program or without the timer program. Without the timer, the "OUT1" is switched to ON.

- The rollers are turned on by flipping the "Roller" power switch on the "ON" position. The heaters and the red indicator light will come on. The indicator light will pulsate on and off as the temperature controller maintains the desired heat.
- The current temperature will be displayed on the upper register while the lower register will show the current setpoint. Temperature is adjusted by the up and down arrow.

While using the timer

The day of the week was selected for each start and finish (ON/OFF) operation. The "h" and "min" buttons were pressed in order to set the correct time for the "ON" to begin the cycle. Instantly, the "UP" arrow blink. The turn off time is activated by pressing the "WRITE" button and after pressing the "WRITE" button, the down arrow blinks. The day of the week for each ON/OFF operation was selected. The "h" and "min" buttons were pressured to set the targeted time for the "OFF" cycle to end. The "DOWN" arrow blinks. Then the "WRITE" button was pressed again. The switch was set to "P2" for the oven to start running. And lastly, the bar (-) displayed the days of operation.

3.3. Experimental Procedure

3.3.1. Phase-I

In this phase of the experimental study, nanoparticles were synthesised using the sol-gel process. This process involves two stages (1) hydrolysis of the precursor TEOS (tetraethyl orthosilicate) and condensation to form the silica nanoparticle structure [246]. A gel is formed during the chain network formation process because a large amount of the solvent will be impregnated in the network. In phase 1, 3 grams of ammonia hydroxide, 1 gram of TEOS and 4 grams of ethanol were added in water and magnetically stirred for $1\frac{1}{2}$ hours at ambient conditions. Another 2 grams of TEOS plus 8 grams of ethanol were added dropwise, and the mixture magnetically stirred for another 2 hours. A gel-like solution was formed which was centrifuged and then kept in the oven for 24 hours at 100 °C.

In general, from the hydrolysis reaction (Eqn 3.2), through the addition of water replaces alkoxide groups (OR) with hydroxyl groups (OH).

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{H_2O} \xrightleftharpoons{\text{hydrolysis}} \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{ROH} \tag{3.2}$$

The hydrolysis leads to the formation of silanol groups ((Si-OH). These are only intermediate species. As demonstrated below for silicate condensation, the silanol groups (Si-OH) involved in the condensation processes (Eqns 3.3 - 3.4) form siloxane bonds (Si-O-Si), and the byproducts are typically water or alcohol.

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{HO} - \mathrm{Si} \xrightleftharpoons{\substack{\text{Alcohol condensation} \\ \text{-alcoholysis-}}} \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{ROH} \tag{3.3}$$

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{HO} - \mathrm{Si} \equiv \xrightleftharpoons{\substack{\text{Water condensation} \\ \text{-hydrolysis-}}} \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{H2O} \tag{3.4}$$

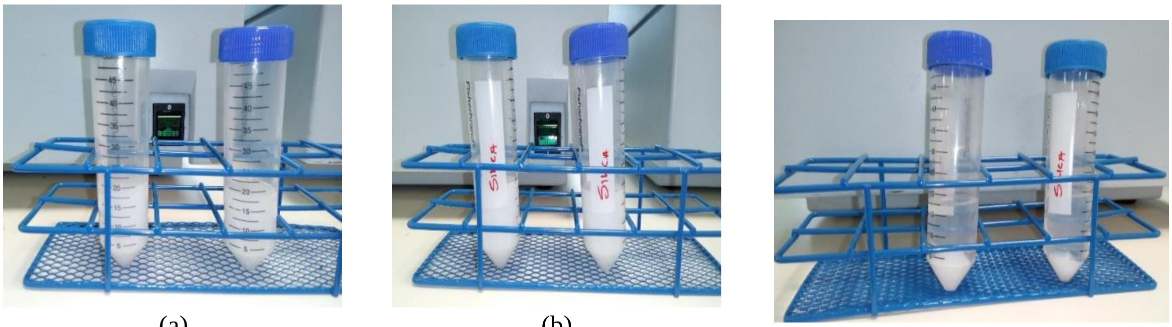
Subsequent condensation reactions produce siloxane bonds (Si-O-Si) plus the byproducts alcohol ROH. This reaction is a simplification of the complex condensation processes. Silica gel formed by the process leads to rigid, interconnected three-demensional network which is caused by TEOS (has four ethoxy groups three and fourfold reaction lead to 3D networks) consisting of submicrometer pores and polymeric chains. The reverse of reaction 3.3 and 3.4, siloxane bone alcoholysis and siloxane bond hydrolysis, promote bond breakage and renovation process that permit complete restructuring of the growing polymer. The overall reaction can be divided into two parts. The first part is the initiation part where the primary particles are formed followed by the growth of the particles as long as silicic acid is available. Although hydrolysis can occur without addition of an external catalyst, it is most rapid and complete when catalysts are employed. The catalysts can either be hydroxyl ions (base catalysis) such as minerial acids (HCl) and ammonia which are the most generally used. In summery, hydrolysis reaction in general follows:

Mainly hydrolysed TEOS monomer [(OR3) Si (OH)] are produced by the hydrolysis reaction. Eventually, this intermediate reaction produced condenses to lastly form silica [192]

$$\mathrm{Si(OR)_4 + H_2O \quad \rightarrow \quad (OR)_3SiOH + ROH} \tag{3.5}$$

The hydrolysis of the silicone alkoxides $Si(OR)_4$ and subsequent polycondensation is due to the gelation of silicon alkoxide solutions which leads to the formation of polymers and particles with siloxane bonds [225].

$$\mathrm{(RO)_3Si(OH) + H_2O \quad \rightarrow \quad SiO_2 + 3ROH} \tag{3.6}$$



(a) Synthesized Silica Nanoparticles in ethanol solution

(b) Synthesized Silica Nanoparticles in ethanol solution after circulation before centrifuge

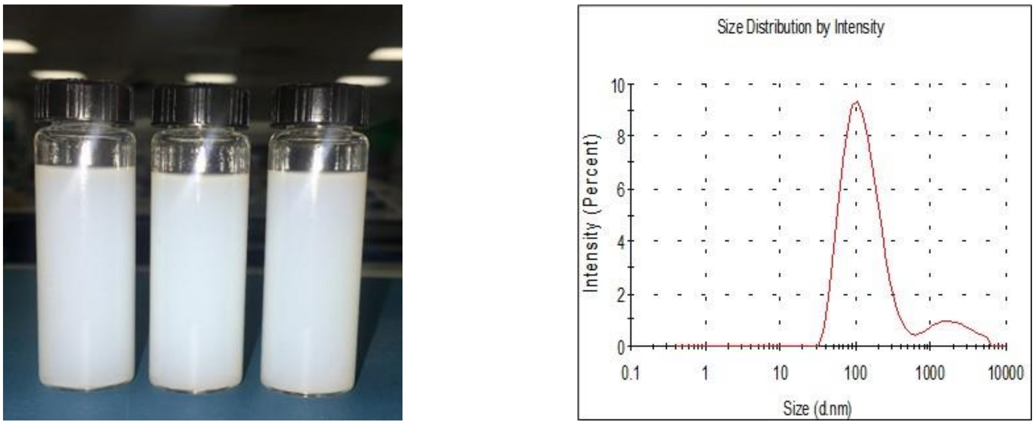
(c) Synthesized Silica Nanoparticles in ethanol solution after centrifuge

Figure 3.17: Synthesized Silica Nanoparticles

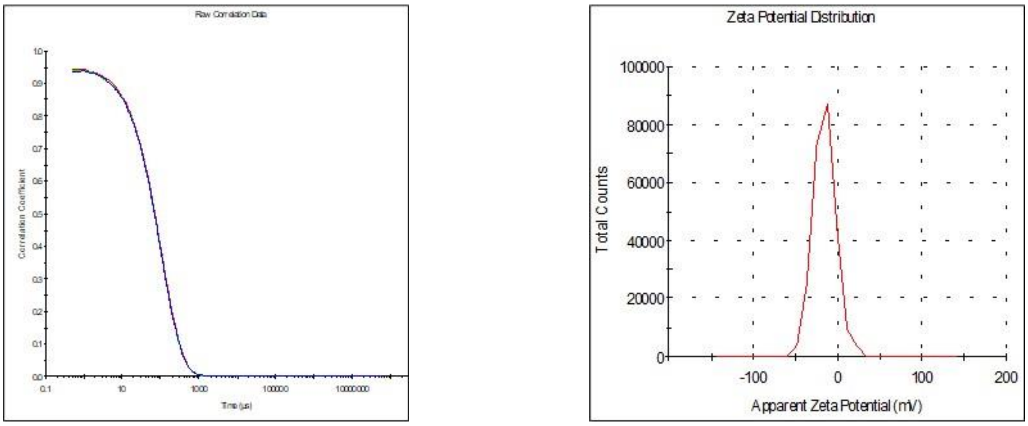
The dried powder was grounded as seen in Figure 3.18 and used in the mud fluid samples. Other samples were synthesised following the same procedure but altering the conditions and the chemical amounts.

Figure 3.18: Silica nanoparticles in powdered form

The size and zeta potential of the silica NP was characterised by the Dynamic light scattering (DLS). Figure 3.17a – 3.17c shows silica nanoparticles dispersed in ethanol while Figure 3.19b shows silica nanoparticle good dispersion as this can be witnessed from the shape of the peak. The sharpness of the peak implies that there were no aggregations in the dispersion hence implying that the particles can disperse well. From Figure 3.20b, the size of the nanoparticle was 110 nm measured from the DLS and the zeta potential from Figure 3.20d was found to be -15.2 mV. From Figure 3.20c, it is evident that the sample didn't contain large particles/aggregates as the measured intercept value was lesser than 1. From the correlation graph, the baseline was not elevated but flat which shows that the sample contained no fluctuations but dispersed well. Afterwards, the dispersed nanoparticles were oven dried heated at 100 °C for 24 hours, and powdered silica nanoparticles were then dispersed in bentonite suspensions. Lastly, the silica nanoparticles were tested for rheological properties and fluid filtration properties in Phase 2 using the model M1100 viscometer and API filter press in the drilling mud.



(a) SiO_2 NPs dispersed in ethanol (b) SiO_2 NP diameter



(c) SiO_2 NP correlation function (d) SiO_2 zeta potential

Figure 3.19: Nanoparticle size measurement and analysis

3.3.2. Phase-II: Mud Formulation

In this phase, different drilling mud formulations were designed. Bentonite water-based mud was made as a reference mud (R). Synthesised nanoparticles were dispersed in the water-based mud in different quantities. The mud formulations were then analysed under LPLH conditions and under HPHT conditions after aging. The Model 1100 viscometer was used to measure the rheological properties of the mud samples and the HPHT filter press was used to measure the filtration properties of the mud samples. Analysis was carried out on the results obtained to determine the stability of drilling mud formulation at HPHT conditions. Stable formulations with nanoparticles were then used in Phase 3 where silica nanoparticles were modified before being applied into the mud samples and tested.

3.3.2.1. Drilling mud formulation (R)

The electric scale was purposed to measure the amounts of additives and the jar was used to measure the water in ml. WBMs purposed for this experiment included 25 g bentonite and 400 mL water. The mixture of bentonite and freshwater were mixed for 30 min at room temperature by the Hamilton Beach mixer (Fig 3.11). All the drilling muds were mixed at the same rate of 11,500 RPM to enable the muds to mix well without coagulation or forming of solids of bentonite. The muds were kept to age for 16 hours at room temperature to fully hydrate. The mud properties were then analysed at room temperature using the Model 1100 viscometer (Fig 3.12). Tables 3.1 presents the materials purposed for the drilling mud preparations and silica NPs (SNPs) synthesis. The mud formulation at this phase was kept simple and the aim was to study silica nanoparticle performance on its own in a bentonite suspension. API standard (API 13B-1 2009) was followed.

3.3.2.2. Mud with Silica NPs (SNPs)

Different samples of WBMs with silica NPs (SNPs) were formed by adding three different concentrations of NPs in WBMs of (0.3 wt.%, 0.5 wt.% and 1.0 wt.%) as presented in Table 3.3. The three concentrations were selected purposely because with less than 0.3 wt.%, there was no great impact on the filtrate loss and rheological properties and adding NPs above 1.0 wt.% wouldn’t be cost effective. Sodium hydroxide (NaOH) was added to bring the pH to ± 9.5 for better colloidal solution stability. All samples were initially tested at room temperature for their rheological and filtration properties. Then, all samples were pressurised in aging cells (Figure 3.14) to evaluate the feasibility of using the muds in ultra-deep formations. To avoid boiling up when exposed to 100 °C and over, the mud samples were first pressurised and then dynamically aged in the hot roller oven (Figure 3.16) for 16 hours at different temperatures. The muds were then tested for their rheological and filtration properties at room temperature after cooling. The API HPHT filter press (Figure 3.15) was purposed to analyse the filtrate loss of all the mud samples and the tests were carried out based on the standard API filter press test.

Table 3.3: Drilling mud formulations with unmodified nano silica

		Mud Name			
		US 1	**US 2**	**US 3**	**US 4**
Additives	Water (mL)	350	350	350	350
	Bentonite (g)	22.5	22.5	22.5	22.5
	Silica nanoparticles (g)	-	0.3	0.5	1.0
	Barit (g)	-	-	-	-
	polyanionic cellulose (g)	-	-	-	-

3.3.3. Phase-III: TEOS

In this phase of the study, nanoparticle surface modification was performed in order to study the effects of nanoparticle surface charge on the rheological properties of the mud systems. The standard operating procedures, experimental equipment used, calibration, safety measures, accuracies and source of error are all explained in sub-sections 3.2.1 – 3.2.11. The objective of this phase was to determine if modifying the surface charge of silica nanoparticles could improve their dispersion abilities in water-based drilling muds while optimising the functionality of the drilling mud over a wide range of conditions to include high temperature and high-pressure drilling environments and formations. The thermal stabilities of the mud formulations at HPHT were investigated through aging tests to mimic borehole conditions. The rheological properties of the mud formulations were measured using the Model 1100 viscometers. The obtained results were studied to determine the stable mud formulations at high temperatures. Zeta potential analysis was key in this phase as this phase also aimed to determine the best cationic surfactant concentration that would give the highest absolute zeta potential values. This was to help establish the effects of repulsive and attractive forces in play that affect the performance of silica nanoparticles in mud systems. The surfactant used for the purposes of surface modification was Hexadecyltrimethylammonium bromide (CTAB).

3.3.3.1. CTAB solution formulation

To alter the surface charges, Hexadecyltrimethylammonium bromide (CTAB) cationic surfactant was used to improve the interaction between colloidal particles and silica NPs in drilling mud. Positively charged cationic functional groups are found at the heads of cationic surfactants. Cations possess a higher surface wettability, emulsifying and solubilization ability, and are pH resistant [247]. They are also thought to be biodegradable materials [248]. CTAB concentration dissolved to 50 ml of deionized water was 5.0 wt. %. Th solution was stirred for 30 minutes at room temperature. After, the solution was added in silica nanoparticle solution for modification.

3.3.3.2. Modification of nano silica

Different concentrations of CTAB (0.25 wt. percent, 0.5 wt. percent, 1.0 wt. percent, and 2.0 wt. percent) were added to silica solution, to ascertain the best concentration that could effectively alter the surface charges of silica nanoparticles. The mixture was stirred constantly for 10 min with the Homogenizer at a constant rotational speed of 2000 RPM, followed by 15 minutes of sonication to produce a well-distributed solution. The solutions were then dried in the oven before adding silica in a bentonite mud.

3.3.3.3. The Reaction processes

The nano particle size modified was 67.54 nm hence the contact area between CTAB and silica NPs would be large enough leading to a large surface area for interaction. Furthermore, the pH value was maintained at 10 by adding 0.1 M NaOH to enable enough hydroxyl groups to occur on the silica surface. Since silica surface charge is negative, addition of CTAB to the system will lead to formation of the organic chain of CTAB array around nano silica due to the ionic interaction between the negative and positive charges on the surface of silica NPs. Lastly, cation reacts with the hydroxyl groups on the silica surface, resulting in the surfactant being grafted on the silica surface and thus lowering the surface energy of silica NPs. On the other hand, after the organic chain of CTAB grafting on the surface of silica NPs, the steric among the NPs increases, resulting in a more mono-dispersed colloidal solution.

3.3.3.4. Formulation of Reference mud

The WBM developed for this investigation adhered to the (API 13B-1 2009) standard and composed of 22.5g bentonite, 20.3g barite, 0.5g polyanionic cellulose and 350 ml deionized water. The mixture of bentonite, water and other additives was mixed for half an hour at normal temperature by the Hamilton Beach mixer. All the drilling muds were mixed at the same rate of 11,500 RPM to enable the muds to mix well without coagulation or forming of solids of bentonite. The pH of all the mud samples was kept in the range of 9.5 – 10 for better colloidal solution stability by adding Sodium hydroxide and sulfuric acid. The samples were kept to age for 16 hours at normal temperature to fully hydrate. The samples prepared for this study are summarized in Table 3.4. All tests were repeated 3 times to check repeatability and reproductivity of the results to ensure that accuracy is maintained.

3.3.3.5. Formulation of mud with modified silica

WBM with modified silica NPs were designed by adding 0.5 wt.% of modified nano silica dispersed in the CTAB surfactant prepared earlier to the reference mud at the same rate of 11,500 RPM to enable the muds to mix well without coagulation or forming of solids of bentonite and other additives. Sodium hydroxide and sulfuric acid were added to modify the mud fluid pH in the range of 9.5 – 10 for better colloidal solution stability. The same procedure as mentioned earlier for the preparation of the reference mud was followed thereafter.

Table 3.4: Drilling mud formulations with modified silica

	Mud Name					
Additives	**MS 1**	**MS 2**	**MS 3**	**MS 4**	**MS 5**	**MS 6**
Water (mL)	350	350	350	350	350	350
Bentonite (g)	22.5	22.5	22.5	22.5	22.5	22.5
Barit (g)	20.3	20.3	20.3	20.3	20.3	20.3
polyanionic cellulose (g)	0.5	0.5	0.5	0.5	0.5	0.5
Silica nanoparticles (g)	-	0.5	0.5	0.5	0.5	0.5
CTAB (g)	-	-	0.25	0.5	1.0	2.0
Zeta potential (mV)	-	-17.7	20	28.2	35.4	37.1

3.3.3.6. Zeta potential analysis

From Figure 3.20, addition of CTAB in the nanoparticle solution led to increase in the zeta potential value. It should be noted that silica NP without CTAB had a negative zeta potential of -17.7 mV and with CTAB, the zeta potential changed because of the decreasing surface energy of silica NPs with addition of CTAB as seen from Figure 3.20. This is because the cation molecules initially dissociate into positively charged Centrimonium ions. Because of the electrostatic attraction between the positively charged Centrimomium ions and the negatively charged surface of silica NPs, ionic interaction takes place due to the establishment of an organic chain of CTAB array which reduces the surface energy of the silica nanoparticles.

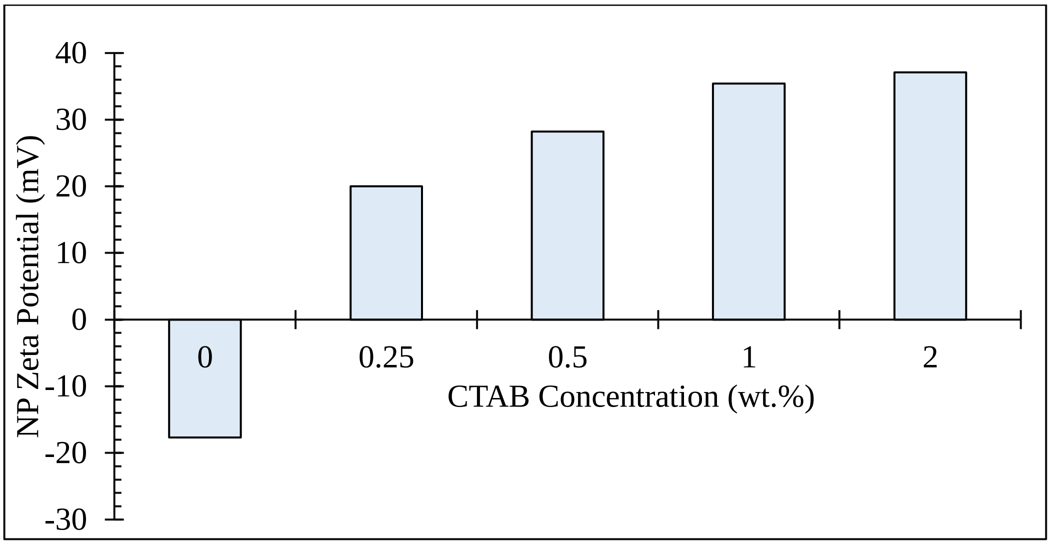


Figure 3.20: Analysis of zeta potential at different CTAB concentrations (wt.%)

3.3.4. Phase-IV: New Mud System and Base Mud

In this phase, tests were carried out to establish if a cheap novel additive would improve the filtration and rheological properties of a water-based mud system under HPHT conditions. The aim is to reduce costs since nanoparticles in large volumes of nanofluids are expensive therefore, the key is to reduce the amount of additives used in formulating a drilling mud system hence leading to an overall low cost in a drilling operation. A new additive was introduced in a water-based mud and tested for its performance under elevated conditions. The rheological properties were analysed, and filtration capabilities studied against a reference mud.

3.3.4.1. Novel drilling mud formulation

A control mud similar to the one listed in sub-section 3.6.7 was initially formulated following the (API 13B-1 2009) standard [249]. Two different sized novel additives were added gradually to the control mud formulations in concentrations of 0.5 wt.%. The five different samples prepared were then aged at seven different temperatures and pressures. After aging, the mud samples were placed in a cold-water bath to cool down, stirred again for 15 minutes at room temperature before testing for their filtration and rheological properties at 25 ^{o}C using the Model 1100 viscometer.

Table 3.5: Drilling mud formulations with sand additives

	Mud Name				
Additives	**S 1**	**S 2**	**S 3**	**S 4**	**S 5**
Water (mL)	350	350	350	350	350
Bentonite (g)	22.5	22.5	22.5	22.5	22.5
Barit (g)	20.3	20.3	20.3	20.3	20.3
polyanionic cellulose (g)	0.5	0.5	0.5	0.5	0.5
Nano sand (35-70 micro) (g)	-	0.5	-	-	-
Nano sand (149-420 micro) (g)	-	-	0.5	-	-
Nano silica (67.45 nm) (g)	-	-	-	0.5	-
Nano silica (149 nm) (g)	-	-	-	-	0.5

3.4. Chapter summary

In this section, the experimental work performed in this study is summarised. The equipment used and their accuracies, safety measures, procedures of operation, sources of error and calibration were described in depth. The additives (materials) purposed for this study are presented. The procedures for formulating the drilling mud formulations are explained in detail. Furthermore, different drilling mud systems formulated for this study and their compositions are also presented. Silica nanoparticle synthesis and surface modification was performed, and the analysis done using the Dynamic Light Scattering (DLS). All rheological and filtration property analysis was performed using the Model 1100 viscometer and the results are presented and discussed in detail in the next chapters.

Chapter 4: Results and Discussion

4.1. Overview

The results obtained from the experimental work as outlined in the methodology flow charts Figures 3.1 to 3.4 are presented. The equipment described in Chapter 3 were used for different purposes such as, nano silica synthesis process, to examine the rheological characteristics of the drilling mud formulations, to determine the ideal CTAB concentration required to modify nano silica surface and to study the stability of nano silica and nano sand in the drilling mud system under high pressure and high temperature (HPHT) conditions. Nanoparticles investigated in this study were synthesised in the lab under controlled conditions and tested for their thermal stability under HPHT conditions. Bentonite on its own in water-based mud degrades under elevated temperatures therefore, other additives must be added to stabilise bentonite water-based mud systems. For a successful, safe and cost-effective drilling operation, a drilling mud that is thermally stable and can retain its rheological properties under elevated temperature conditions is always required. Therefore, the research into enhanced filtration properties and rheological properties of conventional water-based bentonite muds (WBMs) under high pressure and high temperature (HPHT) conditions should be prioritised. In this regard, several challenges always present themselves, i.e. the breakdown of additives and polymers for example Polyanionic-Cellulose (Pac) used as a fluid loss preventer and rheological stabiliser [250] due to high temperature conditions in the borehole. One solution proposed has been the use of thermal extenders to enhance the thermal stability of the drilling mud solution though the concern of disintegration of additives is still not completely and effectively solved. The mechanism under which drilling muds degrade still needs attention and this study therefore exploited nanoparticles in drilling mud in order to enhance the mud stability under high temperatures. Nanoparticle dispersion mechanism in the mud was studied with attention and focus given to the repulsive and attractive forces in the drilling mud between nanoparticles and drilling mud additives. Nanoparticles were modified by altering their surface charges using a cationic surfactant and then tested in the mud. It is still difficult to select the optimum combination of additives that can improve the thermal stability of water-based mud system while also considering the economic benefits and environmental concerns. Therefore, the research also intended to introduce a cheap, environmentally friendly additive.

4.2. Phase-II: Synthesis and analytical characterisation of unmodified silica nanoparticles in water-based bentonite muds

The experimental results were collected and presented to assess the performance of synthesised unmodified silica nanoparticles in water-based mud systems and to establish the optimum concentration of silica nanoparticles that could improve rheology and filtration properties. Tables 4.1 presents the measured rheological and filtration properties such as, PV, YP, 10-sec gel strength, filtrate loss and mud cake of the formulations with silica nanoparticles in concentrations of 0.3 wt.%, 0.5 wt.% and 1.0 wt.%. The reference mud R was the control mud formulation. The stability temperature of the mud systems was defined as the temperature that a fluid can be exposed to for 16 hours without losing more than half of its viscosity [251]. The viscosities of drilling formulations with synthesised unmodified silica were compared with the control mud comprising of bentonite to analyse the fluid formulation's performance, stability and nano silica optimum concentration. From the results presented, stable drilling mud formulations were selected, and the optimum concentration established. The selected optimum concentration was adopted onto the next phase.

Table 4.1: Properties of Muds formulated with unmodified synthesised nano silica before and after aging at different temperatures

Drilling mud	Temp (^{o}C)	Pressure (psi)	Plastic Viscosity (cP)	Yield Point (lb/100 ft^2)	10 sec Gel (lb/100 ft^2)	30 mins Filtration Loss (ml)	Cake Thickness (mm)
R	26.3	14.7	11.81 ± 1.122	70.51 ± 3.84	37.67 ± 0	19 ± 0	0.8 ± 0
	100	25	9.94 ± 0.901	66.73 ± 4.07	44 ± 3.56	20 ± 0	0.5 ± 0.05
	121	50	8.74 ± 0.67	62.6 ± 3.30	55 ± 3.74	23 ± 0	0.8 ± 0.05
	149	100	17.78 ± 0.53	94.19 ± 10.64	93 ± 2.06	26 ± 0	1.0 ± 0
	179	150	11.71 ± 0.172	49.36 ± 2.198	61 ± 0	30 ± 0	1.2 ± 0
US 0.3 wt.%	26.3	14.7	11.0 ± 0.098	63.3 ± 1.44	34.8 ± 2.93	18.5 ± 0	0.6 ± 0
	100	25	6.7 ± 0.098	34.8 ± 1.34	23.3 ± 1.79	27 ± 0	0.5 ± 0
	121	50	6.9 ± 0.102	26.5 ± 1.77	18.5 ± 0.5	29 ± 0	0.7 ± 0
	149	100	4.6 ± 0.10	44.3 ± 0.719	50.3 ± 1.48	52.5 ± 0	0.9 ± 0.1
	179	150	9.3 ± 0.117	10.1 ± 0.672	13.3 ± 0.43	32.5 ± 0.471	1.2 ± 0
US 0.5 wt.%	26.3	14.7	10.2 ± 0.18	65.89 ± 1.925	37.6 ± 1.79	21 ± 0	0.6 ± 0
	100	25	9.5 ± 0.207	43.4 ± 5.32	35.5 ± 0.5	20 ± 0	0.7 ± 0
	121	50	10.6 ± 0.082	53.1 ± 3.33	43.8 ± 1.48	21.5 ± 0	0.8 ± 0
	149	100	7.22 ± 0.27	34.4 ± 3.23	52 ± 2.16	33 ± 0	0.7 ± 0
	179	150	7.9 ± 0.023	36.7 ± 1.03	23.3 ± 0.433	30 ± 0	0.9 ± 0
US 1.0 wt.%	26.3	14.7	10.2 ± 0.318	60.9 ± 1.15	32 ± 0	20.5 ± 0	0.6 ± 0
	100	25	7.7 ± 0.051	33.1 ± 0.064	22 ± 0	18.5 ± 0	0.7 ± 0
	121	50	9.6 ± 0.275	54.6 ± 3.04	37 ± 0	21 ± 0	0.5 ± 0
	149	100	8.9 ± 0.266	51.2 ± 1.81	32 ± 0.82	22 ± 0	0.8 ± 0
	179	150	11.1 ± 0.24	58.4 ± 0.998	78.3 ± 3.86	28 ± 0	1.0 ± 0

4.2.1. Effects of temperature on mud fluid with unmodified nano silica

This section presents the recorded results obtained from the measurement of the rheological and filtration properties of the water-based bentonite mud containing synthesized unmodified silica nanoparticles. The aim is to study the dispersion capabilities of silica nanoparticles in a bentonite mud fluid formulation and establish the optimum concentration and perform future modifications basing on the performance of the mud formulations. The thermal stability of nanoparticles in the mud is tested by conducting hot-rolling aging tests to mimic drilling mud circulation in the wellbore annulus.

Bentonite mud without nano silica was adopted as the control mud. Table 4.1 summaries the measured rheological properties of the drilling formulations. Stability of drilling mud is when the mud system retains half of its viscosity and fluid loss after aging for 16 hours at a chosen temperature [251]. From the data collected, most mud fluids maintained their rheology as temperature increased. Temperature effects were observed as nanoparticle muds exhibited a non-monotonic trend with temperature changes, which is attributed to temperature effects. Temperature exerts a complex influence on the rheology of drilling muds and the effects can be classified as (i) high temperature thinning, (ii) high temperature thickening and (ii) high temperature solidification [2]. It is true that the reference mud performed better than nanoparticle muds up to a temperature of 121 ^{o}C and after that temperature, the reference mud degraded. Bentonite WBMs can maintain their stability up to 121 ^{o}C and exhibit shear thickening behaviour at temperatures greater than 121 ^{o}C. This will lead to gelling and filtration problems in the borehole [252].

4.2.2. Plastic viscosities of the mud fluid containing unmodified nano silica

Figure 4.1 shows the effect of temperature on the plastic viscosity of the drilling muds formulated with unmodified nano silica before and after aging for 16 hours at different temperatures and pressures. At 100 °C samples were aged at 25 psi, the 121 °C samples aged at 50 psi, the 149 °C samples aged at 100 psi and the 176 °C samples aged at 150 psi. Drilling mud fluids are known to contain dispersed solids in continuous phase of the fluid. Plastic viscosity is a combination of the friction of solids and liquid in the drilling mud which together constitutes to the total resistance to flow. The experimental data shows a decrease in plastic viscosity with increase in temperature. The steady decrease in plastic viscosity is due to the effective dispersion of nano silica around bentonite platelets, as well as the exchange of cations that results in the negative charge of nano silica neutralising the positive charge on bentonite surfaces converting them to negatively charged bentonite [253]. This increases the repulsive forces between bentonite platelets, increasing the distance between bentonite particles and resulting in less friction [131]. Decrease in plastic viscosity uncontrollably could be due to deflocculation and poor dispersion of the mud particles after aging at a high temperature. High plastic viscosity is not desired in drilling muds as it causes borehole problems such as, low bit penetration rate, increase in surge and swab pressure, a possibility of pipe sticking and increase in torque and drag. Therefore, a lower plastic viscosity at high temperature indicates a mud formulation that can lubricate the bit and possesses fast rate of penetration (ROP) abilities.

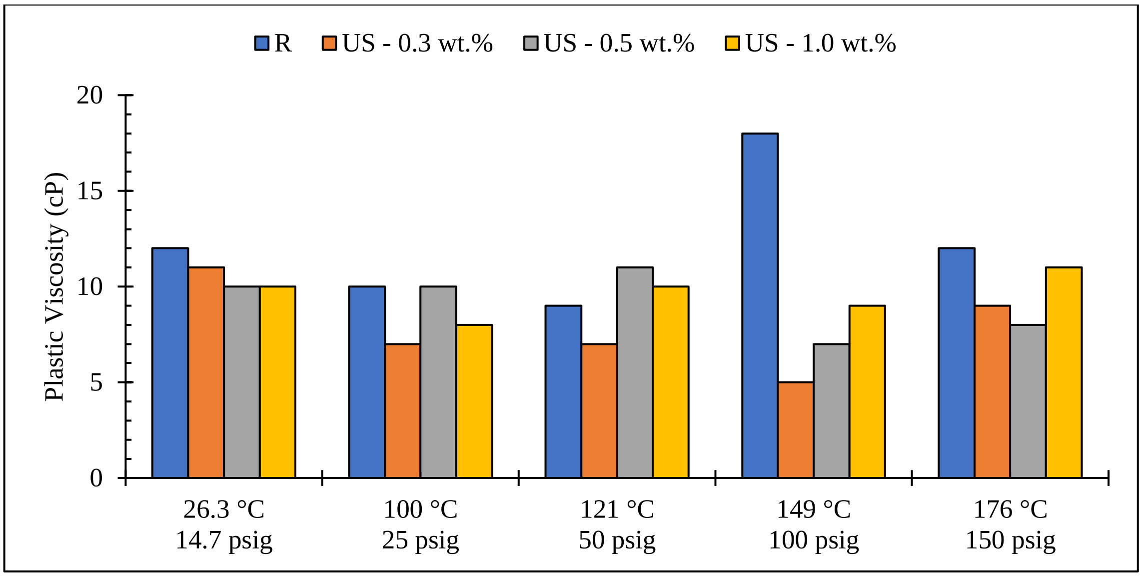


Figure 4.1: Plastic viscosity of mud containing unmodified silica nanoparticles

4.2.3. Yield point of the mud fluid containing unmodified nano silica

Figure 4.2 shows the yield point of the drilling mud formulations at different aging temperatures and pressures. There was a decreasing trend in yield point with increase in temperature. Yield point is a critical value that needs to be exceeded by a shear stress for initial fluid flow [254, 255]. It must be high enough to enable the carrying of drilled cuttings and weighting materials out of the wellbore. Yield point shows the ability of the mud system to lift cuttings from the wellbore to the surface and a mud with a higher yield point than the other is always preferred though not too high to create excessive pump pressure when mud circulation begins. Moreso, a high yield point implies that a drilling mud system is non-Newtonian and can carry cuttings better than any mud with a lower yield point. It is evident from Figure 4.2 that most muds exhibited favourable yield point values after aging at different temperatures. Though there was uncontrolled increase in yield point for the reference mud formulation at a temperature of 149 °C inconsistent with the rheological profile. This indicates the start of rheological and cutting currying capability loss due to bentonite breakdown caused by HPHT conditions. Elevated temperature causes bentonite to hydrate and passivate thus affecting the properties of clay. At the temperature 176 °C the mud with 0.3 wt.% silica concentration showed a decrease in yield point compared to other mud formulations. This is an indication of deteriorating cutting carrying abilities and initiation of mud failure. This could be due to the poor dispersion of 0.3 wt.% silica concentration in the bentonite mud. The concentration amount was not effective enough to disperse well in the colloidal mixture of bentonite.

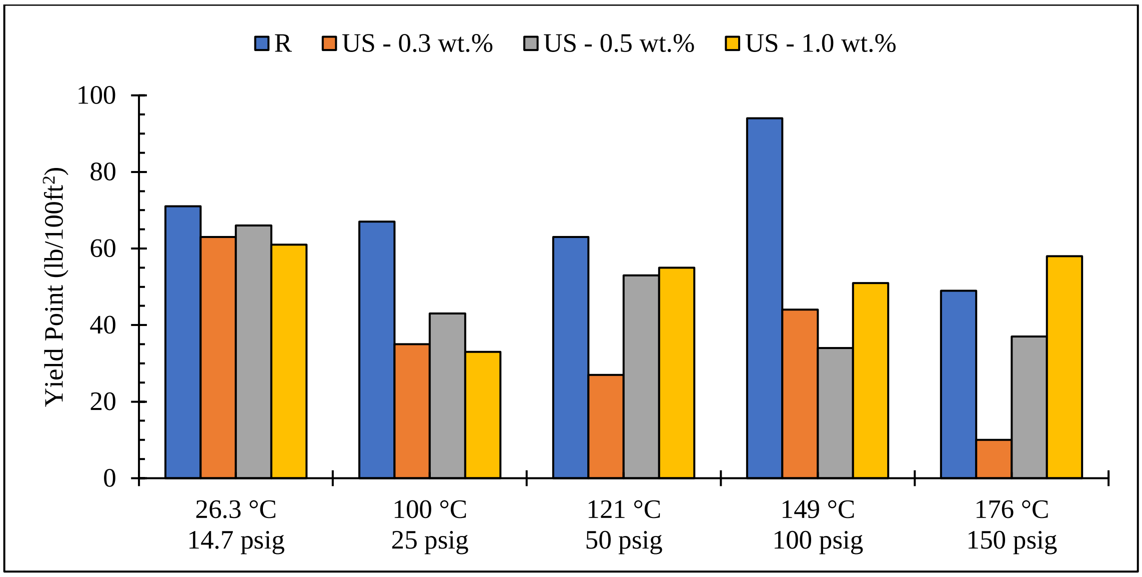


Figure 4.2: Yield point of mud containing unmodified silica nanoparticles

4.2.4. Gel strength of the mud fluid containing unmodified nano silica

The effects of temperature on the gel strength of the mud formulations are shown in Figure 4.3. Gel strength is the measure of the attractive forces in the drilling mud when the mud is quiescent [256]. Very high gel strength is not desirable as it may lead to borehole problems such as swabbing, surging which may result to difficulties removing the cuttings. On the other hand, low gel strength is undesirable as the mud will not be able to suspend and hold cuttings and weighting materials when drilling is stopped hence a balance needs to be maintained. Problems such as pipe sticking may arise if the cuttings and weighting materials settle at the bottom of a drilled borehole. From Figure 4.3, gel strength of the mud formulations starts to decrease with increase in temperature up to a temperature of 100 °C and thereafter, there is a steady increase in gel strength witnessed except for the mud with 0.3 wt.% silica concentration whose increase starts at 149 °C and at 179 °C, the gel strength drastically decreases. All mud formulations were affected at 176 °C, as it is observed that there was either a radical increase in gel strength or a radical decrease of which both scenarios are undesirable. Again at 149 °C, a sharp radical increase in gel strength is observed by the reference mud and thereafter, gel strength decreases rapidly. This is because bentonite muds can maintain their stability up to a temperature of 121 °C and exhibits a shear thickening behaviour at temperatures above 121 °C [252]. Dilution could be a quick solution for decreasing gel otherwise dispersant can be used to treat the condition. Mud fluids with high gel strength than others possess higher cutting carrying capacity and thixotropic property which is needed for any good drilling mud system. Muds with 0.5 wt.% and 1.0 wt.% exhibited stable strength profiles compared to other formulations.

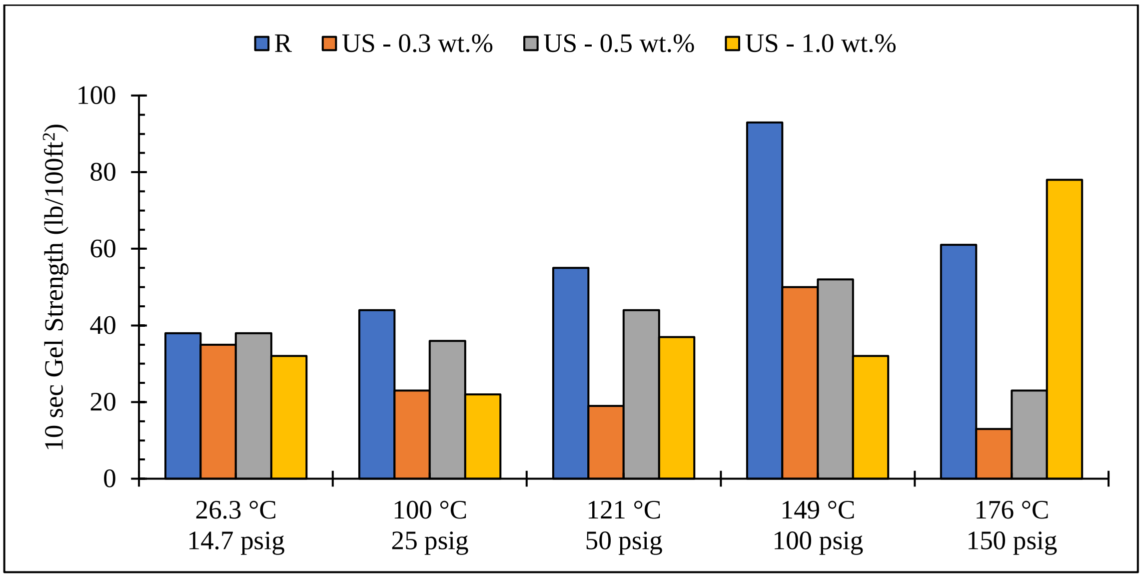


Figure 4.3: Gel strength of mud containing unmodified silica nanoparticles

4.2.5. Filtration loss of the mud fluid containing unmodified nano silica

Figure 4.4 shows the filtration abilities of the mud formulations at different aging temperatures and pressure. The amount of filtrate lost from the drilling mud under HPHT into the permeable formation was analyzed. According to Figure 4.4, nanoparticle mud US - 0.3 wt.% lost more filtrate as temperature increased than the reference mud. That means that at nanoparticle concentration of 0.3 wt.%, the effect of nanoparticles was drastic. At low concentration of 0.3 wt.%, a thicker, loose, high permeable and high porous filter cake was produced resulting to relatively high fluid loss than that of mud fluids with higher nanoparticle concentrations which in return yielded a thinner compact low permeable filter cake resulting in low fluid loss. The increase in filtrate loss is partly due to the deflocculation of bentonite particles caused by electrostatic repulsion between nano silica and bentonite particles [142]. At a temperature of 149 °C, there was unexpected uncontrolled increase in filtrate loss by US - 0.3 wt.% differing from the previous pattern. This is because in HPHT conditions, bentonite solutions aggregate and flocculate resulting in the decrease of the mud fluid rheology and capacity to control filtration loss. The mud with 1.0 wt.% silica concentration improved the filtration properties of the mud formulations better than other mud formulations. There was a steady increase in filtration loss with increase in temperature. The reference mud showed superior performance compared to some nanoparticle muds as it maintained a low filtrate loss with increase in temperature.

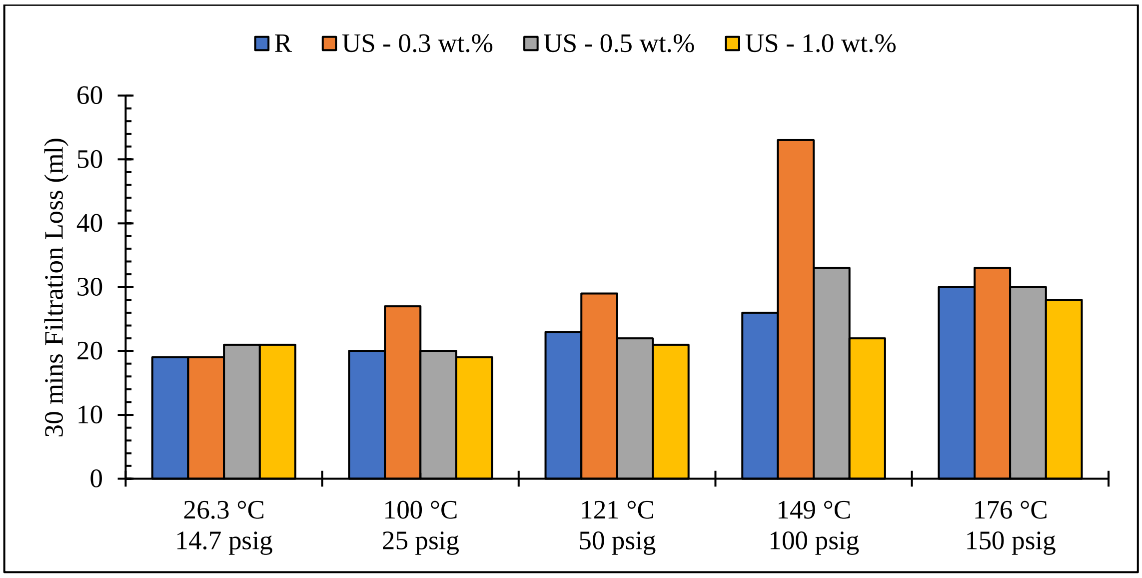


Figure 4.4: Filtrate loss of mud containing unmodified silica nanoparticles

4.2.6. Mud cake of the mud fluid containing unmodified nano silica

Figure 4.5 shows the mud cake thickness of the mud formulations after aging the mud samples at different temperatures and pressures. A mud cake is an impermeable wall formed between the wellbore and the reservoir. It prevents the possible invasion of filtrate into the formation. If filtrate loss is not prevented, it could result in wellbore damage thus decreasing the effective permeability near wellbore region. Increasing temperature resulted in increase in mud cake thickness for all mud formulations. The reference mud and mud with 0.3 wt.% silica concentration exhibited a reduction in mud cake thickness with increase in temperature which is highly recommended for a good drilling mud system, but this changed when the temperature exceeded 100 °C as seen from Figure 4.5. As temperature increased above 121 °C, mud samples with 0.5 wt.% and 1.0 wt.% silica concentration resulted in a thin mud cake compared to other mud formulations which is desirable.

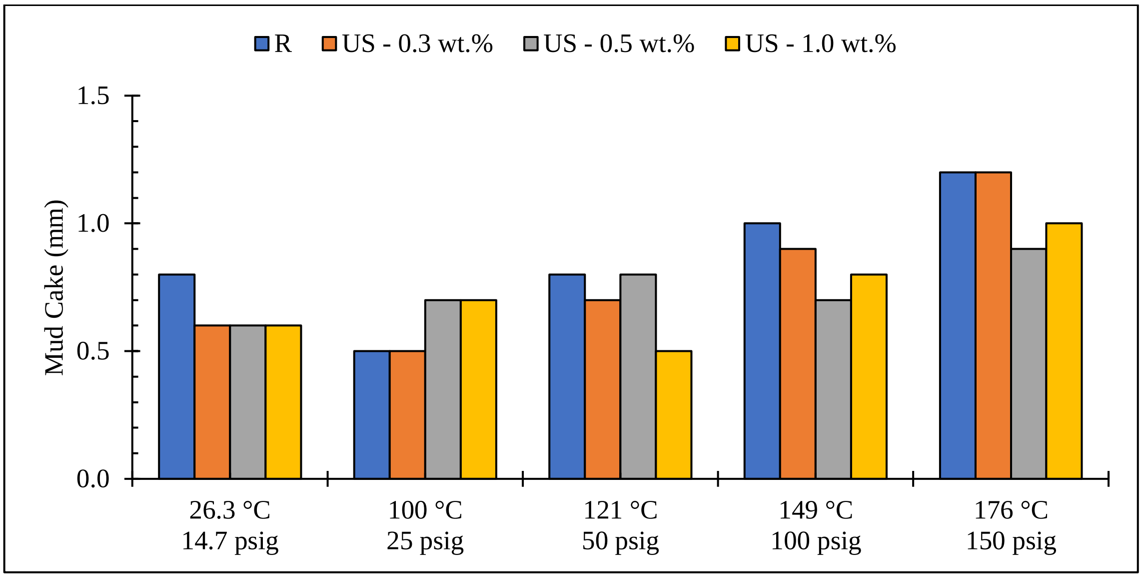


Figure 4.5: Mud cake of mud containing unmodified silica nanoparticles

Figure 4.6 represents the mud cakes formed from nanoparticle mud and bentonite reference mud. Nanoparticle muds produced a thin smooth mud cake compared to a thick permeable mud cake produced by reference bentonite mud. Producing a thin mud cake prevents borehole problems such as raised pressure surge due to reduced hole diameter, tight hole leading to excessive drag, differential sticking because of increased pipe contact with mud cake and many other problems that might happen during drilling operation as mentioned earlier. It is evident that nanoparticles in concentration of 0.5 wt.% performed better when compared to other concentrations. Therefore, nanoparticle at this concentration will be considered for further analysis on the next phases.

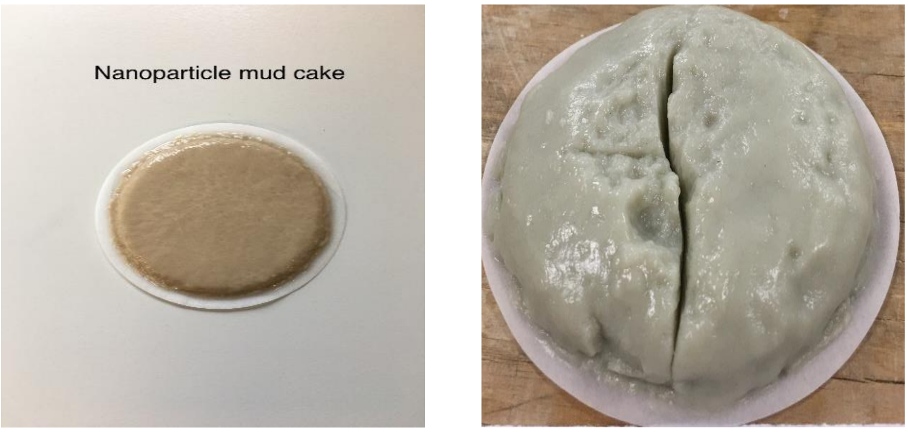


Figure 4.6: Filter cake at HPHT conditions

(LEFT) silica NP aged at 179 °C, and (RIGHT) reference bentonite mud aged at 179 °C

4.3. Phase-III: Modified nano silica analytical characterisation in water-based mud

In phase 3, the experimental results were collected and presented to study the effects of modified silica in water-based drilling mud systems. The previous phase had determined that the optimum concentration of silica nanoparticles was 0.5 wt.%. Therefore, the aim of this Phase 3 is to determine the effects of surface charge on the dispersion abilities of silica nanoparticles in water-based mud. Silica nanoparticle surface was altered with different absolute values of zeta potential using a cationic surfactant and after dispersed in water-based bentonite mud formulations. The rheological and filtration properties of the mud formulations were analysed under high pressure and temperature. Table 4.2 presents the measured rheological and filtration properties such as, PV, YP, 10-sec gel strength, filtrate loss and mud cake for the formulations with silica nanoparticles. From the results collected, stable drilling mud formulations were selected and the best performing absolute zeta potential value was selected. Establishing the key dynamics that affect silica dispersion in drilling mud is key and this phase aimed to address that.

Table 4.2: Properties of Muds formulated with modified synthesised nano silica before and after aging at different temperatures

Drilling mud	Temp (ºC)	Pressure (psi)	Plastic Viscosity (cP)	Yield Point (lb/100 ft^2)	10 sec Gel (lb/100 ft^2)	30 mins Filtration Loss (ml)	Cake Thickness (mm)
MS-1	26.3	14.7	11.50 ± 0.21	16.5 ± 0.63	9.5 ± 0.24	9 ± 0	0.35 ± 0.005
	100	25	18.02 ± 0.36	14.99 ± 1.4	11.75 ± 0.43	9.7 ± 0	0.4 ± 0
	121	50	19.5 ± 0.24	12.58 ± 0.73	6 ± 0	16.7 ± 0	0.5 ± 0.1
	149	100	25.9 ± 0.16	5.66 ± 0.43	6.2 ± 0	17.5 ± 0	0.55 ± 0.04
	176	150	26.20 ± 0.66	6.30 ± 1.46	3 ± 0	19.6 ± 0	0.89 ± 0
	204	250	27.30 ± 2.47	7.10 ± 2.48	4.5 ± 0.5	20.85 ± 0	0.95 ± 0
	232	300	26.82 ± 2.93	7.30 ± 0.96	37.37 ± 4.18	25 ± 0	1.1 ± 0
MS-2 (-17.7 mV)	26.3	14.7	14.70 ± 0.07	8.19 ± 0.55	5.3 ± 0	9.0 ± 0	0.2 ± 0.005
	100	25	30.65 ± 0.82	10 ± 2.18	8 ± 0	13 ± 0	0.6 ± 0
	121	50	26.1 ± 1.44	13.2 ± 3.77	5 ± 0	13.5 ± 0	0.6 ± 0
	149	100	26.20 ± 0.58	13.5 ± 1.77	22.5 ± 2.96	19.06 ± 0	0.65 ± 0
	176	150	28.5 ± 0.3	11.3 ± 0.117	11 ± 0	17.4 ± 0	0.67 ± 0.05
	204	250	30.9 ± 0.23	10.20 ± 0.59	24.5 ± 0.5	20.22 ± 0	0.72 ± 0.02
	232	300	32.60 ± 0.3	9.2 ± 1.59	25.75 ± 0.83	22.95 ± 0	0.85 ± 0
MS-3 (20 mV)	26.3	14.7	13.82 ± 0.29	7.04 ± 0.84	6.5 ± 0	10 ± 0	0.3 ± 0
	100	25	25.53 ± 0.064	14.91 ± 0.051	6.0 ± 0	10.33 ± 0	0.6 ± 0
	121	50	24.23 ± 1.09	25.20 ± 1.83	7.75 ± 0.43	9.24 ± 0	0.53 ± 0.02
	149	100	25.29 ± 0.63	10.3 ± 0.5	19.5 ± 0.47	14.32 ± 0	0.6 ± 0
	176	150	19.64 ± 0.8	9 ± 1.77	28.5 ± 0.87	14.81 ± 0	0.62 ± 0.02
	204	250	16.25 ± 3.94	10 ± 7.83	22.25 ± 1.79	20.12 ± 0	0.63 ± 0
	232	300	15.20 ± 3.32	9.60 ± 7.5	34.75 ± 8.58	23.10 ± 0.72	0.65 ± 0.25
MS-4 (28.2 mV)	26.3	14.7	9.96 ± 0.25	6.46 ± 0.70	5 ± 0.47	9.3 ± 0	0.3 ± 0
	100	25	26.34 ± 0.47	19 ± 0	8.67 ± 0.47	13 ± 0	0.4 ± 0
	121	50	29.46 ± 1.38	21.93 ± 0.09	5 ± 0	9 ± 0	0.4 ± 0
	149	100	25.12 ± 2.81	16.20 ± 3.19	2 ± 0	13.3 ± 0	0.6 ± 0.02
	176	150	23.60 ± 0.998	15.20 ± 0.5	21.25 ± 1.09	16.92 ± 0	0.7 ± 0
	204	250	25.23 ± 0.51	16 ± 0.62	23 ± 0	20.77 ± 0	0.72 ± 0.05
	232	300	26.33 ± 0.47	20.3 ± 4.11	19 ± 8.29	22.56 ± 0	0.69 ± 0

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Drilling mud	**Temp (ºC)**	**Pressure (psi)**	**Plastic Viscosity (cP)**	**Yield Point (lb/100 ft^2)**	**10 sec Gel (lb/100 ft^2)**	**30 mins Filtration Loss (ml)**	**Cake Thickness (mm)**
MS-5 (35.4 mV)	26.3	14.7	11 ± 1.15	18 ± 0.318	12 ± 0	9.72 ± 0	0.47 ± 0
	100	25	22.3 ± 1.25	33.34 ± 0.47	21 ± 0	8.23 ± 0	0.6 ± 0
	121	50	21.33 ± 0.47	29.34 ± 2.49	20 ± 0	15.31 ± 0	0.56 ± 0
	149	100	17.67 ± 1.25	30.33 ± 2.20	22 ± 0	15.20 ± 0	0.52 ± 0.04
	176	150	19.33 ± 0.47	30.34 ± 6.34	21 ± 0	15.31 ± 0	0.65 ± 0.05
	204	250	13 ± 0.82	30.20 ± 0.82	20.5 ± 0	15.85 ± 0	0.72 ± 0.05
	232	300	13.81 ± 3.78	32.25 ± 3.59	19 ± 4.56	17.90 ± 2.74	0.67 ± 0.08
MS 6 (37.1 mV)	26.3	14.7	9.2 ± 0.27	7.20 ± 0.31	9 ± 0	10.04 ± 0	0.33 ± 0.05
	100	25	16.18 ± 0.27	9.89 ± 0.14	10.20 ± 0	9.74 ± 0	0.5 ± 0
	121	50	13.25 ± 0.73	16.14 ± 3.65	10.8 ± 0	6.55 ± 0	0.35 ± 0.05
	149	100	15.78 ± 1.93	16.64 ± 0.69	14 ± 0	10.9 ± 0	0.43 ± 0.82
	176	150	14.66 ± 2.9	15.19 ± 0.9	20 ± 0.8	14.6 ± 0	0.52 ± 0
	204	250	12.50 ± 7.3	17.80 ± 9.24	19 ± 0.82	15 ± 0	0.6 ± 0.17
	232	300	11.96 ± 2.63	20 ± 3.81	25.70 ± 0.47	16.60 ± 0	0.65 ± 0.14

4.3.1. Effects of temperature on mud fluid with modified silica nanoparticles

This section presents the results obtained from the measurement of the rheological and filtration properties of water-based bentonite formulations containing synthesized modified silica nanoparticles. It is evident that the properties of the mud formulations increased with temperature increased. Nanoparticle and bentonite muds showed a non-monotonic trend. This is true because nanoparticles will disperse and interact differently in a mixture of other additives and when temperature is involved, it creates other effects.

4.3.2. Plastic viscosities of the mud fluid containing modified nano silica

Figure 4.7 below presents the plastic viscosity of the mud formulations after aging at different temperatures and pressures. Temperature increase affects the efficiency of mud fluid additives to protect bentonite clay particles. A high plastic viscosity is an undesirable condition because it reduces the drilling mud pumpability, increases pump pressure expenses and jeopardizes drilling mud efficiency. From Figure 4.7 below, the mud formulation with unmodified silica exhibited the highest plastic viscosity at all tested temperatures compared to other formulations. The plastic viscosity was even greater than bentonite control mud. This is due to the repulsive forces between unmodified silica and bentonite clay which affects free movement of particles in the drilling mud formulation resulting in increasing plastic viscosity. Bentonite formulation again exhibited steady plastic viscosity increase up to 121 °C and thereafter, plastic viscosity increased. On the other hand, mud formulations with modified silica maintained a similar plastic viscosity profile up to a temperature of 149 °C and thereafter, a steady decrease was observed. Stable viscosity at high temperature indicates the ability of NPs to suppress viscosity decrease therefore showing the same rheological behaviour at various temperatures. Clearly, nano silica with the highest absolute zeta potential values produced the most stable mud fluid plastic viscosity profiles seen from mud formulations MS-5 and MS-6 at all temperatures.

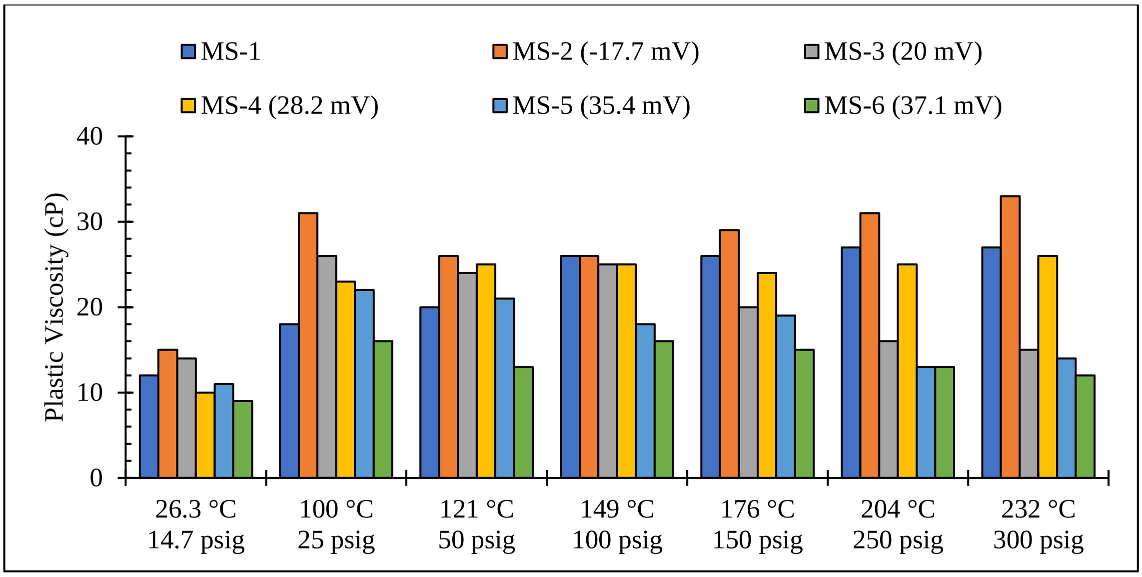

Figure 4.7: Plastic viscosity of mud containing modified silica nanoparticles

4.3.3. Yield point of the mud fluid containing modified nano silica

From Figure 4.8 below, the yield point of the mud formulations is presented after aging as below. The bentonite mud maintained yield point up to a temperature of 121 °C and thereafter, yield point started to decrease. This inconsistent in rheological profile indicates the start of rheological loss and loss of cuttings carrying abilities of the mud fluid system. It was observed that the reference mud performed better than the mud with unmodified and modified silica at low temperature and low pressure conditions. Mud formulations with modified silica nanoparticles performed better than mud formulations with unmodified silica nanoparticles from the temperature of 100 °C all throughout indicating better stability at HPHT condition. It is evident that the YP of the modified nanoparticle muds was higher than that of mud samples containing unmodified silica. This is because of the interaction of the negatively charged bentonite and positively charged modified nano silica which results in formation of bigger particles in the dispersion resulting in lower viscosity and higher yield point. It was also observed that mud samples with modified nanoparticles having a higher absolute zeta potential value performed better than other muds with a smaller absolute zeta potential value at HPHT conditions. Adding unmodified negatively charged silica increased the electrochemical repulsive forces between the negative bentonite clay platelets and negative silica surface charge leading to deflocculation of the platelets hence resulting in lower yield point and higher viscosities.

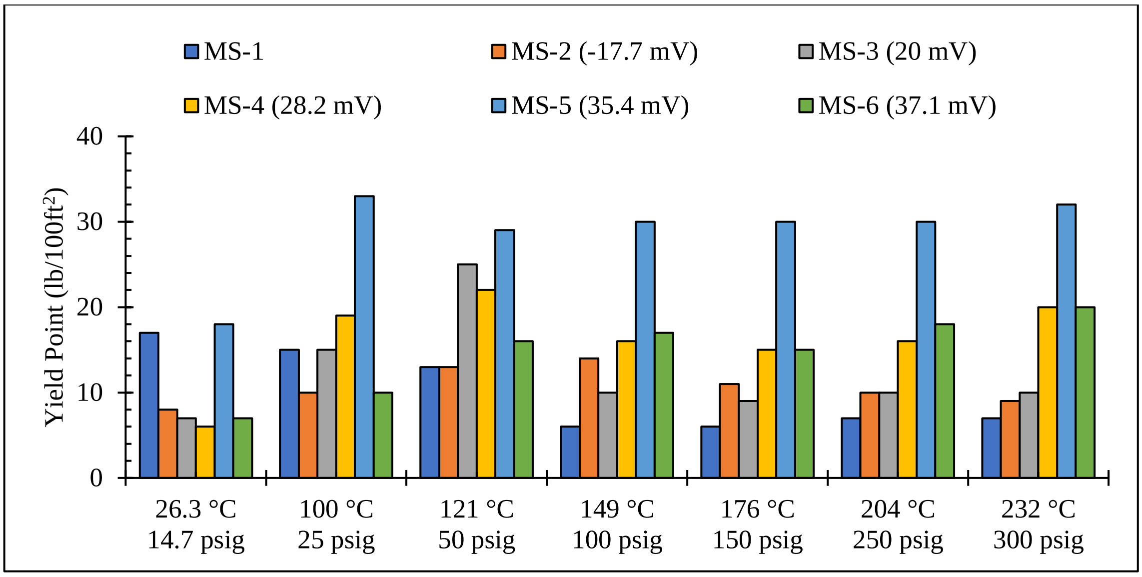

Figure 4.8: Yield point of mud containing modified silica nanoparticles

4.3.4. Gel strength of the mud fluid containing modified nano silica

Figure 4.9 below shows the 10 sec gel strength of the mud formulations after aging at different temperatures and pressures. Gel strength increased with increase in temperature for mostly all the mud formulations. As mentioned earlier in the previous phase, the same procedure was followed when measuring the gel strength.

As shown in this Figure 4.9, bentonite WBM exhibited the lowest gel strength compared to all other mud samples. This gel reached maximum at a temperature of 232 °C. This behaviour indicates the complex effects of temperature resulting in high temperature thickening and solidification, and thus failure of the mud system. The mud with unmodified silica MS-2 showed a slightly higher gel strength from temperature of 149 °C. Temperature reduces the ability of nanoparticles to protect clay particles. This together with the repulsive forces affected the dispersion abilities of the formulation.

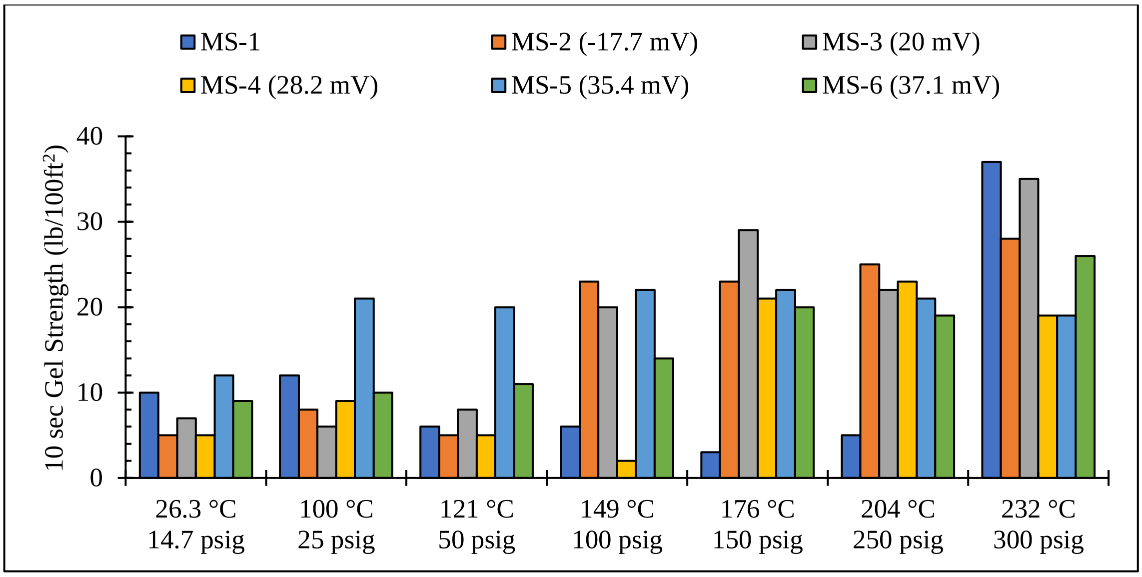

Figure 4.9: Gel strength of mud containing modified silica nanoparticles

The gel strength of muds with modified nano silica increased steadily with increase in temperature especially MS-5 and MS-6 formulations containing silica with the highest absolute value of zeta potential. This was due to the formation of the heterocoagulation structure, which improves water retentivity within the drilling mud system, reducing the temperature effects of high temperature thickening and solidification, which would have resulted in gelling and filtration issues.

4.3.5. Filtration loss of the mud fluid containing modified nano silica

From Figure 4.10 below, the filtration properties of mud formulations at various temperatures were investigated. It is clear that as temperature increased, filtrate loss of the mud formulations increased. The HP/HT filter press test was applied for this task under a differential temperature condition and pressure of 100 °C and 500 psi, respectively. From Figure 4.10 below, filtration loss at LTLP to 100 °C for both reference and nanoparticle muds showed no major, or statistically significant variation in the fluid loss across the samples, with the reference mud performing similarly or better than the nanoparticle muds. Nanoparticle muds generally exhibited a higher filtrate loss at LPLP conditions until a temperature of 100 °C. As temperature increased above 100 °C, the filtrate loss from the reference mud MS-1 and mud with unmodified silica MS-2 was higher than the filtrate loss from the muds with modified nano silica. From the temperature of 121 °C, the reference mud lost the highest filtrate. This was because of the sensitivity of bentonite to temperature and in HPHT conditions, the polymers degrade leading to increasing fluid loss and poor upward carrying of cuttings abilities. Addition of unmodified nano silica did not solve the problem neither as filtration loss was similar or greater than the reference mud. The high volume of filtrate loss was due to deflocculation of bentonite particles because of the electrostatic repulsion between nano silica and bentonite particles via face-to-face interaction which resulted in failure to form a linked structure. Modified silica performed better than unmodified silica as the volume of filtrate loss was less compared to other mud samples especially muds containing silica nanoparticles with a higher absolute value of zeta potential. The performance of modified silica was due to the face-to-face electrostatic attraction between (modified silica and bentonite) and the edge-to-face (positive edge bentonite -negative face bentonite) [257] leading to the formation of a heterocoagulation structure. This formed structure holds and retains the fluid within the formation hence reducing filtrate volume loss [258].

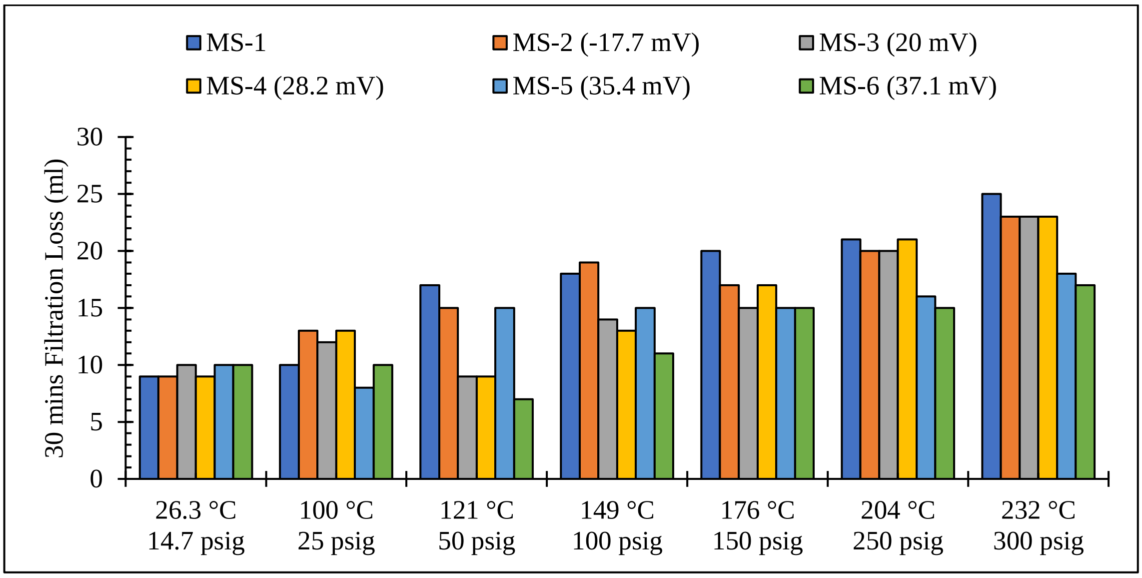

Figure 4.10: Filtrate loss of mud containing modified silica nanoparticles

4.3.6. Mud cake of the mud fluid containing modified nano silica

The quality of the mud cake produced by a mud system is very important during a drilling operation because, a good mud cake reduces filtrate loss from a mud system by acting as a barrier on the borehole wall. If filtrate loss is not controlled, it may lead to borehole problems addressed in the previous phase. Figure 4.11 below presents the mud cake thickness produced by different formulations after aging at different temperatures. There was an increase in mud cake thickness with temperature increase for all the samples. The control bentonite mud and the mud formulation with unmodified nano silica produced thicker mud cakes compared to other mud formulations. On the contrary, formulations with modified nano silica produced thinner mud cakes especially formulations MS 5 and MS 6 containing nano silica with the highest absolute zeta potential values. A thin unerodable mud cake which is smooth and impermeable is always desirable as it prevents filtrate loss into the formation. The formation of thin mud cakes by formulations containing modified nano silica confirms the theory of heterocoagulation structure between bentonite and modified silica because of the electrostatic attractive forces. Therefore, modified nano silica when used would improve the filtration properties of the mud fluid by producing a thin impermeable mud cake.

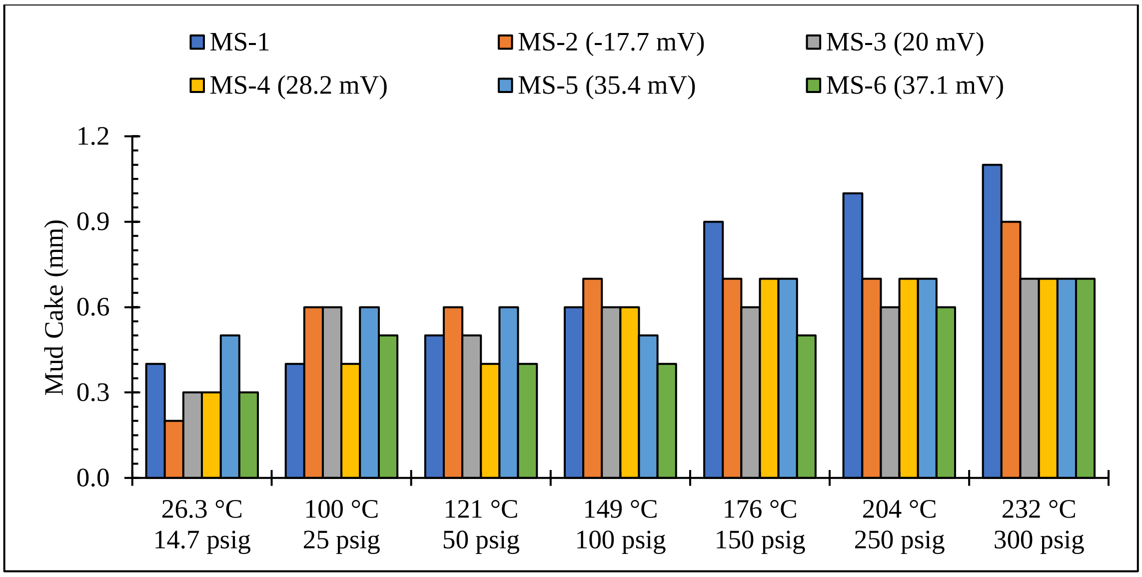

Figure 4.11: Mud cake of mud containing modified silica nanoparticles

4.4. Phase-IV: Formulation of an environmentally friendly cheap mud system utilising nano sand

In phase 4, a new additive nano sand was introduced into a water-based mud to improve the filtrate and rheological properties of the mud. Its effectiveness was then studied and compared to commercial additives. The rheology of the mud was determined to evaluate the behaviour of the drilling mud during circulation. Rheology plays an important role in borehole cleaning, penetration rate, and stability. Having established the optimum concentration in Phase 2, the same concentration was adopted. The aim was to investigate the performance of a new environmentally friendly and low-cost additive in a water-based mud. The rheology and filtration properties of the novel mud system were recorded and compared to nano silica additives. Previously, it was concluded that nano silica improved the properties of the mud at a concentration of 0.5 wt.% in Phase 2. Modifications were made to nano silica in Phase 3 and it was discovered that nano silica surface modification further enhanced both the filtration and rheological properties of the mud system. The industry is currently looking for a low-cost additive which is environmentally friendly. The modification method is costly and involves high capital costs. Purchasing sufficient quantities of silica nanoparticles for a drilling operation is also very expensive. Therefore, this phase introduces a new additive nano sand. The results obtained from the rheological measurements of the mud samples containing nano sand and nano silica are given in Table 4.3.

Table 4.3: Properties of Muds formulated with both a novel additive and nano silica

Drilling mud	Temp. (ºC)	Pressure (psi)	Plastic Viscosity (cP)	Yield Point (lb/100 ft^2)	10 sec Gel (lb/100 ft^2)	30 min Filtrate loss (mm)	Cake thickness (mm)
S1	26	14.7	11.5	16.5	9.5	9	0.35
	100	25	18.02	14.99	11.75	9.7	0.4
	121	50	19.5	12.58	6	16.7	0.5
	149	100	25.9	5.66	6.2	17.5	0.55
	176	150	26.20	6.3	3	19.6	0.89
	204	250	27.30	7.1	4.5	20.85	0.95
	232	300	26.82	7.3	37.37	25	1.1
S2	26	14.7	9	12	7	9.83	0.38
	100	25	9.7	14	7.6	8.45	0.32
	121	50	12.7	14.3	5	10.18	0.35
	149	100	13	6.5	6	14	0.4
	176	150	7.6	19.4	6	19.68	0.55
	204	250	17.7	11.3	6	17.44	0.43
	232	300	18.8	12.25	6	17.62	0.6
S3	26	14.7	10.6	8.6	24.8	9.6	0.35
	100	25	11.5	25	12	14.1	0.5
	121	50	14.8	19.3	15.3	12.3	0.58
	149	100	19.6	28.5	19.8	16.5	0.56
	176	150	20.9	35.6	13	15.1	0.72
	204	250	22.7	11.1	8.8	19.9	1.1
	232	300	19.7	11	7.5	24.3	1.32
S4	26	14.7	14.69	8.19	5.3	9	0.2
	100	25	30.65	10	8	13	0.6
	121	50	26.10	13.2	5	14.5	0.6
	149	100	26.20	13.5	22.5	19.06	0.65
	176	150	28.50	11.3	22.65	17.4	0.67
	204	250	30.90	10.2	24.5	20.22	0.72
	232	300	32.60	9.2	27.7	22.95	0.85

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Drilling mud	Temp. (ºC)	Pressure (psi)	Plastic Viscosity (cP)	Yield Point (lb/100 ft^2)	10 sec Gel (lb/100 ft^2)	30 min Filtrate loss (mm)	Cake thickness (mm)
S5	26	14.7	10.79	7.86	5	8.67	0.3
	100	25	25.10	16.94	4	10.06	0.4
	121	50	22.42	33.76	11.67	13.43	0.63
	149	100	21.89	46.25	25.67	21.81	0.8
	176	150	16.23	23.79	27	23.87	0.5
	204	250	14.33	34.15	35.23	19.67	0.6
	232	300	13.12	59.74	41.25	22.17	1.23

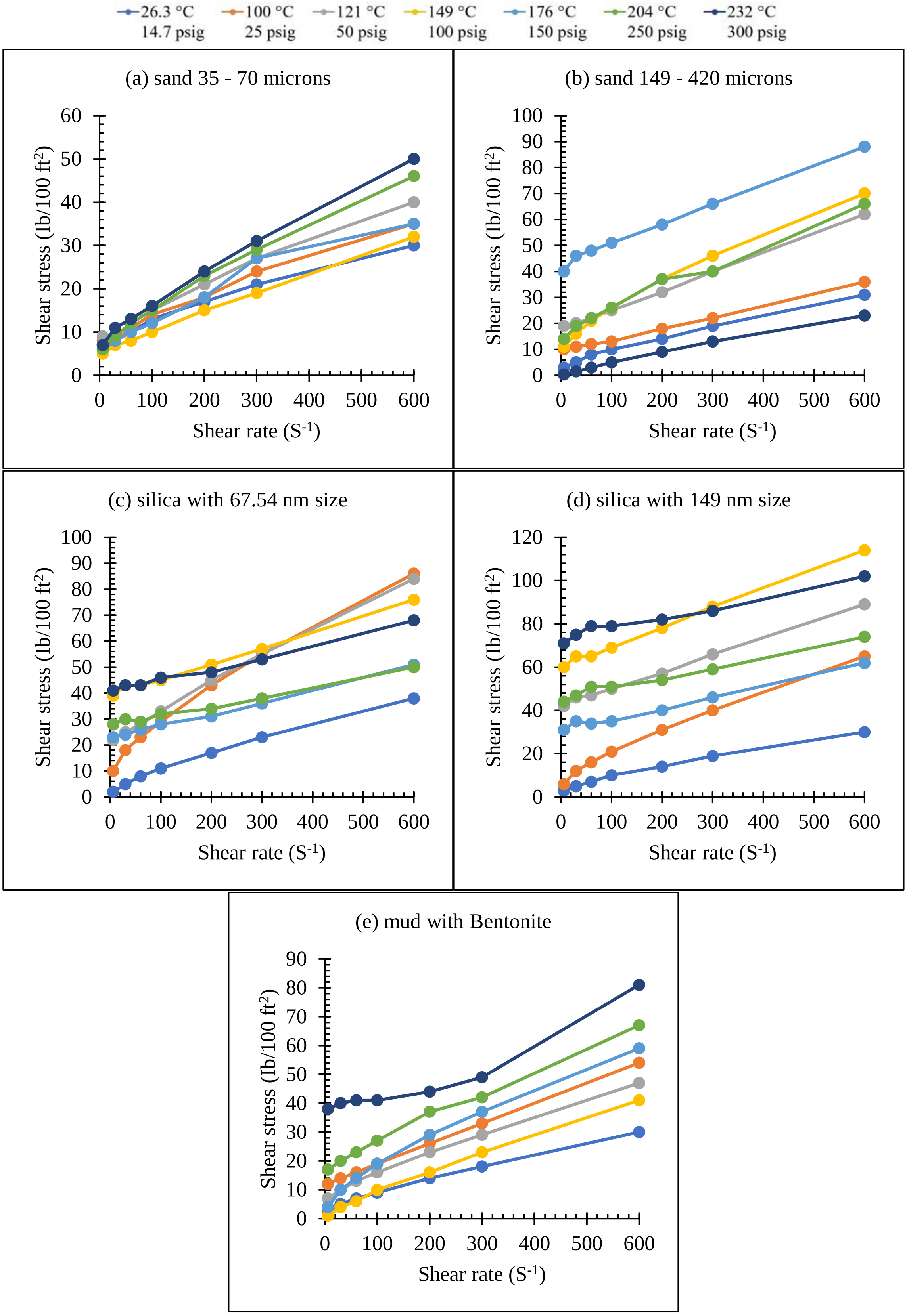
From Table 4.3 above, the mud properties of the formulations varied differently. The yield point of the mud formulations varied considerably with increase in temperature. As mentioned earlier, a mud with a high yield point will possess better cutting carrying abilities and will suspend the cuttings better compared to one with a low yield point. Mud formulations with sand and silica nanoparticles exhibited a higher yield point at mostly all temperatures compared to the bentonite reference mud except at room temperature where the reference mud exhibited higher yield point values. The gel strength of almost all of the muds increased with increasing temperature, though mud samples containing silica nanoparticles had higher gel profiles starting at 121 °C. When temperature increased above 121 °C, the trend of increasing gel profiles with both the reference mud and muds with sand nanoparticles changed. On average, mud fluids containing sand nanoparticles enhanced the filtration properties better than other mud samples, with the reference mud performing better or similar to mud samples containing silica nanoparticles. When compared to other mud samples, sand nanoparticles improved the filtration properties of the mud samples. It was also clear from Table 4.3 that the mud cake produced by muds containing sand nanoparticle was thinner than other mud samples, particularly with formulations containing sand nanoparticles of size (35-70 micron).

4.4.1. Viscosities of the new mud fluid containing nano sand

The shear-stress versus shear rate curves for the formulations comprising of nano silica and two distinct novel nano sand sizes are presented below in Figure 4.12. The graphs in Figure. 4.12 show a non-monotonic trend in the behaviour of the mud samples with changes in temperature. Temperature changes affected the mud samples differently with some mud samples exhibiting a shear thinning effect while other samples displayed a shear thickening effect. Shear thinning behaviour is desirable because it reduces pumping pressure and improves the rate of penetration when the viscosity in the pipes is low and where the shear rate of the drilling mud is high

Experimental results show that all samples behaved as plastic fluids at 26.3 to 232 ^{o}C. From the values of the best fit model parameters, the Bingham plastic and Power law models give wildly different predictions at particularly low shear rates meaning very high yield point in Bigham plastic, very high k value and low n value in Power law. This data therefore fits the Herschel-Bulkley model better which contains Bigham plastic and Power law. From the curves of the novel mud (a and b) below, the relationship between shear stress and shear rate is not linear between 0 and 300 rpm, but linearity increases up to 600 rpm, therefore, the two-parameter Bingham plastic model which assumes a linear relationship between shear stress and shear rate can partly describe the behaviour of these samples. This shows that the formulations have the acceptable flowing characteristics. The gradient of Bingham plastic model which is the ratio of shear stress to shear rate denotes the level of mud viscosity. When a fluid exhibits Bingham plastic behaviour, it won't flow until the shear stress surpasses a critical number known as the yield point. The plots show a gentle gradient throughout the dial speed indicating that the mud samples have the characteristics of least resistance to flow due to interparticle friction. From Figure 4.12 curve (a), shear stress steadily increases with increase in temperature at high shear rate. The steady increase shows the stability of the mud sample under increasing temperature. This mud sample retained its rheological properties under elevated conditions. On the other hand, Figure 4.12 curve (b) shear stress slightly decreased with increase in temperature at high shear rate. This is attributed to thermal dehydration and thermal dispersion of clay particles in the suspension. Though plastic viscosity of the fluid increases with the degree of dispersion of solid particles, its structural viscosity decreases with increasing shear rate. The decrease in structural viscosity was higher than the increase in plastic viscosity. Therefore, shear stress at high shear rate reduced rapidly with increasing temperature.

Rheograms also show that higher temperatures resulted in higher shear stress especially with addition of nanoparticles at high shear rates. This is because nanoparticles acted as chain joiners by reinforcing the bonds between the polymer matrix. Effective hole cleaning is achieved when the yield stress and gel strength are as low as possible [259]. The increase in yield point with increase in temperature was due to bentonite flocculation in the presence of nanoparticles. At low shear rates, shear stress increased when temperature increased and there was a divergence of the shear stresses towards different values for formulations in Figure. 4.12 (b), (c), (d) and (e). On the other hand, Figure 4.12 (a) shows that, there was a convergence of the shear stress towards similar values at least for the temperature tested. This behaviour indicates stability of the mud formulation. Stable viscosity profiles with increase in temperature indicates nano sand's ability to suppress viscosity reduction thereby yielding similar rheological behaviour with varying temperatures.



(a) sand 35 - 70 microns

(b) sand 149 - 420 microns

(c) silica with 67.54 nm size

(d) silica with 149 nm size

(e) mud with Bentonite

Figure 4.12: Viscosities of drilling mud at different shear rates

4.4.2. Plastic viscosities of mud fluid containing nano sand

Drilling muds are typically composed of randomly distributed particles in a continuous phase. Solid-to-solid mechanical friction causes plastic viscosity, which accounts for the entire flow resistance. Figure 4.13 below presents the plastic viscosity of the mud formulations after aging at different temperature. There was an increase in plastic viscosity with increase in temperature as seen in Figure 4.13 below. There was a slight reduction in plastic viscosity at room temperature with addition of nano particles except for sample S4. This reduction was because of nanoparticle’s ability to stop gel formations in the mud formulation which would have been caused by the colloidal mud particle interaction [260]. It should be noted that a mud with the lowest viscosity is preferred as it results in increased rate of penetration (ROP), provides better cooling and lubrication functions to borehole equipment, reduces fluid loss to the formation, and decreases pump pressure needed to facilitate circulation [131, 261]. It was observed that after a temperature of 121 °C, the plastic viscosity of S1 and S4 formulations increased, suggesting high temperature thickening and solidification effects. Uncontrolled increase in plastic viscosity is undesirable because it causes flocculation, which causes pump pressure loss, surge and swab pressure increases, and increased pump pressure costs. Mud formulation S2 and S 3 with nano sand exhibited stable plastic viscosity profiles at all temperatures. Stable viscosity at high temperature indicates the ability of nanoparticles to suppress viscosity decrease, resulting in the same rheological behaviour at different temperatures. This trend and behaviour of nano sand can be explained by the fact that nano sand particles were well dispersed around and between the bentonite platelets and cation exchange occurred in which the negatively charged nano sand neutralizes the positive charge on the bentonite surfaces, hence converting them to negatively charged bentonite platelets overall. This negative charge strengthened the repulsive force among bentonite platelets and led to an increase in the distance among bentonite particles; as a result, less friction was experienced [131]. Additionally, if a formulation is more complex with a wider range of particles size distribution including a rise in particle size less than 0.001 mm and larger nanoparticles with particle size distribution around 10-100 nm, it is more likely to result in a desired effect [252]. Hence the larger the particle size is, the lower the viscosity would be [262]. Therefore, nano sand in formulation S2 performed better than other formulations as seen from Figure 4.13 below.

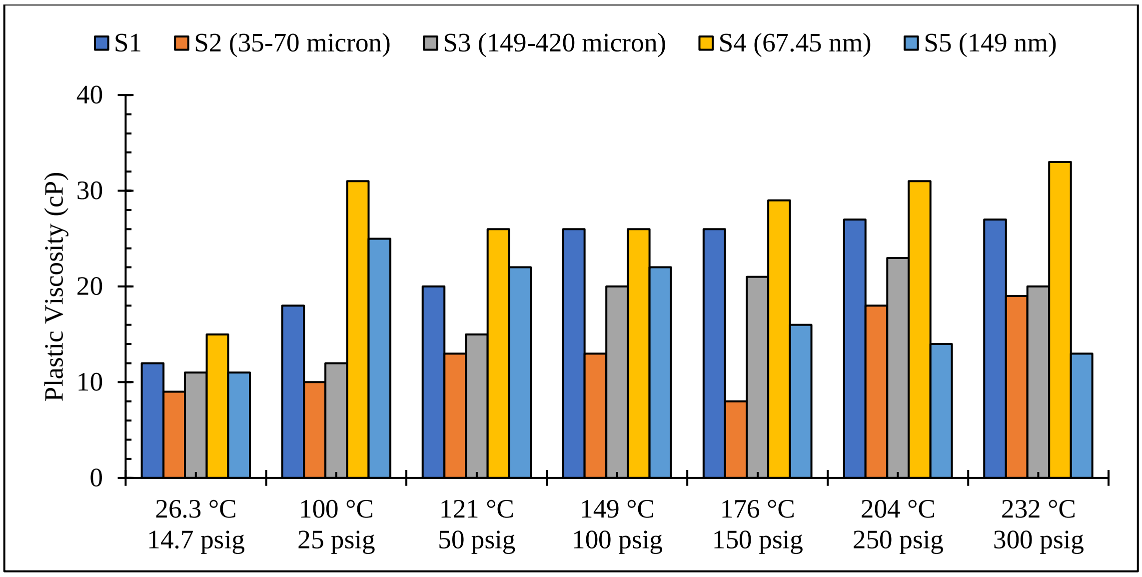


Figure 4.13: Plastic viscosity of the mud containing nano sand

4.4.3. Yield point of the mud containing nano sand

The flow resistance produced by electrochemical attractive forces in the mud particles is known as the yield point. Positive, negative, or neutral charge can be found on the surface of scattered particles in mud. Under dynamic conditions, these charges create electrochemical attractive or repulsive forces, causing the yield point to rise or fall [263, 264]. Figure 4.14 below presents the Yield point of muds with nano sand, nano silica and without nanoparticles before and after hot rolling at different temperatures. The ideal yield point suggested by Scomi Oil Tools [265] is below 25 Ib/100ft^2 for low temperature conditions and between 10 and 25 Ib/100ft^2 for HPHT conditions. As observed from Figure 4.14, at LPLT conditions, formulation S2 containing nano sand and S1 bentonite reference mud yield point values were within the recommended range at 26.3 °C. As temperature increased above 121 °C, the reference mud S1 yield point decreased below the recommended range. This is due to bentonite break down at HPHT conditions as increase in temperature causes bentonite to hydrate and passivate hence affecting clay properties. Though S5 formulation exhibited the highest yield point values when temperature increased above 121 °C, mud formulation S2 and S3 maintained a stable yield point profile with increasing temperature within the recommended range. This novel mud system with a new additive exhibited better cutting carrying abilities up to a temperature of 176 ^{o}C and thereafter, all nanoparticle mud fluid samples showed similarly the same yield point profile. Nanoparticle muds showed better cut carrying capabilities compared to the reference mud. This stability in yield point is due to the strong repulsive force between the negatively charged nano sand and the negatively charged bentonite. The strong electrostatic repulsion between negatively charged particles prevents coagulation, and thus a strong clay platelet network forms in the drilling mud system, increasing yield point [161]. Sample S3 performed better than S2 and S5 performed better than S4. Samples S3 and S5 both had a slightly bigger size than their counterpart. The performance of samples S3 and S5 containing bigger nanoparticle sizes then other samples is because, a more complicated formulation with a broader range of particle size distribution, such as a decrease in particle size smaller than 0.001 mm and larger nanoparticles with a particle size distribution of 10-100 nm, is more likely to produce the intended results [252]. Larger particles act as balls within the dispersion, preventing coagulation and resulting in higher yield point and low plastic viscosity. It is evident that nano sand improved the yield point property of the mud system.

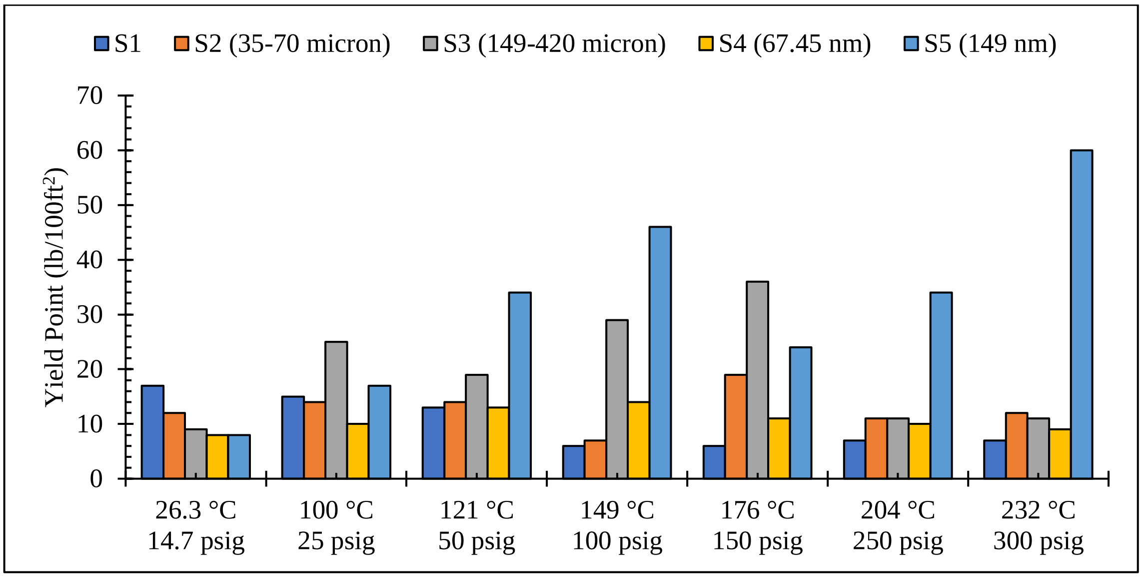


Figure 4.14: Yield point of the mud containing nano sand

4.4.4. Gel strength of the mud fluid containing nano sand

The gel strength of the mud formulations is presented in the Figure 4.15 below. The suggested range for the 10 sec gel strength of water-based mud is less than or equal to 15 Ib/100 ft^2 for formulations before aging and for formulations aged at LPLT and HPHT conditions [265]. Most of the formulation were outside of the suggested specification for 10 sec gel strength. The gel strength of all the formulations varied non-monotonically with temperature increase. As temperature increased up to 121 ^{o}C, most mud samples exhibited similarly the same gel strength apart from sample S3 whose gel was higher.

As temperature increased above 121 °C, formulations S2, S3 and the reference muds gel remained steady, but the trend changed for samples S4 and S5 as they exhibited higher gel strengths at temperature of 204 °C and 232 °C. It can be concluded that sample S2 maintained a stable gel strength with increase in temperature exhibiting the same gel strength at all temperature changes. It should be noted that very high gel strength is unwanted as it might lead to increase in pumpability costs in case drilling resumes, surging, swabbing and may lead to difficulties in removing cutting to the surface [22]. Also, low gel strength is not desirable as the mud will not be able to hold and suspend drilled cuttings and weighing materials when drilling is stopped therefore a balance needs to be maintained. Problems such as pipe sticking may arise if the cuttings and weighting materials settle to the bottom of a drilled borehole. There was also a change in trend at 232 °C for the reference mud as a rapid increase was observed different from the previous trend. This is an indication of total failure of the mud system. The unwanted increase in gel strength was because, as temperature increases, the mud fluid loses more of the fluidity property from the dispersion [266]. Temperature reduces the effectiveness of NP additives to protect the clay particles hence resulting in a high temperature thickening effect [252, 266].

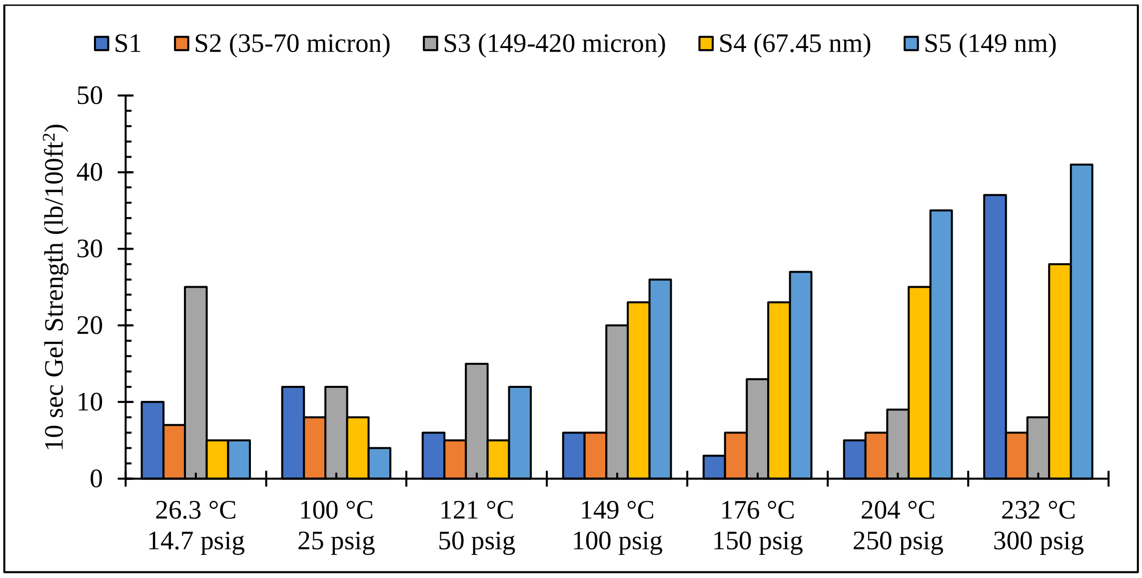


Figure 4.15: Gel strength of the mud containing nano sand

4.4.5. Filtration loss of the mud fluid containing nano sand

The filtration properties of the formulations were studied before and after aging. Figure 4.16 below shows that filtration loss increased with increase in temperature. The recommended value of HPHT fluid loss is that, it should be less than or equal to 25 ml after 30 min of filtration test [265]. Despite the increase in filtrate loss with increase in temperature, almost all fluid losses from the formulations were below 25 ml after 30 min HPHT filtrate test. The reference mud performed equally or slightly better than nanoparticle muds at LPLT conditions as all mud formulations lost similarly the same filtrate. As temperature increased, this trend changed, with the reference mud registering the highest filtrate loss of 16.7 ml, 20.85 ml and 25 ml at 121 ^{o}C, 204 ^{o}C, and 232 ^{o}C respectively. Increase in filtrate loss is due to the fact that bentonite WBMs may retain stability up to 121 ^{o}C and exhibit shear thickening behaviour at higher temperatures. This will cause borehole gelling and filtration issues [252]. On the other hand, addition of silica nanoparticles did not completely solve the problem as filtrate loss increased with addition of nano silica. This is because of bentonite particle deflocculation caused by the repulsive electrostatic forces between the negative bentonite surface and negative silica surface interaction leading to failure to form strong linked structures to strengthen the chains between bentonite and nanoparticles [142, 266-268]. Nano sand on average lost the least filtrate compared to the reference bentonite formulation and formulations with nano silica. Mud formulation S2 lost the least filtrate at all temperatures except at 176 ^{o}C. This is partly due to the size of the nano sand which facilitated the blocking and sealing of the nano pore throats of clay hence reducing filtrate loss. Fluid loss containing nano sand is provided by hydraulic flow or diffusion into the pore structure where the precipitated nano sand act as a physical barrier, preventing additional pore penetration and filtrate invasion. As a result, the wellbore and formation are pressure separated, and fluid loss is halted. Furthermore, edge-to-face (positive edge bentonite-negative face bentonite) facilitated the formation of clusters that trapped nano sand between clay particles forming heterocoagulated formation which traps the fluid within the structure hence reducing fluid loss [258, 269]. This is because, when two particles of distinct characteristics such as size, charge or chemical composition interact, it will lead to a formation of clusters and lastly result in the formation of a gel like structure known as heterocoagulation structure [269].

At a temperature of 204 ^{o}C and 232 ^{o}C, filtrate loss for all mud formulations increased except for formulation S2 whose filtrate loss remained the same at elevated temperatures. At the same temperatures, the reference mud exhibited the highest filtrate loss of 20.85 ml and 25 ml respectively. Formulation S2 performed better than formulation S3 because the bigger size of nano sand in S3 failed to block or plug the pores hence resulting in more filtrate loss.

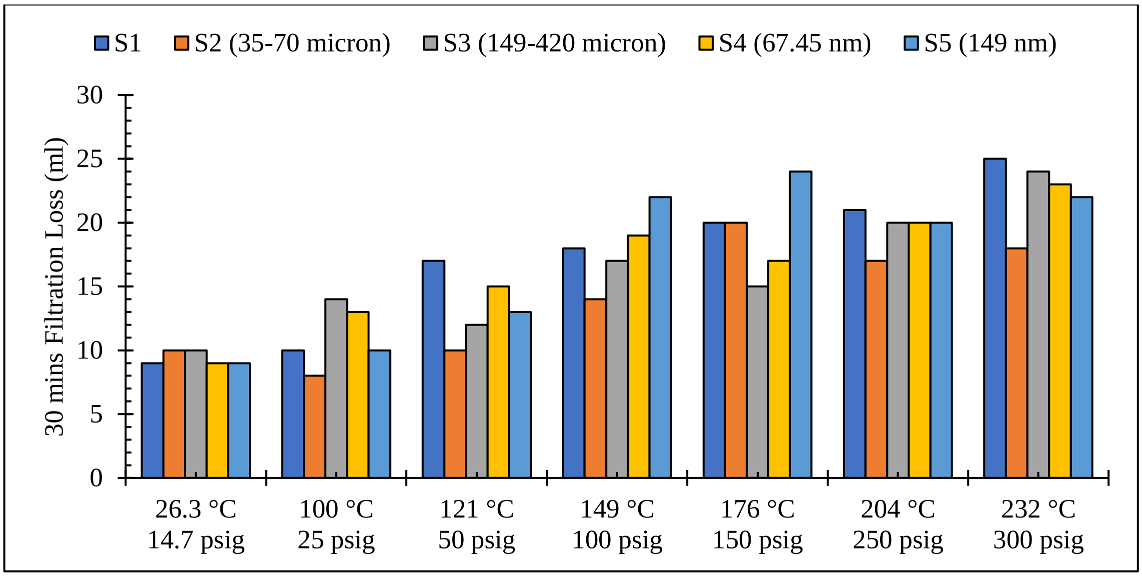


Figure 4.16: Filtration loss of the mud containing nano sand

4.4.6. Mud cake of the mud fluid containing Nano sand

A filter cake or mud cake will form at the wellbore across the porous zone when filtrate is lost from the wellbore into the formation through the permeable zone. Excessive filtration loss can damage the formation. Any successful mud formulation must produce a thin, firm impermeable filter cake when filtration loss occurs to minimise additional formation contamination due to filtrate loss and a blocked pipe due to an uneven or too thick mud cake. [270]. Practically, the filter cake from API or HTHP fluid loss test should be less than or equal to 1/16 inch (1.6mm). Figure 4.17 below present the mud cake formed by the formulations before and after aging. The reference mud produced a thinner mud cake up to a temperature of 149 ^{o}C. It is evident that the reference mud performed better compared to formulations with nanoparticles except for formulation S2. Above 149 ^{o}C, the mud cake of the reference mud started increasing indicating the beginning of flocculation and failure. Almost all formulation mud cakes thickness increased as temperature increased. This problem was aggravated by the thermal degradation of filtrate control additives and viscosifiers. This is because, at 149 ^{o}C, starch undergoes a process known as hydrolysis and depolymerization of thinners, or irreversible chemical processes, which results in the drilling mud's full degradation [271].

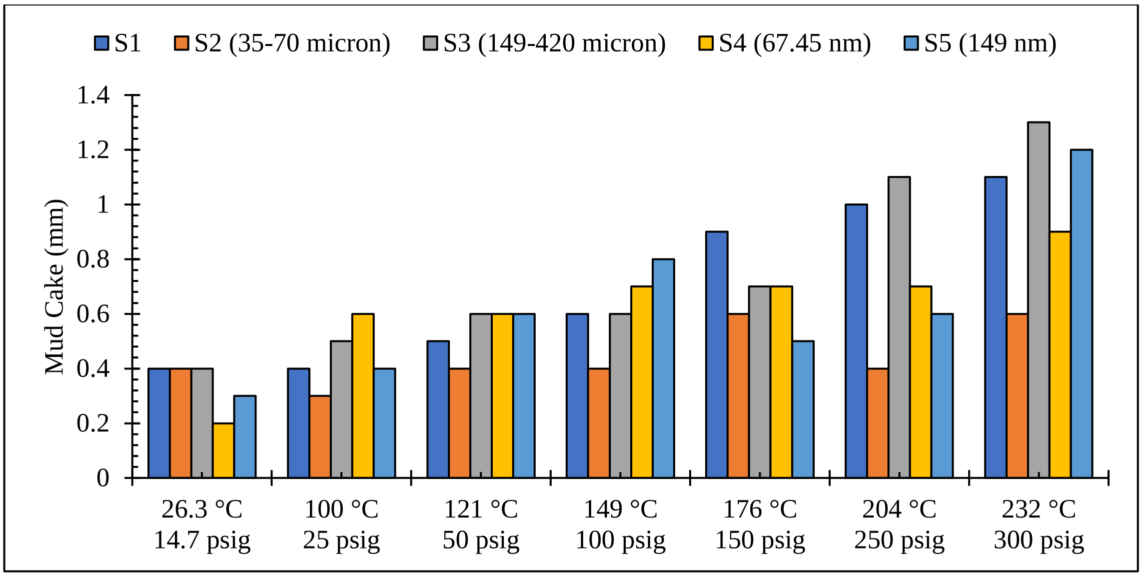
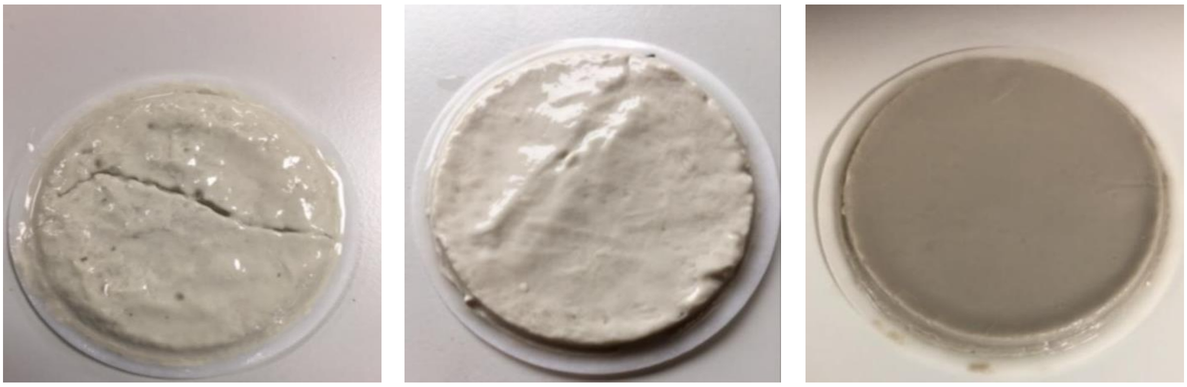


Figure 4.17: Mud cake of the mud containing nano sand

Mud formulation S2 with nano sand produced a thinner mud cake compared to all other formulations which explains the least amount of filtrate loss from this sample compared to other samples at almost all temperatures. The permeability of the mud cake formed by formulations containing nano sand was low compared to formulations containing nano silica and the reference mud according to the observation presented in Figure 4.18 below. In addition to the above, sample S2 filter cake was thinner and non-erodible, but for samples with nano silica and the reference mud, the mud cake produced was soft and more highly permeable. This supports the theoretical idea of the formation of the rigid structure network between bentonite and nano sand because of the electrostatic attraction around edge-to-face (the positive edge bentonite negative face bentonite). The attraction trapped nano sand between bentonite particles and formed a linked structure retaining the fluid within the structure and resulting in reduction in the filtrate volume loss. From this analysis, it can be stated that nano sand would be the best choice for preventing fluid loss, but a lower percentage might be chosen if a lower viscosity and yield point are required for WBMs to have a higher drilling efficiency. S2 performed better than S3 formulation, S 4 and S 5 produced a thinner mud cake compared to the reference mud above temperatures of 149 ^{o}C.



Reference Silica NPs Sand NPs

Figure 4.18: Mud cake produced by mud containing nano silica and nano sand

4.4.7. Effects of pressure on the rheological properties

Figure 4.19 below presents the effect of pressure on the rheological properties of a WBM. Temperature was kept constant at 121 ^{o} C. The impacts of pressure can be perceived to be less visible than the effects of temperature. It can be seen from Figure 4.19 that as pressure changed, rheology changed slightly, and in some cases, there was no significant difference or change in rheology as pressure incresaed. In all investigated ranges of imposed pressure, viscosity showed a slight increment with increasing pressure. The influence of pressure on gel strength is essential for the start -up procedure after process stoppages [272]. Therefore, we can say that pressure affects the behavior of drilling muds in the solid-like regime, mainly the deformation required to break up the gel and initiate flow after the mud has been quiescent for some time . The results agree with the work done by Amani and Al-Jubouri, Wang et al. and William et al. who urgued that pressure is negligible for aqueous suspensions and that temperature is more predominant [273-275]. G´essica et at, also concluded that the impact of pressure is more relevant in the soild than in the liquid like regime [42]. Another point to address is that the concept that pressure affects the material only above a particular value is valid only for the liquid-regime in which the viscosity is not much affected for the case 270 bar applied pressure [42]. In this study, the maximum pressure tested was 26 bar. This was because of the limitations on the equipment used. As a result, the effects of pressure were not felt.

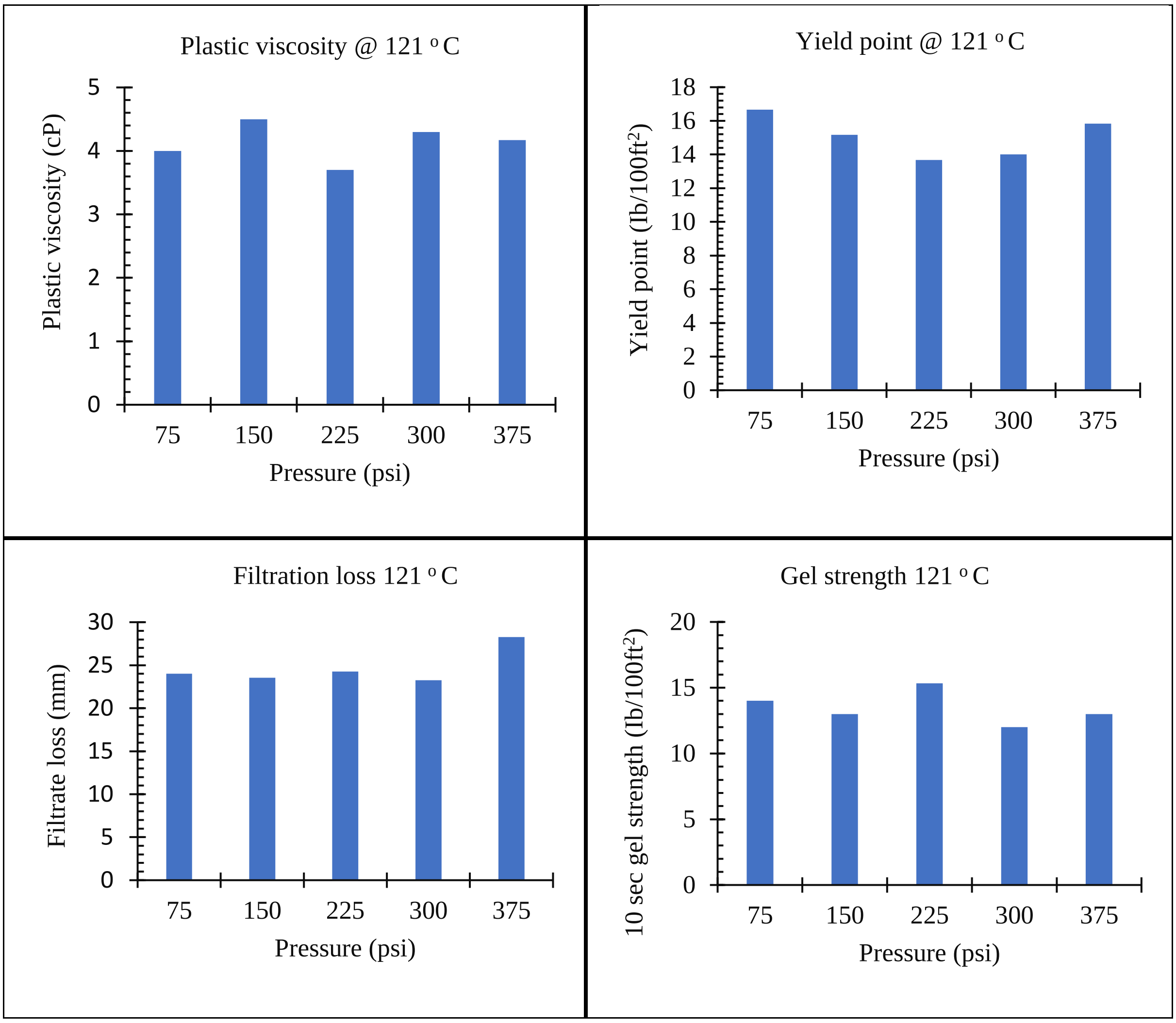


Figure 4.19: Effects of pressure on the rheological properties of bentonite WBM at a constant temperature of 121 °C

4.5. Chapter Summary

The rheology of water-based mud fluids tends to decrease when temperatures exceed 121 ^{o}C. Bentonite WBMs are stable up to 121 ^{o}C and exhibit shear thickening behaviour at temperatures above 121 ^{o}C. This will result in borehole gelling and filtration issues [252]. Temperature exerts a complex influence on the rheology of drilling muds and the effects can be classified as (i) high temperature thinning, (ii) high temperature thickening and (ii) high temperature solidification [2]. Therefore, water-based muds need to be improved in order to perform in high pressure and high temperature environments. In drilling engineering, nanotechnology has been widely used in the design of drilling mud fluid. This research therefore exploited silica nanoparticles as a way of stabilising water-based muds in HPHT environments. It was observed in the early stages of this research that negative drastic results had been reported in the literature on silica nanoparticle performance by using silica in the size of 15-30 nm. As a result, this research decided to investigate a larger sample size than previously reported. Nanoparticles of size 100 and above were tested and the results showed that there was improvement in the rheological properties. If a formulation is more complex with a wider range of particles size distribution including a rise in particle size less than 0.001 mm and larger nanoparticles with particle size distribution around 10-100 nm, it is more likely to result in desired effects [252]. It was found that silica at a concentration of 0.5 wt.% produced the desired rheological properties and reduced filtrated loss by 7.5%, 9.1%, 15.4% and 6.7% when temperature increased to 100 °C, 121 °C, 149 °C and 176 °C respectively.

Formulations with nano silica exhibited stable profiles with temperature increase. However, filtration capabilities were lacking and therefore other dynamics affecting silica dispersion in water-based muds, such as repulsive and attractive forces and their effects on colloidal interaction and zeta potential, were investigated to understand the forces that affect stable dispersion of colloidal mixtures. In order to study the effects of repulsive and attractive forces on the rheology of the drilling formulations, a cationic surfactant called hexadecyltrimethylammonium bromide (CTAB) was utilised to alter the surface charge of nano silica. Additionally, the optimum concentration of CTAB that would effectively alter the surface of nano silica was also investigated. From the experimental observations, formulations with nano silica having the highest absolute zeta potential value of 35.4 and 37.1 millivolts (mV) performed better than formulations containing nano silica with low absolute zeta potential value. The effects of repulsive and attractive forces played a vital role in improving the rheological properties further. Filtration loss was reduced on average by 11.4, 17.6 and 29.5% by mud samples MS 4, MS 5 and MS 6 respectively at all temperatures when compared to the reference mud and mud with unmodified silica. The optimal amount of CTAB to modify nanoparticles was found to be between 1.0 and 2.0 wt.%. This concentration when added to nano silica resulted to effective surface modification which led to enhanced rheology when used. The effects of pressure on the rheology of WBMs was not noticeable, as pressure variations resulted in little or negligible changes in rheology.

This research main aim was to come up with a novel, cheap and environmentally friendly additive that could perform similarly or even better than commercial additives when used in HPHT drilling conditions. Having investigated the dispersion of silica in colloidal solutions in the early stages of this research, nano sand was introduced to study its performance in drilling mud. Observations proved that nano sand improved both drilling mud rheology and filtration properties. Compared to silica nanoparticles, nano sand exhibited similarly or better stable rheological profiles as temperature increased better than formulations with nano silica. It was evident that Sample S 2 (35-70 micron) exhibited the ability to effectively improve the rheological properties of WBM. Sample S 2 (35-70 micron) filtrate loss was reduced by 16.35% and 29.52% at temperatures of 204 °C and 232 °C respectively. At the same temperatures, the mud cake thickness was reduced by 54.74% and 45.45% respectively by the same mud sample compared to other formulations. This novel, cheap and environmentally friendly drilling mud additive can suite operations in HPHT environments.

Chapter 5: Conclusion, Recommendations, and Future Work

5.1. Overview

In this study, the dynamics that affect the dispersion abilities of silica nanoparticles in water-based mud system at high temperature were investigated. Nanotechnology is widely used in oil and gas industry and the drilling industry has benefited vastly from this technology. Despite its success, this technology has been found to be very expensive, and its toxicity has not been fully addressed. The process of nanoparticle synthesis and surface modification alone is costly, not to mention the large quantities of nanoparticle materials required during a drilling operation. Therefore, the industry is now in need of a non-toxic, environmentally friendly, less expensive, and biodegradable additive that will similarly perform like commercial additives. Commercial additives have also been found to degrade under elevated temperatures and their stability is limited to a certain temperature therefore, other additives must be added to nano drilling mud systems to supplement and stabilise these mud systems under HPHT. This has always resulted to increased drilling operation costs which the industry is trying to avoid. The industry has gone as far as employing hybrid drilling muds, a new form of nanofluids using metallic nanoparticles such as gold, zinc, titanium together with carbo nanoparticles such as silica, carbon nanotubes, graphene etc which is very expensive hence resulting in increased costs. To stabilise nanoparticles in drilling mud systems, the dynamics through which they disperse and degrade at elevated temperatures and pressures must be understood. In Chapters 2 and 4, it is evident that bentonite and nanoparticle drilling muds become unstable and degrade under the following mechanisms at high temperatures:

- Hydrolysis and depolymerization of thinners
- Repulsive forces
- Attractive forces
- Partical size
- Zeta potential

As a result, this study sought to comprehend these dynamics and establish how they affect colloidal dispersions. This was to serve as a baseline for developing a novel drilling mud system that would perform similarly to muds containing commercial additives. Chapter 2 further demonstrated that nanoparticles can stabilize mud fluid systems, but they are expensive.

Based on the above mechanisms that effect nanoparticle dispersion, silica nanoparticles with different surface charges and sizes were synthesised and analyzed to identify a combination that would improve mud rheology and filtration properties at elevated conditions. The evaluated nanoparticles are presented in Table 3.4. All the efforts by researchers as highlighted in Chapter 2 have brought to the forefront the attempts made in stabilizing water-based fluids at HPHT but none has however considered the combination used in this work as presented in Table 3.5.

Almost all results show that as temperature increases, there is a peak and a fall, indicating a nonlinear trend of results. This is inherently the nature of non-Newtonian fluids, you get a peak, and it starts to fall. When the weight% volume fraction was observed, there was an upper limit 1.0 wt.% above which the continuous increase in nanoparticle concentration resulted in no improvement in rheology and filtration properties, but rather a counter reaction that resulted in other effects such as sedimentation. During drilling operations, the bit is always rotating, and this creates Coriolis force effect and when nanoparticles are added to a drilling formulation, it creates agglomeration (big chunks) hence affecting smooth movement and when HPHT effects are added on top of that, you will never see a nice smooth increment or trend from left to the right. This explains the non-monotonic trend in the behaviour of mud fluid formulations at all varying temperatures.

5.2. Conclusion

The objective of carrying out this research was to investigate the performance of silica nanoparticles, understand the dynamics that affect silica nanoparticles in colloidal systems and based on the findings, design a novel, cheap, environmentally friendly drilling mud system using nano sand. The study involved running laboratory experiments in which mud formulations containing nano silica and nano sand were aged at various temperatures and pressures before being tested for rheology and filtration properties. The equipment described in Chapter 3 were used to prepare the mud formulations and to measure the drilling mud properties. The following conclusions were drawn from this study based on the findings of the results obtained.

1. The optimum nanoparticle concentration was found to be 0.5 wt.%. Above 0.5 wt.% would have been a waste of resources and below 0.5 wt.%, there was no significant effect observed.

2. Modified nano silica improved the rheology and filtration characteristics of the water-based formulations.
3. The drilling muds formulations with nano sand exhibited shear thinning and thixotropic characteristics. Shear thinning and thixotropic properties indicate good cuttings carrying abilities, good weighting material suspension and transport and good hole cleaning capabilities.
4. Mud formulations S 2 and S 3 with nano sand maintained stable plastic viscosity profiles with increase in temperature which indicates the ability of nano sand to suppress viscosity reduction hence resulting in similar rheological behaviour at changing temperatures.
5. Compared to other formulations, the bentonite formulation and formulation containing nano silica, plastic viscosity increased with increasing temperature which is unwanted except for formulation S 5.
6. Silica nano particles when compared to the reference bentonite mud performed better by improving the rheological and filtration properties at HPHT conditions though their performance was lacking when compared to the novel formulation with nano sand.
7. When compared to reference bentonite formulation, the new additive nano sand exhibited better cutting carrying abilities up to a temperature 176 ^{o}C and thereafter, all NP mud fluid samples showed similarly the same yield point profile.
8. Formulation S 3 containing (149-420 micro) maintained a yield point values similarly to formulation S 5 with nanoparticles.
9. There was no statistically significant variation in plastic viscosity and yield point across the samples with nano sand when compared to samples with silica nanoparticles, with formulations containing sand nanoparticles performing similarly or better than formulations containing silica nanoparticle muds.
10. Sample S 2 containing nano sand (35-70 micron) filtrate loss was reduced by 16.35% and 29.52% at temperatures of 204 °C and 232 °C respectively compared 5.66% and 11.32% by formulation S 5 containing nano silica.
11. At the same temperatures, the mud cake thickness was reduced by 54.74% and 45.45% respectively by the same mud sample S 2 compared to 36.84% and 11.81% by sample S 5. This new mud system can suite operations in HPHT environments. Therefore, nano sand improved the filtration properties of the water-based mud better than nano silica.

12. The mud cake produced by formulations containing nano sand was thinner, smoother and less permeable compared to the one produced by the formulations containing nano silica and the reference mud.
13. Nano sand formulations were cheaper as sand can be found freely compared to formulations containing silica. Silica had to be synthesised and the materials used costed a lot more than free sand.

5.3. Limitations

Though the intended goals of this study were achieved, there was some limitations encountered during the experiment such as.

- According to the equipment, the maximum ageing temperature and pressure was at 232 °C and 300 psi. There for the formulation could not be tested above those condition to evaluate Ultra-HPHT environments
- Nano sand size could not be reduced any further as there was an issue with the machine therefore, the sizes tested were kept at 35-70 micro and 149-420 micro

5.4. Recommendations and future work

The aims and objectives of this current study have been met within its scope following the analysis of the experimental results. However, there is still need to carry out further investigations on the effects of other mud additives which are environmentally friendly and cheap but also outside the scope of this current study. Further studies will contribute massively to the knowledge and reduce the gap in knowledge with regards to the mud additives used in the current study. For those reasons, the following recommendations are made:

1. Further work could focus on the effects of added additives on the pump life cycle and equipments used in drilling operations.
2. The maximum temperature tested was at 232 °C as this was the maximum operating temperature of the ovens used in this study. Nowadays, deeper and hotter wells are drilled, in that regard, further research should be undertaken to establish the effects of temperatures above 232 °C on nano sand in water-based mud.
3. Further research could concentrate on the chemistry of the mud formulations and their effects on the reactive shale rocks.

4. Future research can focus on modifying the surface of nano sand as it had been established in Phase 3 that surface modification can further increase the performance of silica nanoparticles.
5. Further investigations could concentrate of reducing the size of nano sand further and establish the effects of smaller nano sand performance.

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