

https://dspace.org/

Investigation of the use of nanomaterial surfactants for oil emulsion drilling muds for deep-hole conditions

Kgwete, Maele Noma

2018

https://hdl.handle.net/10539/26594

Kgwete, Maele Noma, (2018) Investigation of the use of nanomaterial surfactants for oil emulsion drilling muds for deep-hole conditions, University of the Witwatersrand, Johannesburg, https://hdl.handle.net/10539/26594

Downloaded from a DSpace repository. https://dspace.org/



Investigation of the use of nanomaterial surfactants for oil emulsion drilling muds for deep-hole conditions

Prepared by

Maele Noma Kgwete

(Student number: 552591)

(MSc (50/50) Research Report in Oil and Gas Engineering)

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa

September 2018

DECLARATION:

I declare that this report is my own, unaided work. I have read the University Policy on Plagiarism and hereby confirm that no Plagiarism exists in this report. I also confirm that there is no copying nor is there any copyright infringement. I willingly submit to any investigation in this regard by the School of Chemical Engineering and I undertake to abide by the decision of any such investigation.

_____ 20 September 2018

Signature Date

ABSTRACT

The challenges faced by recovery methods for the extraction of oil and gas from reservoirs are related to existing drilling operations. Consequently, the muds become susceptible to poor heat transfer, disintegration, gelation, pipe sticking, poor cleaning ability, and poor lubrication. The challenges in drilling operations at high temperature and high pressure (HTHP) conditions can be mitigated when rheological properties are controlled and monitored. This research focusses on the investigation of the use of nanomaterial surfactants for oil emulsion (OBM) drilling muds in order to address the challenges in HTHP conditions.

Emulsion drilling fluids with and without nanoparticle were prepared. ZnO nanoparticle was selected for this research based on its unique thermal stability properties. The drilling fluid package comprised 100 g of distilled water, 1 wt% of NaCl, 1 wt.% of $CaCl_2$, various amount of surfactant (Triton® X-100 or DTAB) and + 6 wt.% of bentonite. The surfactant concentration varied from 0.25 to 1.25 % with 0.25 intervals. To evaluate and compare the contributions of surfactants and nanomaterial, the prepared drilling fluids were subject to rheological and filtration test.

The results showed that DTAB surfactants-based drilling mud with ZnO nanoparticle showed a more stability compared to Triton. The decrease in viscosity with DTAB did not have a significant impact of the filtration loss in the presence of ZnO nanoparticles. The drilling fluids showed a dilatant and shear thickening behavior. The filtration test showed that 1 % of surfactant loss minimal amount of fluid and ZnO nanoparticle reduced the fluid lost capacity. The emulsion contained DTAB as surfactant and ZnO nanoparticle performs better in terms of retaining water and/or liquid in the mud; therefore, making it suitable for drilling at HTHP conditions.

DEDICATION

I dedicate this report to my beloved father and mother

Freddy Kgwete and Ngwanaleshega Dorcas Kgwete

And

To my sister ***Bakedi Kgwete***

For all the battles she fought in 2017 and 2018, this research echoes her strength!

ACKNOWLEDGEMENT

This is the sweetest last part writing of my research. I thank God for the strength He instilled in me to arrive at this point. It has been a fruitful journey. It is now associated with my current passion for renewable energy and energy in general.

First, I must commence with thanking my supervisor Dr Nkazi who pushed me to always work to the best of my ability and constantly held phone calls to offer advice and guidance in my research. My gratitude goes to his ever-spirited advice and encouragement to go from average to the best, acknowledge my gratitude for him believing that a mining engineer can relate to chemical engineering discipline.

I would like to express special thanks to CHIETA for sponsoring me with a full bursary to pursue my studies. I got the opportunity to work under TOTAL Professeurs Associès and therefore deeply obliged for their support.

I am thankful for Witwatersrand chemical engineering lecturers for their input towards my education and the wisdom I received from the guest international lectures.

Lastly, I would not be where I am without my family. They are the source of my strength and encouragement. Sincere gratitude to my parents for always encouraging me to go the extra mile in life! As a personal note, I place a profound appreciation to my siblings; Nogane, Bakedi, Mokwena, Oupa and Mpumi for always being there for me and making my life the best.

TABLE OF CONTENTS

Content **Page**

DECLARATION: i
ABSTRACT i
ACKNOWLEDGEMENT iii
LIST OF FIGURES vi
LIST OF TABLES vii
NOMENCLATURE viii
CHAPTER 1 : BACKGROUND AND MOTIVATION **1**

1.1 Background 1
1.2 Problem statement 2
1.3 Objective of the study 3
1.3 Delimitation of the study 3
1.4 Justification of research report 4
1.5 Structure of the report 4
CHAPTER 2 : LITERATURE REVIEW **6**

2.1 Introduction 6
2.2 Drilling mechanism 6
2.3 WBM vs OBM 8
2.4 Drilling muds in HTHP 9
2.4.1 Challenges at HTHP Operations 10
2.5 Rheology properties 11
2.5.1 Shear stress 12
2.5.1 Yield stress and Thixotropy 12
2.5.2 Gel strength 13
2.6 Rheological Challenges 15
2.6.1 Filtration Limitations 15
2.6.2 Thermal Conductivity 18
2.6.3 Surface Area 19
2.6.4 Pipe Sticking 21
2.6.6 Wellbore instability 21
2.7 Rheology models 21
2.8 Drilling Fluid Additives 24
2.8.1 Surfactants and brines 24
2.8.2 Deep-hole operations 25
2.9 Nanomaterial design and application 26

2.9.1 Nanotechnology 26
2.9.2 Properties of nanomaterial 28
2.9.3 Advantages and limitations of nanomaterial 28
2.10 Nanomaterials Synthesis 29
2.10.1 Metal oxide nanoparticles 29
2.10.2 Metallic nanoparticles 30
2.10.3 Carbon nanotubes (CNTs) 31
2.10.4 Cost of nanoparticle synthesis 31
2.12 ZnO nanoparticle 32
CHAPTER 3 : Experimental procedures AND ANALYTICAL TECHNIQUES 33
3.1 Materials used 33
3.1.1 Nanoparticle 33
3.1.2 Surfactants 33
3.1.3 Fluids used 34
3.1.4 Sample Used 34
3.2 Synthesis of emulsion-based drilling fluid 34
3.3. Measurement of mud filtrate loss 36
CHAPTER 4 : RESULTS AND DISCUSSION 38
4.1 Rheological test 38
4.2 Mud Viscosity 40
4.3 Emulsions stabilities 41
4.4 Filtration test 42
4.5 Effect of water content 44
CHAPTER 5 : Conclusion AND RECOMMENDATIONS 46
5.1 Conclusion 46
5.2 Recommendations 47
Below are the recommendation for future investigations 47
REFERENCES 48
APPENDIX 51
APPENDIX A: RHEOLOGY 51
APPENDIX B: FILTRATION LOSS 63

LIST OF FIGURES

Figure 2.1: Illustration of a drilling rig on an offshore platform 7
Figure 2.2: Drilling cost estimation 11
Figure 2.3 Base drilling mud and nanomaterial base muds 14
Figure 2.4: Flow behaviour of OBM (30 %v water) showing the effect of nano silica and nanoclay 15
Figure 2.5: The effect of the composition of Pal to rheological properties 15
Figure 2.6: Graphical representation of recovery factor vs. pore volume at different flooding test 16
Figure 2.7: A 5000 magnification of filter cake resulting from HTHP filtration test 17
Figure 2.8: An illustration of decreasing nanoparticle size to increase surface area 19
Figure 2.9: An illustration of the same volume of materials showing surface area variation (Amanullah & Al-Tahini, 2009; Fakoya & Shah, 2017) 20
Figure 2.10: Illustration of the laminar behaviour of different drilling fluids 22
Figure 2.11: The available categories used to optimise EOR 26
Figure 2.12: Design and applications of nanotechnology in the petroleum industry 27
Figure 2.13: Example of current nanoparticles 30
Figure 2.14: An illustration of the mechanism salt reduction synthesis to form of metallic nanoparticles formation 30
Figure 3.1: Brine-oil ratio (9:1) 35
Figure 3.2: (a) Hielscher UP200S Ultrasonic Process (b) Ohaus Explorer EP413 balance 36
Figure 3.3: (a) Rheometer (b) Schleicher & Schuell No.1505 filter 37
Figure 4.1: Shear stress versus shear rate of emulsion-based drilling fluid 39
Figure 4.2: Viscosity versus shear rate of emulsion-based drilling fluid 40
Figure 4.3: Emulsion based drilling fluids with (a) DTAB and (b) Triton® X-100 41
Figure 4.4: Filtration loss of drilling fluid with 1Wt% DTAB 42
Figure 4.5: Filtration loss of drilling fluid with 1Wt% Triton® X-100 43
Figure 4.6: Filtration loss of drilling fluid with 1Wt% DTAB + ZnO 43
Figure 4.7: Filtration loss of drilling fluid with 1Wt% Triton® X-100 + ZnO 44
Figure 4.8 : Filtrate volume over time 45

Figure 4.9: Filtration loss of drilling fluid with different surfactants 45

LIST OF TABLES

Table 2.1: Chemical and physical properties of ZnO 32
Table 3.1: Chemical properties of surfactants 33
Table 3.2 : Brine fluids 34
Table 3.3 : Synthesis of emulsion-based drilling fluids..... 34
Table 3.4 : The ratios of the n-Wt. % of the surfactants..... 35

NOMENCLATURE

HTTPS	High Temperature High Pressure
LTLP	Low Temperature Low Pressure
ROP	Rate of Penetration
IFT	Interfacial Tension
MLR	Multiple Linear Regression
EOR	Enhanced Oil Recovery
OBM	Oil-based mud
WBM	Water-based mud
GBM	Gas-based mud
API	American Petroleum Institute
BYM	Bourgoyne and Young's mode
ANN	Artificial neural network
CNT	Carbon nanotubes
DTAB	Dodecyl Dodecyltrimethylammonium bromide
HCL	Hydrochloric Acid
FOR Rheology Models:	
cp	Centipoise
$\tau_\circ$	Yield Stress
Θ (lb/100ft^2)	Gel strength in pounds per square feet
ρ	Density
μ_{Pl}	Plastic Viscosity
RPM	Revolution per Minute
μ	mud viscosity
Pa.s	Pascal - second
s^{-1}	Revolutions per second
psi	Pounds per square inch
kPa	Kilopascal
γ	Shear rate
τ	Shear Stress

CHAPTER 1 : BACKGROUND AND MOTIVATION

1.1 Background

The peak of energy demand is fast approaching, proponents of the oil and gas industry foresaw the definite need that requires the full utilization of resources. According to Mahendranath, et al (2015), the energy consumption demand is predicted to increase. However, the continuous decreasing availability of hydrocarbons and increasing extraction costs due to the continuous development of global energy demand presents the need for new techniques. To assist with the improvement of penetration rates that results in better productivity. The major challenges associated with the increasing cost of extractions in the petroleum industry include unrecovered resources left in-situ reservoirs, the damage of equipment due to drilling, and the limited knowledge on the exploration of the unconventional reservoir (Mahendranath, et al., 2015).

In addition, Kasiralvalad (2014) distinguished that some of the biggest expenses in the drilling and production operations are associated with the costs of drilling fluids (herein 'drilling muds'). In another study by Husein (2012), it was estimated that the loss of drilling mud can cost the petroleum industry approximately $800 million per year. The study also signifying that the cost factor is associated with drilling operations, which is highly subjected to the application of drilling muds. In recent studies the application and selection of nanotechnology as a solution to these challenges is appealing.

Nanotechnology coupled with drilling mud technology is an advanced technique that is currently being considered to enhance oil recovery (Kasiralvalad, 2014). The most apparent application of nanotechnology is the development of nanomaterial based fluids ("smart fluids" or "nanofluids") in the upstream operations (Sun, et al., 2017). Nanofluids are nanoformulations of micro-emulsions and surfactants, which are created by synthesising nanosized particles to fluids to enhance their rheological properties. The technical benefits of these fluids can present significant solutions in enhancing stability against sedimentation, drag reduction, corrosion control, provide lubrication, wettability alteration and intensify drilling fluid quality. Among these more recent developments included metal oxide nanoparticles (TiO_2, ZnO, MgO, Al_2 O_3,

F_2O_3 and SiO_2). These particles offer heat transfer and conductivity properties which enhances the mobility of drill cuttings.

Although extensive research in nanomaterial has been done over the past five decades, the complex operations involved in the current oil and gas drilling means that the application of nanotechnology is in its early stages (Kasiralvalad, 2014). Some of the new developed nanoparticles (nanosilica and bentonite clay) and are not water absorbing some cannot withstand the extreme HTHP conditions (Geng, 2015). Hence several researchers have noted that custom made nanoparticles to enhance their rheological properties is more effective. Moreover, the dimension of nanomaterial, in general, has unique properties, that offer technical benefits. However, it is noted that the integration of these processes and techniques still needs to be further researched to pave the way for the industry to upscale research into real-world oilfield application.

Therefore, the aim of this research is to investigate the use of nanomaterial surfactants for oil emulsion drilling muds for deep-hole drilling in the petroleum industry based on current advancement. First, investigate the challenges of conventional drilling fluid at HTHP operations. Second, create emulsion based drilling fluids and evaluate the rheological properties by varying concentrations of surfactants in nanomuds and conventional muds. Third, find out the rheological properties that can increase the efficiency of drilling muds and address severe drilling problems at HTHP operations.

1.2 Problem statement

The current challenges of depleting conventional reservoir and low recovery rates in unconventional reservoirs, coupled with the increased operating costs and money lost to drilling mud led to the need to evaluate and suggest an customised drilling muds for HTHP conditions. The current degrading status of surfactants used at deep-hole drilling shows that they do not have the appropriate rheology and high-temperature transfer. Therefore, there is a need for the demonstration of how the behaviour of nanomaterial surfactants for oil emulsion drilling can address the most common problems in drilling operations of HTHP conditions.

1.3 Objective of the study

The aim of this research report is to investigate the use and the effect nanomaterial surfactants for oil emulsion drilling muds for deep-hole conditions. The nanoparticle ZnO and surfactants (Dodecyltrimethylammonium bromide and triton) are considered in this investigation. The aim of this research report will be achieved with the following objectives:

- **Objective 1**: Investigate to what extend does the synthesis of emulsion-based drilling fluids using Dodecyltrimethylammonium bromide and triton surfactants can aid in mitigating the challenges faced in deep-hole drilling operations. This will be done through the study of various synthetic methods for each surfactant concentration, an essential task to be conducted.
- **Objective 2:** Investigate the rheological and fluid loss properties that need to be improved for oil emulsion drilling muds. Also including the evaluation of the significant thermal properties of deep-hole drilling and compare with conventional ones to understand why conventional OBM are not suitable for deep-hole operations. In addition, we need to establish the applications that allows the modification of drilling fluid rheology for specific operation challenges

1.3 Delimitation of the study

There are different types of drilling fluids available on the petroleum industry, which all promote different technical benefits. The conventional drilling muds with chemical additives still present limitations (Al-Yasiri & Al-Sallami, 2015). The subsequent revival of oil emulsion drilling muds with the synthesis of nanomaterial surfactants creates a formalised framework for a scientific research for deep-hole drilling, which consequently serves as the primary focus of this dissertation.

The author notes that there is a certain level of uncertainty that is not accounted for in their work. For example, the temperatures modelled in a lab environment is not the same as the on exhibited in the wells. One would argue that the difference is insignificant, but due to other factors that

affect temperature, it should be accounted for. An anomaly presented in results might make a difference to the outcome.

1.4 Justification of research report

The need to conduct the research is justified by the following:

- Nanomaterial surfactants offer improved rheological properties
- The opportunity to enhance oil recovery by using proven nanomaterial emulsion based muds
- The need to find applications that allow the modification of drilling mud rheology for specific operation challenges
- The need to minimise formation damage by maintaining wellbore stability and minimise fluid loss which results in cost-effective operations

The ultimate outcome is that the industry requires an optimum drilling process with enhanced OBM drilling muds for deep-hole oil and gas operations. To highlight the optimal control variables that could yield the whole operation to an efficient process in HTHP conditions.

1.5 Structure of the report

In **Chapter 2** of the research, the author reviews and studies drilling process literature and the advancement of nanomaterials being utilised in drilling muds for deep-hole oil and gas operations. This provides a clear context to the research question. It enables the understanding of conventional drilling fluids used in LTLP conditions, therefore formulating the foundation to understand their needs.

Chapter 3 demonstrates the methodology of work that is to be followed by detailed outline of experimental work and investigations.

Chapter 4 Results obtained from the investigation of the use of nonmaterial surfactants are evaluated and presented with linkage to the literature review.

Lastly, **Chapter 5** concludes the on the use of nanomaterial for OBM in relation to the current advancement in the oil and gas industry then propose some recommendations.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

The context of the research is based on the investigations of oil emulsion drilling muds for deep resources, which encompasses the conditions of HTHP. In this chapter the review of the literature starts off with a brief outline of the basic drilling process with drilling fluid approach. Then establish the differences between the water-based muds and oil-based muds. This serves as the most fundamental postulation to be understood to achieve the goals of the project. This also includes an extensive literature on the properties of drilling mud with or without the synthesis of nanomaterials and their rheology. This enables the opportunity to establish the most economical and environmental friendly nanomaterial additives that may improve the functions of drilling muds for deep-hole drilling.

The approach to literature defines the conditions for what is considered deep-hole drilling, because the drilling fluid properties change under those conditions (Al-Yasiri & Al-Sallami, 2015). In deep-hole drilling temperatures and pressures can be very high, therefore, the drilling fluids rheology should be modified to accommodate the deep-hole conditions.

The literature attempts also to summarise the significant known nanomaterials that are currently being used in the oil industrial for enhancing oil recovery. The aim of this enables the justification of the use of nanomaterial. The literature also outlines the common nanomaterials and their technical benefits and evaluates their level of enhanced recovery in different operating conditions. The results from the qualitative analysis presents a platform for the most dominant nanoparticles that can be the practical focus for future research.

2.2 Drilling mechanism

To understand the background and purpose of nanomaterial in drilling muds, one must comprehend the basics of drilling operations with the approach of drilling mud objectives. The mechanism of rotary motion forms the framework of drilling; there are several main systems within hole boring. By exploration a reservoir is located; it is solid rock that has oil pockets

trapped in pores. To extract the oil, a drilling circuit requires the rotary system that rotates the drill bit, lifting system for vertical movement of the drill string and a circulation system that circulates the drilling fluid (Van Dyke, 1998). These systems work together to recover the oil. Figure 1.2 illustrates a schematic representation of a steady-state drilling process.

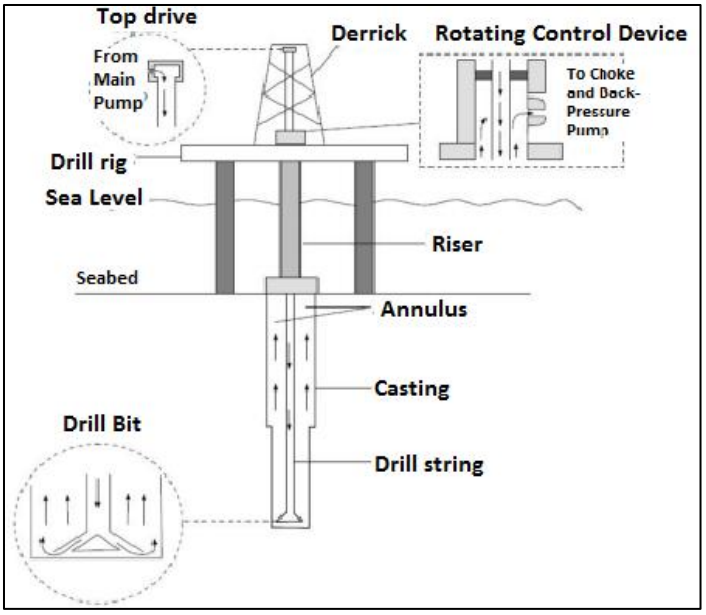


Figure 2.1: Illustration of a drilling rig on an offshore platform

(Helgestad, 2010)

The following presents a brief process of a drilling process (Vryzas & Kelessidis, 2017);

- A rotational force is applied to the drill bit which transforms the drill bit into a cutting tool. The drill bit rotates and fragments the contact rock into smaller sizes (cuttings).
- Concurrently drilling mud is circulated from a surface pump and is pumped through the top drive through the drill string pipe to reach the drill bit faces.
- When the drilling mud reaches the drill bit face, it lifts the fragmented rock cuttings through the casting to the surface.
- The drilling mud and cuttings then reach the control rotating device where separation occurs. This device separates the cuttings from the drilling mud, where the drilling mud is pumped back into the drill string as a continuous process.

The illustration of a drilling operation clearly points out the importance of the role of the drilling mud in use. Drilling muds main functions are to transports fragments of rock, which in turn creates hydrostatic pressure to the borehole formation (Helgestad, 2010). Thus, drilling muds form a variable that can be manipulated to create an efficient drilling operation. The emergence of nanomaterial surfactants oil emulsion drilling muds and many more other ones (which will not be covered in this research) allows for the functions to be expanded.

In a study conducted by Helgestad (2010), noted that some muds can perform specific functions such as corrosion control, sealing formations that present permeable conditions and provide stability. All these functions address different drilling problems in different operations, for this research the focus is on the deep-hole operations as most of the shallow reserves have been attained.

As established before, drilling muds perform various functions but to understand their objective in a drilling operation, a parallel comparison between blood and drilling muds is drawn. In an overview of the significance of drilling fluids by Al-Yasiri and Al-Sallami (2015), it is explained how blood is like drilling muds, the mud pump representing the heart and the deoxygenated blood is the cuttings from the drilling as it is pumped out to be cleaned so it is ready for circulation.

The historic review on drilling fluid dates to use of water to remove cuttings, which presented limitations in the achievable drilling depth, as a result, more drilling muds were introduced. According to Al-Yasiri and Al-Sallami (2015), bentonite clay formed the basis of the current conventional muds. In their research, they noted that drilling muds are mainly a composition of oil, gas, water and various chemical additives for performance enhancement.

.

2.3 WBM vs OBM

Characteristically of the American Petroleum Institute (API), drilling fluids are classified as oil-based mud (OBM), gas-based mud (GBM) and water-based mud (WBM). The generic term of ‘drilling mud’ is simply a composition of clay and water. The use of OBM in a drilling

operation is highly depended on the type of formation within the reservoir of interest. It is, therefore, useful to recognise and study the formations and the geological compositions that consequently affect the drilling operations

There is countless research conducted on both the emergence of nanotechnology in terms of nanomaterial advancement in drilling, reservoir management, and production. These nanomaterials have mostly been tested in experiments and some with detailed modelling investigation. As discussed previously, WMB is commonly used for LTLP drilling conditions whilst OBM is preferred for HTHP because of the morphology.

According to literature, it is evident that there is more research on nanomaterials for WBM, this is only so because of reserves were for a long time not at the record depths as current wells. Hence, more research is currently directed the improving of OBM and design nanoparticles that will enhance their rheology. Although there are reported successful attempts in the design and application of nanomaterial for wellbore strengthen the efforts were for LTLP operating conditions. Moreover, there is a need to investigate, design and apply suitable nanomaterial for field testing. More literature on scaling-up wellbore strengthening research towards HTHP conditions.

2.4 Drilling muds in HTHP

To understand the severe operational conditions that OBM are subjected to, it is imperative to understand what defines HTHP conditions. A standard definition of HTHP drilling operation is explained as an operation where the pressure exceeds 25,000 psi and borehole static pressure (BHST) is more than 177° (Agarwal, et al., 2013). However, drilling operations in places like the Gulf of Mexico have become more severe and reaching record depths with a pressure of 40,000 psi and BHST of 315° (Gusler, et al., 2007). Another example of HTHP conditions is the Menegai oilfields found in Kenya which in 2011 it reach depths of 2218 (Miyora, 2014). Drilling muds at these conditions are subjected to breakdown of polymeric additives, gelation and degrading of weighting materials. The breakdown of polymeric additives means the ability of surfactants, viscosifiers and fluid loss is affected and leads to the poor performance of rheological properties which can result in barite sag.

Although, given the emerging nanotechnology advances the designing, producing and applying of nanomaterial to OBM have become much more complex due to their behavioural chemistry (nanoscience) at HTHP (Nasser, et al., 2013). The concept of drilling objectives has remained the same. The function of drilling muds is to maximise oil recovery at an efficient rate.

It is apparent that drilling muds at HTHP conditions have many identified challenges, and extensive research in the petroleum industry has investigated different possible solutions to address these challenges. Hence, proponents recommend the use of oil-based drilling muds because of the better resistance towards gas hydrate formation and by contaminants allowing better stability which offers faster drilling (Agarwal, et al., 2013; Al-Yasiri & Al-Sallami, 2015; Gusler, et al., 2007). Altogether, it is noted that OBM is more inclined to maintain rheological properties within an acceptable range compared to WBM and GBM when subjected to HTHP (Gusler, et al., 2007). Moreover, highlighting the justification of the investigation of nanomaterial for OBM and objectives outlined by the author for this research.

2.4.1 Challenges at HTHP Operations

The petroleum industry has embarked on reducing costs at deep-hole drilling operations because the deep the operation the higher the operating costs. The cost of extracting oil calculation is primarily based on the depth and location of the well as a function of operating parameters; labour, equipment availability and efficiency, geological features, drilling techniques etc., thereby the cost of drilling is nonlinear (see Figure 2.2). Generally, the oil and gas industry define a problem as anything that hinders on safety, profits and the environment. Therefore, the industry has focused on identifying problems because of their effect the viability of drilling projects.

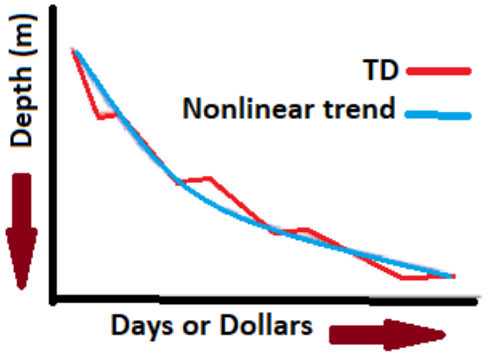


Figure 2.2: Drilling cost estimation

(Hossain, 2015)

For deep-hole drilling conditions apart from the experience of HTHP harsh conditions, there are numerous identified problems. The following is a list of some problems relevant to this research:

- Wellbore instability
- Drag and torque
- Harmful gases (hydrogen sulphide)
- Pipe sticking borehole wall
- Lost circulation
- Fluid loss

Globally, the trend emerging with problems in HTHP conditions are associated with drilling operations. The inevitable master problem being the depth at which wells are located. The deeper the operations the more problems, delaying the time to extract reserves which directly escalates operating costs (see Figure 2.2).

2.5 Rheology properties

The profile for the application of drilling fluids at deep-hole operations depends on the properties the flow in a circulating system. Rheology can be described as the analysis physical properties fluid in terms of flow and deformation behaviour. Harry et al (2017) suggested that rheology is the analysis of viscosity behaviour when subjected to variable shear rate settings. The measurement of inertia in drilling mud is viscosity. Shear stress is the frictional drag that is exerted to a surface at different velocities. Rheological properties are discussed in this section.

Drilling fluids must have rheological flexibly because during the drilling process at different rates of penetration fluid flow becomes unconventional in the annulus. Therefore, different viscosity standards of fluid at different elevations are used, because at shallow depths low viscous fluids are idea, whist at deep-hole operations more viscous drilling muds are required (Harry et al, 2017).

Drilling fluid properties are strained even more and forced to change under those conditions. The balance of maintaining stable rheological properties and ensuring that the performance of drilling fluid is efficient can be difficult at harsh HTHP drilling conditions.

2.5.1 Shear stress

The relationship between shear rate and shear stress is. Fluids are classified as Newtonian or non-Newtonian depending of the flow behaviour. Flow behaviour is the relationship between the flow rate and pressure of the fluid which is the measurement of shear stress and strain (Miyora, 2014). This concept is illustrated by the Newtonian fluid formula: $\tau = \mu\gamma$

Where τ = Shear stress, Pa;

μ = Viscosity, Pa-s

γ = Shear rate, s-1

2.5.1 Yield stress and Thixotropy

For drilling mud to flow, stress (load) must be applied to it. The ability of a fluid to support their own weight to a certain degree is defined as yield stress. Thixotropy in drilling muds is defined as the adjustable decrease of viscosity relative to time when in motion. Depending on the degree of thixotropy on drilling fluids Thixotropy can be evaluated using and loop test and is classified under several categories for drilling fluids:

- Negative thixotropy occurs when low shear is applied to a fluid which causes it to thicken at a high rate and maintains its state at rest whilst viscosity lowers.

- Positive thixotropy is often an observed property in drilling fluids. This state is when a fluid after apply shearing, it does not recover which causes high viscosity.
- Rheopexy is a behaviour where when shearing is applied to a fluid, it accelerates structural recovery. This state is also similar too negative thixotropy, however when low shearing is applied stress does not decrease.

According to Hughes and Maxey (2007) yield stress and thixotropy are separate rheological properties, however in most instances they can be observed in the same fluid.

2.5.2 Gel strength

Gel strength is a property that is used to evaluate the ability of drilling mud to lift and suspend drill cuttings, it is measured with a viscometer. Gel strength should be monitored because low value means cuttings settles (causes stuck drill string) whilst excessive means that retention at the surface and results in fluid loss and can fracture the formation.

Agarwal, et al. (2013) conducted experimental work to investigate the optimum nanomaterial to use between nano-silica and nanoclay to stabilize OBM (invert emulsion) when drilling at HTHP conditions. They concluded that when investigating the use of nanomaterial for OBM, the muds should show the gel-like structure with the yield stress because this attribute means that drilling cuttings do not settle but rather flow as desired. This correlates with work done by Abdo & Haneef (2012) although different nanomaterials were tested.

Vryzas, et al. (2016) performed several experimental works to compare their ability to lift and suspend fragmented drill cuttings (gel strength) when using bentonite mud and nanomaterials-based mud. The results were then compared (see Figure 2.3), the muds with nanoparticle showed low gel strength as compared to the bentonite mud. The evaluation noted two factors: the nanomuds were able to prevent pipe sticking, hole clogging because the mud did not cause accumulation as the gel strength is responsible for distributing suspension which eliminates problems. Furthermore, the behaviour caused by the flat gel strength helps to reduce the equivalent circulation density.

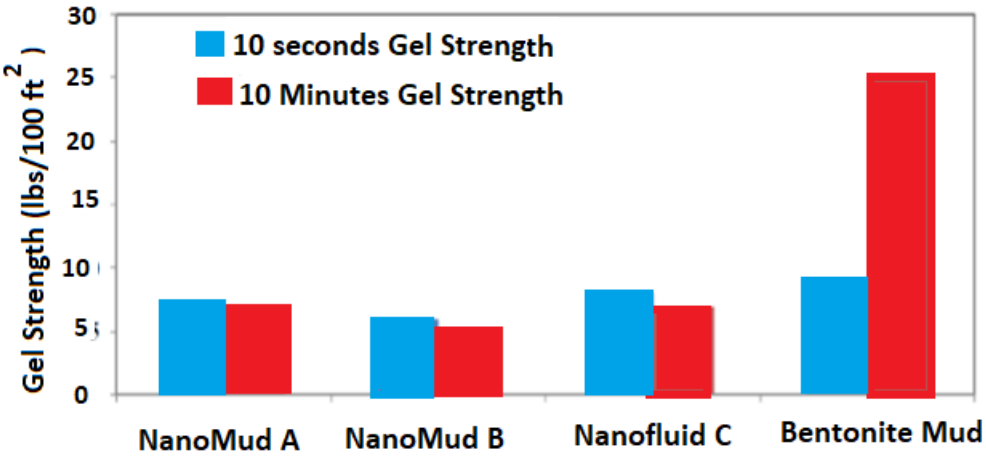


Figure 2.3 Base drilling mud and nanomaterial base muds

(Vryzas, et al., 2016)

The keys outcomes form both researches regarding gel strength, shear stress, and viscosity (see Figure 2.4 and Figure 2.5):

- Drilling muds must have low viscosity to suspend drill cuttings while maintaining low shear rates
- During drilling operations increase viscosity to reduce drilling costs
- Yield stress and viscosity is sensitive to dispersion property of nanomaterial
- Gel strength showed that carry capacity of drill cuttings was improved by 200% due to the application of nanomaterial

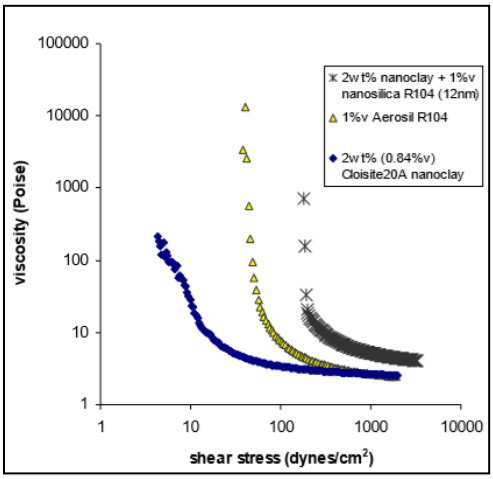


Figure 2.4: Flow behaviour of OBM (30 %v water) showing the effect of nano silica and nanoclay

(Agarwal, et al., 2013)

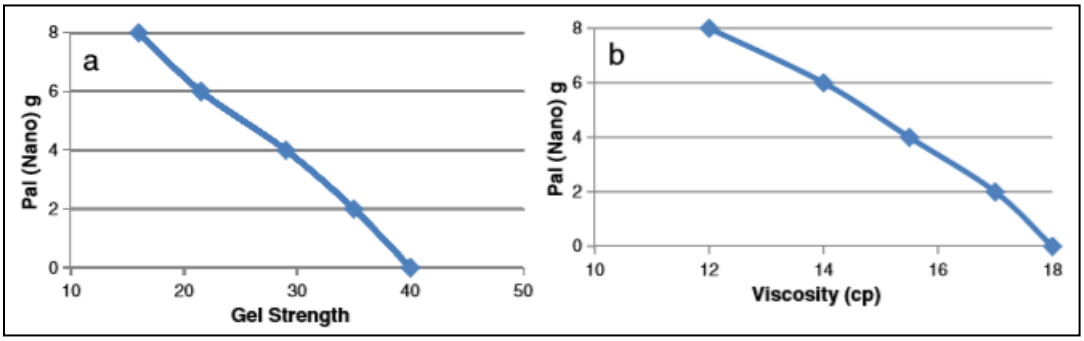


Figure 2.5: The effect of the composition of Pal to rheological properties

(Amanullah & Al-Tahini, 2009; Abdo & Haneef, 2012)

2.6 Rheological Challenges

2.6.1 Filtration Limitations

Youssif, et al. (2017) proposed that further investigation of the effects of using silica nanoparticles (SiNPs) for deep reservoirs drilling muds to enhance recovery. Silicon dioxide (herein silica-SiO_2) is currently a commonly used nanoparticle because composed of sandstone or quartz a natural environmentally benign rock. The group noted that the secondary recovery methods using silica nanomaterial are not as effective as it ought to be. Therefore, they modified the secondary recovery method by applying water flooding followed tertiary recovery by nanomaterial flooding at different concentrations (0.5 wt. %, 0.2 wt. % 0.1 wt. % and 0.05 wt. %). The increase of silica nanomaterial concentration (> 0.1 wt. %) resulted in increased oil recovery factor. This is possible because by delaying the water breakthrough more oil is produced which in turn maintains undamaged formation. This scenario presented contradictory property manipulation; if silica nanomaterial is at high concentration it may increase rock morphology while increasing oil recovery. But at low silica flooding rate, the formation damage is decreased. In their observations, it was also noted that the optimum silica concentration of 0.1 wt. %, because at this constraint, oil recovery was reported as 54%, compared to of ±42 % when water was flooded alone (as shown in Figure 2.6).

- WF: water flooding alone
- NF: silica nanomaterial flooding
- PV: pore volume
- RF: recovery factor

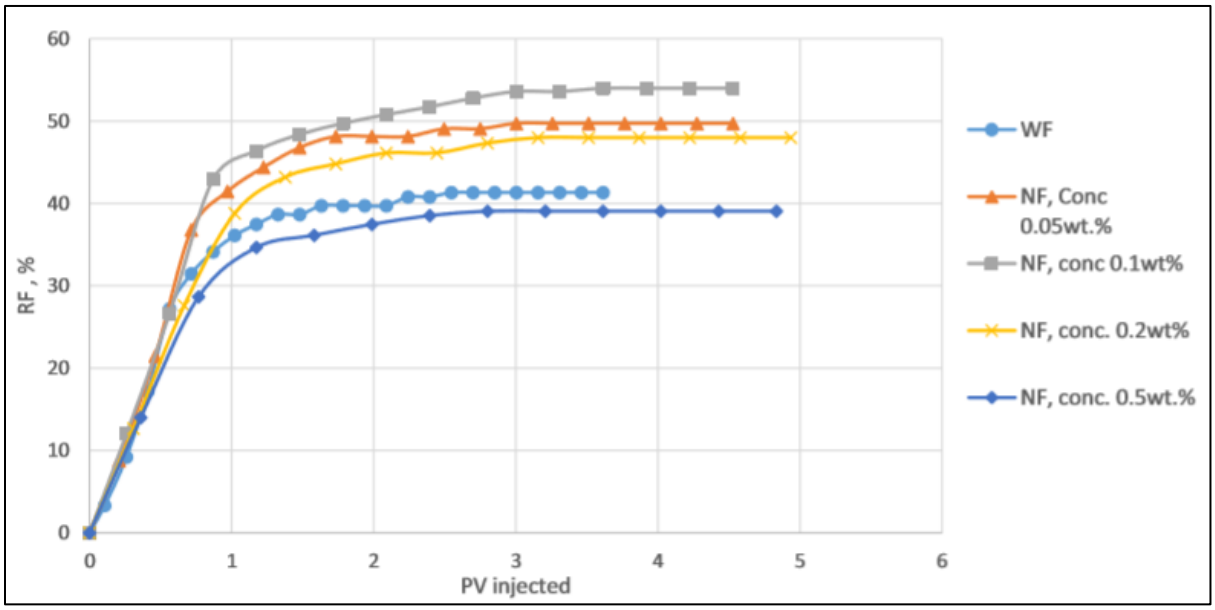


Figure 2.6: Graphical representation of recovery factor vs. pore volume at different flooding test

(Youssif, et al., 2017)

Srivatsa and Ziaja, (2011) carried a comparative analysis on laboratory work review were colloidal silica nanoparticles (concentrations of 30, 20 and 10% wt./wt.) to investigate fluid loss. The results illustrated that polymer-surfactant provided better filtration properties. Which could be used to control drilling mud cake thickness, to address sticking challenges.

They conducted an experiment using a filter press and drilling muds, which was composed of 3% silicon volume particles and the other without nanoparticles. This resulted in a significant reduction of filter cake from the mud embedded by nanoparticles compared to the drilling mud without nanoparticles. Their research presented the notion that when silica nanoparticles are knitted (a nanomaterial) into drilling muds then filtrate loss is possible as the particles present low porosity and permeable features.

Furthermore, in a parallel research outcome, noted by Fakoya & Shah (2017) and Zakaria (2013) fluid loss, rheology properties and formation damage can be improved using nanomaterial surfactant drilling muds for deep-hole operations. For example, in an experimental investigation by Vryzas et al (2016) where they evaluated filtration loss at HTHP conditions (300 psi and 250 □ F) with a custom-made Fe_3O_4 nanoparticle (diameter 8 nm) is added in an OBM of bentonite at different concentration. They reported that yield stress and the viscosity at varied shear stress was sensitive to temperature. The relationship between temperature and yield stress was linear. Their results showed that the thickness of filter cake increased, this was possible because of the increased surface area (see Figure 2.7).

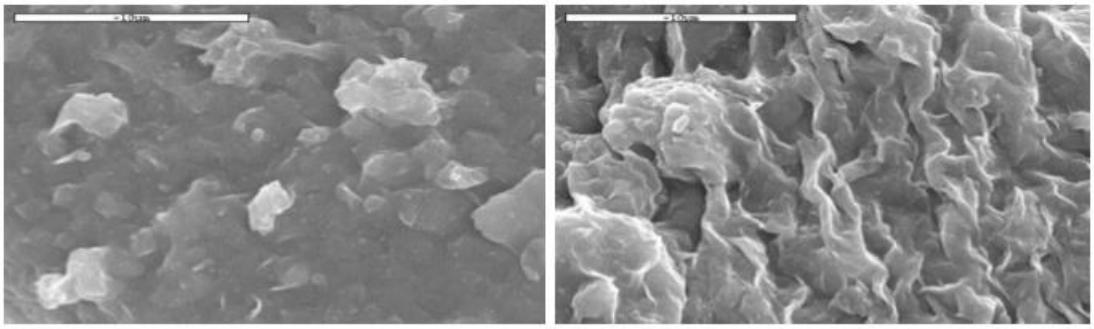


Figure 2.7: A 5000 magnification of filter cake resulting from HTHP filtration test

(Vryzas, et al., 2016)

Kang, et al (2016) reported increased EOR when using OBM with the assistance of silica nanoparticles. They conducted a swelling rate, imbibition and transit time experiments in a shale formation to evaluate if nanoparticle containing OBMs may offer solutions that would address wellbore instability problems. They claimed that since high dosage of nanoparticles in a shale formation can be used for plugging the shale pores in water-based muds (WBM). Therefore, establishing a framework to investigate if the same nanoparticle exhibits the same plugging effect when OBM are tested. The team monitored yield point, plastic viscosity and filtration properties.

The key outcomes from their work were that they observed that when the silica nanoparticles were applied to OBM, the nanoparticles did not disperse and exhibited higher filtration absorption as compared to WBM. Although for both muds, the application silica nanoparticle (at

concentrations of 5wt. % and 10 wt. %) resulted in higher yield point and pore volume. Furthermore, they concluded that the application of nanomaterial OBM lead to crack propagation due to increased filtration and Young's modulus cannot be considered to mitigate wellbore instability. However, a study by Srivatsa and Ziaja (2011) where they used filter press and drilling muds (with and without silica nanoparticles), presented results showed that when silica nanoparticles offer better filtration results when the polymer-surfactant blend is used.

2.6.2 Thermal Conductivity

A stable drilling mud at harsh HTHP conditions is of utmost importance, because if not it could hinder on the cooling and thermal conductivity properties. In general, the drill bit is subjected to friction as it interacts with the rock; this friction is mitigated with the lubrication of drilling mud which is depended on the heat transfer properties. However, given the deepening reservoirs with inherent HTHP challenges, consequently the drill bits are exposed to excessive heat as the rock surface exhibit high temperature and the morphology of the drilling muds are affected at those conditions. The excessive heat experienced by the drilling equipment leads to overheating and affects the rate of penetration and in extreme scenarios, the whole operation can come to a halt. Hence, the emphasis to design drilling muds that improves the thermal properties enhancing the heat transfer property. In this section, the author delivers a brief review research conducted on improving thermal conductivity in OBM.

Hassani, et al (2016) used silica/ multiwall CNT's to investigate thermal conductivity of nanomaterial base muds. Their results showed that thermal property of mud is sensitive to temperature and velocity and high Reynolds numbers were attained at varied concentrations, therefore, validating that CNT's show heat transfer enhancement.

One of the consequences of lack of heat transfer properties is excessive friction, which leads to damaging drilling equipment. The friction cause resistance to penetration and in more instances, the drill crew puts more force to the drill bit to counter the friction which increases torque. It was noted that the incorrect application of torque wears the drill string which causes the drill string to fail. (Solberg, 2012)

2.6.3 Surface Area

According to Fakoya and Shah (2017) the conventional drilling muds currently used in the industry contain micro and macro-sized nanoparticles and there are favoured due to the high surface to volume ratio. Figure 2.8 illustrates how the atoms of the nanoparticle surface area are increased by decreasing the size (Sun, et al., 2017). These particles possess distinctive structural properties which are attributed to their size and the surface area. In a study on smart fluid application conducted by Amanullah and Al-Tahini (2009) they drew a comparison of several spherical particles (with radius; 1 mm, 1 nm and 1 µm) from the same material, to investigate the surface area to volume.

Their results graphically represented (see Figure 2.9), it is apparent that if particles on millimetre scale require conversion to nano-scale particles to increase their surface area. An OBM that has an increased surface area nanoparticle embedded into a material (a nanomaterial) becomes a smart mud. Such drilling muds that have enhanced filtration, rheological properties, lost circulation and possesses the ability to improve the formation mud cake (Fakoya & Shah, 2017).

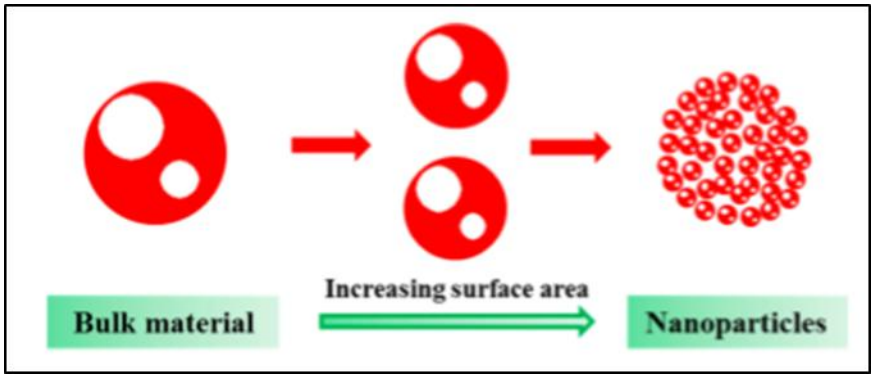


Figure 2.8: An illustration of decreasing nanoparticle size to increase surface area

(Sun, et al., 2017)

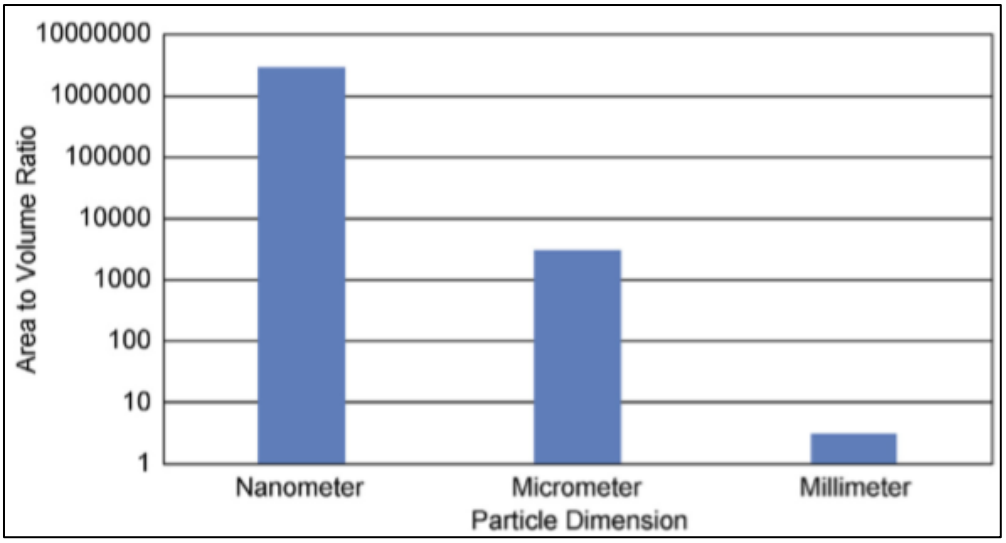


Figure 2.9: An illustration of the same volume of materials showing surface area variation

(Amanullah & Al-Tahini, 2009; Fakoya & Shah, 2017)

For example, currently, the solution for drilling problems is the dispersion of bentonite clay (WBM) into colloidal particles to stabilise emulsions, resulting in the creation of large surface area. The expanded surface area is the reason why bentonite is used to stabilize emulsions (Nasser, et al., 2013; Mahendranath, et al., 2015; Afolabi, et al., 2017). Moreover, even when the concentration of the smart muds is less, the large surface area property allows the nano-muds exhibit intense interactions with the surroundings. This feature enhances the drilling operations at HTHP by providing mobility control, wettability alteration and sand consolidation.

Vryzas and Kelessidis (2017) reported comprehensive reviews of several experimental works, he noted the following key finds regarding wellbore and shale stability:

- 10 wt. % of 20-35 nm nanoparticle is recommended for pore plugging
- Bigger pores can be plugged by bulk nanoparticles
- Addition of nanoparticles reduces mud loss into shale formations
- Nanomuds are stable at HTHP, also showing improved rheology properties
- A combination of nanoparticles and the bio-polymer surfactant is a thermally stable (at a temperature of up to 350 □ F) drilling mud and can aid in wellbore strengthening.

2.6.4 Pipe Sticking

Paiaman et al. (2009) reported their experimental studies on methods to mitigating drill pipe sticking to the mud cake in complex formations by using drill mud nanoparticles composition. They used carbon black nanomaterials and their results showed that there was a decrease in mud cake thickness which meant that the probability of pipe sticking less.

2.6.6 Wellbore instability

Globally, it is common know that wellbore instability is the definitive problem that constantly needs to be monitored. It can cause drilling delays due to stuck pipe and or lost circulation. Hence, the drilling industry spends millions to put controls that mitigate the wellbore instability problems. Literature review indicated that the most common control measure used is the application of nanoparticles, there specifications in studies is that the size of the nanoparticles should not exceed 34% of pore throat Al-Yasiri and Al-Sallami (2015). According to Vryzas and Fellsides (2017), they suggested the long-term mitigating measure is to apply wellbore strengthen from the first stage of exposing the shale to steady-state production. Several studies have been recorded in attempted to a better design for well strengthen by flooding of nanomaterial downhole. The principle is that the nanomaterial pumped would attempt to become a stop block, which fills fractures and prevents fluid loss while at the same time, strengthen the wellbore. There are two ways this works; the material generally blocks the whole fracture or just blocks the pore throat of the fracture. By blocking the fractures, it prevents further propagation (Vryzas and Kelessidis, 2017).

2.7 Rheology models

It is important to understand the inertial properties. As discussed earlier, we know that their different types of drilling muds (OBM, WBM and GBM), these are classified according to the foundation of their flow behaviour.

The general flow behaviour of fluids is further grouped under following flow models: Newtonian (a), Bingham (b), pseudo-plastic (c) Herschel-Bulkley (d), and dilatant (e), these can either be turbulent or laminar (Miyora, 2014). However, in a parallel research by (Agarwal, et al., 2013), it

was noted that although the models are proven in some instances the data from experiments might not fit the available models. Therefore, the consideration of applying a sensitivity analysis would be advantages, as it might address anomalies. Figure 2.10 shows the rheology behaviour expected from conventional drilling muds, a high friction between particles is attributed to high shear rates.

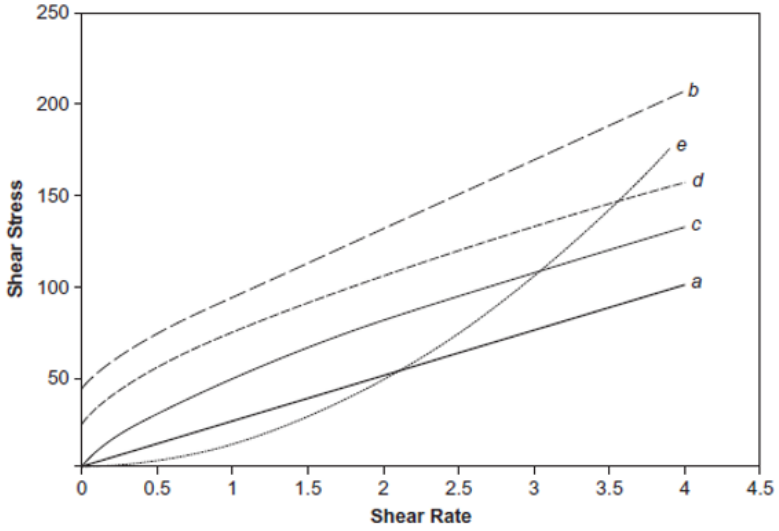


Figure 2.10: Illustration of the laminar behaviour of different drilling fluids

(Miyora, 2014).

The model becomes important in estimating the fluid loss by understanding the relationship between shear stress and shear rate of OBM. Gucuyener (1983) mentioned that the key to ensuring efficient drilling performance and minimise deep-hole problems is in key flow management, and this starts with understanding the relationship between shear stress and rates exhibited by drilling muds.

Bingham Plastic (B-P)

This is widely used model that defines plastic viscosity which is attributed to the direct proportionality relationship between shear stress and shear rate. However, this model fails in characterizing fluids that are non-linear and fluids with high or low shear rates.

Power Law (P-L)

This model describes non-linear fluids with high shear rates and considers no yield stress to initiate flow. Within the Power law, there are fluids with viscosity that decreases and increases with shear rate. The fluid with increasing fluid is called dilatant and latter is pseudo-plastic. Most fluids exhibit Bingham Plastic and Power Law characteristics to formulate the model of Herschel-Bulkley (Powell, 2014)

Dilatant

This flow behaviour also known as shear thickening is observed when shear strain to a fluid is applied causing the viscosity to increase. It is an example of a non-Newtonian fluid and is controlled by particle size, distribution.

Pseudo-plastic

These are fluids whose viscosity decreases when subjected to shear strain. The rheology of the fluid resembles a shear thinning non-Newtonian behavior. It does not show time dependent effects on the properties of materials.

Herschel-Bulkley (H-B)

A blend of two models to form a model for Plastic fluids. This model is widely used at drilling operations as it provides informative trends in viscosities of drilling muds. Although it is the ideal model at drilling sites, the limitations arise in the inaccurate capture of shear stress at low shear rates in relation to viscosities. Therefore, confining this model to be used when designing drilling muds for a specific application.

Casson

Although this model was originally designed for pigments, it also favours drilling muds. It is thought of as a Bingham and Power law hybrid model, like the Herschel-Bulkley model. This model has been observed to accurately describe drilling fluid with high concentrations of bentonite at very low shear rates.

2.8 Drilling Fluid Additives

At some point during the drilling process, it is necessary that the OBM is displaced by another mud (referred to as a spacer) to avoid contamination. According to (Fakoya & Shah, 2017) during cementing job cement spacers formed by nanomaterial OBM can effectively remove the OBM from within the casing surface. Concurrently it can also reverse the wettability of the faces to help acts as an adhesion for the excavated hole and cement slurry.

It is a common notion that reservoir failures and the integrity of the wellbore are attributed to cementing related problems. These problems can be related to cementing stability, and these can be one of the biggest problems, and problems mean costs and lost time (Fakoya and Shah, 2017). There the introduction of smart muds has recently become of interest since the introduction of nanomaterials. The common additives (nanomaterials) to be added according to literature is summarised by Khalil et al. (2017) as CuO, Al_2O_3, Fe_2O_3, TiO_2 and ZnO_2. The main function is to enhance properties such as increased permeability, strength, control leaching, assist in hydration and most importantly serve as a self-cleaning agent.

2.8.1 Surfactants and brines

Organics compounds from a group of hydrophobic and hydrophilic, surface active substances are referred to as surfactants (OLKOWSKA, et al., 2013). Their further noted that the hydrophilic group may either be positively charged (cationic compounds) or no formal charge (non-ionic compound). The purpose of brines in deep-hole operations is to assist in debris removal, formation pressure management, avoid well damage, and enable repair and clean-up operations.

The integral part of the providing oil emulsion drilling muds that are thermally stable, is to focus on the control and monitor the rheological properties (Vryzas & Kelessidis, 2017). As the efficiency of OBM in performing tasks is possible because of a specific rheological and heat transfer property. Thus, it makes sense to draw focus on improving the performance of drill muds, with the notion of increasing the heat transfer function of the drilling mud using nanomaterial

To understand the rheology of drilling muds at HTHP, it is important to understand the significant alterations to their rheology properties when the muds are used during drilling. The

rheological performance profile of drilling muds is strongly depended on the effects of dynamic pressure, temperature and shear properties of deep-hole reservoirs. This also means that there is a necessity for a deep understanding of the base mud properties which includes the flow, heat transfer properties and structure of the muds.

2.8.2 Deep-hole operations

To understand the background of the challenges presented by deep reservoirs, one must quantify what is meant by deep-hole operations. In 1978, Shell's Gulf of Mexico cognac drilling field reached the water depths of approximately 304 m this has since then been used as a benchmark for the definition of deep-hole operations (Kilisek, 2014). The Gulf of Mexico reaching record water depths of approximately 2900 m. These great depths are now defined as ultra-deep-water (Kilisek, 2014).

Beyond pressure control problems at these depths, there are several problems that hinder the efforts or EOR, in some projects the drilling operations are inefficient with high operating costs. The deep-hole operations present challenging subsurface conditions which due to the depth is subjected to high temperatures and high pressures (HTHP).

HTHP formations are associated with reservoirs at depths greater than conventional wells. These harsh formations (HTHP) mean challenges of filtration and rheological properties is expected, thus requiring exceptional innovation to exploit these complex resources. There are several innovative categories that are currently available in the petroleum industry; thermal, chemical, and gas methods. For this research, the focus is on chemical methods. Figure 2.11 shows the several methods that are currently used to improve EOR in complex reserves.

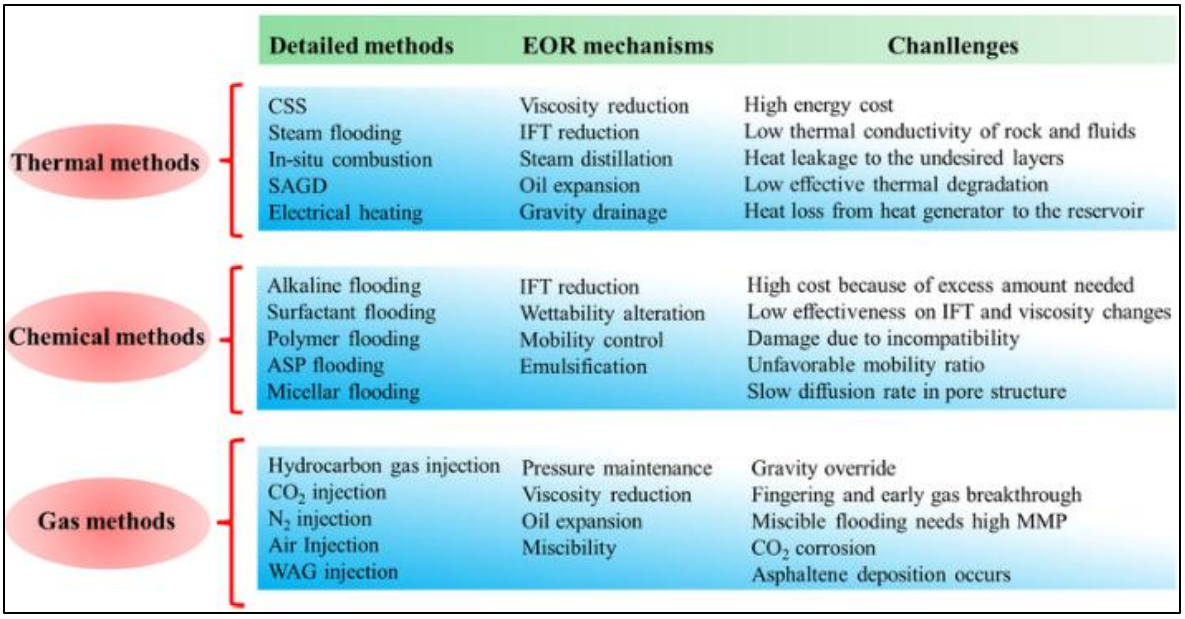


Figure 2.11: The available categories used to optimise EOR

(Sun, et al., 2017)

Chemical methods have various options as illustrated in Figure 2.11, the author draws attention to the application of detergent-like surfactants that helps to lower the interfacial tension (IFT) and increase oil recovery factor. Because drilling operations take place in highly salinity conditions, nanoparticles may not disperse as desired (Zhang, et al., 2014).This assists to inhibit oil droplets from infusing through a reservoir (Sun, et al., 2017). However, the methods also present challenges that may hinder efficient recovery rates. Hence, the introduction of nanoparticles to enhance the efficiency of drilling muds to help address the challenges noted.

2.9 Nanomaterial design and application

2.9.1 Nanotechnology

Nanotechnology is a wide industry where nanomaterials are applied, depending on the required objectives. They play significant roles including but not limited to pharmaceuticals, reservoir monitoring, advanced materials and environment fields. Currently, in reservoir drilling

operations, nanomaterials are embedded into the structure of muds to enhance their properties that adjust to the HTHP conditions of deep wellbores.

The product of knitting materials into nanoparticles is called nanomaterial. There are several identified methods that can be used to produce nanomaterial; plasma arcing, synthesis, chemical disposition and couple with the use of natural particles (Fakoya & Shah, 2017). These chemical methods are collectively known as methods designed for EOR. Figure 2.12 shows the sections where the application of nanomaterial is applicable in the petroleum industry.

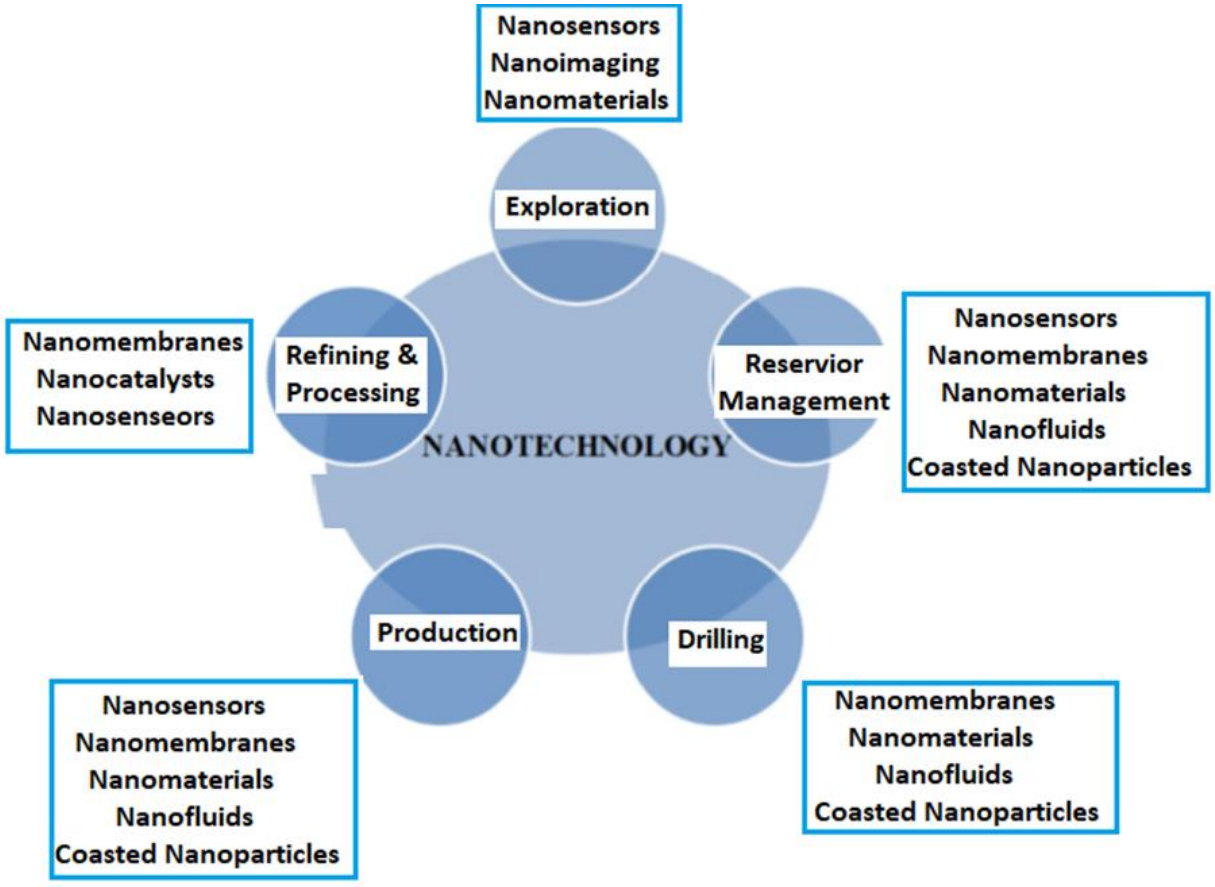


Figure 2.12: Design and applications of nanotechnology in the petroleum industry

(Khalil, et al., 2017)

This section outlines of the relevant literature regarding current studies of nanoparticles and nanomaterial for OBM. It enables the author to critically review the gaps in this emerging technology and present a framework that could pave the way for researchers who are interested

in up-scaling nanotechnology to deep-hole reservoirs. Notable properties are briefly summarised here (Subhankar, n.d):

2.9.2 Properties of nanomaterial

- At elevated pressures, nanoparticles with a high surface area to volume ration provide a tremendous diffusion rate.
- In material size, bulk material should have constant physical properties, but nanoparticles are exhibit size-dependent properties as the atoms at the surface of the material increases and therefore creates a large surface area.
- The effect of nanoscale properties enables nanomaterial to show quantum effects and show optical properties.
- The interaction of nanoparticles surface with the solvent make suspension possible due to overcoming of different densities.

2.9.3 Advantages and limitations of nanomaterial

The science of nanomaterial narrows the gap between atomic structures and bulk material. Despite this notion, there are several limitations that hinder on the link. For example, Subhankar (n.d) obeserved that nanoparticles have surface modification issues and release control limitations. It was noted that although nanoparticles posses the advantages of large surface area, their small size makes it difficult for nanpoparticles to land due to particle aggregation.

Khalil, et al. (2017) extensively reviewed on the recent development of the design, applications and challenges on nanotechnology, presenting the impact on the industry. Their review revealed that the main challenges encountered in nonmaterial design is the controlling of colloidal stability knitted in the particles. For example, the particles failed to prevent formation damage and high surface energy from aggregation (increased surface area). Which resulted in the absorption of other particles, thus altering the chemical and physical properties. This shows that there is a gap between the stabilization of nanoparticle.

2.10 Nanomaterials Synthesis

Several nanotechnology proponents conducted research coupled with experiments on formulating the ideal combination of nanomaterial to OBM. There are several methods of creating nanoparticles, which is presented in this discussion. According to Geng (2015), nanoparticles used in reservoirs are not water absorbing, the most common ones are carbon, silica and magnetic. As the synthesis and applications of nanoparticles are currently the most popular for HTHP operations. The author reviews the outcomes of experiments conducted, to identify gaps and further opportunities that could be addressed.

Some typical extraction oil reservoir methods recollect approximately 70% of the oil. Then when considering deepening reserves this estimation is less, i.e. employing the usual techniques at HTHP, will result in the extraction of half a barrel out of three of oil from a well. Although they have been promising inventions of employing nanomaterial to enhance oil recovery, many of the reported research is still only in the lab scale stages.

There are several derived methods of synthesising designed of nanomaterials in attempt to have full control on morphological properties (size and shape). The nanoparticles can either be prepared by chemical, physical or gas procedures and furthermore synthesised by 'bottom-up' or 'top-down' method. In their research, four common used nanoparticles for synthetic protocols were discussed; a metal oxide, metallic nanoparticles and carbon nanotubes.

2.10.1 Metal oxide nanoparticles

These particles offer heat transfer and conductivity properties that can be embedded in OBM, which enhances the mobility of drill cuttings. Metal oxide examples are TiO_2, ZnO, MgO, Al_2O_3, F_2O_3 and SiO_2 (see Figure 2.5). The applicable fabrication method at HTHP conditions is presented as a liquid-solid phase. This is because the morphological features can be controlled when microemulsion synthetic method is applied.

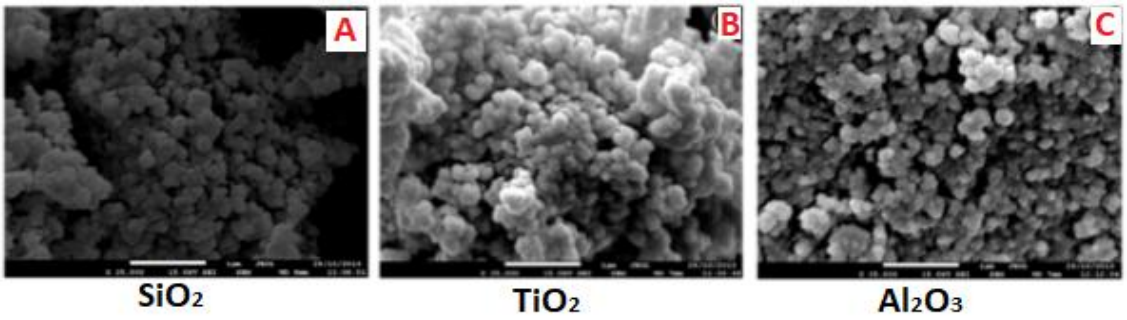


Figure 2.13: Example of current nanoparticles

(Sun, et al., 2017)

2.10.2 Metallic nanoparticles

Salt reduction is the common method to synthesize metallic nanoparticles (such as Au, Ag, Cu, Os and Pd). The reduction process is followed clustered metallic nanoparticles that aggregate to form nuclei, which is then stabilized using surfactants (see Figure 2.6). Surfactants act as a control parameter as it changes the surface energy of the nanoparticle. Therefore, allowing to grow in such a way that it limits the absorption of other surrounding particles if it grows into their direction.

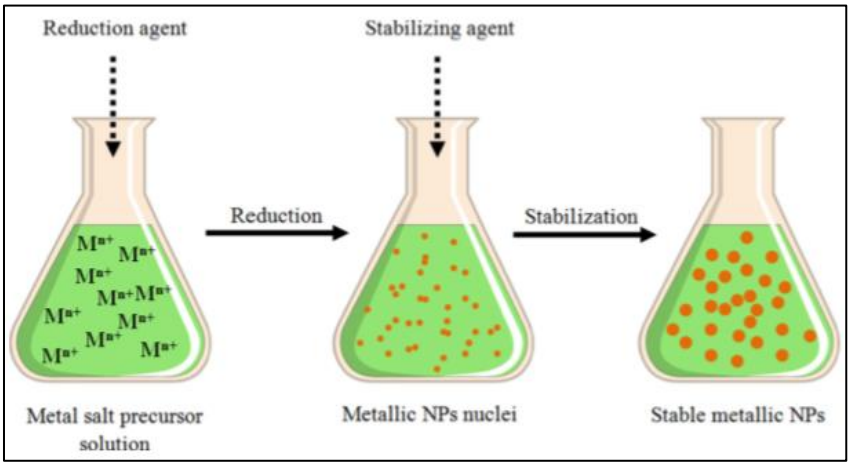


Figure 2.14: An illustration of the mechanism salt reduction synthesis to form of metallic nanoparticles formation

(Khalil, et al., 2017)

2.10.3 Carbon nanotubes (CNTs)

These are known to offer physical attributes such as mechanical flexibility, electrical and strength properties earning the potential to apply as emulsion stabilizers and or as an additive for OBM of deep-hole operations.

The overall review of Khalil et al (2017)**,** there are more gaps, which hinder on the success of achieving high recovery rates at low operational costs for deep-hole operations. The four common nanoparticles revealed that there is an urgent need to design simple low cost one. As currently emerging research outcomes show that nanoparticles are still produced from old unproductive equipment that still uses non-environmental friendly raw materials. This challenge limits producing nanomaterial for oilfield utilisation to achieve EOR, because oilfields require large dosages of nanomaterials for OBM and its limited by ineffective equipment's. Thus, this application ends up increasing drilling operation costs.

2.10.4 Cost of nanoparticle synthesis

Nanotechnology industry has identified the benefits of the application of nanomaterial, in drilling, explorations, refining and processing. Which are all sound and the results show potential enhanced oil recovery and efficient drilling operations. According to literature, it is identified that the cost of synthesising is expensive and the limiting manufacturing equipment.

To attempt the application of nanomaterials to improve base muds attempt oilfield trials, it is apparent that nanomaterial is required at high dosage, which can become costly. Throughout the review of experimental work, what was prevalent is that the development of nanoparticles is still highly depended on the use of ineffective equipment and to increase the dosage would escalate the operating cost. Therefore, within the investigation of the use of nanomaterial cost models should be inclusive. However, proponents have suggested that since some of the common nanoparticles are naturally occurring and is in abundance could mean that the cost is not as discouraging as thought out to be.

For example, Afolabi et al. (2017) conducted research on prospects of Nigerian bentonite clay for drilling mud development. They outlined the benefits of the rheological properties when used to modify drilling muds. As this mineral is vastly available and Nigeria has oilfields, this serves

as an advantage when considering using bentonite nanoparticles. This could reduce the cost implications attached to the application of nanomaterial to achieve efficient drilling operations.

2.12 ZnO nanoparticle

Modern advancement in nanotechnology has increased the scope of the characteristics of nanomaterial. Metal oxide nanoparticles (such as TiO_2, ZnO, MgO, $Al_2 O_3$, F_2O_3 and SiO_2), have received noteworthy considerations due to their morphological features can be controlled when microemulsion synthetic method is applied. Zinc oxide (ZnO) nanoparticle is one that presents unique properties that offers various capability functions in different industries.

Properties of ZnO nanoparticles

Zinc oxide (also known as zinc white) is an inorganic white crystalline compound powder that is colourless and odourless. It rarely occurs in nature; thus, it is widely produced commercially. ZnO possess thermochromic effects, as it changes from white to yellow colour when subjected to heat and reverts to white when cooled. It also reacts to alkalis and acids and when exposed to air it can absorb carbon dioxide and water vapour. ZnO shows stability when decomposition takes place. Table 2.1 is a summary of chemical and physical properties of ZnO (Omkar and Subhankar, n.d).

Table 2.1: Chemical and physical properties of ZnO

Relative density	5.6.6 g/ cm^3
Melting Point	1975 ^{0}C
Molecular Weight	81.38 g/ mol
Solubility in Water	0.0004% (17.8 ^{0}C)
Crystal Structure	Wurtzite
Band Gap	3.3 eV

.

CHAPTER 3 : EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES

3.1 Materials used

3.1.1 Nanoparticle

ZnO nanoparticle (white powder) was supplied by Sigma Aldridge, with an average particle size <10 nm. This nanoparticle had molecular weight of 81.39 g/mol.

3.1.2 Surfactants

Two organic cationic and non-ionic surfactants compounds were used to investigate the use of nanomaterial surfactants for oil emulsion drilling muds for deep-hole conditions. These are: Triton® X-100 and Dodecyl Dodecyltrimethylammonium bromide (DTAB). Table 3.1 illustrates the chemical properties of these surfactants. These surfactants are used in drilling operations to aid drilling mud rheology.

Table 3.1: Chemical properties of surfactants

Surfactant	**Dodecyl Dodecyltrimethylammonium bromide**	**Triton® X-100**
Appearance	White Powder	Liquid/Colourless
Molecular weight	308.34 g/mol	625 g/mol
Chemical formula	$C_{12}N\ (CH_3)_3Br\ 0.22$	$C_{14}H_{22}O(C_2H_4O)_n$ (n=9-10)
Viscosity	-	240 cps at 25 ^oC
pH	-	pH 6-8
Type of surfactant	Cationic	Non-ionic
Supplier	Sigma Aldridge	Sigma Aldridge

**The HLB of the surfactant is 13.5, so this can help generate oil in water emulsions.*

3.1.3 Fluids used

Table 3.2 : Brine fluids

Brine type	Brine Formula	Density range (ppg)
Chloride Salt	NaCl	8.4-10
Chloride Salt	$CaCl_2$	8.4-11.3

Brine solution was prepared by mixing distilled water with NaCl and $CaCl_2$. The products were then used to prepare surfactant solution and a nanoparticle aqueous solution. Emulsions contained surfactants (DTAB or Triton®X-100), brine; crude oil; bentonite and zinc oxide nanoparticles.

3.1.4 Sample Used

The crude oil sample used was supplied by Sasol Natref from the refinery tank F29107

3.2 Synthesis of emulsion-based drilling fluid

There are several identified methods for synthesising nanoparticles, and the use of water-in-oil emulsions has become the most prominent method used. For this work, oil emulsion drilling fluids were prepared by emulsifying distilled water in nanoparticle that contained crude oil. Another drilling mud was prepared without using nanoparticle. The composition of the drilling fluids are illustrated in Table 3.3.

Table 3.3 : Synthesis of emulsion-based drilling fluids

Emulsion drilling fluid with nanoparticle
100 g Distilled water + 1 wt% NaCl + 1 wt.% $CaCl_2$ + 1 n-wt.% Triton® X-100+ 1 wt.% ZnO + 6 wt.% bentonite
100 g Distilled water + 1 wt.% NaCl + 1 wt.% $CaCl_2$ + 1 n-wt% DTAB + 1 wt.% ZnO + 6 wt.% bentonite
Emulsion drilling fluid without nanoparticle
100 g Distilled water + 1 wt.% NaCl + 1 wt.% $CaCl_2$ + n-wt% Triton® X-100 + 6 wt.% bentonite
100 g Distilled water + 1 wt.% NaCl + 1 wt.% $CaCl_2$ + n-wt.% DTAB + 6 wt.% bentonite

Nan-ionic surfactants as emulsifier to create emulsions, water is a function of surfactant ratio. For water solubility to reach its peak, a certain surfactant ratio must exist. The specification of the w/o emulsion ratios of surfactants used are tabulated in Table 3.4. The hydrophilic-lipophilic (HLB) value of the surfactant is 13.5, so this can help generate oil in water emulsions. This was attained by mixing different rations of DTAB and Triton® X-100.

Table 3.4 : The ratios of the n-Wt. % of the surfactants

Wt.% of Surfactants	
DTAB	Triton® X-100
0.25	0.25
0.50	0.50
0.75	0.75
1.00	1.00
1.25	1.25

Figure 3.1 shows the preparation of emulsion with the water to oil ratio of 9:1.

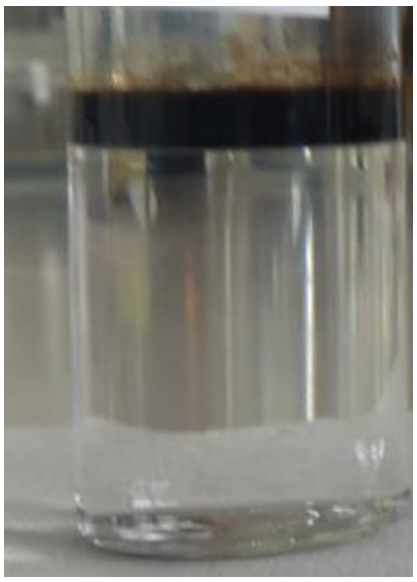


Figure 3.1: Brine-oil ratio (9:1)

Rheological properties of the drilling muds were tested by Anton Paar rheometer, under a various ranging shear rates to determine their viscosities and torque. The shear rates from 1 to 100 S^{-1} were used to determine the apparent shear rates, with a controlled temperature of at 25 °C. Other geometries includes stainless steel cup (27.2 mm-diameter) and a spindle (26 mm).

3.3. Measurement of mud filtrate loss

The process of drilling fluid filtrating into a permeable formation is defined as fluid loss. A good drilling fluid exhibits low fluid loss characteristic. Deep-hole drilling operations means that the drilling muds are subjected to HTHP. Filtration test was conducted the temperature of 25 °C and pressure of 50 KPa, with measurements taken every 2 minutes for 14 minutes to determine the filtration loss. The filtration test was done for different samples.

3.4 Analytical equipment

The investigations were confirmed via the following instruments:

- A hielscher UP200S Ultrasonic Processor (200 watts, 24 kHz) was used to mix the aqueous solutions and the crude oil (see Figure 3.2 a).
- An Ohaus Explorer EP413 milligram balance was used to weigh the chemicals in preparation of the aqueous solutions (see Figure 3.2 b)

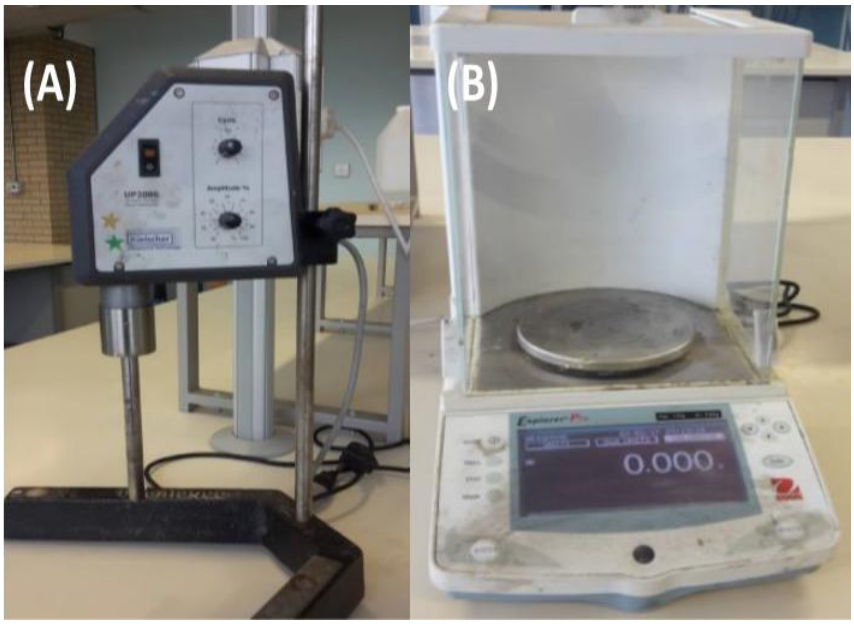


Figure 3.2: (a) Hielscher UP200S Ultrasonic Process (b) Ohaus Explorer EP413 balance

- Rheology studies were done using a rheometer and the filtration loss was determined using the Schleicher & Schuell No.1505 filter (Figure 3.3).

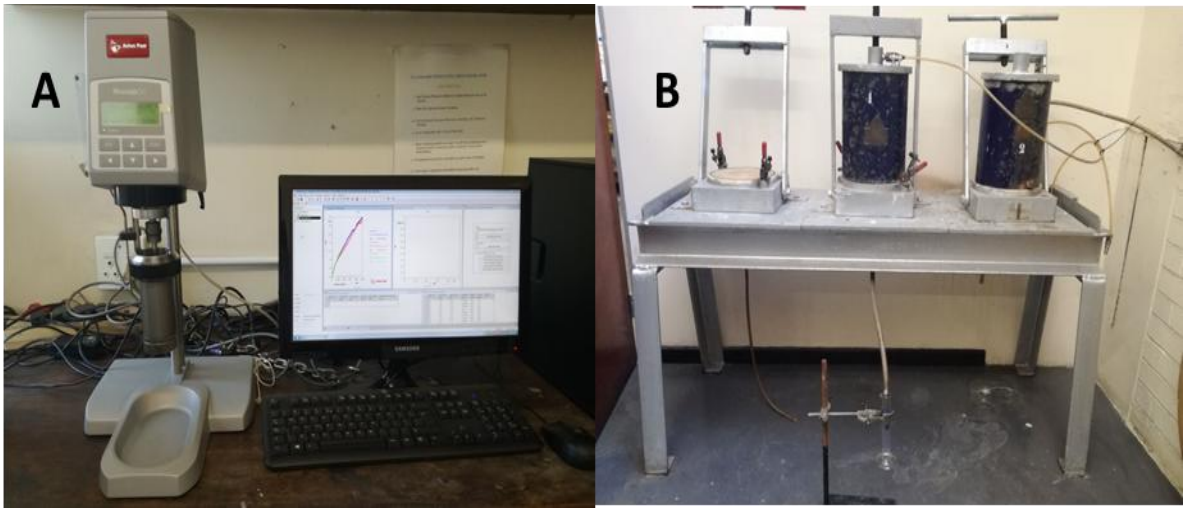


Figure 3.3: (a) Rheometer (b) Schleicher & Schuell No.1505 filter

- The stress applied during rheological studies in the fluid – cup system by the spindle/rotator rotation mimics that of the drilling process whereby the drilling bid rotates and applies a certain amount of stress to the fluid – well wall.
- Determination of viscosities and deformation of the drilling fluid were determined using Anton Paar rheometer.

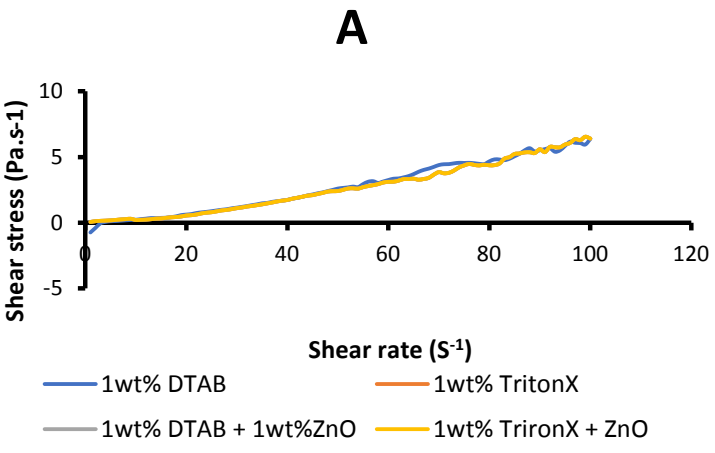
CHAPTER 4 : RESULTS AND DISCUSSION

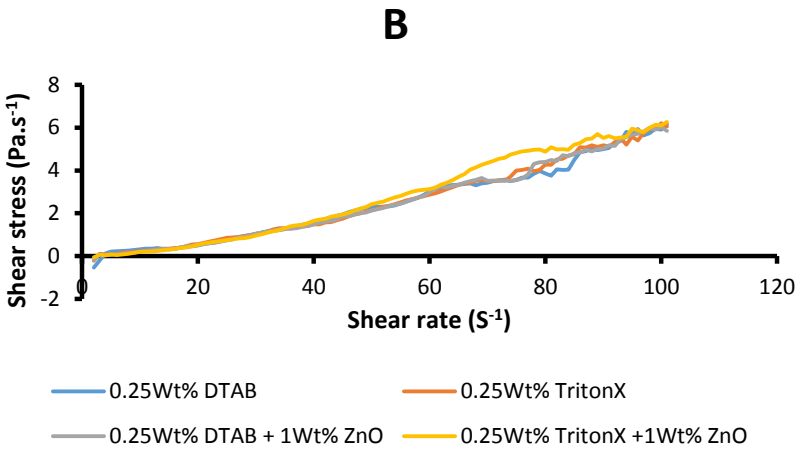
4.1 Rheological test

The conventional drilling muds for LTLP operating conditions have been observed by proponents that there are not efficient in HTHP conditions. The integral efforts of controlling and monitoring rheological properties of conventional drilling muds is a useful guide for HTHP conditions. This can be enhanced by the use of nanomaterial surfactant and the understanding of drilling fluid rheology.

To control and monitor the effects of the use of nanoparticle surfactants on rheological properties, 1 wt.% ZnO and various concentration of surfactants ranging from 0.25 to 1.25 wt.% were used. Figure 4.1 (a - e) illustrates the effect on rheological property of nano based material with varying surfactant concentrations. The rheological studies of the emulsion-based drilling fluid results showed that irrespective of the type of surfactant used, the flow behavior is relatively the same. The shear stress increases with an increasing shear rate.

To further evaluate the shear rate-shear stress relationships, rheological models such as the Herschel-Buckley model, power law model and plastic model. It observed that as the concentration of surfactants increases, the flow curve exhibited dilatant behaviour. The plotted data shows that with an increased concentration of surfactants, the drilling mud reduced its fluid loss ability.





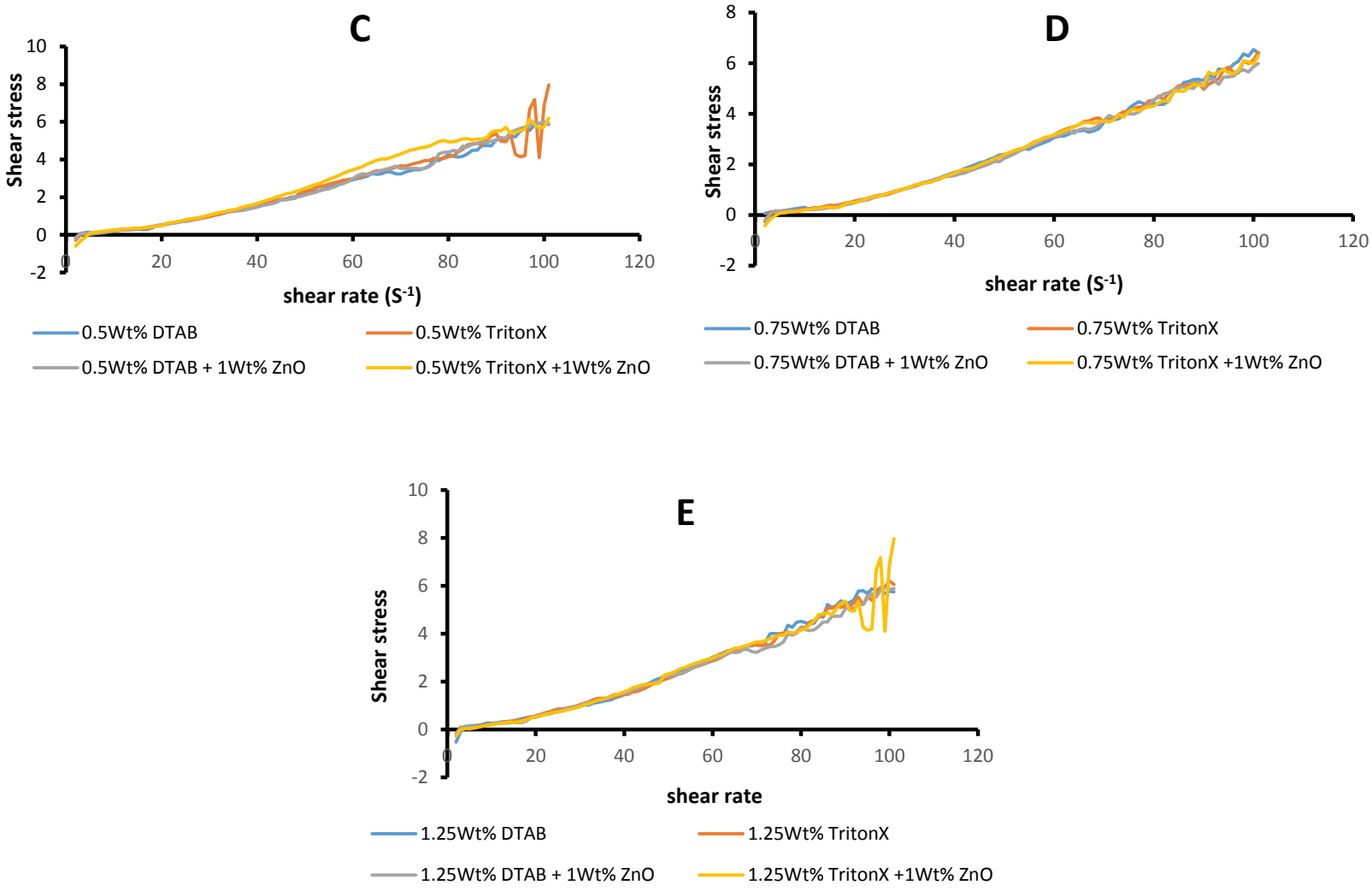


Figure 4.1: Shear stress versus shear rate of emulsion-based drilling fluid

The above graphs showed a dilatant model behavior and shear thickening of the emulsions. As more shear stress is applied, the emulsions become thicker and they did not return to their original state after deformation. This showed inelastic and non-Newtonian behavior. When comparing the different behavior of the surfactants, it is noted that the DTAB with ZnO showed more prominent behavior compare with that of the Triton® X-100.

4.2 Mud Viscosity

Miyora (2014) noted that the common assumption of drilling fluids is that there are considered as shear thinning non-Newtonian trend, which shows that when viscosity decreases when shear rate is increased. Drilling muds that exhibit shear thinning means that they can easily pumped down-hole.

The increase in weight of the emulsions by adding ZnO shows a significant effect in viscosity and not on shear stress. Drilling muds must have low viscosity to suspend drill cuttings while maintaining low shear rates. The emulsion with a mixture of Triton® X-100 and ZnO show a significant effect of shear rate on viscosity; whereby it decreases rapidly at first and then stabilizes. This mixed combination shows shear thinning behavior, and makes it the idea fluid when pumping it in deep-hole operations. On the other hand, the emulsion with DTAB shows an increase in viscosity as shown in Figure 4-2 (a-b). For other surfactant concentrations, more graph are illustrated which follow the same trend in the Appendix A.

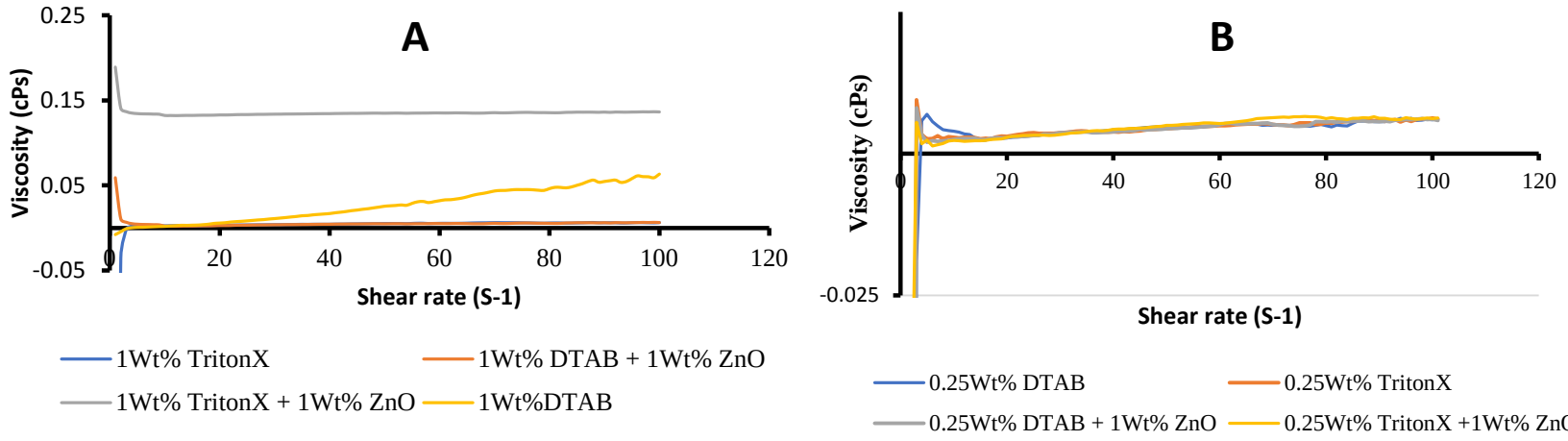


Figure 4.2: Viscosity versus shear rate of emulsion-based drilling fluid

4.3 Emulsions stabilities

According to literature emulsions are mostly considered unstable. This is attributed to the fact that water and oil tend to separate over time. However, in this investigation, the surfactant used proved to act as good stabilizing agents for the emulsions. Emulsions of different ranging concentrations (0.25, 0.5, 0.75, 1.0, and 1.25 Wt %) of surfactants were placed in poly vial bottles. Observation was done on emulsions to investigate if the emulsions are not separating at room temperature. This is a technique that can determine if a fluid is stable on not. Figure 4.3 (a) and b) shows the outcome of the surfactant stability. The observed heights of mixed materials were constant over the period two weeks before the characterization of the synthesized samples. The most stable emulsion was found to be the emulsion with DTAB as a surfactant (see Figure 4.3 a). The separation was due to the absorption of other particles, thus altering the chemical and physical properties. Hence, it shows that there is a gap between the stabilization of nanoparticle.

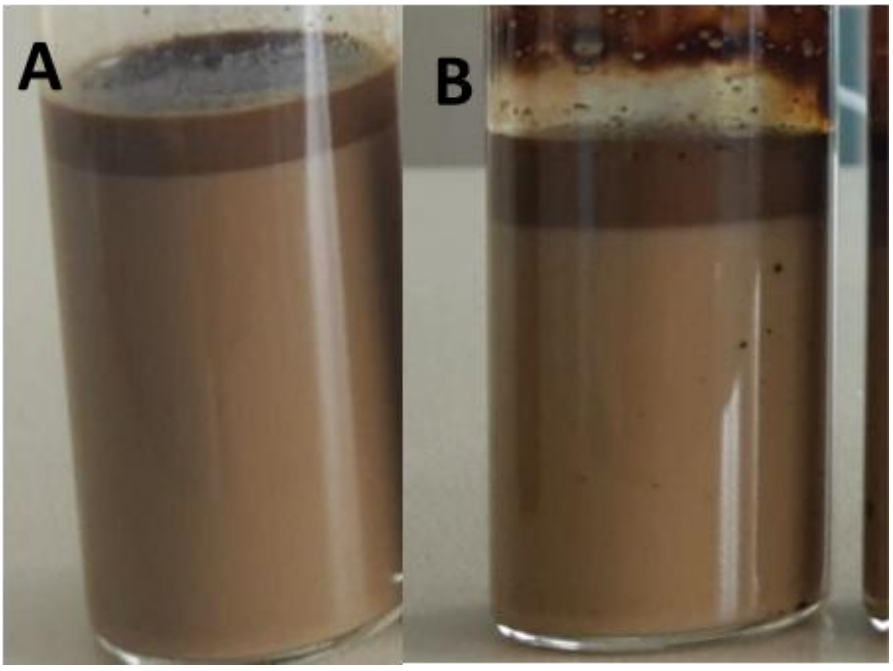


Figure 4.3: Emulsion based drilling fluids with (a) DTAB and (b) Triton® X-100

4.4 Filtration test

Beyond rheology, fluid losses is another property that drilling operations should mitigate to curb expensive drilling operations and maintain safety. The filtrate volume of different surfactant has shown a similar trend with or without ZnO nanoparticles. Figure 4.4 illustrates that fluid loss was less at the concentration of 1 wt. % of DTAB, where the filtrated volume was at its lowest (58 ml). When examining the 0.75 wt. %, the filtrate volume was 111 ml. Hence, making the 1 wt. % the more stable concentration.

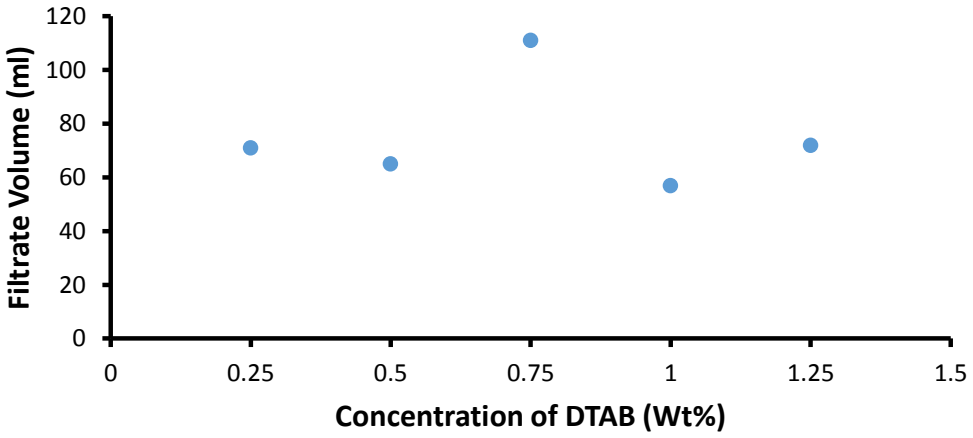


Figure 4.4: Filtration loss of drilling fluid with 1Wt% DTAB

Further observations showed that for all the surfactants at 1 wt. %, there is the lowest volume filtrate. From Figure 4.5, 4-6 and 4-7 the following observations infer that nano-muds exhibit low fluid loss:

- Lowest volume of filtrate at 1wt%,
    - DTAB + ZnO = 53ml
    - Triton® X-100 + ZnO = 53 ml
    - Triton® X-100 = 66 ml,
- Highest filtrate volume was at 1.25 wt. % for
    - Triton® X-100 + ZnO (160 ml)
    - DTAB + ZnO (80 ml)
    - Triton® X-100 90 ml)

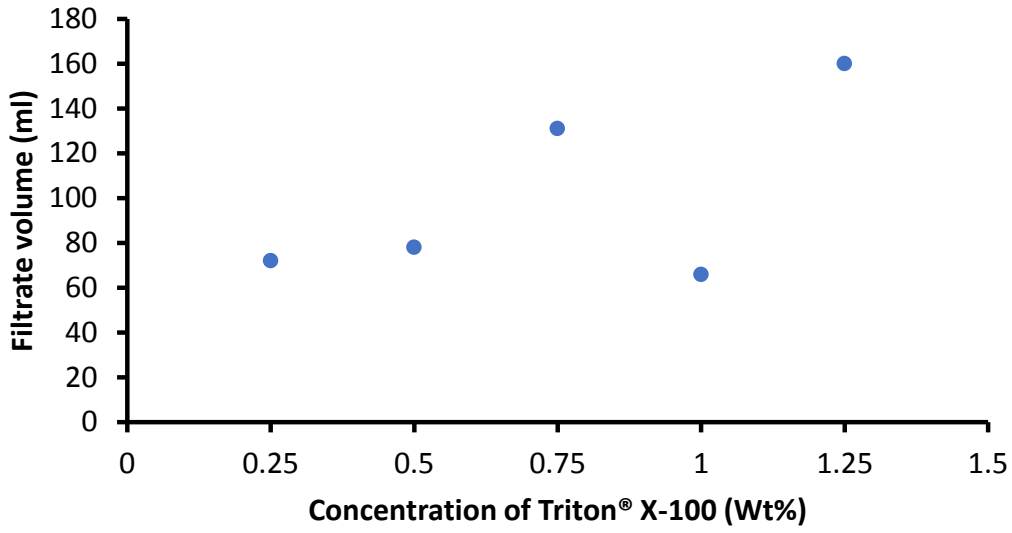


Figure 4.5: Filtration loss of drilling fluid with 1Wt% Triton® X-100

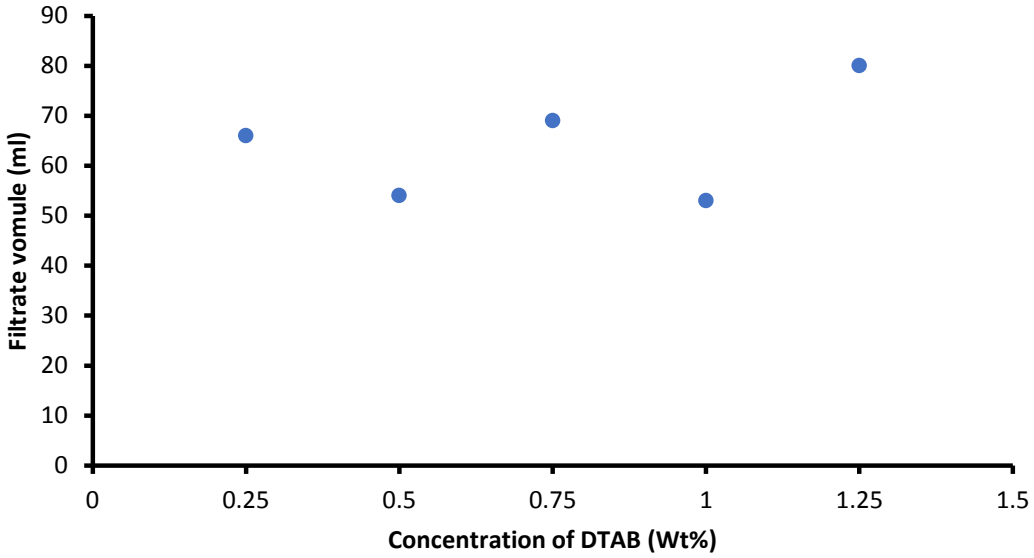


Figure 4.6: Filtration loss of drilling fluid with 1Wt% DTAB + ZnO

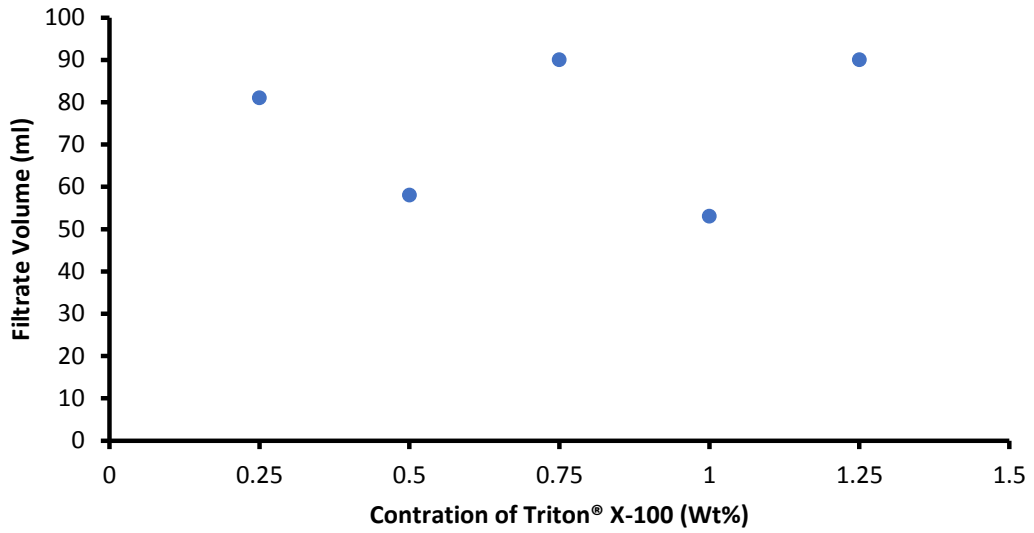


Figure 4.7: Filtration loss of drilling fluid with 1Wt% Triton® X-100 + ZnO

4.5 Effect of water content

There are various reasons that drilling fluid properties in HTHP conditions changes over time. One of the reasons is that over time water within the formation gets incorporated in the drilling mud which alters the rheological properties. The applied filtrate tests explores and show shows graphs with varying nanoparticle content and maintaining water content. Several graphs illustrating volume of filtration loss over time where plotted, with varying surfactant concentrations. Figure 4.9 is an example of the graphs (see Appendix B for more illustrations and it follows the same trend).

In a summary of filtrate test, an observation of the drilling mud combination that showed the lowest filtrate volume was at the 1Wt%, for both the nanoparticle and surfactant (see Figure 4.8). An examination of the test study illustrated that the best possible combination of nanoparticle and surfactant it is the drilling fluid that contained both ZnO and DTAB. This combinations show the lowest filtration. According to literature, drilling fluids should poses adequate additives to enable emulsify water content within a drilling fluid. Therefore, there should be enough nanoparticles that incorporates excess water to attain a stable emulsion. This factor is of utmost importance because it plays the role of regulating temperature by lubricating and cooling the drilling string and bit. This also fulfils the functionality of aiding with corrosion mitigation.

Another concern, is that a drilling fluid that cannot retain water content, can increase drilling operations at HTHP costs significantly, because of the limited capacity of transportation medium for drilling debris. As a consequence, the hydraulic pressure becomes challenging to regulate. With this study, it is observed that the use of nanoparticle creates stabilized drilling emulsions, which is able to incorporate water within the drilling fluid. It can be inferred that have nano-muds less fluid loss and drilling emulsions without nanoparticles lose their fluidity with increased HTHP.

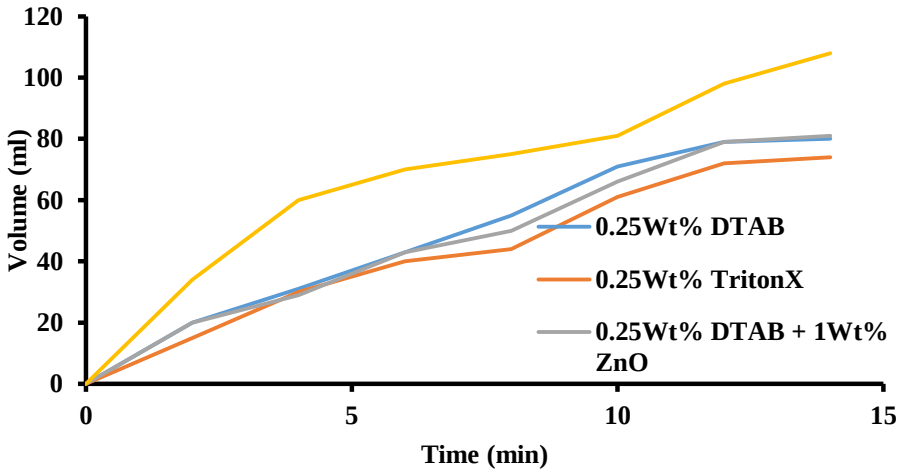


Figure 4.8 : Filtrate volume over time

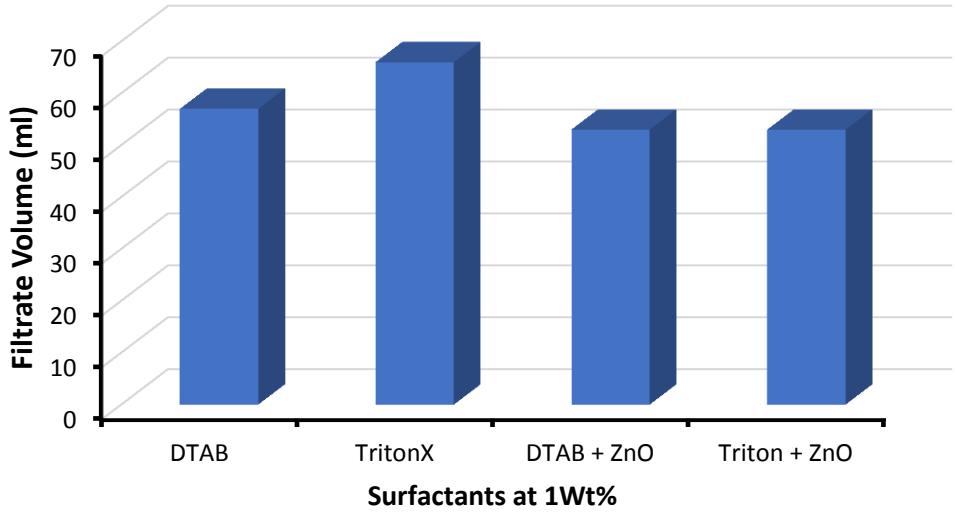


Figure 4.9: Filtration loss of drilling fluid with different surfactants

CHAPTER 5 : CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Experimental oil emulsions were prepared using ZnO nanoparticles as emulsion stabilisers and emulsion without nanoparticle. Rheological properties were measures to evaluate the effects of nanomaterial surfactants (Dodecyltrimethylammonium bromide and triton), at varied concentrations. The results showed the following

- This investigation has highlighted that the use of nanomaterial surfactants for drilling muds for deep-hole conditions
- Custom made nanoparticles has the potential to enhance the rheological properties of drilling muds at HTHP and make them more effective. .
- DTAB surfactants-based drilling mud with ZnO nanoparticle showed a more stability
- The optimum emulsion based drilling fluid is the one that contained DTAB as a surfactant because the emulsion showed a decrease in viscosity and did not show a significant impact of the filtration loss in the presence of ZnO nanoparticles.
- The emulsion that contained 1wt% DTAB and ZnO showed better performance in terms of its ability to retain the water and/or liquid in the mud. This shows that drilling can take place at HTHP depths as lubrication can be retained for longer, also without increasing the cost in regards to supplying energy to increase pressure.
- It can be inferred that have nanomuds less fluid loss and drilling emulsions without nanoparticles lose their fluidity with increased HTHP

The harsh drilling operating conditions at HTHP, means that drilling muds are constantly subjected to stresses at various degrees. For these reasons, their rheology should be modified to accommodate the deep-hole conditions.

The combined effect of pressure, temperature, shear and time history on rheology properties is a daunting task towards characterization of drilling mud rheology. It requires accurate understanding and determination of rheology. When critically reviewing the current research, nanomaterial application to drilling techniques is a potential solution. However, it is noted that the integration of these processes and techniques still needs to be further researched to pave the way for the industry to upscale research into real-world oilfield application.

Hence, future further studies should entail rheological studies and stability studies of the emulsion based drilling fluids with and without the nanoparticles at different temperatures and pressure.

5.2 Recommendations

Below are the recommendation for future investigations

- The effect of temperature on the rheological and filtration behaviour should be investigated.
- The effect of pressure on the filtration behaviour should be investigated.
- The effect of mixing surfactants should be investigated.

.

REFERENCES

Afolabi, R. O., Orodu, O. D. & Efeovbokhan, V. E., 2017. Properties and application of Nigerian bentonite clay deposits for drilling mud formulation :Recent advances and future prospects. *AppliedClayScience,* Volume 143, pp. 39-49.

Agarwal, S. et al., 2013. Nanoparticle-stabilised invert emulsion drilling fluids for deep-hole drilling of oil and gas. *The Canadian Journal of Chemical Engineering,* Volume 91, pp. 1641-1649.

Al-Yasiri, S. M. & Al-Sallami, T. W., 2015. How the drilling fulids can be made more efficient by using nanomaterials. *American Journal of Nano Research and Applications,* 3(3), pp. 41-45.

Amanullah, M. & Al-Tahini, A. M., 2009. Nano-Technology-its significance in smart fluid development for oil and gas field application. *SPE Saudi Arabia Section Technical Symposium*.

Ayoub, M., Shien, G., Diab, D. & Ahmed, Q., 2017. Modeling of Drilling Rate of Penetration Using Adaptive Neuro-Fuzzy Inference System. *International Journal of Applied Engineering Research,* 12(22), pp. 12880-12891.

Bahari, A. & Seyed, A. B., 2009. Drilling cost optimization in a hydrocarbon fi eld by combination of comparative and mathematical methods. *Petroleum Science,* Volume 6, pp. 451-463.

Bataee, M., Kamyub, M. & Ashena, R., 2010. *inverstigation of various (ROP) Models and optimization of drilling parameters for Ppc and roller - cone bits in shadegoan oil field.* Beijin, China, CPS/SPE international oil and gas conference and Exhibition.

Berg, P. V. & Tveit, S. O., 2016. *Model for evaluating drilling efficiency based on the concept of Mechanical Specific Energy,* Norway: Norwegian University of Science and Technology.

Fakoya, M. F. & Shah, N. S., 2017. Emergenc of nanotechnology in the oil and gad industry: Emphasis on the application of silica nanopacticles. *Petroleum,* pp. 1-15.

Geng, J., 2015. *Synthesis of different sizes& functions nanoparticles,* Missouri: Missouri University of Science and Techology.

Gusler, W. et al., 2007. A New Extreme HPHT Viscometer for New Drilling Fluid Challenge. *SPE Drilling and Completion,* June.Volume 81.

Halali, M. A., Ghotbi, C., Tahmasbi, K. & Ghazanfari, M. H., 2016. The role of carbon nanotubes in improving thermal stability of polymeric fluids: Experimental and modeling. *Ind. Eng. Chem,* 55(27), p. 7514–7534.

Hareland, G. & Hoberock, L. L., 1993. *Use of Drilling Parameters to Predict In-Situ Stress Bounds.* Amsterdam, The Netherlands, SPE paper 25727: SPE/ IADC Drilling Conference.

Hassani, S. S. et al., 2016. The effect of nanoparticles on the heat transfer propoerties of drilling fluids. *Journal of Petroleum Science and Engineering,* Volume 146, pp. 183-190.

Helgestad, D.-E., 2010. *The Drilling Process: A Plantwide Control Approach*, Norway: Norwegian University of Sciecne and Technology.

Hossain, M. E., 2015. *Fundamentals of Sustainable Drilling Engineering,* s.l.: s.n.

Husaevg , M. A., 2015. *ROP Modelling and Analysis,* s.l.: University of Stavanger.

Husein, M., 2012. *Enhancing drilling fluid performance using nanotechnology.* Calgary, Alberta, University of Calgary.

Kang, Y., Zhang, H., You, L. & Song, M., 2016. Strengthening shale wellbore with silica nanoparticles drilling fluid. *Petroleum,* Volume 2, pp. 189-195.

Kasiralvalad, E., 2014. The great potential of nanomaterials in drilling and drilling fluid applications. *International Journal of Nano Dimension,* 5(5), pp. 463-471.

Khalil, M., Jan, M. B., Tong, W. C. & Berawi, A. M., 2017. Advance nanomaterils in oil and gas industry: Design, application and challenges. *Applied Energy,* Volume 191, pp. 287-310.

Kilisek, R., 2014. *Breaking Energy.* [Online]
Available at: https:breakingenergy.com/2014/04/08/gulf-of-mexico-to-drive-global-deep-water-drilling-innovation/
[Accessed 25 Febrauary 2018].

Mahendranath, A., Varkey, S. & Mazumder, S., 2015. Application of nanotechnology in petroleum industry. *Internation Journal of Recent Scientific Research,* 6(9), pp. 6152-6157.

Mehennaoui, S. & Khochemane, L., 2015. Optimization of Settings Parameters of Rotary Drillng Rig Using SIMHYRAULICS Toolbox. *Contemporary Engineering Sciences,* Volume 8, pp. 115-120.

Miyora, T. O., 2014. *Modelling and Optimization of Geothermal Drilling Parameters - A Case Study of Well Mw-17 In Menengai, Kenya,* Reykjavík, Iceland: University of Iceland.

Nascimento, A. et al., 2015. Mathematical Modeling Applied to Drilling Engineering: An Application of Bourgoyne and Young ROP Model to a Presalt Case Study. *Mathematical Problems in Engineering : Hindawi,* 20 August, pp. 1-9.

Nasser, J., Jesil, A., Mohiuddin, T. & Al Ruqeshi, M., 2013. Experimental Investigation of Drilling Fluid Performance as Nanoparticles. *World Journal of Nano Science and Engineering,* Volume 3, pp. 57-61.

Negin, C., Ali, S. & Xie, Q., 2016. Application of nanotechnology for enhancing oil recovery-A review. *Petroleum,* Volume 2, pp. 324-333.

Oakley, D. J. et al., 2000. *Innovation drilling fluid design and rigorous pre-well planning enable success in an extreme HTHP well,* s.l.: In IADC/SPE Asia Pacific Drilling Technology. Society of Petroleum Engineers.

Paiaman, A. M., Al-Askari, M. K., Al-Anazi, B. D. & Masihi, M., 2009. Effect of Drilling Fluid Properties on Rate of Penetration. *NAFTA,* 60(30), pp. 129-134.

Solberg, S. M., 2012. *Improved drilling process through the determination of hardness and lithology boundaries,* Norway: Norwegian University of Science and Technology.

Srivatsa, J. T. & Ziaja, M. B., 2011. *An experimental investigation on use of nanoparicles as fluid loss addivitves in a surfactant-polymer based drilling fluids.* s.l., International Petroleum Technology Conference.

Sun, x., Zhang, Y., Chen, G. & Gai, Z., 2017. Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress. *Energies,* 10(345), pp. 1-33.

Van Dyke, K., 1998. *Drilling fluids,mud pumps, and conditioning equpment,* Austin, Texas: University of Texas at Austin Petroleum.

Vryzas, Z. & Kelessidis, V. C., 2017. *Nano-Based Drilling Fluids: A Review,* Basel, Switzerland: Energies.

Vryzas, Z. et al., 2016. *A comprehensive approach for the development of new magnetite nanoparticles giving smart drilling fluids with superior rheological and fluid loss properties for HP/HT applications.*. Bangkok, Thailand, n Proceedings of the International Petroleum Technology Conference .

Youssif, M. I., El-Maghraby, R. M., Saleh, S. M. & Elgibaly, A., 2017. Silica nanofluid flooding for enhanced oil recovery in sandstone rocks. *Egyptian Journal of Petroleum.*

Zakaria, M. F., 2013. *Nanopartilce-based Drilling Fluids with Improved Characteristics (Ph.D Dissertation),* Canada: University of Calgary.

Zhang, H., Nikolov, A. & Wasan , D., 2014. Enhanced Oil Recovery (EOR) Using Nanoparticle Dispersions: Underlying Mechanism and Imbibition Experiments. *Energy and Fuels*, 28(5), p. 3002−3009.

APPENDIX

APPENDIX A: RHEOLOGY

A.1 Viscosity and Torque profiles

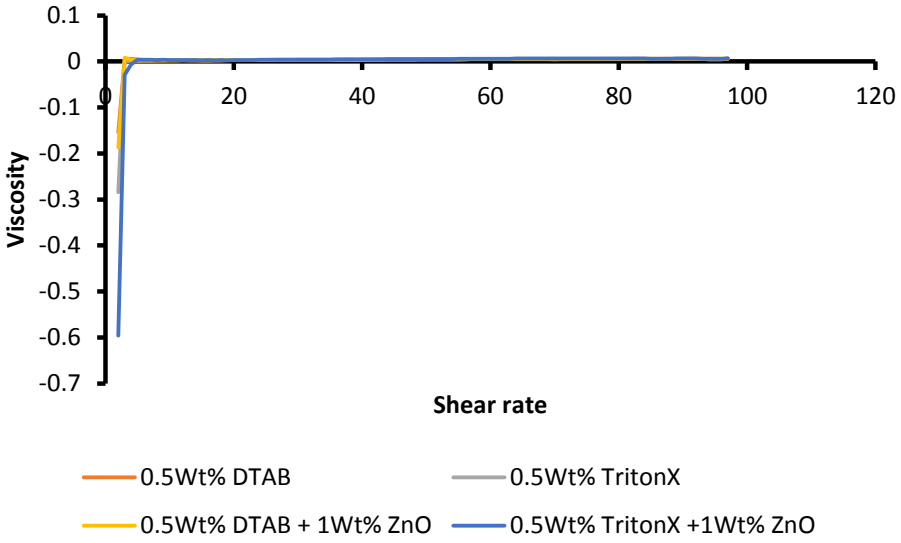


Figure A.1: Viscosity profile for 0.5 wt % DTAB with and without ZnO

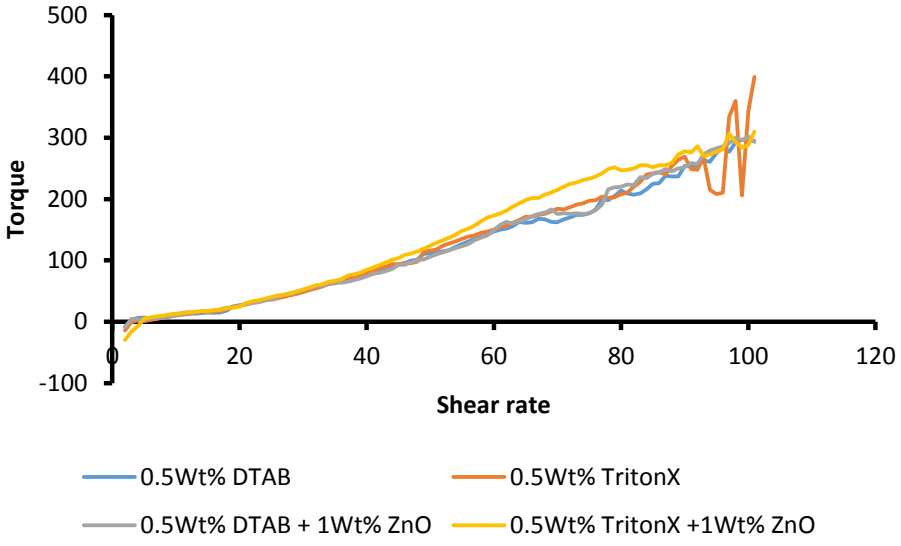


Figure A.2: Torque profile for 0.5 wt % DTAB with and without ZnO

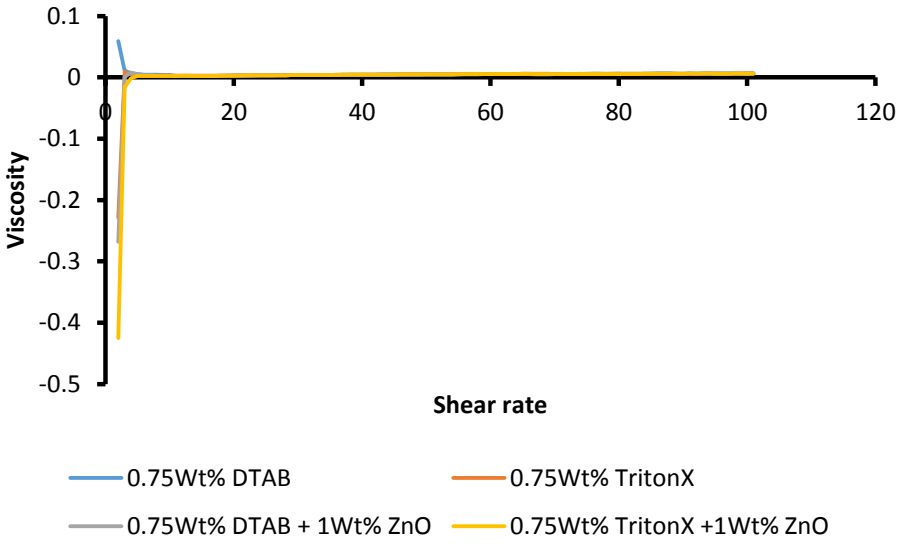


Figure A.3: Viscosity profile for 0.75 wt % DTAB with and without ZnO

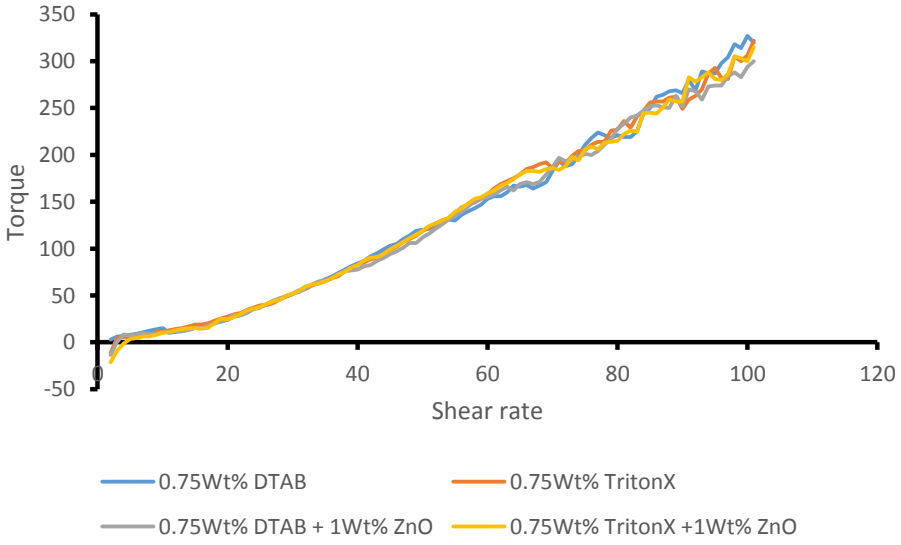


Figure A.4: Torque profile for 0.5 wt % DTAB with and without ZnO

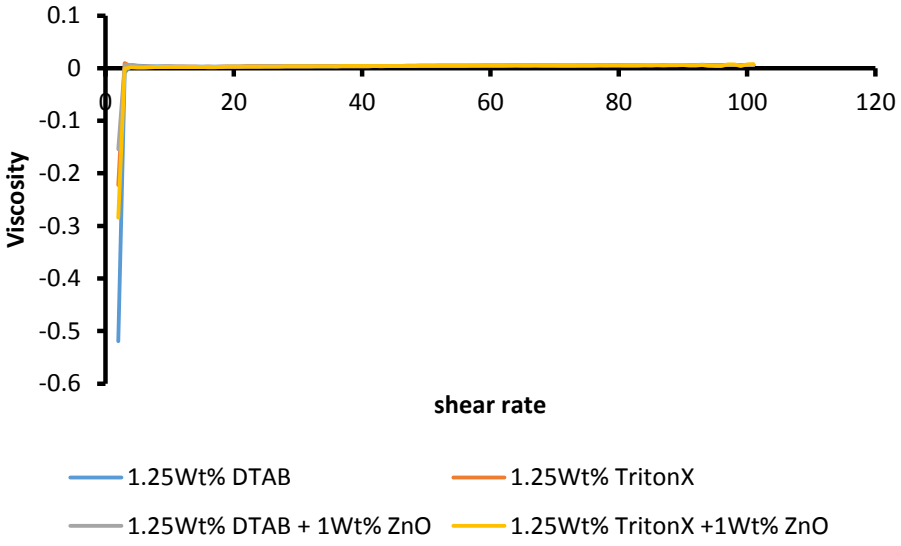


Figure A.5: Viscosity profile for 1.25 wt % DTAB with and without ZnO

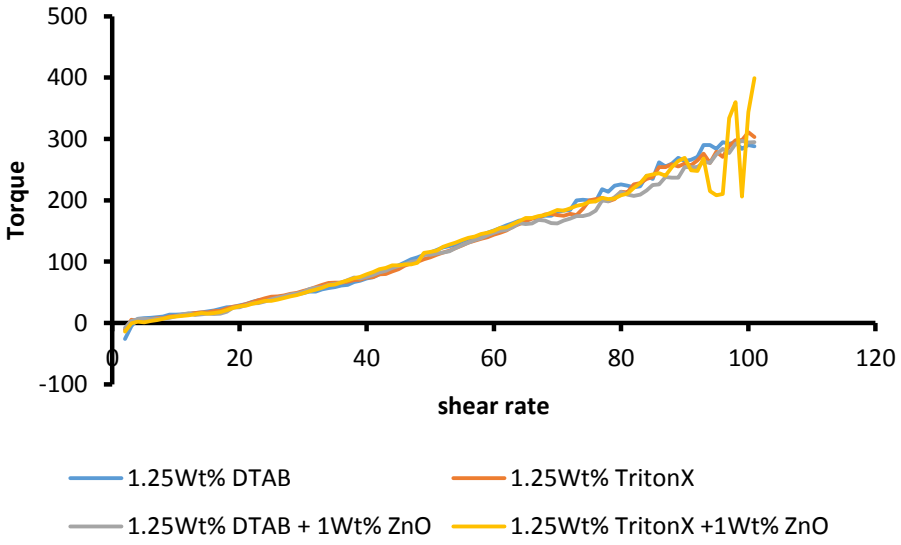


Figure A.5: Torque profile for 1.25 wt % DTAB with and without ZnO

Table A.1: Shear stress against shear rate

Shear Rate [1/s]	Shear stress 1.0Wt%	Shear stress 0.25Wt%	Shear stress 0.5Wt%	Shear stress 0.75Wt%	Shear stress 1.25Wt%
1	-0.778	-0.529	-0.154	0.0591	-0.518
11.1	-0.433	-0.208	0.0649	0.118	-0.099
21.2	-0.0829	0.122	0.128	0.143	0.133
31.3	0.0249	0.217	0.138	0.159	0.155
41.4	0.075	0.233	0.111	0.183	0.166
51.5	0.087	0.25	0.134	0.212	0.187
61.5	0.116	0.259	0.143	0.25	0.207
71.6	0.142	0.29	0.171	0.275	0.273
81.7	0.17	0.325	0.224	0.302	0.269
91.8	0.187	0.349	0.277	0.205	0.282
102	0.233	0.352	0.31	0.224	0.307
112	0.271	0.373	0.264	0.236	0.323
122	0.314	0.335	0.28	0.269	0.34
132	0.307	0.311	0.304	0.31	0.371
142	0.329	0.339	0.288	0.326	0.41
152	0.344	0.408	0.296	0.373	0.458
162	0.389	0.429	0.37	0.412	0.508
173	0.446	0.463	0.495	0.437	0.525
183	0.541	0.504	0.509	0.479	0.576
193	0.578	0.55	0.588	0.55	0.616
203	0.62	0.594	0.63	0.576	0.684
213	0.699	0.634	0.65	0.629	0.734
223	0.748	0.691	0.697	0.712	0.759
233	0.787	0.745	0.771	0.765	0.803
243	0.839	0.807	0.821	0.802	0.839
253	0.893	0.87	0.869	0.866	0.873
263	0.946	0.93	0.923	0.936	0.907
273	0.987	0.986	0.958	0.976	0.937
284	1.057	1.04	1.01	1.04	0.966
294	1.107	1.09	1.1	1.11	1.03
304	1.167	1.15	1.14	1.16	1.02
314	1.227	1.19	1.16	1.23	1.1
324	1.297	1.22	1.24	1.28	1.13
334	1.357	1.26	1.27	1.34	1.17
344	1.437	1.33	1.31	1.4	1.22

354	1.467	1.38	1.4	1.47	1.24
364	1.547	1.47	1.48	1.54	1.33
374	1.597	1.52	1.45	1.62	1.38
384	1.647	1.59	1.5	1.68	1.45
395	1.697	1.65	1.56	1.73	1.49
405	1.787	1.73	1.65	1.83	1.59
415	1.857	1.79	1.69	1.9	1.65
425	1.937	1.89	1.79	1.98	1.79
435	2.037	1.95	1.85	2.06	1.88
445	2.107	2.05	1.91	2.1	1.97
455	2.197	2.13	1.99	2.19	2.07
465	2.267	2.2	2.02	2.27	2.13
475	2.367	2.24	2.21	2.37	2.22
485	2.457	2.3	2.21	2.4	2.3
495	2.557	2.3	2.25	2.41	2.37
506	2.607	2.3	2.31	2.5	2.45
516	2.647	2.32	2.34	2.6	2.5
526	2.707	2.37	2.44	2.62	2.56
536	2.667	2.46	2.53	2.59	2.66
546	2.897	2.55	2.61	2.71	2.74
556	3.077	2.63	2.7	2.79	2.8
566	3.117	2.73	2.76	2.86	2.86
576	2.987	2.86	2.85	2.94	2.94
586	3.097	3.02	2.93	3.06	3.02
596	3.207	3.12	3	3.11	3.1
606	3.307	3.19	3.04	3.12	3.17
617	3.327	3.29	3.12	3.2	3.26
627	3.407	3.32	3.26	3.32	3.32
637	3.507	3.34	3.22	3.32	3.34
647	3.657	3.36	3.24	3.35	3.42
657	3.837	3.4	3.35	3.27	3.42
667	3.977	3.31	3.34	3.33	3.49
677	4.077	3.4	3.25	3.41	3.5
687	4.207	3.42	3.23	3.66	3.61
697	4.347	3.5	3.33	3.85	3.66
707	4.407	3.53	3.4	3.76	3.68
717	4.417	3.57	3.47	3.8	4
728	4.477	3.5	3.47	3.97	4.02
738	4.517	3.56	3.54	4.21	3.99
748	4.507	3.66	3.66	4.36	3.96
758	4.517	3.67	3.99	4.47	4.36

768	4.487	3.84	3.95	4.4	4.27
778	4.437	3.98	4.1	4.36	4.48
788	4.417	3.86	4.26	4.41	4.52
798	4.627	3.76	4.17	4.37	4.47
808	4.777	4.06	4.13	4.38	4.4
818	4.767	4.03	4.18	4.5	4.45
828	4.717	4.04	4.31	4.88	4.8
839	4.827	4.49	4.49	4.99	4.69
849	5.017	4.85	4.5	5.23	5.23
859	5.207	4.91	4.74	5.27	5.09
869	5.467	5.04	4.74	5.35	5.19
879	5.627	4.95	4.73	5.36	5.37
889	5.377	4.99	5.06	5.3	5.27
899	5.467	5.06	5.07	5.59	5.31
909	5.557	5.33	5.06	5.37	5.42
919	5.627	5.36	5.26	5.77	5.79
929	5.357	5.8	5.21	5.74	5.8
939	5.467	5.67	5.49	5.74	5.68
950	5.807	5.93	5.67	5.95	5.88
960	6.127	5.63	5.54	6.07	5.83
970	6.037	5.74	5.84	6.36	5.88
980	6.017	5.95	5.92	6.28	5.67
990	5.907	5.9	5.86	6.54	5.78
1 000	6.337	6.16	5.89	6.4	5.75

Shear Rate [1/s]	Shear stress 1.0Wt%	Shear stress 0.25Wt%	Shear stress 0.5Wt%	Shear stress 0.75Wt%	Shear stress 1.25Wt%
1	0.0621	-0.0574	-0.596	-0.425	-0.284
11.1	0.121	0.0615	-0.321	-0.18	-0.00495
21.2	0.146	0.0369	-0.145	-0.0256	0.0377
31.3	0.162	0.0745	0.108	0.0741	0.0257
41.4	0.186	0.0552	0.142	0.0947	0.0583
51.5	0.215	0.0799	0.18	0.127	0.0991
61.5	0.253	0.111	0.194	0.128	0.137
71.6	0.278	0.159	0.24	0.163	0.183
81.7	0.305	0.191	0.264	0.198	0.203
91.8	0.208	0.209	0.278	0.217	0.233
102	0.227	0.218	0.316	0.253	0.254
112	0.239	0.25	0.325	0.283	0.282
122	0.272	0.279	0.349	0.3	0.319

132	0.313	0.3	0.345	0.306	0.306
142	0.329	0.333	0.381	0.288	0.325
152	0.376	0.377	0.39	0.313	0.359
162	0.415	0.413	0.434	0.414	0.416
173	0.44	0.45	0.454	0.5	0.492
183	0.482	0.522	0.49	0.497	0.537
193	0.553	0.583	0.602	0.544	0.563
203	0.579	0.629	0.667	0.606	0.628
213	0.632	0.679	0.695	0.679	0.672
223	0.715	0.712	0.749	0.719	0.715
233	0.768	0.753	0.801	0.755	0.722
243	0.805	0.788	0.852	0.825	0.765
253	0.869	0.822	0.878	0.87	0.816
263	0.939	0.842	0.923	0.912	0.864
273	0.979	0.891	0.995	0.991	0.908
284	1.043	0.959	1.05	1.04	0.965
294	1.113	1.02	1.12	1.1	1.04
304	1.163	1.09	1.19	1.19	1.08
314	1.233	1.16	1.22	1.23	1.15
324	1.283	1.21	1.3	1.25	1.23
334	1.343	1.3	1.33	1.31	1.25
344	1.403	1.39	1.39	1.36	1.32
354	1.473	1.44	1.49	1.44	1.38
364	1.543	1.45	1.54	1.51	1.46
374	1.623	1.55	1.59	1.59	1.5
384	1.683	1.64	1.68	1.65	1.58
395	1.733	1.71	1.76	1.75	1.65
405	1.833	1.74	1.84	1.8	1.75
415	1.903	1.84	1.93	1.82	1.8
425	1.983	1.88	2.01	1.88	1.87
435	2.063	1.95	2.08	1.98	1.88
445	2.103	2.02	2.18	2.06	1.91
455	2.193	2.13	2.21	2.13	1.91
465	2.273	2.21	2.3	2.22	1.95
475	2.373	2.29	2.37	2.29	2.27
485	2.403	2.42	2.47	2.38	2.32
495	2.413	2.48	2.57	2.47	2.36
506	2.503	2.54	2.66	2.54	2.47
516	2.603	2.65	2.73	2.6	2.56
526	2.623	2.74	2.84	2.66	2.61
536	2.593	2.82	2.95	2.77	2.7

546	2.713	2.91	3.04	2.85	2.77
556	2.793	3	3.14	2.96	2.82
566	2.863	3.07	3.27	3.06	2.9
576	2.943	3.1	3.38	3.1	2.94
586	3.063	3.13	3.45	3.17	2.99
596	3.113	3.2	3.54	3.24	3.09
606	3.123	3.33	3.62	3.33	3.11
617	3.203	3.43	3.75	3.4	3.21
627	3.323	3.55	3.86	3.48	3.32
637	3.323	3.69	3.96	3.58	3.4
647	3.353	3.83	4.03	3.65	3.41
657	3.273	4.04	4.03	3.65	3.48
667	3.333	4.14	4.12	3.63	3.51
677	3.413	4.26	4.21	3.7	3.6
687	3.663	4.35	4.29	3.72	3.66
697	3.853	4.44	4.4	3.67	3.65
707	3.763	4.54	4.5	3.76	3.73
717	3.803	4.59	4.54	3.96	3.8
728	3.973	4.74	4.61	3.87	3.86
738	4.213	4.81	4.65	4.11	3.94
748	4.363	4.89	4.72	4.18	3.95
758	4.473	4.92	4.83	4.12	4.07
768	4.403	4.97	4.96	4.24	4.04
778	4.363	4.98	5.02	4.27	4.06
788	4.413	4.88	4.93	4.3	4.15
798	4.373	5.08	4.94	4.44	4.21
808	4.383	4.98	5	4.5	4.39
818	4.503	5	5.1	4.49	4.55
828	4.883	4.97	5.1	4.9	4.79
839	4.993	5.21	5.04	4.89	4.83
849	5.233	5.28	5.09	4.88	4.87
859	5.273	5.46	5.08	5.02	4.79
869	5.353	5.48	5.17	5.18	5.06
879	5.363	5.69	5.46	5.12	5.27
889	5.303	5.51	5.54	5.13	5.36
899	5.593	5.6	5.51	5.64	4.98
909	5.373	5.5	5.71	5.55	4.94
919	5.773	5.53	5.4	5.64	5.35
929	5.743	5.58	5.45	5.76	4.28
939	5.743	5.95	5.53	5.61	4.15
950	5.953	5.88	5.61	5.59	4.2

960	6.073	5.79	6.14	5.71	6.68
970	6.363	5.99	5.86	6.08	7.18
980	6.283	6.13	5.66	6.05	4.11
990	6.543	6.1	5.74	5.98	6.88
1 000	6.403	6.26	6.19	6.29	7.97

Shear Rate [1/s]	Shear stress 1.0Wt%	Shear stress 0.25Wt%	Shear stress 0.5Wt%	Shear stress 0.75Wt%	Shear stress 1.25Wt%
1	0.0591	-0.187	-0.187	-0.268	-0.154
11.1	0.118	0.0894	0.0894	0.00588	0.0649
21.2	0.143	0.0707	0.0707	0.167	0.128
31.3	0.159	0.0626	0.0626	0.145	0.138
41.4	0.183	0.0946	0.0946	0.162	0.111
51.5	0.212	0.11	0.11	0.194	0.134
61.5	0.25	0.135	0.135	0.173	0.143
71.6	0.275	0.167	0.167	0.174	0.171
81.7	0.302	0.205	0.205	0.216	0.224
91.8	0.205	0.24	0.24	0.211	0.277
102	0.224	0.271	0.271	0.237	0.31
112	0.236	0.298	0.298	0.243	0.264
122	0.269	0.329	0.329	0.266	0.28
132	0.31	0.326	0.326	0.301	0.304
142	0.326	0.352	0.352	0.302	0.288
152	0.373	0.407	0.407	0.356	0.296
162	0.412	0.456	0.456	0.397	0.37
173	0.437	0.479	0.479	0.463	0.495
183	0.479	0.516	0.516	0.48	0.509
193	0.55	0.581	0.581	0.583	0.588
203	0.576	0.604	0.604	0.579	0.63

213	0.629	0.641	0.641	0.641	0.65
223	0.712	0.687	0.687	0.703	0.697
233	0.765	0.74	0.74	0.743	0.771
243	0.802	0.78	0.78	0.808	0.821
253	0.866	0.882	0.882	0.888	0.869
263	0.936	0.895	0.895	0.921	0.923
273	0.976	0.953	0.953	0.976	0.958
284	1.04	1.05	1.05	1.04	1.01
294	1.11	1.09	1.09	1.07	1.1
304	1.16	1.15	1.15	1.15	1.14
314	1.23	1.18	1.18	1.23	1.16
324	1.28	1.24	1.24	1.3	1.24
334	1.34	1.28	1.28	1.3	1.27
344	1.4	1.27	1.27	1.37	1.31
354	1.47	1.3	1.3	1.45	1.4
364	1.54	1.36	1.36	1.52	1.48
374	1.62	1.41	1.41	1.53	1.45
384	1.68	1.48	1.48	1.55	1.5
395	1.73	1.56	1.56	1.62	1.56
405	1.83	1.6	1.6	1.65	1.65
415	1.9	1.65	1.65	1.74	1.69
425	1.98	1.72	1.72	1.8	1.79
435	2.06	1.86	1.86	1.88	1.85
445	2.1	1.85	1.85	1.94	1.91
455	2.19	1.93	1.93	2.02	1.99
465	2.27	2	2	2.12	2.02
475	2.37	2.04	2.04	2.11	2.21
485	2.4	2.12	2.12	2.23	2.21

495	2.41	2.19	2.19	2.32	2.25
506	2.5	2.25	2.25	2.41	2.31
516	2.6	2.33	2.33	2.52	2.34
526	2.62	2.4	2.4	2.61	2.44
536	2.59	2.45	2.45	2.7	2.53
546	2.71	2.54	2.54	2.78	2.61
556	2.79	2.65	2.65	2.89	2.7
566	2.86	2.73	2.73	3	2.76
576	2.94	2.82	2.82	3.08	2.85
586	3.06	2.98	2.98	3.1	2.93
596	3.11	3.16	3.16	3.15	3
606	3.12	3.25	3.25	3.23	3.04
617	3.2	3.2	3.2	3.31	3.12
627	3.32	3.28	3.28	3.23	3.26
637	3.32	3.34	3.34	3.37	3.22
647	3.35	3.43	3.43	3.41	3.24
657	3.27	3.5	3.5	3.38	3.35
667	3.33	3.56	3.56	3.42	3.34
677	3.41	3.65	3.65	3.57	3.25
687	3.66	3.52	3.52	3.73	3.23
697	3.85	3.53	3.53	3.93	3.33
707	3.76	3.52	3.52	3.85	3.4
717	3.8	3.53	3.53	3.88	3.47
728	3.97	3.51	3.51	3.96	3.47
738	4.21	3.54	3.54	4	3.54
748	4.36	3.62	3.62	3.99	3.66
758	4.47	3.82	3.82	4.07	3.99
768	4.4	4.31	4.31	4.21	3.95

778	4.36	4.38	4.38	4.34	4.1
788	4.41	4.4	4.4	4.56	4.26
798	4.37	4.48	4.48	4.65	4.17
808	4.38	4.44	4.44	4.79	4.13
818	4.5	4.71	4.71	4.83	4.18
828	4.88	4.67	4.67	4.94	4.31
839	4.99	4.8	4.8	5.03	4.49
849	5.23	4.85	4.85	5.06	4.5
859	5.27	4.96	4.96	5.02	4.74
869	5.35	4.89	4.89	5	4.74
879	5.36	4.99	4.99	5.24	4.73
889	5.3	5.02	5.02	5.03	5.06
899	5.59	5.17	5.17	5.38	5.07
909	5.37	5.14	5.14	5.35	5.06
919	5.77	5.44	5.44	5.16	5.26
929	5.74	5.56	5.56	5.45	5.21
939	5.74	5.66	5.66	5.46	5.49
950	5.95	5.71	5.71	5.48	5.67
960	6.07	5.81	5.81	5.66	5.54
970	6.36	5.99	5.99	5.74	5.84
980	6.28	5.9	5.9	5.65	5.92
990	6.54	6.02	6.02	5.86	5.86
1 000	6.4	5.85	5.85	5.99	5.89

APPENDIX B: FILTRATION LOSS

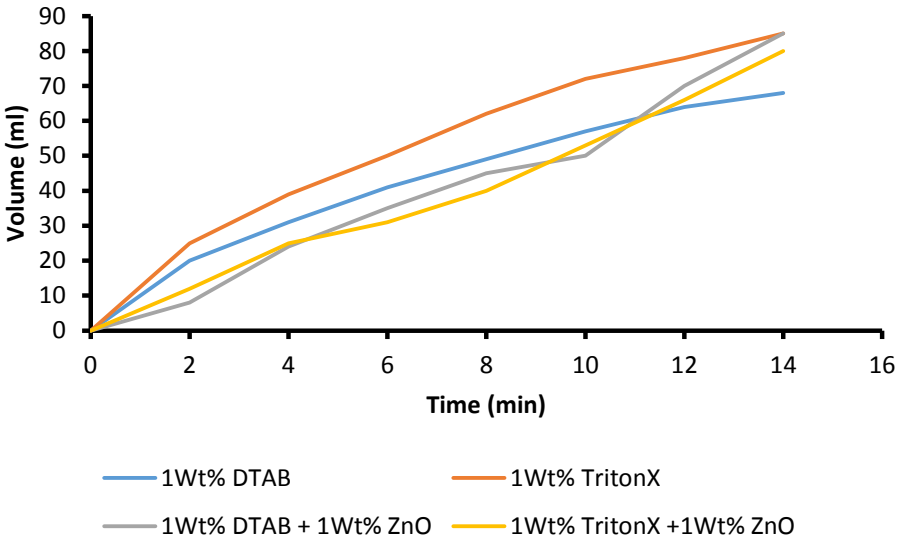


Figure B.1: Filtration loss profile for 1wt % DTAB with and without ZnO

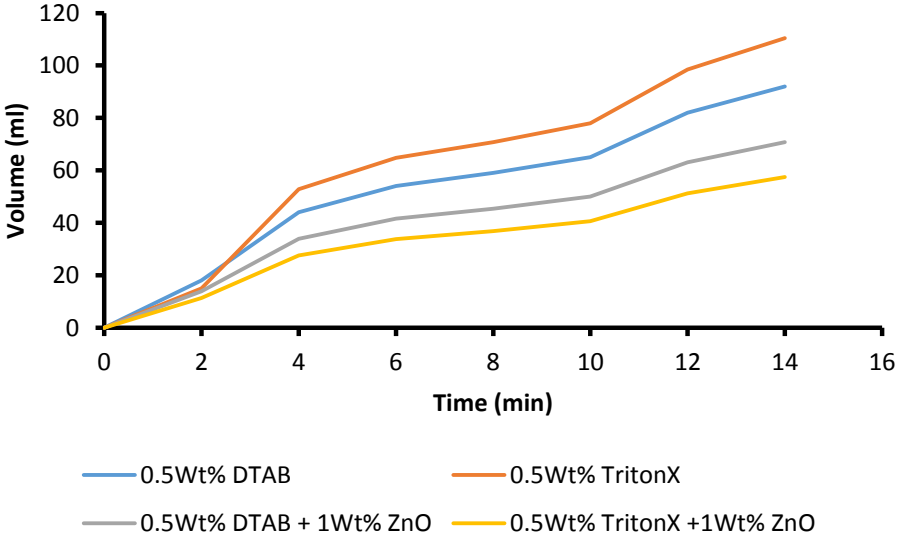


Figure B.2: Filtration loss profile for 0.5 wt % DTAB with and without ZnO

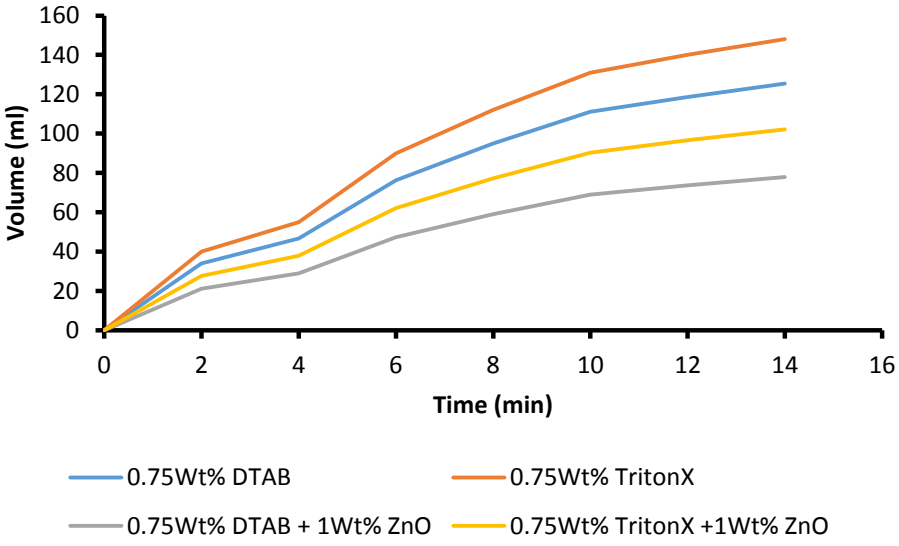


Figure B.3: Filtration loss profile for 0.75wt % DTAB with and without ZnO

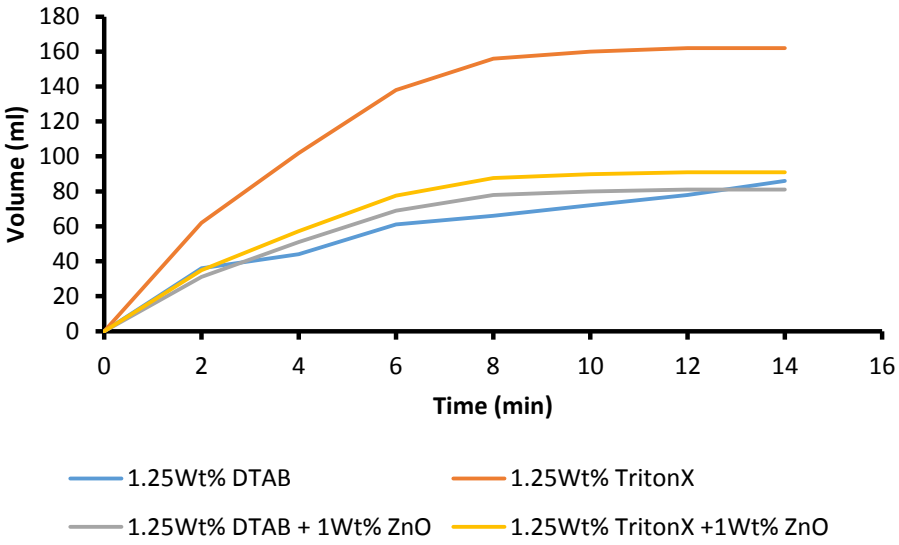


Figure B.4: Filtration loss profile for 1.25wt % DTAB with and without ZnO