INVESTIGATION OF THE EFFECTS OF ZINC OXIDE NANOPARTICLES AND SYNTHESIZED CELLULOSE NANOCRYSTALS (CNCs) ON EMULSION-BASED DRILLING FLUIDS

Msc Research Dissertation

Prepared by

Tiemele wilfried Anderson Aka (1754832)

Supervisor: Dr Diakanua Nkazi

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

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Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Masters of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Tiemele Wilfried Anderson Aka

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Abstract

Drilling Mud holds an important role in the drilling process in such a way that it is a determinant key to the success of the operation as well as the money spent throughout the process. Indeed the success and the cost of the operation can be severely impacted by some challenges experienced while drilling such as temperature and pressure conditions which leads to fluid loss, fluid deterioration...As a result there is a need to formulate a fluid with desirable rheological properties to withstand such undesirable parameters.

Therefore this work was aimed to improve emulsion drilling fluids (EDFs) based nanoparticles with enhanced properties. Many investigations were performed to find a proper emulsion stability as well as a good drilling fluid performance. The stability of the prepared emulsion drilling fluids was done using surfactant with different concentrations for several days. After several days of preparation, the EDFs containing DTAB as surfactant have showed a better emulsion stabilizer compared to the Triton X-100 ones.

In addition an investigation combining both NPs and surfactants confirmed the used of NPs to improve DF and revealed the effective use of ZnO NPs for drilling fluids application and preferentially with DTAB as surfactant.

Following that result, the 2nd part of the work was based on the synthesis and characterization of CNCs as NPs to formulate EDF with DTAB as surfactant. The CNCs NPS were successfully obtained via the method of oxidation of microfibrillated cellulose through TEMPO-mediate and after characterization using TEM, spherical NPs with small size varying from 10-50nm were observed. The FANN® Model 35 viscometer served to display the behavior of the shear stress and viscosity of the prepared fluids against variable shear rate at variable NPs and temperature concentration.

The rheological and filtration properties were increase with increase in CNCs content from 0.8 to 1.2% of fluid in room temperature and with an increase in temperature.

Dedications

To my family members

Acknowledgements

All glory be to God the Father of my Lord Jesus Christ, for all things are made possible with his grace.

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List of Symbols

μ: Viscosity

$\dot{\gamma}$: shear rate

τ: shear stress

ζ_y : yield point

n: flow behavior index

μ_p: Plastic viscosity

ρ: density of the fluid [kg / m3].

μ_{d1}: and μ_{d2}: respectively represent the dynamic viscosity of the solution and of the solvent,

P: Training pressure; in Kgf / cm2

H: Depth of the layer crossed; in m

d: Density of the mud.

K = consistency factor

ζ = shear stress

F: shearing force

S: surface

μ_{rel}: Relative viscosity

μ_{sp}: Intrinsic viscosity

μ_s: Specific viscosity

t: time

x: abscissa

u: distance

μ_a: The dynamic or apparent viscosity

h: Depth of the layer crossed; in m

ν: The kinematic viscosity.

C: Concentration

List of abbreviations

AFNOR: Association Française de Normalisation (French Standardization Association)

API: American Petroleum Institute

CNC: Cellulose Nanocrystal

CNF: Cellulose Nano-Fiber

DF: Drilling Fluid

EDF: Emulsion Drilling Fluid

GBM: Gas Based Mud

HLB: Hydrophilic-Lipophilic Balance

HTHP: High Temperature High Pressure

LTLP: Low Temperature Low Pressure

NPs: Nanoparticles

OBM: Oil Based Mud

o/w: Oil in water

o/w/o: Oil in water in oil

PV: Plastic Viscosity

TEM: Transmission Electron Microscopy

WBM: Water Based Mud

w/o: Water in oil

w/o/w: Water in oil in water

YP: Yield Point

ZnO: Zinc Oxide

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CHAPTER 1. INTRODUCTION

1.1 Background and motivations

Essentially, any material derived from crude oil and processed in oil refineries is called Petroleum products. Then, vaporizators, motor oils, fuel, deodorants, tyres, perfumes, lipstick, toilets seats, and many other items are petroleum products (Speight, 2015). Hence, petroleum holds an important place in our daily life. So for several years, the need for drilling deeper for oil and gas production is becoming urgent due to the depletion of the oil stocks combined with the increasing worldwide energy demand and population. For example likewise many countries, South Africa government allocates a significant part of its budget in crude oil importation, which is a major source of importation of the country in term of energy supply (Yousef and Adam, 2008). All stipulated above confront the petroleum technologists all around the world to search for solutions to face the current challenges day after day.

Different steps are involved in the oil and gas production process. Among all those steps, the drilling is an important step namely because of the cost of its operation. Unfortunately, the oil and gas exploration subjected upon some conditions such as the compressibility of fluids and initial pressure of the reservoir both primary and secondary methods for oil recovery can only produce one third (in the range of 15–30%) of the total amount of available oil (Green *et al.*, 1998). The proper solution to ensure better production may include improving tools, materials, skills, use of down-hole rotation tools and any other innovative techniques that can improve drilling operations in order to recover more oil. However, practically all those equipment are almost ineffectual if they are not used in the presence of an accurate drilling fluid (DF) (Caenn *et al*., 2011).

DF also called as drilling mud, is the complex fluid used to facilitate the drilling of oil and gas wells. Nevertheless, the current and conventional wells are depleting which lead the drilling engineer to deep and ultra-deep wells (more than 1500m). These new generations of wells cause real difficulties to the current and basic drilling fluids. Indeed, the rheological performances of current drilling fluids are deteriorating due to harsh hole environmental conditions such as high temperature and high pressure (HPHT) faced during extended reach drilling operations (Annis and Esso, 1967; Bourgoyne, 1986). Lack of performance of any of these rheological functions in such environments leads to severe drilling problems such as lost circulation, fluid instability due to changing conditions and high torque and drag (Adriana *et al.,* 2009; George and Scott, 1951; Mendes *et al.,* 2003; Ryan and Douglas, 2008; Yarim *et al.,* 2007). Therefore, the use of current resources and techniques might not be able to keep up with this increasing demand. This has forced drilling technologists to look for innovative methods and technologies for oil and gas extractions from both onshore and offshore reservoirs. Moreover, the techniques should also be more economical, efficient and environmentally sound to extract more hydrocarbons.

Emulsion based drilling fluids have emerged as an important class of drilling fluid systems, which have gained a significant interest in modern drilling operations. Emulsions are the colloidal systems in which fine droplets of one liquid are dispersed in another liquid where the two liquids are otherwise immiscible. Emulsions are prevalent in the food industry, pharmaceutical industry, paints, cosmetics, agriculture products and petroleum industry (Hunter *et al.,* 2008; Jha *et al.,* 2014, Caenn *et al*., 2011). The focus of this research will be in the petroleum industry, where emulsion plays an important role particularly in drilling fluids. Experiments conducted for the suitability of these fluids in HPHT conditions have shown that emulsion based drilling fluids provide a greater degree of well bore stability when compared to water-based drilling fluids (Kelly *et al,* 1980). The use of a stabilizing agent known as surfactant is necessary in order to avoid any destabilization of the emulsion system. Polymers and bridging agents are also used to control the rheological and filtration properties of the drilling fluid systems. Unfortunately, the surfactants only fail to fulfil completely all their expected previously listed missions with satisfaction in emulsions mud at HPHT; and they are also subject to severe environmental regulations in many countries (Gomari, 2015)**.** Therefore, there is a need to formulate the DFs with fewer surfactants and propose additives, which can help to perform better their role and withstand HPHT conditions.

The use of nanoparticles has remarkably impacted many important industries, such as healthcare energy and aeronautics (Borzabadi-Farahani, Borzabadi and Lynch, 2014; Dinca *et al*., 2012; Luther *et al*., 2015). Moreover, literatures revealed that the use of nanofluids has showed their efficiency in a wide range of applications such as drilling, cementing, and enhanced oil recovery (Saidur *et al.,* 2011; Evdokimov *et al.,* 2006; Zitha, 2005; Hendraningrat *et al.,* 2013). One major emerging application of nanotechnology in oil reservoir engineering is in the sector of developing new types of smart fluids for enhanced oil recovery and drilling (Igor *et al.,* 2006). Nanoparticles exhibit many attractive properties including highly enhanced physico-mechanical, chemical, electrical, thermal, hydrodynamic properties and interaction potential.

Considering the issues related to drilling fluids, the present study can promote the development approach towards oil and gas drilling operations, reducing pollution due to the use of oil-based mud and surfactants, protecting the environment and minimizing the costs of the drilling operation.

1.2 Research Questions

This research project aims to investigate whether zinc oxide nanoparticles and cellulose nanocrystals (CNCs) can be used as a viscosifying agent for DF type “emulsion based drilling fluid” under high temperature and high pressure conditions. Thus, the research intends to answer the following questions:

- Can CNCs and zinc oxide (ZnO) nanopartices be used as suitable additives for emulsion DF by fulfilling the drilling fluid’s requirements?
- Can mineral oil mixed with attapulgite clay be used in emulsion DF by fulfilling drilling fluid’s requirements?
- Can crude oil mixed with attapulgite clay be used to withstand HTHP conditions?
- Are CNCs and ZnO nanoparticles another alternative to reduce the additive cost of DF cost?

1.3 Research aim and objectives

The aim of this research project is to investigate the effects of ZnO nanoparticles and synthesized cellulose nanocrystals (CNCs) on emulsion-based drilling fluids. The following are the set objectives to meet the aim of this research project

- To formulate an emulsion drilling fluid (EDF) package with a selected surfactant and evaluate the optimum concentration of surfactant to be used;

- To investigate the effectiveness of ZnO nanoparticles as EDF additive;
- To investigate the effect of mixed with CNCs - crude oil or mineral oil on the emulsion drilling mud based;
- To investigate the rheological behavior and fluid loss properties;

1.4 Report Outline

This work is divided into five parts.

The background related to this work in a general introduction furthermore, this part addresses the research questions, the aim of the study and the steps undertaken to achieve the work are addressed in the first part.

In the second part an inspection upon the state of current knowledge about DFs in general and emulsions drilling fluids used in oil and gas industry. Then a discussion on the rheological behavior of the drilling fluids, focusing on the phenomena, which affect the rheology of DFs. In addition, the report provides general knowledge on the effect of surfactant on the stability of the emulsion. Finally, a necessary literature on the use of nanoparticles and clays in drilling fluids, and their properties allowing them to confer an affinity to the emulsion muds.

The third part describes all the materials used and details of the experimental procedure of the synthesis of CNCs and preparation of the emulsion mud samples.

The results obtained from the CNCs synthesis as well as emulsion mud from the analysis made are presented in the fourth part. The effect of different types of surfactant and their concentration on the EDF properties, the ZnO nanoparticles effect on EDF properties. This report investigate the effect of CNCs at different concentration on the rheology stability of the EDF at variable temperature and fluid loss at variable pressure.

Lastly a brief summary and conclusion of the study are provided in the fifth part by suggesting functionalized ZnO nanoparticles and CNCs are able to act as good viscosifier as well as stabilizer for EDF. In addition, it provides recommendations for future works in the same direction.

CHAPTER 2. LITERATURE REVIEW

2.1 Drilling fluids

2.1.1 Introduction

Oil drilling is part of the set of operations needed to locate and extract hydrocarbon deposits in the subsoil from reservoir rock. Several drillings are needed to result in the exploitation of a deposit: Exploration drilling to confirm the presence of hydrocarbons, evaluation drilling which makes it possible to estimate the economic viability of the development, and finally the development wells that lead to the start of production (Garcia and Parigo, 1968). Drilling efficiency became more important in such a way that the wells are becoming deeper. Hence the implication of DFs is a major tool for the success in any oil and gas drilling process and a lot of money are spent to get the better formulation according to a given drilling process. DFs are generally classified into three different classes such as water based mud (WBM), oil based mud (OBM) and gas based mud (GBM) performing multiples functions and properties. Therefore, those functions and properties cannot be performed without several additives which make the mud a very complex mixture. In this chapter it is question to look over through the complex universe of the drilling mud to know their role, present each family and their use, the properties which regulate them as well as the additives that they need to enhance their work underground.

2.1.2 Oil and gas drilling fluids: definition and functions

Among the different factors involved in the drilling operation, the selection and application of the drilling fluid are the determining factors which contribute to the success of any drilling operation. Drilling fluids also called drilling “mud” can be defined as a system composed of different fluids combinations containing a multitude of additives used for the drilling of oil and gas wells (Khodja, 2010). Indeed the complex design of the drilling fluids must simultaneously fulfill several functions (Lummus and Azar, 1986; Darley and Grey, 1988);

- Clean the well, hold the cuttings in suspension,
- Maintain the stability of the well bore.
- Reduce friction between the drill string and sides of the well

- Prevent the fluid loss to the formation;
- Avoid formation damage and differential pipe sticking by making thin impermeable filter cakes,
- Cool and lubricate the drilling tools and most importantly help in the evaluation of formation by raising the cuttings from the well bore bottom to the surface.

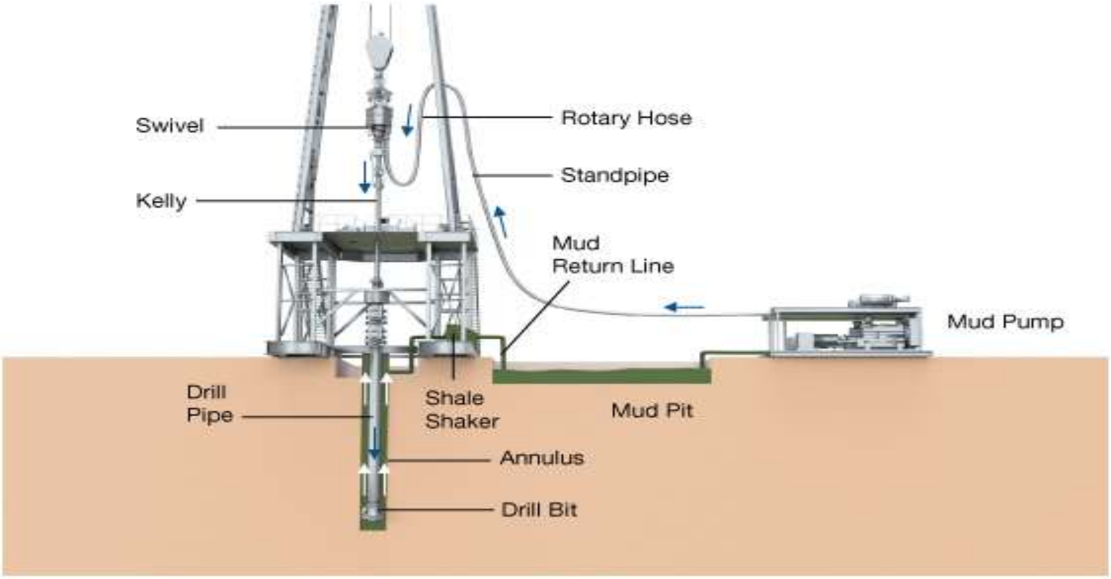

Figure 1: Drilling fluid cycle during a drilling process (Kodja *et al*., 2010)

2.1.3 Types of drilling fluids

DFs are commonly classified into three different families according to the fluid Base used in their preparation: air, water or oil (Ryan and Chillingar, 1996). They are so made depending on the challenges to be faced due to the complexity of the problems encountered in petroleum drilling operation.

2.1.3.1 Water Based Mud (WBM) family:

Water based muds are most used in the field of drilling (Amoco Production Company, 1994). WBM is mud in which the continuous phase is water, eventually, they are generally constituted by suspensions of bentonite clay, inert solids, and its rheological characteristics are corrected by addition of viscosifying polymers. They are usually used to drill the sections that are superior in a well, they are generally relative easy to build, inexpensive to maintain and less polluting and can be applied to overcome most drilling challenges (Amoco Production Company, 1994).

However, the thermal degradation of the polymers used in these formulations has a major disadvantage for the smooth running of a drilling operation (Rossi *et al*., 1999; Mohammed, 1990).

2.1.3.2 Oil Based Mud (OBM) family:

The use and preparation of OBM is different from that of the water based mud. The continuous phase is oil and the dispersed phase is aqueous which is emulsified within and stabilized by surfactant (Khodja *et al*., 2010). Moreover by definition the OBM with more than 5% water are called inverse emulsion drilling fluids (the continuous phase is an organic or mineral oil such as crude oil, gas oil, etc.); and OBM with less than 5% water (IDF, 1988). OBM is used when shale/clay parts of the well are expected to be troublesome. The oil based mud is chosen for its stability at high temperatures, lubrication and its stabilizing attributes of the well. They are also applicable when drilling highly deviated or horizontal wells due to their high natural degree of lubricity (Adebayo, 2012). However, due to the less water content of OBM than WBM, hydration of the shale sections will be minimal. Unlike WBM, these fluids have an insensitivity to contaminants (NaCl, KCl, clay). In addition, a reduction of the friction of the seal on the walls of the well and a limited damage of the formation are observed when using OBM, hence they show a better productivity (Adebayo, 2012). Unfortunately they are environmentally problematic due to the pollution that their use generates, they can likely act as contaminant and they are very expensive (Simpson *et al*., 1994; Friedheim *et al.*, 1999; Young and Maas, 2001; Patel *et al.*, 2001; Schlemmer *et al*., 2002). Currently, fluids based on non-toxic oil are increasingly used to remedy that situation.

2.1.3.3 Gas based mud (GBM);

The gas based muds are known as any mud which continuous phase is gas mixed with water in varying proportions. The gas may be air, natural gas, foam or fog (Bourgoyne, *et al.*, 1986). The

GBMs are used when their pressure is lower than that exerted by the petroleum located in the pores of the rock formation (Shah *et al.*, 2010). These fluids are called ‘underbalanced fluids’, this underbalanced drilling technology is generally adopted for poorly consolidated and/or fractured formations.

The cost of the drilling fluid represents 10-15% of total drilling costs (Zhao, 2013), with a single well costing approximately $ 8.7million in 2013 according to the Petroleum Services Association of Canada. Therefore, the drilling fluids that are easy to use, inexpensive and environmentally friendly are highly preferred. Since the water-based fluids have a relatively low cost, they are majorly used for drilling operation. Unfortunately the drilling fluids cannot achieve their purpose to facilitate the drilling process due to HPHT drilling operations (Mullen *et al.*, 2005). OBMs are becoming increasingly subject to environmental regulation in Europe, as oil based drilling fluids are prohibited and hence WBMs are used to drill HPHT wells (Tehrani *et al.*, 2009).

2.1.4 Drilling fluids properties

Mud functions are majorly dependent on mud properties; therefore, it is crucial to measure particular properties of mud in order to control its ability to perform the required function(s) (Ljones, 2013). The following properties are known as essential properties of mud, they include mud’s weight or density, viscosity, gel strength and filtration loss which control drilling operation in oil and gas field.

2.1.4.1 Mud Weight:

Mud weight or generally called mud density is the ability of mud to endure formation pressure in order to prevent blow out and break down formation. The density of any fluid is directly related to the amount and average specific gravity of the solids in the system. Therefore, the control of density is critical since the hydrostatic pressure exerted by the column of fluid is required to contain formation pressures and to aid in keeping the borehole open (Annis and Smith, 1974; Darley and Gray, 1988). It must be high enough to counteract the pressure exerted by the inflow of water, oil and gas and consequently the eruptions (Caenn *et al.*, 2011). WBM is used for desired density greater than 1 on the contrary for desired density lower than 1 OBM is used (kodja, 2010). It must also not exceed the resistance limit of the walls of the well (formations crossed) not to break them and not have a loss of mud during its circulation (Caenn, 2011). The mud exerts a pressure on the walls of the well given by the following expression:

$$P = \frac{h \cdot d}{g} \qquad \text{equation 1}$$

Where:

P: Training pressure; in Kg / cm2

h: Depth of the layer crossed; in m

d: Density of the mud.

g: Gravity.

However, the common method for checking the density of any drilling fluid is the mud balance. The mud balance consists of a supporting base, a cup, a lid, and a graduated beam carrying a sliding weight. But more and more for a purpose of accuracy and precision the use of pressurized mud balances is taking over in different locations.

2.1.4.2 Viscosity

Viscosity is the velocity of the fluid to flow and it is generally defined as the internal friction produced by a fluid when a force is applied to initiate a flow (Sandvold, 2012). This internal friction is a result of the attraction between the molecules of a liquid. Viscosity is dependent on mud rheology to clean the base of a bore hole. Consequently it is a quantity of vital interest in rheology; its knowledge is sometimes enough to accurately characterize the rheological behaviour of the material (Kristensen, 2013). Different viscosity coefficients are defined:

- **The dynamic or apparent viscosityμ_a.**

This is the ratio of the stress to the corresponding shear rate:

$$\mu_a = \frac{\tau}{\dot{\gamma}} \qquad \text{equation 1}$$

Where,

τ = shear stress

μ_a = viscosity

$\dot{\gamma}$ = shear rate.

- **The kinematic viscosity ν.**

$$\nu = \frac{\mu_a}{\rho}\ [m^2 / s] \qquad \text{equation 2}$$

ρ: density of the fluid [kg / m3].

- **Relative, specific and intrinsic viscosity**

It is often used in the study of solutions or suspensions to determine the respective influences of the solute and the solvent on the rheological behaviour. The following viscosities are frequently used:

- Relative viscosity:

$$\mu_{rel} = \frac{\mu}{\mu_s} \qquad \text{equation 3}$$

- Specific viscosity:

$$\frac{\mu - \mu_s}{\mu_s} = \mu_{rel} - 1 \qquad \text{equation 4}$$

- Intrinsic viscosity:

$$[\mu] = \lim_{\substack{c \to 0 \\ \dot{\gamma} \to c}} [\frac{\mu_{sp}}{C}] \qquad \text{equation 5}$$

μ_{d1}: and μ_{d2}: respectively represent the dynamic viscosity of the solution and of the solvent,

C: represents the concentration of solution,

μ_{rel} and μ_{sp}: are dimensionless quantities,

[μ]: is homogeneous in the opposite of a concentration.

For most drilling fluids, the effective viscosity will be relatively high at low-shear rates, and relatively low at high-shear rates (Growcock and Harvey, 2005; Darley and Gray, 1988). In other words, the effective viscosity decreases as the shear rate increases. When a fluid behaves in this manner, it is said to be shear thinning. Shear thinning is a very desirable characteristic for drilling fluids (Bourgoyne *et al.*, 1991).

2.1.4.3 Gel Strength:

A drilling mud left to rest gradually builds a structure that increases its rigidity and can be reduced by agitation which is called gel strength. Gel strength is also the ability of mud to develop and retain a gel structure in static condition (Caenn, Darley, and Gray, 2011). Gel strengths indicate the thixotropic properties of a drilling fluid and are the measurements of the attractive forces under static conditions in relationship to time (Caenn, Darley, and Gray, 2011). The term thixotropic refers to the fact that this phenomenon is reversible and not instantaneous. Moreover, the gel strength is a measurement of the shear stress necessary to initiate flow of a fluid that has been quiescent for a period of time. Generally, only gel 10s, 10mn and 30mn are reported (Annis and Smith, 1974**)**. Gel strengths occur in drilling fluids due to the presence of electrically charged molecules and clay particles which aggregate into a firm matrix when circulation stops. Generally two types of gel strength occur in drilling fluids, these are progressive and fragile gel strength (Darley and Gray, 1988). A progressive gel strength increases substantially with time, this type of gel strength requires an increase in pressure to break circulation after shutdown. A fragile gel strength increases only slightly with time, but may be higher initially than a progressive gel. It must be noted that there is no well-established means of mathematically predicting gel strengths in any fluid system. Generally, gel strengths will increase with time, temperature, and increase in solids (Sweet, 1989).

Therefore, the drilling fluids technician must be concerned about the initial gel strength that has to be sufficient, yet not having excessive long-term gel strength. Gel strengths assume great importance with regard to suspension properties under static conditions and when performing swab and surge analysis.

2.1.4.4 Filtration or fluid loss property

The knowledge of the causes of the phenomenon of clogging of the well's surroundings by the drilling mud is of obvious interest. Indeed, as far as possible the prevention of catastrophic damage can be realized by the choice of a suitable fluid and suitable conditions of implementation. The factors to be taken into account regarding clogging are related to the rock (permeability, porosity, pore distribution, mineralogical nature, wettability), the fluids and its contains (nature, chemical properties, physicochemical characteristics, pressure, temperature), the mud itself (composition, rheological characterization) and its filter elements, the cake (thickness, permeability, mechanical strength, particle size) and filtrate (nature, chemical and physicochemical properties) (Annis and Smith, 1974).

When the drilling fluid is in contact with a newly drilled surface, it immediately enters that surface. Then, the penetration being limited, some pores are obstructed by particles suspended in the fluid. Therefore mud systems should be designed to seal permeable areas as quickly as possible with smooth, thin cakes. In high permeability formations with large pores, all mud could invade the formation depending on the size of the solid particles in the mud (Saboori *et al*., 2018). In general the more particles there are in the colloidal size range, the lower the cake permeability (Saboori *et al*., 2018). The obstruction of the porous medium is even faster when the concentration of particles is higher. Once the obstruction begins, the finer elements are in turn retained. Only the liquid phase invades the formation, while the solid phase is deposited outside, along the wall, constituting the outer cake.

It is quite important to know that two kinds of filtrations occur during drilling: static filtration during shutdown of the fluid circulation, and dynamic filtration during fluid circulation which causes erosion of the formed cake (Saboori *et al*., 2018). As shown on Figure 2, different zones can be distinguished from the well to the formation such as the outer cake lining the wall, the inner cake and the zone invaded by the filtrate during the immediate penetration.

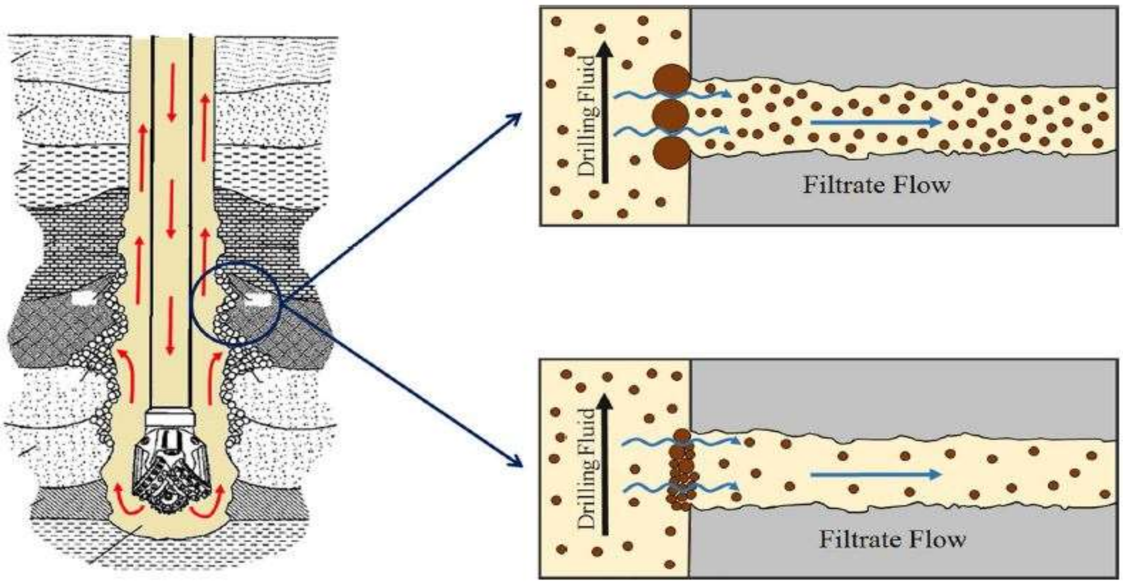

Figure 2: Effect of particles size on the DF filtration performance (Saboori *et al*., 2018)

One of the critical parameters for the prediction of the invasion of the mud formation is the permeability of the cake and its variation with the pressure. The presence of soluble salt in clay mud increases the permeability of the filter cake sharply, but certain organic colloid enable low cake, low permeability to be obtained even in saturation salt solution (Sweet, 1989). Filtration property of drilling fluids is evaluated and controlled by API tests using a standardized press filter. These tests can be performed at high pressures and high temperatures depending on the investigation to be done.

By keeping the DFs' properties at a good level, it is possible to maintain long term stability of the mud. It is therefore important to control the properties during drilling and in particular the rheological properties. However, constant variations are encountered during the drilling process, for which the drilling fluid has to be incorporated with different types of additives in order to achieve some required properties (Agarwal *et al*., 2013; Bourgoyne *et al.*, 1986; Coussot *et al., 2004;* Shah *et al*., 2010).

2.1.5 Drilling fluids additives

Additives are well designed to enhance several properties as well as reduce negative effects of the drilling fluids (Bloys *et al.*, 1994). According to World Petroleum Magazine, there are more than 3000 drilling fluid additives that are known to date (Skalle, 2012). The type and amount of additives depend on the drilling requirements and the type of reservoir to be drilled and accordingly modify particular properties and rheological behaviour for the drilling fluid (Max *et al*., 1974). The properties required of drilling muds are multiple and can sometimes even be contradictory. The mud must, for example, be very viscous to ensure the recovery of the cuttings, but the viscosity must not be too high to reduce the pressure losses due to the flow and avoid fracking of the formation. Some additives can only be used in OBM and air/gas systems and some other only for WBM. In the table 1 represented below the additives commonly used in drilling muds are broadly classified into 20 categories (Economides *et al*., 1988).

Table 1: drilling fluid additives (Economides *et al*., 1988; Company, 2008).

Alkalinity controller	Lubricant
Bactericides	Decoupling
Anti-calcium	Inhibitor of swelling of clays
Corrosion Inhibitor	Products facilitating separation
Anti-foam	High temperature stabilizer
Foaming agent	Defloculant
Emulsifier	Viscosifier
Filtrate reducer	Weighting
Flocculants	Aqueous base fluid (brine)
Clogging agent	Oleaginous base fluid

In fact as it is necessary to select a suitable fluid for a particular well for a better oil and gas drilling operation, we need to understand that a simpler drilling fluid that contains less additives allows easier maintenance and better control of properties. When accessing the design and maintenance of mud, it is crucial to understand the factors that influence its functions. It is, therefore, necessary to measure or to predict the rheology of fluids at high temperatures and pressures, and the strength of additives subject to these conditions (Nguyen, 1993).

2.1.6 Summary

The drilling fluids are WBM, OBM and GBM; they exhibit several functions which help to perform an oil and gas drilling process. Four fundamental properties characterize them such as the density, the viscosity (rheology), Gel Strength and the filtration. However, each drilling is to be applied for a specific drilling process depending on the challenge to be faced. In fact, each of them is endowed with a distinctive property according to the additives used for their formulation to perform its task within the well throughout the drilling process. Therefore, a better understanding of the rheology of these fluids and the conditions which influence them throughout the drilling process is vital in a formulation for a good mud.

2.2 Rheology and conditions affecting drilling fluids

2.2.1 Partial introduction

Etymologically, rheology is a discipline that deals with the flow and deformation of materials under the action of constraints. Rheology has been developed to describe the properties of materials with poorly defined and intermediate behavior between that of the perfect elastic solid and that of the Newtonian fluid (Darby, 1976). The following chapter aims to define the main rheological parameters as well as the different types of fluid flow.

2.2.2. Rheology of drilling fluids

2.2.2.1 Generalities

One of the major elements in the formulation of drilling fluids is the study of rheological behavior of these fluids. Rheology is the study of the aptitude for all form of substance to flow as a function of shear rate, time and special orientation (Darby, 1976). Therefore, some external parameters from the substance itself may affect its rheology namely rate and duration of the shear and notably temperature and pressure (Kristensen, 2013). According to a common point of view, drilling fluids are identified as either Newtonian fluids where viscosity (μ) is independent of shear rate or non-Newtonian fluids, where viscosity is function of shear rate $\mu = \mu\ (\gamma)$ (Caenn *et al*., 2011; Bailey *et al.*, 1994; Ibeh, 2007).

Several rheological models have been implemented in order to more easily describe the behavior of fluids which are indeed based on. They have been implemented on the basis of an experimental or semi-empirical way (Azar and Samuel, 2007; Growcock and Harvey, 2005; Mezner, 2011; Caenn *et al*., 2011).

2.2.2.2 Rheological Parameters

- Notion of laminar shear movement.

Any material subjected to a set of forces is liable to be deformed, the movements of the different points of that material depending of course on the distribution and the intensity of the applied forces. A laminar shearing motion is generated for some distributions of these forces. During such a movement, it is considered that the material has a structure in lamellae, in adjacent layers. The deformation of the material is effected by relative sliding of the different layers, without the transfer of material from one layer to another. Laminar shear movements are generated using rheometers. It is from such movements that the rheological parameters of the fluids can be determined.

- Shear stress.

The shear stress (τ) is the fundamental dynamic quantity in rheology. During a laminar shear movement, two successive layers in contact with each other move relative to one another. It appears at the interface of these two layers of friction forces exerted tangentially on the surface of the layer: they are called shear force (Darby, 1976).

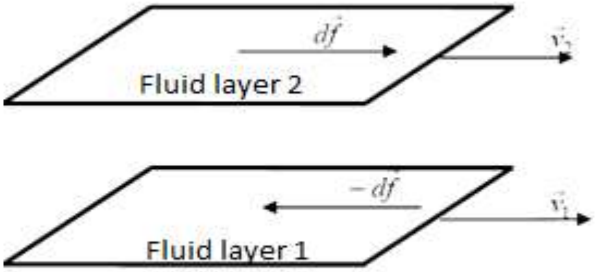

Figure 3: Forces acting on two neighboring layers

Assuming that the layer (1) is driven by a speed v1 greater than the speed v2 of the layer (2), the layer (1) exerts on the layer (2) a shear force df parallel to the movement and tending to accelerate the layer (2). The layer (2) exerts on its layer (1), a shearing force – df tending to slow it down. By relating these shear forces to the surface unit, we define the shear stress τ:

$$\tau = \frac{\mathrm{d}f}{dS} \qquad \text{equation 6}$$

τ: represents a force per unit area; it is expressed in newton per m^2 or more conveniently in Pascal (Pa) and dS is the elementary surface of the considered entity.

It should be noted that in the calculation of the resultant forces, the pressure forces acting perpendicular to the surface are not taken into account, because of their low value in comparison with the shear forces.

- Deformation and shear rate.

These two quantities constitute the basic kinematic quantities in rheology. The definition of shear deformation is presented in the simplest case of a shearing motion with plane symmetry. The material is sheared between two parallel planes, one moving, the other motionless (Figure 4).

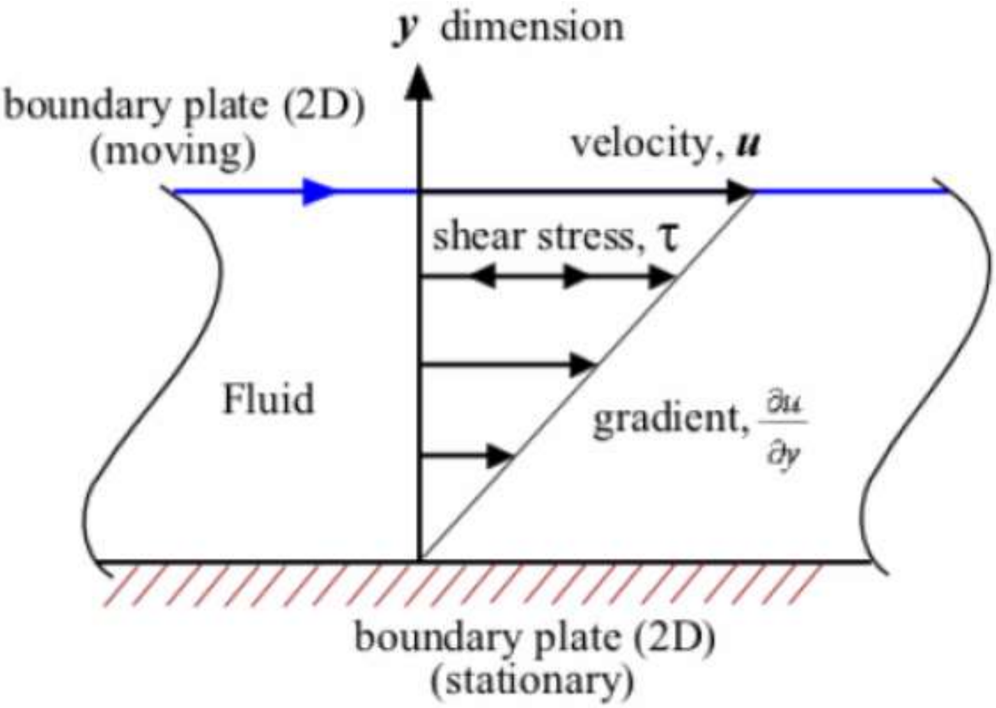

Figure 4: Laminar shear motion between two parallel planes (Ibeh 2007).

It is arbitrarily considered that the material particles of two adjacent layers are at time t = 0 in a straight section. At t time later, the particles will have traveled the distance u (x, t) for the particle located at the abscissa x and u (x + dx, t) for the particle located at the abscissa x + dx.

Shear deformation is defined by Equation 7:

$$\gamma = \frac{du(x,t)}{dx} \qquad \text{equation 7}$$

This magnitude is dimensionless; it does not depend on the displacement u (x, t) itself but on the variation of this displacement when one goes from a layer to an infinitely close layer.

The expression of the shear rate ($\dot{\gamma}$) is given by Equation 8, it is the derivative with respect to the time of shear deformation:

$$\dot{\gamma} = \frac{d\gamma}{dt} \qquad \text{equation 8}$$

$\dot{\gamma}$ has the dimension of the inverse of a time and is expressed in s^{-1}.

- State equation.

The determination of these two quantities (shear stress and deformation or shear rate) makes it possible to define the rheological equation of state of the material (Jaali, 2015; Sandvold, 2012). The rheograms plotted from the data obtained rheometer are the curves that graphically translate the rheological equation of state of the material. The most common representation consists in expressing the variation of the shear stress with that of the shear rate.

2.2.2.3 Rheological Models

- **Newtonian Fluid Model**

The Newtonian Fluid Model has been formulated to describe the behavior of such fluids which have a low molecular weight and that the molecular structure is simple and stable (American Petroleum Institute). Fluids such as water, gases, thin motor oil tend to exhibit Newtonian flow characteristics.

The characteristic equation of Newtonian fluids related the shear stress (τ) and the shear rate ($\dot{\gamma}$) is given by a linear relationship established as follow:

$$\tau = (\mu).(\dot{\gamma}) \qquad \text{equation 9}$$

Where,

τ = shear stress

μ = viscosity

$\dot{\gamma}$ = shear rate

The figure below show a straight line graph $\tau = f(\dot{\gamma})$ at variable and constant temperature (μ remain constant).

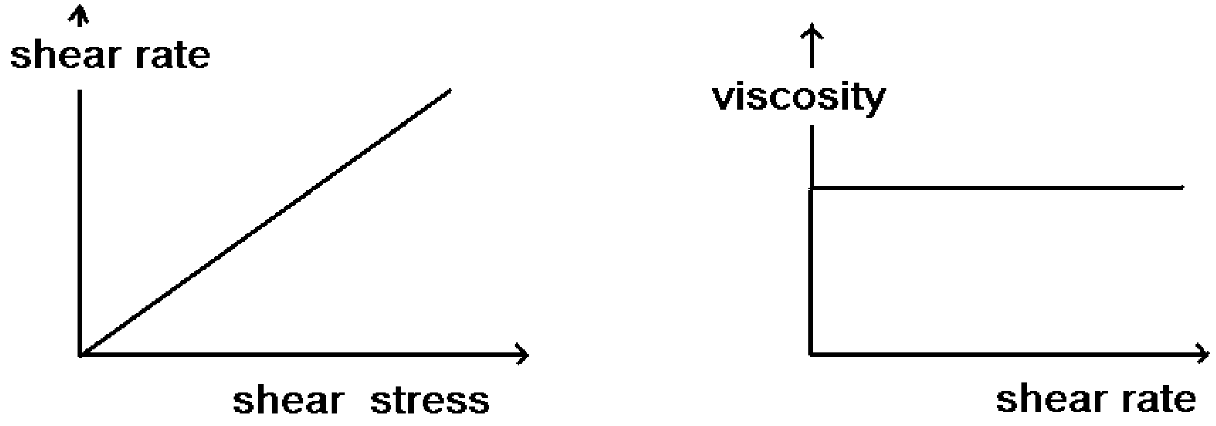

Figure 5: diagram showing shear rate vs shear stress and viscosity vs shear rate (Rheology. (n.d.). Retrieved December 14, 2017, from http://people.sju.edu/~phabdas/physics/rheo.html)

- **Bingham plastic model**

This model describes plastic fluids; they are commonly referred as Bingham plastic fluids due to the fact that in the early 1900s Bingham initially observed the plastic behavior of that kind of fluid (Bingham, 1922). Unlike Newtonian fluids, a finite stress is absolutely required to observe a flow (Caenn *et al*., 2011). In fact, some shearing stress is needed before a Bingham plastic fluid flows, the minimal value necessaire to allow the fluid to flow (τ; $\dot{\gamma}$) is known as yield points. The term "yield point" denotes initiating stress, and "plastic viscosity" denotes slope of the curve. They are both very important drilling fluid parameters, and can be calculated from mud viscometer data. From the yield points it has been observed a linear relationship between the shear rate and the shear stress of this kind and the constant of proportionality is called plastic viscosity, μ_p (Kok, 2009). The mathematical relationship relating shear stress/shear rate for the Bingham Plastic Model is given as follow:

$$\tau = \zeta_y + \mu_p \dot{\gamma} \qquad \text{equation 10}$$

Where,

τ = shear stress

ζ_y = yield point

μ_p = Plastic viscosity

$\dot{\gamma}$ = shear rate

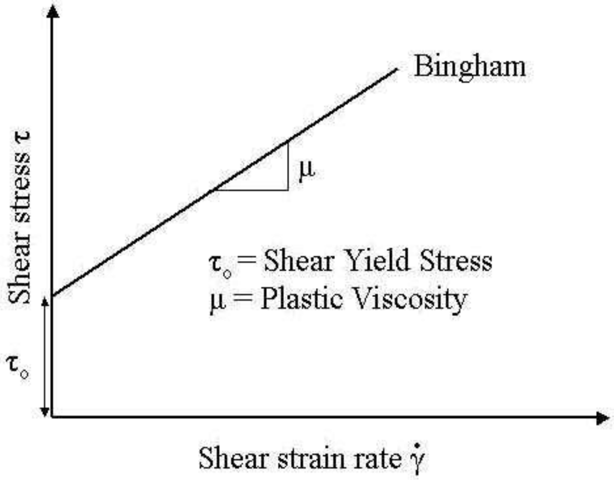

Figure 6: Bingham fluids curve of shear stress vs shear strain (Azar and Samuel 2007)

The Bingham Plastic Model and the terms plastic viscosity (PV) and yield point (YP) are commonly used in the drilling fluids industry. PV is used as an indicator of the size, shape, distribution and quantity of solids, and the viscosity of the liquid phase (Caenn *et al*., 2011). The YP is a measure of electrical attractive forces in the drilling fluid under flowing conditions (Caenn *et al*., 2011). In addition PV and YP are two parameters of a drilling fluid that many industrials still consider to be vitally important in the overall drilling operation. The YP is now considered an outdated concept that has no real meaning or application in drilling operations. The Bingham model is the most traditional model used to fit the viscoplastic behaviour of drilling fluids (Rossi *et al*., 2002); this can clearly be seen when the viscometer readings are plotted on a graph and the resultant line is a curve and not a straight line.

- **Power Law Model**

The Power law model describes the fluids having a behavior that is intermediate between the Newtonian fluids and the Bingham fluids. This particular behavior of those fluids confers them the name pseudo plastic fluids (Metzner, 1956). The Power Law model establishes the relationship between shear stress and shear rate by the following equation:

$$\tau = K\dot{\gamma}^{n} \qquad \text{equation 11}$$

Where,

τ = shear stress

K = consistency factor

$\dot{\gamma}$ = shear rate

n = flow behavior index

Power law model does not relate perfectly to the drilling fluids behavior since it does not include a yield stress and therefore can give poor results at extremely low shear rates. However, the Power Law constants n and K are used in hydraulic calculations that provide a reasonable degree of accuracy. But in the DF engineering when the DF becomes more viscous, then the constant K must increase to adequately describe the shear stress/shear rate relationship. Additionally, n indicates the degree of non-Newtonian behavior.

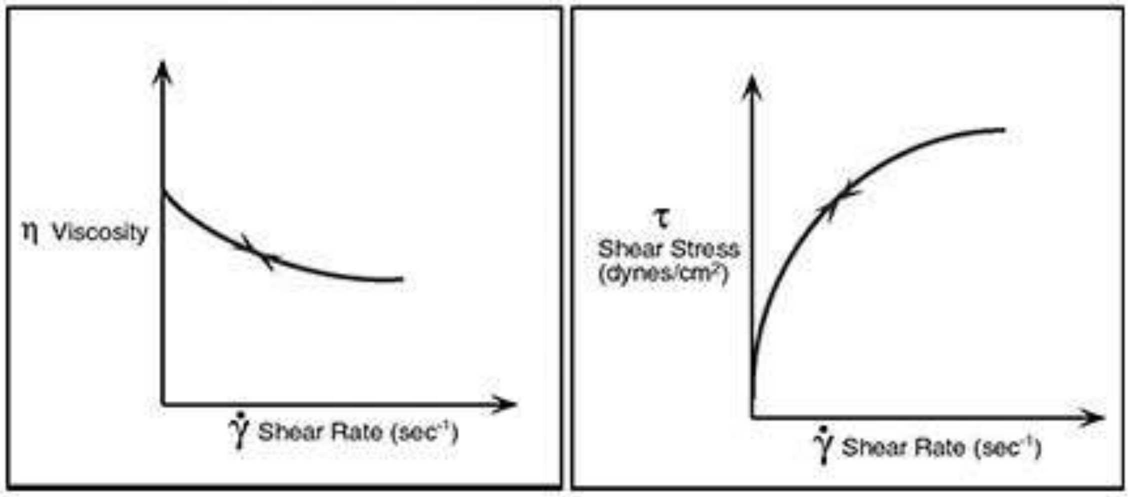

Figure 7: Curves for Power Law fluids: (1) viscosity vs shear rate and (2) shear stress vs shear rate (Retrieved October 14, 2019, from https://www.brookfieldengineering.com/learning-center/learn-about-viscosity/what-is-viscosity)

- **Herschel-Bulkley**

Herschel-Bulkley (1926) model has been implemented to address a limitation of Power Law model at low shear-rates. Those fluids show a behavior quite halfway between those of Bingham Plastic and pseudo-plastic fluids; Herschel-Bulkley model is basically the Power Law model including the yield stress term (Growcock and Harvey, 2005). The Herschel-Bulkley equation is so expressed:

$$\tau = \zeta_y + K\gamma^n \qquad \text{equation 12}$$

A typical drilling fluid actually exhibits behavior significantly close to the one described by Herschel-Bulkley model (Kristensen, 2013). Hence the choice of Helschel-Bulkley model is obvious to describe more accurately most fluids than the simpler Power Law and Bingham models. Therefore, it is being widely used for hydraulics calculations by several DF companies (Barry *et al.*, 2015). It is also judicious to underline that some difficulties are still experienced while making correlations between drilling fluid parameters measured and hydraulic calculations.

2.2.3 Conditions affecting drilling fluids rheological properties

Due to the depletion of oil and gas reserves, a transition has resulted from normal to deep well and ultra-deep well drillings. Due to increase in the depth of the wells, the parameters such as temperature and pressure may vary for different wells.

Moreover, when the target is deep enough or geothermal, additional care has to be taken in order to deal with the HPHT environment that limits the range of available tools and technology to exploit these existing reservoirs (Annis and ESSO, 1967). Basically a well is called HPHT well when the bottom hole static temperature is expected to reach more than 177°C (350^oF) and the bottom hole static pressure is in excess of 170MPa (24500 PSI) (Proehl and Sabins, 2006). It has been noticed that such conditions would affect the performance of drilling fluids by severely deteriorating their characteristic and rheological properties (Mullen *et al.*, 2005; Zamora *et al*, 2000).

In practice, the rheological properties of drilling fluids under downhole conditions may be very different from those measured at ambient temperature and pressure at the surface. Hence, a variation in temperature even inconsiderable can have a significant impact on the rheological properties of drilling fluids (Caenn, Darley, and Gray, 2011). Therefore this situation is deplorable since any drilling fluid is designed with the primary objective of maintaining its design properties throughout the wellbore. Accordingly DFs do not perform in such conditions and so affect the entire drilling process in term of time, cost even production rate (Mullen *et al.,* 2005).

Those impacts can be noticed from physical and chemical points of view. From a physical point of view, it is important to underline that an increase in temperature is consecutive to a decrease in viscosity of the mud (Caenn, Darley, and Gray, 2011). However any increase in pressure results in an increase in density so by analogy the viscosity of the mud (Caenn, Darley, and Gray, 2011). From a chemical point of view, at any temperature above 94°C hydroxide ions (OH^-) tends to react with mineral clays (Caenn, Darley, and Gray, 2011). A vital HPHT parameter is the time that tools, materials and drilling fluids must withstand the severity. Drilling operation in extreme downhole conditions needs extensive planning with special care being paid to environmental impacts (Matthews *et al.,* 2006).

Furthermore a significant gap exist between the current technologies and the drilling requirements in such HPHT wells, hence they are one of the main focus areas of the drilling industry nowadays. Several factors related to the HPHT environment that increase the likelihood of failure in such projects are known. Buchan (1993) has identified some of those issues which are discussed below:

- Heavy casing strings resulting from the considerable depth at which many HPHT wells are drilled. The increased in temperature generally lowers material strength and this has to be accounted for;
- Drilling and completion equipment being operated at the limits of their design. Most current tools are rated to perform up to a maximum of 177°C;
- Drilling fluid related issues resulting in loss of circulation, well control concerns and stuck pipe due to differential sticking caused by excessive overbalance;
- Another major issue in deep wells (not necessarily HPHT) is that a low rate of penetration occurs due to highly competent rock or poor drilling fluid selection and optimization or both;
- These issues can be addressed with the introduction of additives that can resist against the HPHT conditions.

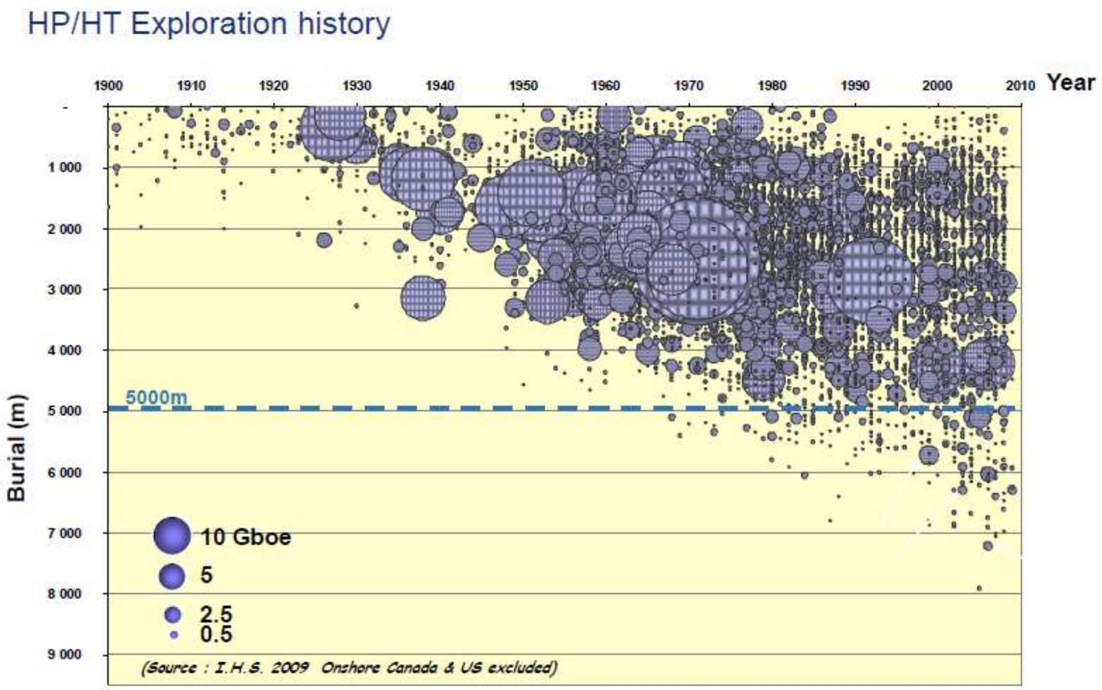

Figure 8: Evolution of the depth of hydrocarbon exploration wells

2.2.4 Summary

Several fluid models have been developed, and depending on the type of fluid a particular model corresponds more or less to it. Moreover the DFs stand as non-Newtonians fluids, indeed only one model among them describes very closely the drilling fluids behavior, which is the Herschel-Bulkley model but we can still include the Bingham and Power models in some cases. The study of rheological properties of a DF is an important factor which aims to understand its behavior according to the model closer to its behavior in order to determine its different characteristics. Also external parameters that are the temperature and the pressure degrade drastically the first properties of the fluids. Therefore, a prepared drilling fluid has to stand against the hostile conditions that can be encountered throughout the drilling process. The next chapter will be talking about a kind of drilling fluid which can be used to meet these requirements.

2.3 Emulsion

2.3.1 Partial introduction

An emulsion can be observed by simply mixing oil and water. Emulsions can be more than mixing oil and water, and are used for different industrial applications. They play a specific role within each industry where they are applied. Likewise their application in drilling industry brings some interesting properties which fit many drilling fluids requirements. Therefore, the success of an emulsion required the presence of a third element which prevents a phase separation called surfactant. Thus, by the use of the surfactants, the emulsions can be maintained for a long period of time to realize the required work. The following point below will give an overview on the emulsions and their different applicants, their application towards drilling fluids and the different mechanism of stabilization.

2.3.2 Emulsion: general concepts

Emulsions are widely used in many fields of daily life namely food, cosmetic, pharmaceutical, paint, and petroleum industries (Vignati *et al*., 2003; Perkins et al., 1974; Zhao *et al.,* 2013; Tan *et al.,* 2014; Tehrani, 2007). Emulsions are colloidal systems in which fine droplets of one fluid are dispersed in another fluid where both liquids are otherwise immiscible and thermodynamically unstable (Tadros and Vincent, 1983; Binks, 1998; Tadros, 2005). Therefore, the use of emulsifiers is required to prevent the coalescence of droplets and to obtain a stable system without macroscopic phase separation (Tan *et al.,* 2014; Fouilloux, 2011). The traditional emulsifier usually used to stabilize emulsions is surface-active molecules (surfactants). Recently these formulations have been questioned, following the evolution of the requirements concerning the protection of the environment, user safety and cost constraints. Therefore moving towards a progressive to decrease the use of synthetic surfactants is required. Besides the traditional use of amphiphilic molecules such as polymeric surfactants, emulsifiers can also be used with nanostructured solid particles that adsorb at the liquid-liquid interface and form a layer of protection between both the dispersed and continuous phases (Caenn *et al*., 2011).

2.3.3 Current applications

The fluids that form emulsions are generally water and oil. An emulsion with water as dispersed phase and oil as continuous phase is called water in oil (W/O) emulsion system and the vice versa is called an oil in water (O/W) emulsion system. It is also possible to produce multiples emulsions (W/O/W or O/W/O): they contain within the dispersed phase a second dispersed phase. Emulsions can be used to confine a molecule in the dispersed phase, leading to pharmaceutical applications with the encapsulation of an active ingredient (Lovelyn and Attama, 2011). Another example is that they can also be used as rooms of reaction in chemical synthesis in order to achieve the synthesis of particles (Fan *et al.*, 2018; sachdev *et al.*, 2016). Finally in drilling fluids, emulsions offer many advantages as they play an integral role in providing enhanced rheological properties and fluid loss characteristics (Stamatakis, Young and Stefeno, 2012, Elkatatny and Nasr-El-Din, 2013, Chilingarian and Vorabutr, 1983). In some cases, the dispersion process is not only an end in itself but also a method of dispersion sometimes matters to form a specific emulsion. This provides their used to facilitate the transport of highly viscous liquids, where the use of bitumen forming a dispersion in an aqueous phase reduces the viscosity of the product and makes handling easier. In the same way, one methods of oil recovery requires the injection of water under pressure into the well thus emulsion forms then oil is easily recovered (Fouilloux, 2011). As a result, emulsions formed have no industrial application as such, but it is inevitable by this process. All these systems have a common feature of having large amounts of interfaces.

However, the increase in interfacial contact between the continuous and the dispersed phase is accompanied by the dispersion of droplets (diameter in micrometers) resulting in an increase in the total free energy of the system (Zwan, 2008; Tadros, 2009). As a consequence, emulsions are thermodynamically unstable systems, which naturally tend to move towards the complete separation of present phase in order to minimize their surface area' (Kokal, 2002). Nevertheless, physically stable (as opposed to thermodynamically stable) emulsion dispersions are most likely to be produced by creating kinetic barriers to drop/drop coalescence. The emulsion stabilization necessarily requires the addition of a stabilizer to limit these destructive phenomena. This stabilizer, called surfactant, allows kinetic stability to be reached by slowing down the process of breaking of the emulsion and separation of the phases (Weaire and Hutzler, 1999). In fact, the formulation and use of stable emulsions have been widely examined in relation to many industries particularly in petroleum production (drilling fluids, oil recovery) (Hunter *et al*., 2008).

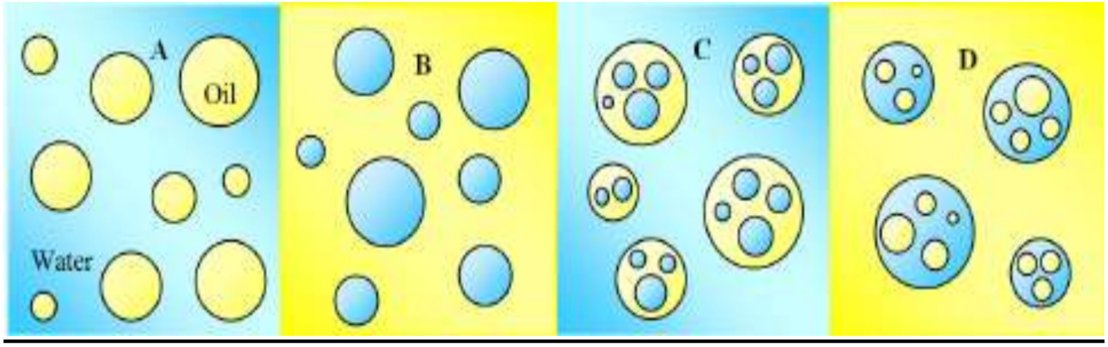

Figure 9: Different types of emulsions A (O/W), B (W/O), C (W/O/W) and D (O/W/O) (Prichapan, and Klinkesorn, 2014)

2.3.4 Emulsion based drilling fluids

The emulsion based drilling fluid can be defined as that category of water based drilling fluids to which oil is added. This system uses different types of oil such as crude oil, diesel and mineral oil. The model of emulsion based drilling fluids brought some advantages over classical drilling fluids. In fact, emulsion based drilling fluids performs better where WBM is limited mostly in HTHP conditions (kelly *et al*., 1980). Emulsion based drilling fluids offer the following advantages (Jha *et al.* 2014);

- Achieve rheological and filtration parameters better than WBM;
- Enhance drilling rate upon the addition of oil;
- Elevate lubricating qualities;
- Suitable for drill formations where bottom hole temperature and pressure exceeds the tolerance level of conventional water based muds;

- Increase ability to perform at HPHT compared to conventional based mud;
- Control the corrosion of drill pipe;
- Less expensive.

Stabilization of these drilling fluids is required in order for these emulsions to be maintained over time so that they can perform better. This stabilization of the emulsion systems requires a suitable stabilizer named as surfactants which protect the droplets against coalescence.

2.3.5 Mechanism of stabilization

It is virtually impossible to obtain a stable emulsion from two pure fluids. Every stable emulsion to be achieved requires two essential criteria: firstly, the destabilization phenomena (coagulation, coalescence, Ostwald ripening) that has to be avoided and secondly, the emulsification process must also be possible. In general, only the addition of one or more emulsifiers can increase the kinetic stability of a given emulsion. The long term stability mainly depends on the formulation, the process also has a key importance, since the droplet's size is often governed by the shear rate of the emulsification process (Aveyard and Clint, 2003; Chevalier and Bolzinger, 2013; Frelichowska *et al*., 2009). However the emulsions is not only a matter of the process but also the stabilizing agents contribute greatly.

2.3.5.1 Surfactant as an emulsions stabilizer

In order to limit all the phenomena leading to the destruction of the emulsions, some species are included to help the stabilization of emulsion droplets of pure components in the system. These species (molecules) named surfactants, which can be small or macromolecular, mainly aim to reduce the interfacial tension between both phases which could form a stable film of emulsion between the two immiscible fluids (Bourrel and Schechter, 1988). This film behaves like a physical barrier, preventing the droplets from likely coalescing when they collide (Caenn *et al*., 2011). A surfactant molecules are amphiphilic, with a hydrophilic (water-soluble) head and a long hydrophobic (water-insoluble/ oil soluble) tail (Jha *et al*., 2014). In addition they are classified into four types according to the ionic nature of the head group and they are defined as; anionic surfactant (this surfactant carries a negatively charged polar head**)**, cationic surfactant **(**this surfactant carries a positively charged polar) nonionic surfactant **(**a nonionic surfactant does not carry any ionic charge) and zwitterionic (It can have both a positive and a negative charge) (Myers, 2005). The adsorption of surfactant at liquid-liquid interface provides the basis for all emulsification processes and thus has a considerable significance. However, the cost of surfactant is normally high, and their recovery is not practical (Agarwal *et al*., 2013). Furthermore, there are some surfactants which cause health problems such as tissue irritation and cell damage (Tang *et al*., 2015.). Moreover due to high temperatures encountered in deep drilling, polymeric surfactants degrade and demulsification occurs; therefore, new types of surfactants resistant to high temperatures are required (Coussot *et al*., 2004. Shah *et al.* 2010; Agarwal *et al*. 2013). Also, the current trend in the drilling fluid development should come up with novel environmentally friendly drilling fluids that will rival oil-based drilling fluids in terms of low toxicity level, performance, efficiency, and cost (Hossain and Al-Majed 2015). Therefore, the use of solid particles as emulsifiers is getting more attention recently due to their low cost, low toxicity, and their remarkable resistance against coalescence compared to the conventional emulsions stabilized by surfactants (Frelichowska *et al*., 2009; Pickering, 1907; Ramsden, 1903).

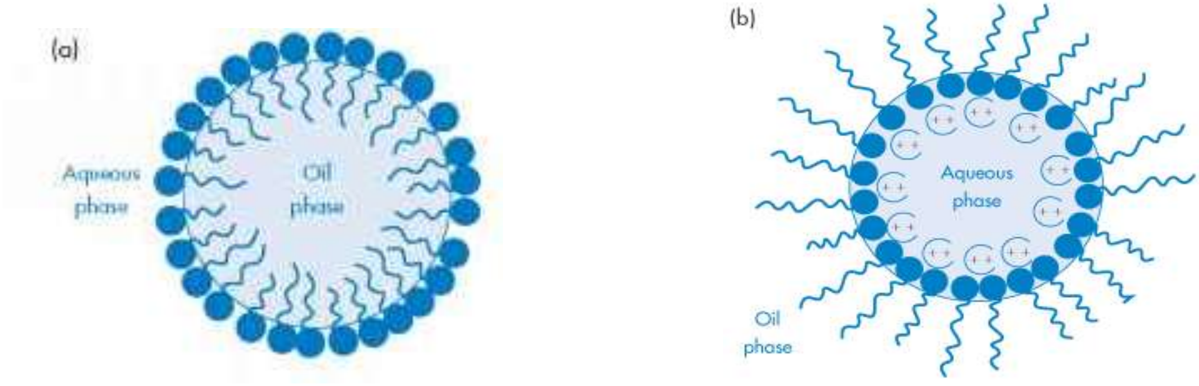

Figure 10: (a) o/w emulsion stabilized by polymeric surfactants; (b) w/o emulsion stabilized by polymeric surfactants

2.3.5.2 Solid particles as emulsions stabilizer

In the early 1900s Ramsden (1904) and Pickering (1907) stabilized emulsions using particles strong and fine of different materials called “Pickering emulsions”. Pickering emulsions like classical emulsion, are also emulsions of any type (oil-in-water, water-in-oil and even multiple) stabilized by solid particles in place of surfactants. The most important work related to stabilization of emulsions by solids is attributed to Masliyah and his collaborators (Pal and Masliyah, 1990; Yan, PAL and Masliyah, 1991). According to the Literature, the solids of less than 1 mm diameter can be wet by an organic or aqueous phase and can stabilize the emulsion direct or reverse (Svetgoff, 1989). Different kinds of solids, either organic or inorganic fulfil the partial wetting condition for most common oils and have been proven efficient stabilizers of emulsions (Aveyard, *et al*., 2003; Wang, *et al.*, 2003).

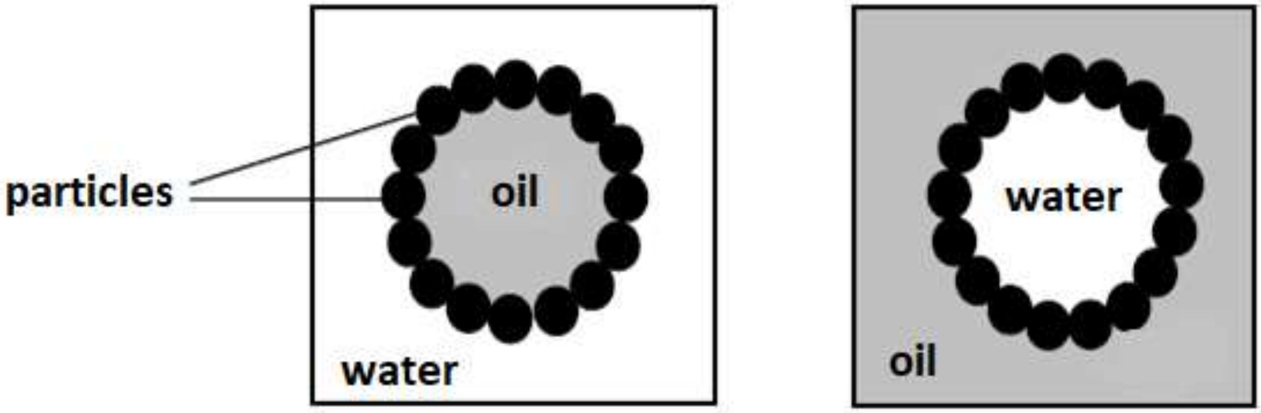

Figure 11: (a) o/w emulsion stabilized by solids particles; (b) w/o emulsion stabilized by solids particles (Frelichowska, 2009)

2.3.6 Summary

The formulation of Drilling fluids based on emulsions exhibits several interesting properties. Due to the unique properties that emulsions bring to drilling fluids, they appear as a good option for the formulation of drilling fluids. However the use of the required surfactant is a challenge to be addressed in the formulation of a good emulsion drilling. In addition any drilling fluid formulation involve the use of clay and nowadays nanoparticles to bring specific properties to enhance the drilling mud. The following chapter will be dedicated to the impact of clays and nanoparticles in drilling fluids.

2.4 Nanoparticles and clays in drilling fluids

2.4.1 Partial introduction

This chapter will cover the use of nanotechnology in drilling fluids as well as the impact of adding clays in a drilling fluids formulation.

Nanotechnology is the study of nanoscale materials. A wide attention has been brought to the implementation of nanotechnology to boost different sectors of industry. Indeed nanomaterials show some amazing characteristics much better than the other materials. Therefore, the drilling fluids engineers did not put themselves aside of the innovation but are taking advantages of that to enhance as much as possible this sector.

Clays are used in drilling fluids to play mainly two major roles such as viscosifier for drilling fluids and mitigate fluids loss. In a quite high percentage of drilling fluids formulation bentonite clays are used because of their properties. But to achieve some others aims, different clays can be also used with success.

2.4.2 Nanoparticles in drilling fluids

More and more, nanoparticles application is gaining special interest in many fields of application due to their remarkable properties, they are environmental friendly and cost effective materials. Different fluids are blinded with nanoparticles to make the so-called nanofluids for different applications ranging from medicine, healthcare, materials, chemical industries, etc (Christian *et al.*, 2008; He and Zhao, 2005; Mahmoud *et al.*, 2016). The upstream oil and gas industry is also positively impacted by the adoption of nanofluids technology within several processes such as exploration, drilling and completion, production and enhanced oil recovery operations (Friedheim *et al.*, 2012; Hendraningrat *et al.*, 2013; Al-Yasiri, and Al-Sallami, 2015).

In the domain of drilling fluids, nanofluids have been explored and found to overcome current drilling issues which are pipe sticking, lost circulation, torque and drag (William *et al.*, 2014; li *et al.*, 2015). Significance impacts of the use of nanoparticles in drilling fluids have also been reported for the first time by Abdo and Danish (2010, 2012) and Abdo *et al*. (2010). Following the same register several nano-sized particles have been successfully integrated to the formulation of drilling fluids to enhance their rheological and fluids loss properties at HPHT (Agarwal *et al.*, 2011; Ponmani *et al*., 2014, Ragab and Noah., 2010; Friedheim *et al.,* 2012; Long *et al.*, 2012; Hendraningrat *et al*.,2013; Al-Yasiri, M.S. and Al-Sallami, W.T., 2015).

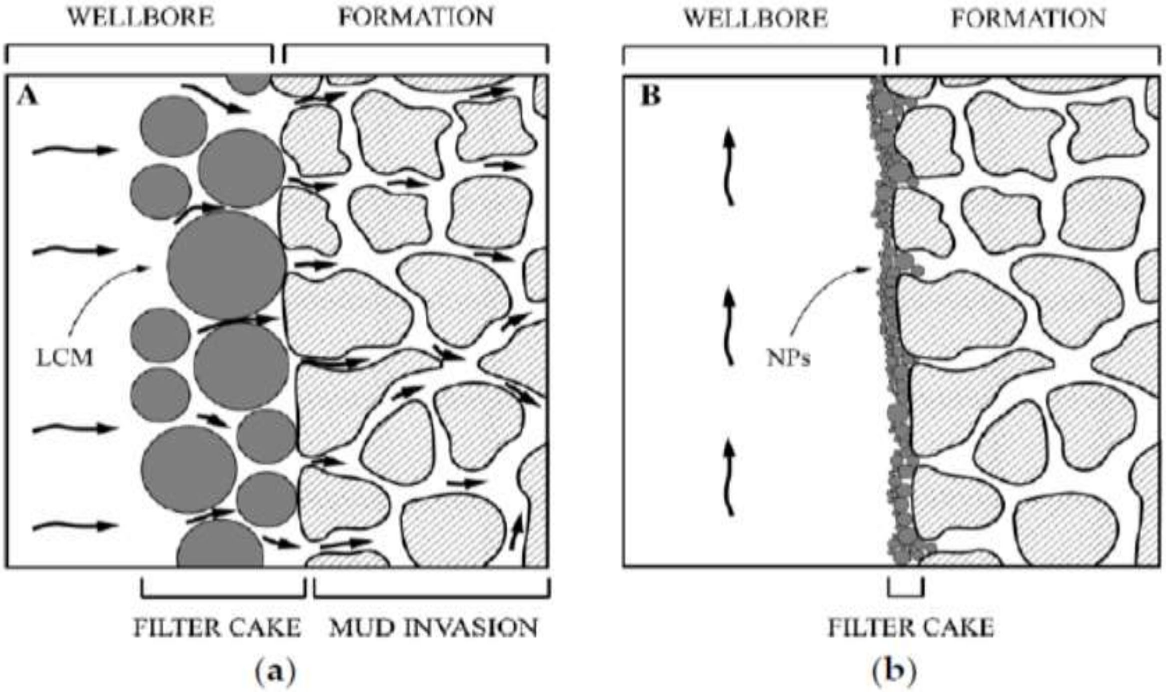

Figure 12: A schematic representation of mud losses while drilling in the case of (a) typical LCM; and (b) NP [2] (Springer, 2015).

2.4.2.1 Cellulose nano-crystals

2.4.2.1.1 Introduction and properties of CNC

The nano scale size of the synthesized cellulose crystals confers them the name of cellulose nanocrystals (CNCs). Among the natural polymer; cellulose can be found in huge quantity; they are well known to be environmental friendly, renewable and biodegradable (Peng *et al.*, 2011; Kumari and Chauhan, 2014). In many fields CNCs have been applied with a remarkable success for example food coatings, biomedical applications, catalysis support structures, transparent-flexible electronics and as additives to adhesives, paper-based, products, cement-based materials and drilling fluids where they play a key role due to their good rheological properties (Song *et al*., 2016; Nurfatimah *et al*., 2014, 2015; Yong *et al*. 2015b; Ashiqur *et al*., 2015).

The dispersion of CNC at low concentration (less than 1%wt) within an aqueous medium show a high viscosity and shear thinning (Pääkkö *et al.*, 2007; Tatsumi *et al.*, 2002) as well, depending on the dilute polymer's concentration in solutions (Ryder and Yeomans., 2006). CNCs exhibit some interesting properties for drilling fluids purpose such as high aspect ratio, high elastic modulus, high tensile strength, low density and surfaces that facilitate their dispersibility within water (Moon *et al*., 2014).

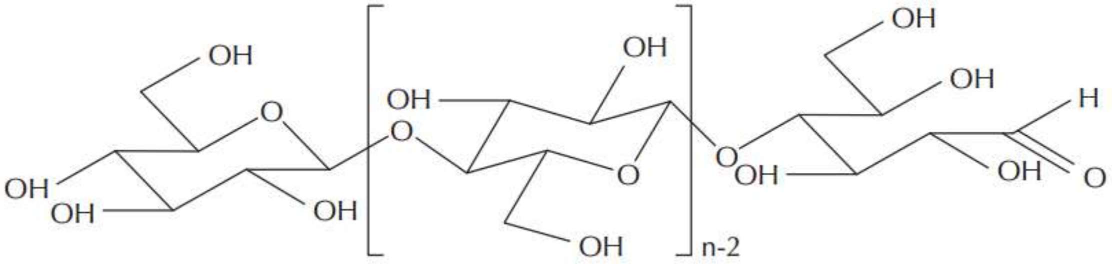

Figure 13: Chemical structure of cellulose chain.

2.4.2.1.2 CNC for drilling fluids

Different types of celluloses are used in the formulation of drilling but limited work has been done on the use of CNCs as an additive in drilling mud. Therefore, an investigation on the impact of a drilling fluid preparation with a small amount of cellulose nanoparticles (CNPs), including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) have been done by Kunlin Song et al. (2015). They results indicated that the low solid fluids exhibited an obvious shear thinning behavior compare to those of traditional fluids without CNPs (Song, 2015)

One other project conducted by of Dr. Yaman Boluk show a significant fluid loss and filtration characteristics due to an addition of CNCs in the prepared DF (Boluk, 2012).

A high viscosity was observed when dispersing CNCs at low concentrations in the formulation of the drilling mud (Pääkkö *et al*., 2007; Tatsumi *et al.*, 2002) with shear thinning behavior as observed on dilute polymer solutions (Ryder and Yeomans, 2006). Generally the biopolymers based drilling fluids exhibit shear thinning characteristics, which is actually highly recommended in drilling fluids since it promotes increased penetration rate thus reduced rig time (Caenn *et al.*, 2011).

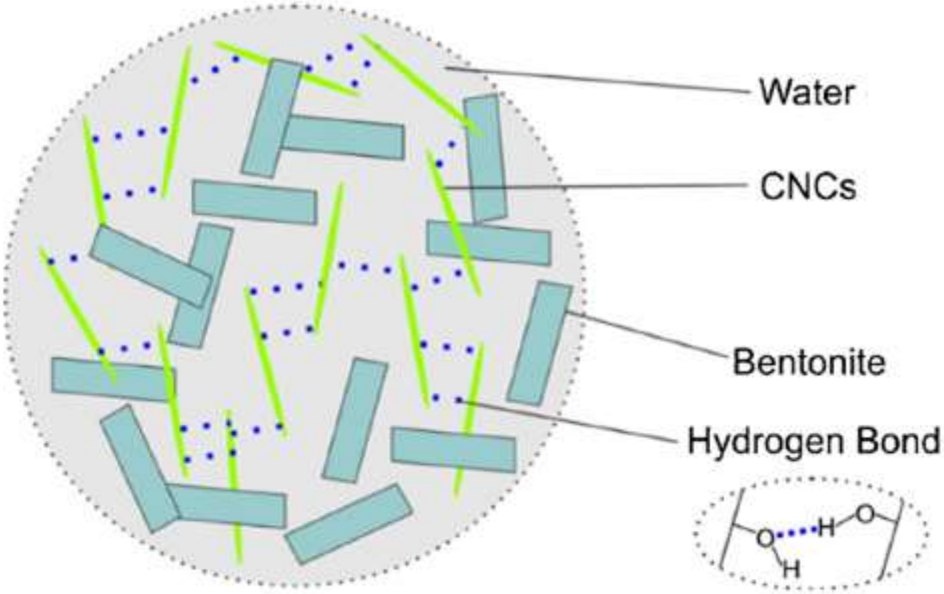

Figure 14: CNCs inside the matrix of the drilling mud (Song *et al*., 2016)

2.4.2.2 Zinc oxide (ZnO)

2.4.2.2.1 Zinc oxide properties

Among different metal oxide nanoparticles, ZnO nanoparticles have their own importance due to their vast area of applications gas sensor, chemical sensor, bio-sensor, cosmetics, storage, optical and electrical devices, window materials for displays, solar cells, and drug-delivery (Baxter and Aydil, 2005; Lyu *et al*., 2002; Wang, 2004; Sawai *et al*., 1996). In addition, due to their non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric property, which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators (Song, Zhou and Wang, 2006). Since ZnO shows different physical and chemical properties depending upon the morphology of nanostructures (Kumar *et al*., 2013), it is a serious candidate to be taken into account to formulate drilling fluids with better rheological and filtration properties.

2.4.2.2.2 ZnO in drilling fluids

The use of ZnO nanoparticles in drilling fluids were usually directed against the presence of hydrogen sulfide, which is highly toxic, corrosive gas and has a harmful effects on drilling process (Aftab *et al*., 2016; Sayyadnejad *et al*., 2008). In this regards, many investigation have shown how the used of ZnO nanoparticles can be effective in removing the hydrogen sulfide from DFs.

Also an investigation has proven that nanoparticles, such as copper oxide (CuO) and zin coxide (ZnO), can be incorporated in an aqueous solution of xanthan gum to prepare nanofluid muds. In this study, a prepared nanofluid containing various nanoparticle concentrations in an XG aqueous system boosted thermal, electrical and rheological properties of the WBM (Ponmani *et al.,* 2014). The latter investigation is the only one found in the literature where ZnO has been used to enhance drilling rheology properties.

2.4.3 Clays in drilling fluids

2.4.3.1 Generalities of clays

The earth's underground from worldwide is full of clays and each of them has its own and particular properties. Due to those properties, clay minerals have been used in a wide range of applications. In addition to the manufacture of construction materials, they are also used for the development of polymer materials, the refining of edible oils, cosmetics or medicine, and DFs (Rautureau *et al.,* 2017; Murray, 2000; Murray, 1991; Eisenhour and Brown, 2009). Among other things, due to their microscopic and macroscopic size properties, and their predominance in the earth's crust, clays have found an important place among the existing materials. A deep understanding of clays can be the most valuable tool for anyone who is going to study mud. The clay can be added intentionally and becomes the active part of the system or it can enter the mud as a major contaminant through the dispersion of drilling solids (Gatlin, 1960; Dolz *et al*., 2006; Fordyce and Baer, 1950). For this reason, it is necessary to understand the basic chemistry of clays to properly control the mud. Clay chemistry is also important with respect to interactions between the mud and other additives that affect the stability of the drilled well (Durand *et al*., 1995a,b; Van Oort, 1997; Zhou *et al.*, 1995).

The clays chosen in drilling fluid are particularly high-swelling which allow a better viscosity and filtration control (Hassan and Abdel-Khalek, 1998; Altun and Serpen, 2005). Furthermore, as stipulated early high-swelling clays are preferred compared to low-swelling clays which enter the drilling fluid in the form of cuttings then are referred to as contaminants (Kodja *et al.*, 2010; Anderson *et al.*, 2010).

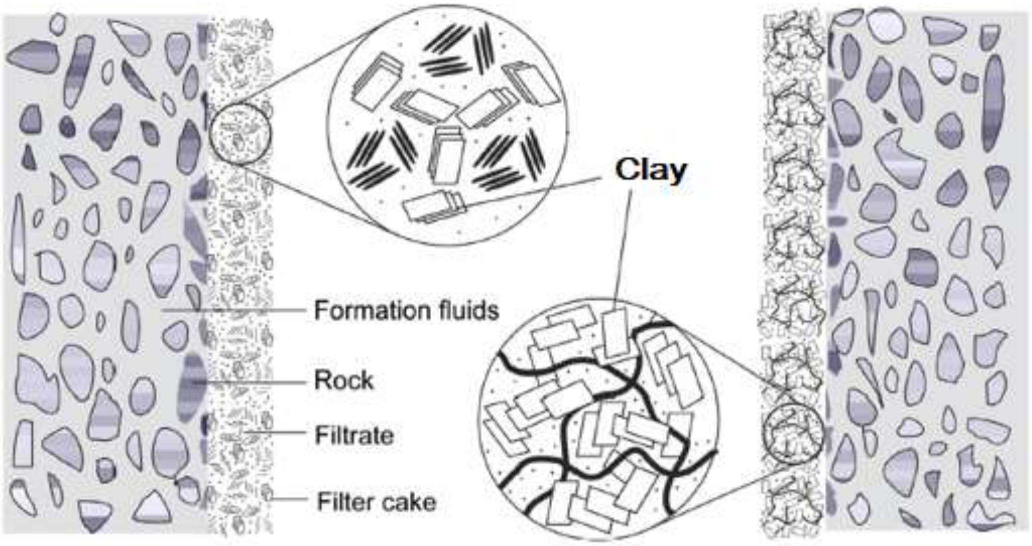

Figure 15: mineral clays in the drilling fluid circulation (Song *et al.*, 2016**)**

2.4.3.2 Bentonite

Geologically, bentonite is a layer of weathered volcanic residue, one of the largest volcanic waste sites in the North America region, now known as "black hills of Wyoming and south Dakota, and the big horn mountains of Wyoming" (Amorin *et al.*, 2004). One of the major components of bentonite is the minerals clay smectite, indeed the term bentonite is used to refer to montmorillonite sodium which is a form of smectite (Dyke, 2000). Bentonite is commonly used in drilling fluids to fulfil two of its important requirements such as increase viscosity and reduce filtration losses (Lebedenko and Plée, 1988; Darley and Gray, 1988). In interaction with water bentonite swells due to its hydrophilic character and adsorbs water. Good quality bentonite when used in drilling fluids will give the required viscosity and acceptable filtration loss (Lebedenko and Plée, 1988; Darley and Gray, 1988; Falode., Ehinola and Nebeife, 2008**)**

Table 2: API standard Bentonite composition (Rabah and Abdelrahman, 2012)

Compound	SiO_3	Al_2O_3	TiO_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	L.O.I
Wt%	59.22	19.18	0.13	5.69	2.49	2.34	1.89	0.62	0.13	0.01	7.55

The figure below shows the structure of the bentonite.

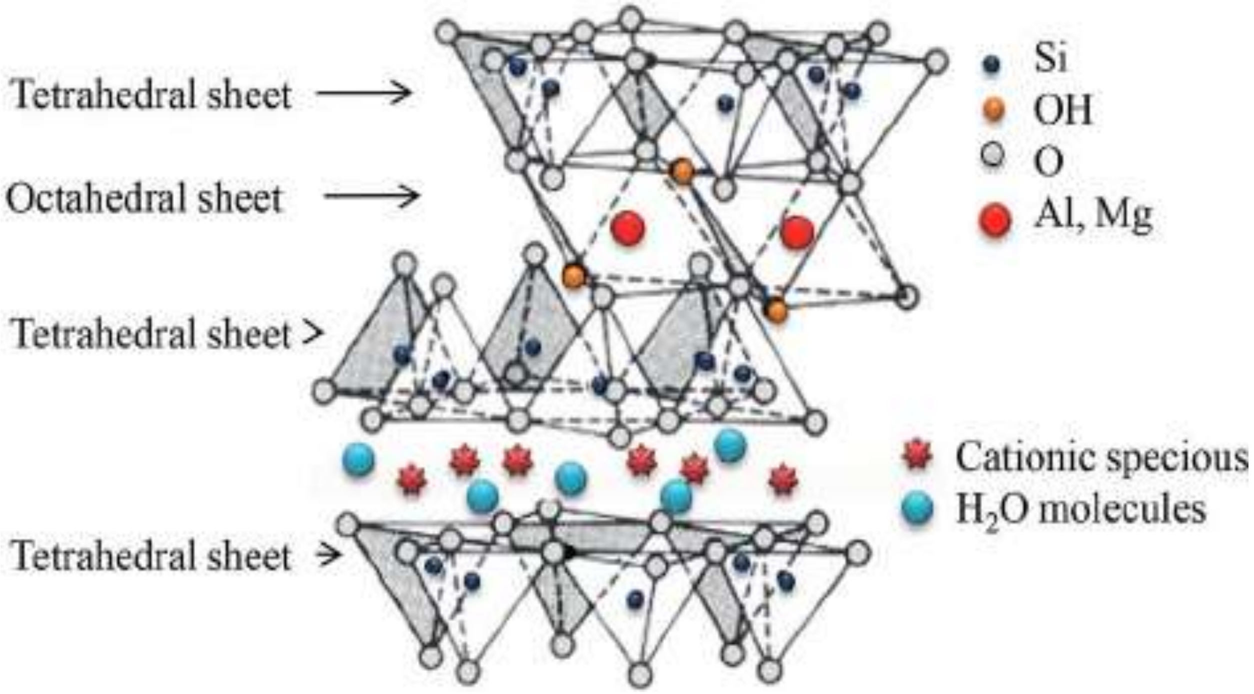

Figure 16: Schematic representation of the montmorillonite (Ghadiri, Chrzanowski, and Rohanizadeh, 2015)

In addition, due to the increase in high temperatures of the well while going deeper, bentonite particles tend to flocculate which causes particles to join together to form a loose and an open network, which consequently increases filtration and affects the performance of bentonite.

2.4.3.3 Attapulgite

Bentonite is the well-known and common clay used in drilling mud. However in some wells, where the salinity of water reaches a certain proportion, the commercial bentonite gets affected after the hydration (Carney, 1979). Hence an alternative fibrous clay known as attapulgite can be used in such condition of higher water salinity instead of bentonite to perform the drilling process (Abdo *et al*., 2016; Altun and Serpen, 2005). Another inconvenient of using bentonite is that bentonite based drilling mud used in geothermal wells are damaged subjected to high temperature (175°C) condition because the plates of the bentonite tend to flocculate (Altun and Serpen, 2005). This flocculation has an undesirable impact on the drilling fluid process and lead to an increase in the drilling cost.

To summarize, the high salinity and the high temperature are hostile to bentonite based drilling fluids which result in drastic rheological and filtration properties. Consequently, there is a huge to formulate an adequate mud system to withstand those hostile conditions, and that requires the search for substitute clays.

Attapulgite, has been proposed as the bentonite replacement for the environments having both high temperature and high saline concentration (Carney, 1979). Attapulgite belongs to a group of a hydrated magnesium aluminium silica mineral. The structural characteristics and physical - chemical properties make attapulgite unique in the clay mineral family. Although there could be temperature dependent changes in crystalline structure, attapulgite is stable up to relatively high temperature and pressure (Abdo, 2013). Some investigators, for instance, have indicated that attapulgite is temperature resistant clay (Altun and Serpen, 2005).

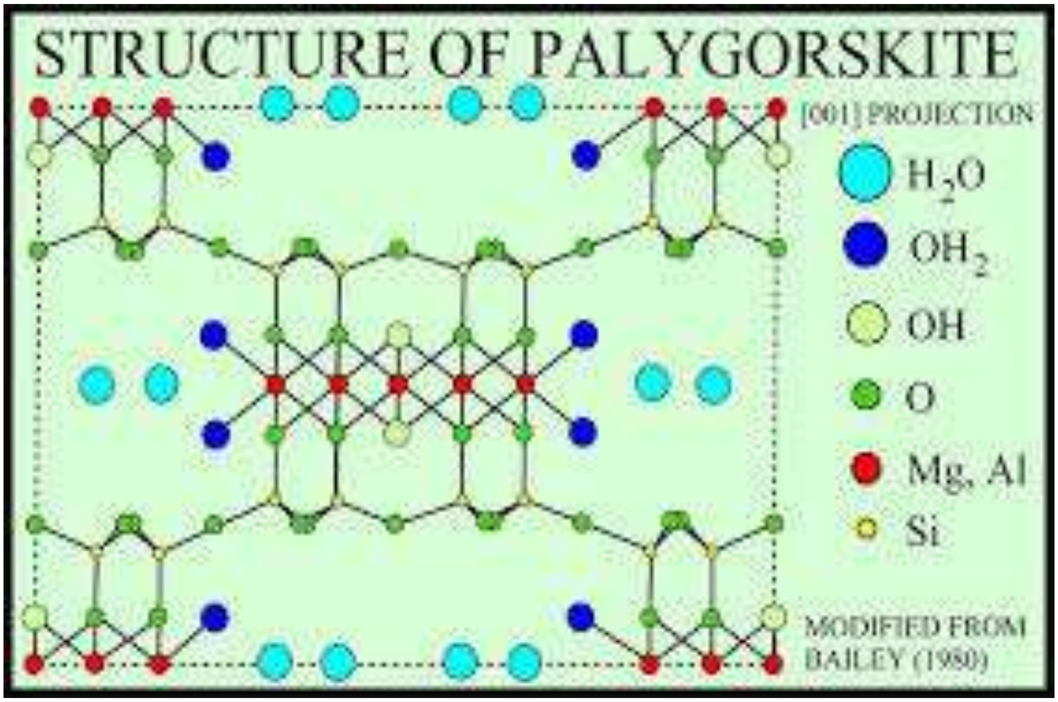

Figure 17: Schematic structure of attapulgite clay

2.4.4 Summary

Clays are an important additive that help the drilling fluids to fulfil their objectives in the way that they mainly ameliorates the viscosity and mitigates fluid loss of the DF. Therefore, depending on the type of the well and the conditions to be encountered, a specific clay must be used in the mud formulation. Likewise nanotechnology is implemented for enhancing drilling fluids properties. Indeed a numerous nanoparticles either polymers or solid particles amazingly impacted muds properties.

CHAPTER 3. EXPERIMENTAL DESCRIPTION AND ANALYTICAL TECHNIQUES

3.1 Experimental description

3.1.1 Material

- Chemicals

A 3.2% microfibrillated cellulose (MFC) suspension obtained from Sappi was used as the source of cellulose material, 13-15% NaClO solution (from Rochelle Chemicals), 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO), attapulgite (from Sigma Aldrich S.A.), NaBr (from Rochelle Chemicals), NaOH pellets together with 32% HCl were obtained from Merck. All chemical were not diluted nor concentrated except for NaOH and HCl of which were converted to 0.5M solutions. Two surfactants were used in this research; cationic Dodecyl Trimethyl Ammonium Bromide (DTAB) and non-ionic Triton® X-100. The DTAB with the formula of $C_{12}N(CH_3)_3Br$ 0.22 has a molecular weight 308.34g/mol at 25^0C and the Triton® X-100 with the formula $C_{14}H_{22}O(C_2H_4O)_n$(n=9-10) and average molecular weight of 625g/mol. Its viscosity was 240cps at 25^oC with pH 6-8 (5% aqueous solution). The HLB of the surfactant is 13.5, so this can help generate oil in water emulsions. ZnO nanoparticle was selected for this project, supplied by Sigma Aldridge. This was in a white powder form with formula weight of 81.39g/mol and particle size <10nm. The brine solution was prepared with NaCl and CaCl2 which were mixed together with distilled water. Surfactant and nanoparticle aqueous solutions were prepared using brine solution. The crude oil sample used was supplied by Sasol Natref (refinery tank F29107) and the mineral oil sample used is a high content 25w-60.

- Instruments:

A hielscher UP200S Ultrasonic Processor (200 watts, 24 kHz) (Figure 3.1) was used to mix the aqueous solutions and the crude oil. An Ohaus Explorer EP413 milligram balance (Figure 3.1) was used to weigh the chemicals in preparation of the aqueous solutions. A Rheolab Quality Control viscometer figure 3.2, from Anton Paar was used to perform the rheology tests and the feed loss was determined using the Schleicher & Schuell No.1505 filter.

The emulsions that were made contained either Cationic dodecyl trimethyl ammonium bromide (DTAB) or non-ionic surfactant Triton®X-100 as surfactants; brine; crude or mineral oil; bentonite or attapulgite as clay and zinc oxide nanoparticles or cellulose nanocristals synthesized as described below.

3.1.2 CNC synthesis procedure

To optimize particles' size some variations has been done in terms of temperature, agitation rate and chemicals' ratio. The synthesis of CNC was based Tempo mediation method through variation of various parameters such as temperature, speed of agitation and stoichiometric ratio. The effect of each parameter was better understood during the fluid behavior analysis using the rheometer and the filter press. The amount of nanoparticle was also optimized using 10 and 50nm, very monodisperse and capable to play an important additive role.

The CNC was generated using the method of oxidation of microfibrillated cellulose through TEMPO-mediated described as follow: 750ml of 3.2% microfibrillated cellulose (24g solids) slurry was further allowed to rest overnight. Then the slurry was diluted in 3877.5ml of distilled water in which 0.369g TEMPO and 3.69g NaBr have been previously added. Both the slurry and distilled water were pre stored at 9°C in a fridge, the suspension was stirred continuously at 400 – 500 rpm with an overhead stirrer. The reaction was initiated by adding 172.5ml of 13-15% NaClO solution and allowed to run for 6hrs under agitation at controlled temperature (10°C) using ice bath varying between 9°C and 11°C and pH was adjusted to 10.0 ± 0.3 with NaOH (0.5 N). A pH meter was used to control the pH of the mixture. After 6hrs the reaction was halted and the contents were filtered. Then the product was washed several times with DI water until the aqueous solution reached neutral pH. The product was then suspended in 1000ml of distilled water prior being sonicated using an ultrasonicator (USM20) for 45min and was stored at 9°C in a tightly sealed container. It is important to note that in order to avoid contamination, the product was placed in a seal Buchner funnel with parafilm during the filtering process and carefully transferred the CNC cake into the storage containers with clean equipment.

3.1.3 Emulsion mud preparation procedure

In general, drilling fluid laboratories recommend a method of preparation and an order of addition for emulsion drilling fluid (EDF) evaluation practices. It is advantageous to first dissolve the surfactants in aqueous medium to promote the production of an oil in water emulsion.

"The continuous phase is one in which the surfactant is the most soluble", but this one remains very much used (Schramm, 1992). Thus, in the EDF domain, it is recommended that the emulsifiers be dissolved in the aqueous (Lashmar *et al*., 1995). The initial addition of the two surfactants in aqueous phase before addition of oily phase promotes the stability of the emulsion. The order of addition thus influences the kinetic stability of the emulsion.

In all preparations, a specific agitation rate and the power of the ultrasonicator was mentioned. The study of the evolution of the electrical stability (defined in the API standard, 2005) as a function of the stirring time shows a considerable influence of this parameter up to a duration of 35 minutes. At 40 min, beyond which the electrical stability remains constant. It is reported that the slow and steady addition of the dispersed phase promotes emulsification (Fouilloux, 2011). On the contrary, some works do not indicate a difference between a slow addition and a quick addition (Vignati *et al.,* 2003; Perkins *et al.,* 1974; Zhao *et al.,* 2013). All emulsions were prepared with an ultrasonicator. It is generally accepted that long, vigorous agitation improves stability. The main factors that affect the optimal emulsification time are the amount and type of surfactant and the stirring speed. The methods used to study the properties and stability of an emulsion are described either in standards or in the specifications specific to each industry. In this part of the study, the stability of the emulsions is evaluated according to several factors often specified in the AFNOR standard T73-409 (1976), namely: the nature of the phases to be emulsified, the nature and the content of the emulsifier, the volume fraction of dispersed phase, the emulsification conditions, the concentration and the content of possible additives.

100g of samples of emulsion were prepared following the protocol below; after having chosen the water: oil ratio of 9:1 to be studied and verified that the two phases to be emulsified are liquid at ambient temperature, the surfactants weighed with an accuracy of 10^{-3} g are introduced into the aqueous phase. The above steps was followed~~;~~

- Pour the aqueous phase at a ratio water: oil (9:1) into a beaker placed on a stirrer and adjust it at a constant speed;
- Addition of bentonite or attapulgite (6%);

- Addition of brine solution ;
- Addition of surfactant (2%);
- Leave the mixture stirring for 10 min;
- Introduce the oily phase to disperse in small quantities for 2 min using a syringe while ultrasonicating the mixture to get microemulsions.

These steps were applied to all the emulsions prepared except for emulsions with nanoparticles, where the aqueous phase was placed first in a beaker, then the desired amount of nanoparticles has been added and ultrasonicated for 30mn. The nanoparticles well dispersed (for emulsion with nanoparticles) the procedure was carry out as followed above. The rheology properties and filtration tests of the emulsions drilling fluids were carried out using the following tests.

3.2 Characterization techniques

3.2.1 Rheometer (Location: Wits University)

3.2.1.1 Equipment description

The FANN® Model 35 viscometer are direct reading instruments which are available in six speed and 12 speed designs for use on either 50 Hz or 60 Hz electrical power. The standard power source is 115 volts but all of the models may be fitted with a transformer, which makes operation with 220/230 volts possible.

These are true couette coaxial cylinder rotational viscometer since the test fluid is contained in the annular space (shear gap) between an outer cylinder and the bob. Viscosity measurements are made when the outer cylinder, rotating at a known velocity, causes a viscous drag to be exerted by the fluid. This drag creates a torque on the bob, which is transmitted to a precision spring where its deflection is measured and then compared with the test conditions and the instrument's constants. This system permits the true simulation of many of the significant flow process conditions encountered in industrial processing.

Viscosity as measured by a couette type viscometer such as the Model 35 is a measure of the shear stress caused by a given shear rate. This relationship is a linear function for Newtonian Fluids, i.e. a plot of shear stress vs. shear rate is a straight line. In many instances, while the fluid of interest may not be Newtonian, its rheology is near enough to Newtonian that this viscometer can be used and the viscosity calculated as though it were Newtonian. It should be noted that the recommended calibration of the Model 35 is a linear or Newtonian calibration. This means that if the sample fluid characteristics are extremely

Non-Newtonian the linear method of calculating the viscosity cannot be used. In this case the Model 35 dial reading and speed along with the dimensional data on the rotor and bob used will have to be calculated using an appropriate formula for a non-linear shear stress/shear rate relationship that closely fits the characteristics of the fluid.

These instruments have been designed so that viscosity in centipoise (or milli-Pascal seconds) of a Newtonian fluid is indicated on the dial with the standard rotor, bob, and torsion spring operating at 300 rpm. Viscosities at other test speeds may be measured by using multipliers of the dial reading. A simple method of close approximation of viscosity in a plastic fluid, such as a drilling fluid is described in Section 6B.

The range of shear rates may be changed by selecting rotor speed and using various rotor-bob combinations. A variety of torsion springs are available and designed to be easily interchanged in order to broaden shear stress ranges and allow the measuring of viscosity in a wide variety of fluids.

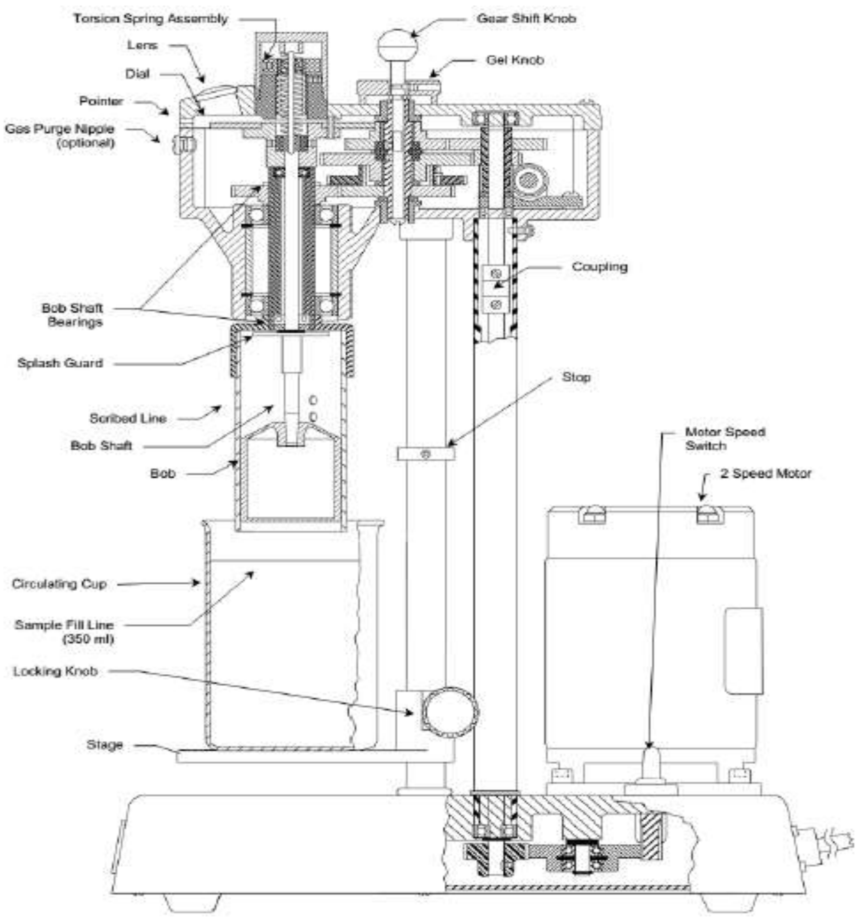

Figure 18 Model 35 Viscometer (Lam and Jefferis, 2014).

3.2.1.2 Description of the rheological measurement procedure

The rheological tests are performed by pouring the prepared emulsion drilling fluids in the cylindrical cup previously disconnected from the equipment. Inside the cup, two concentric circles delimit the minimum and maximum volume of fluid needed. The cup is brought to the equipment for the tests. Since the rheometer is connected to a computer different settings are available in the software design for different measurements purpose. Then it is possible to set the speed of the rotator, the time to run a particular test, the shear range. By the end of the experiment a file with different data is available for analysis and discussion with graphs.

3.2.2 Filtration equipment (Location: Wits University)

3.2.2.1 Equipment description

A measuring filtration behavior and wall-cake building characteristic of a mud is essential to drilling fluid control and treatment. The characteristics of filtrate, such as oil, water, or emulsion content are also important. The types and quantities of solids in the fluid and their physical and chemical interactions affect these characteristics. Temperature and pressure affect the physical and chemical interactions. Performing tests at both low pressure/low temperature and high pressure/high temperature is necessary, and these testing conditions require different equipment and techniques.

The filtration rate is the fluid loss measured in milliliters at ambient temperature and 100 psi (690 kPa) through a special filter paper for 30 minutes.

The filtration properties and wall-building of drilling fluids and cement slurries is mostly determined by the effective mean of the Series 300 LPLT Filter Press. A LPLT Filter Press assemblies consist of these following specifics items:

- Mud reservoir mounted in a frame; where the fluid is poured before the test
- Pressure assembly and regulator; used to vary the pressure for each measurement
- Filter paper; works as the underground pores through which the fluid passes.
- 25 ml graduated cylinder; used to collect the loss fluid and determine the amount of the fluid loss in a function of time.

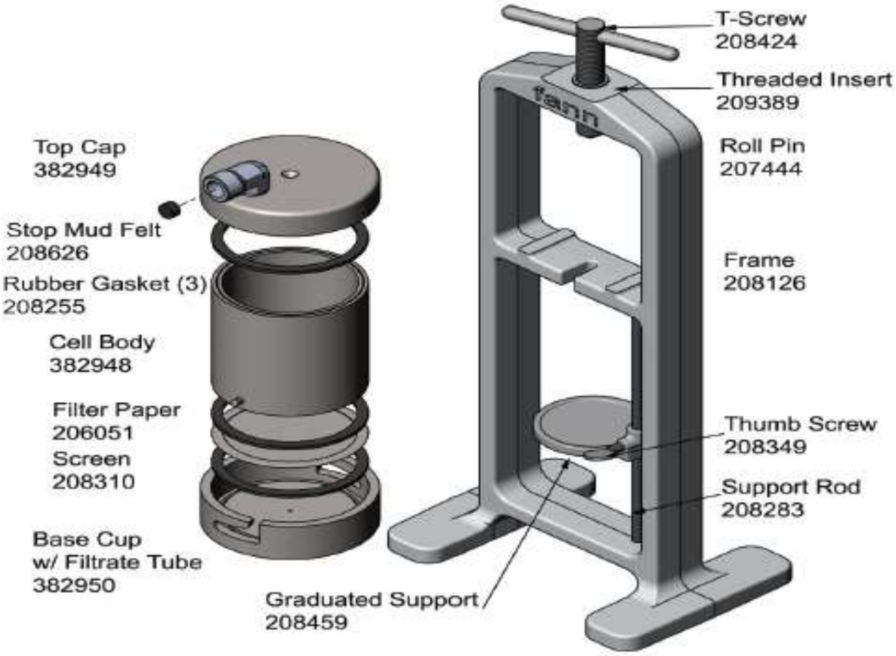

Figure 19 : Standard API filter press equipment

3.2.2.2 Description of the filtration test

Filtration tests were carried out in a standard filter press equipment with Fann filter papers according to the API guidelines (American Petroleum Institute, 2003). This type of filter paper has the particle size retention range from 2 to 5 μm. In each run, 100 mL of the DFs was placed in the filter press at room temperature under a pressure of 100 psi (0.69 MPa) provided by NO_2 gas chargers. The times during which each single volume of filtrate passed through the filter paper were recorded for 30 min after starting each measurement (Kosynkin *et al.*, 2011). Finally a table can be drawn showing either the volume of fluids loss or the time taken for that volume to be collected at a pressure of 100psi, or the volume of water collected within 30mn.

CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Introduction

In some previous works conducted by Tatsumi *et al.* (2002), Pääkkö *et al*. (2007), Boluk (2012) Song (2015) some new DF based cellulose nanomaterials formulations were developed to improve DF properties. The DFs were tested under different conditions and the results obtained were promising.

Hence, significant area of study has to be explored with NPS and namely celluloses NPs for the enhancement of DF.

Therefore, the scope of this research lays upon the previous outputs of the previous ones on DF based CNCs and goes further by evaluating some new formulations under other conditions. This Chapter is consecrated to developing a method of preparation of EDF by finding the right surfactant and estimating the right concentration of surfactant and CNCs from experimental measurement of rheological and filtration properties.

4.2 Rheology and filtration properties of EDFs without and with ZnO

4.2.1 Study of the effect of different surfactants and ZnO on the rheological properties of emulsion based drilling fluids

4.2.1.1 Preparation of emulsion drilling fluids with surfactants only

Table 3 describes the emulsion drilling fluid packages with different amount of surfactant (distilled water : oil (9:1) + 1wt% NaCl + 1wt% $CaCl_2$ + n-Wt% of surfactant (DTAB/Triton X-100) + 6wt% bentonite).

Table 3: Drilling fluid systems with different concentration of surfactant

Additives	Drilling fluid systems				
	DF 1	DF 2	DF 3	DF 4	DF 5
water (g)	165.15	165.2	164.75	164.8	163.85
Oil (g)	18.35	18.3	18.25	18.2	18.15
Surfactant (g)	0.5	1	1.5	2	2.5
$CaCl_2$ (g)	2	2	2	2	2
NaCl (g)	2	2	2	2	2
Bentonite (g)	12	12	12	12	12

Emulsions are mostly unstable; water and oil tend to separate over time. However, the surfactants used proved to act as good stabilizing agents. Emulsions containing different amount of surfactants (0.25, 0.5, 0.75, 1.0, and 1.25 Wt %) were placed in poly vial bottles. A visual observation of the emulsions helps to check the emulsion stability and to ensure that the emulsions are not separating at room temperature as seen in the image below (Figure 20 (a) and (b)). The observed heights of mixed materials were constant over the period of two weeks before the characterization of the synthesized samples. The most stable emulsion was the emulsion prepared with DTAB as a surfactant.

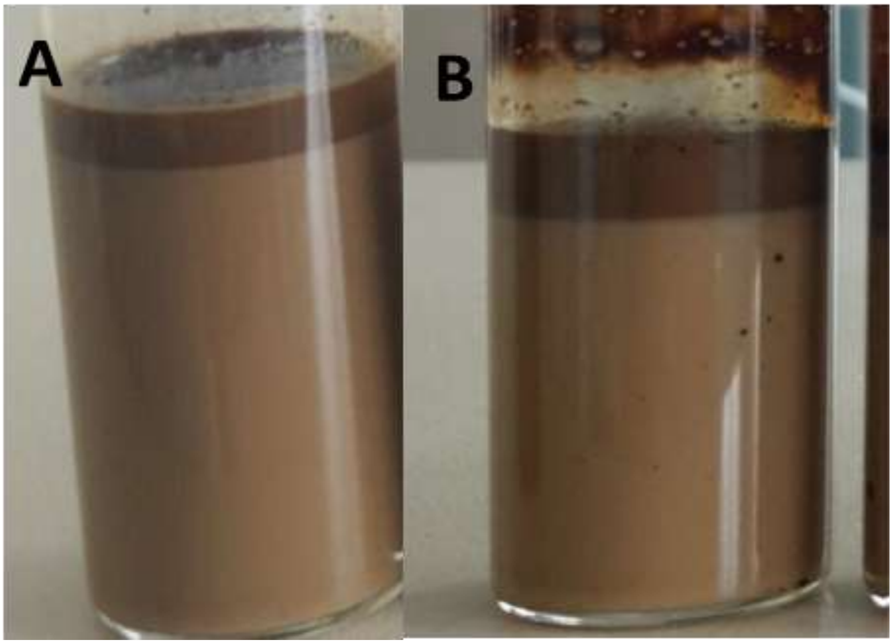

Figure 20: Emulsion based drilling fluids with (a) DTAB and (b) Triton® X-100

4.2.1.2 Preparation of emulsion drilling fluids with ZnO

Table 4 describes the emulsion drilling fluid packages with different amount of surfactant with nano ZnO (distilled water : oil (9:1) + 1wt% NaCl + 1wt% $CaCl_2$ + n-wt% of surfactant (DTAB/Triton X-100 + 1wt% ZnO + 6wt% bentonite)

Table 4: Drilling fluids formulation with different concentration of surfactants

Additives	**Drilling fluid systems**				
	DF 1	DF 2	DF 3	DF 4	DF 5
water (g)	163.35	162.9	162.45	162	161.55
Oil (g)	18.15	18.1	18.05	18	17.95
Surfactant(g)	0.5	1	1.5	2	2.5
$CaCl_2$ (g)	2	2	2	2	2
NaCl (g)	2	2	2	2	2
Bentonite (g)	12	12	12	12	12
ZnO (g)	2	2	2	2	2

Emulsions containing different surfactants such as DTAB and Triton® X-100 at a variable percentage (0.5, 1.0, 1.5, 2.0, and 2.5 Wt %) were placed in poly vial bottles. The emulsions were kept at room temperature and after ten days of visual observation, the emulsions showed good stability. Then the characterization has been done to determine the ideal sample.

4.2.1.3 Study of rheological properties procedure

The deformation and viscosities of the DF were determined using Anton Paar rheometer. 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.

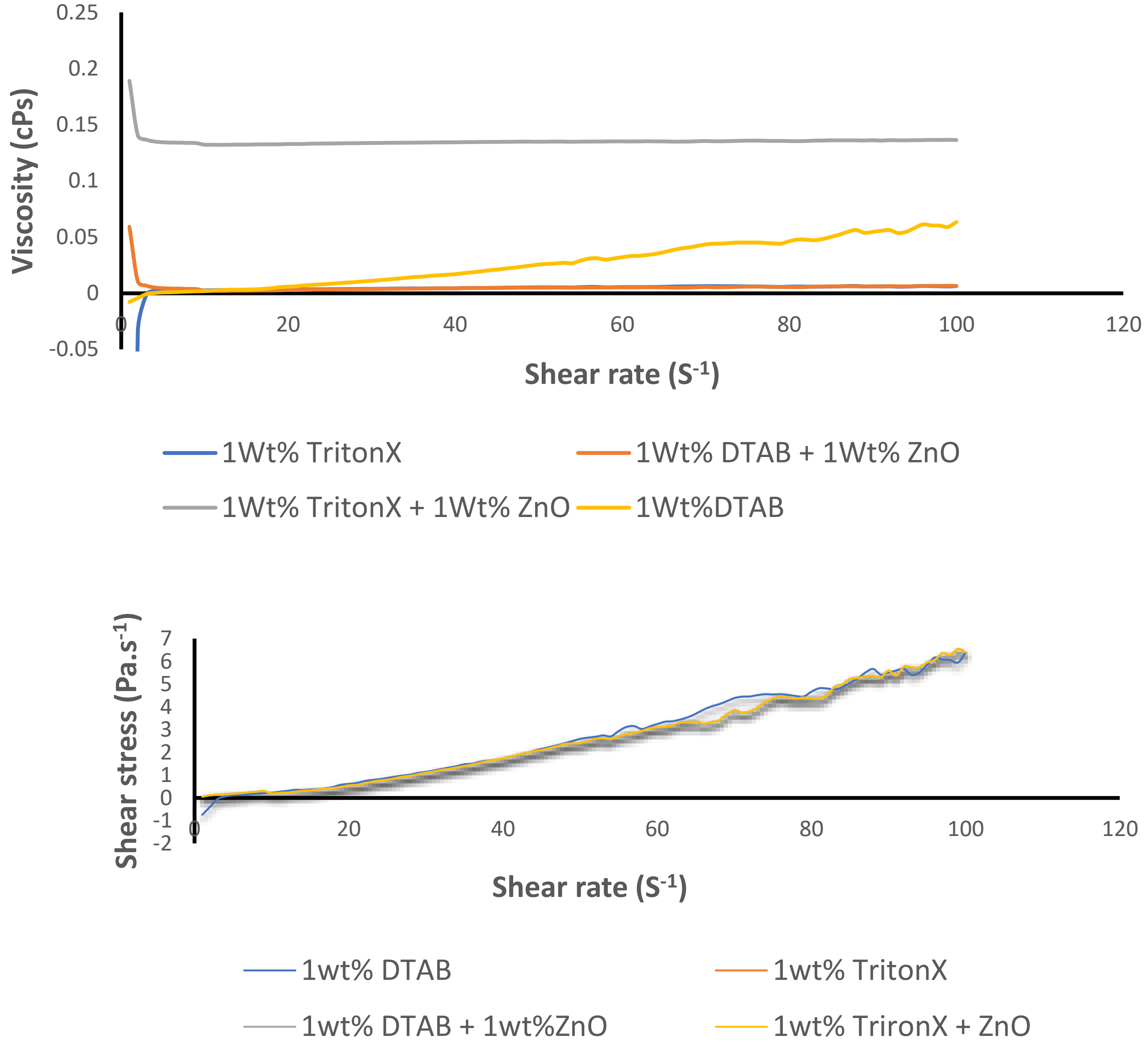

Figure 21: Shear stress versus shear rate of emulsion-based drilling fluid (b) Viscosity versus shear rate of emulsion-based drilling fluid

The rheological studies of the emulsion-based DF show that irrespective of the type of surfactant used, the behavior is relatively the same. The shear stress increases with an increase in shear rate. The emulsions are showing a dilatant behavior, whereby the emulsions are shear thickening; meaning that as the shear stress is applied, the emulsions become thicker. The dilatant behavior is, however, not affected whatever the duration of the applied stress. The emulsions do not return to their original state after deformation, meaning that they are inelastic (Sławomirski, 1975; Jaali, 2015). The emulsion that contained DTAB showed a more prominent behavior as compared to that with Triton® X-100 or a mixture with ZnO as shown in Figure 21.

The increase in weight of the emulsions by adding ZnO shows a significant effect in viscosity and not on shear stress. The emulsion with a mixture of Triton® X-100 and ZnO shows a significant effect of shear rate on viscosity; whereby it decreases rapidly at first and then stabilizes showing a thinning behavior of the fluid. On the other hand, the emulsion with DTAB shows an increase in viscosity as shown in Figure 21.

4.2.2 Study of filtration properties procedure: API filtrate loss measurement

Figure 22 shows the measured API filtrate values for 5 drilling fluids formulated containing a different concentration of DTAB. The DF with 1%wt of DTAB shows lower filtrate loss, which is desirable for a drilling fluid formulation.

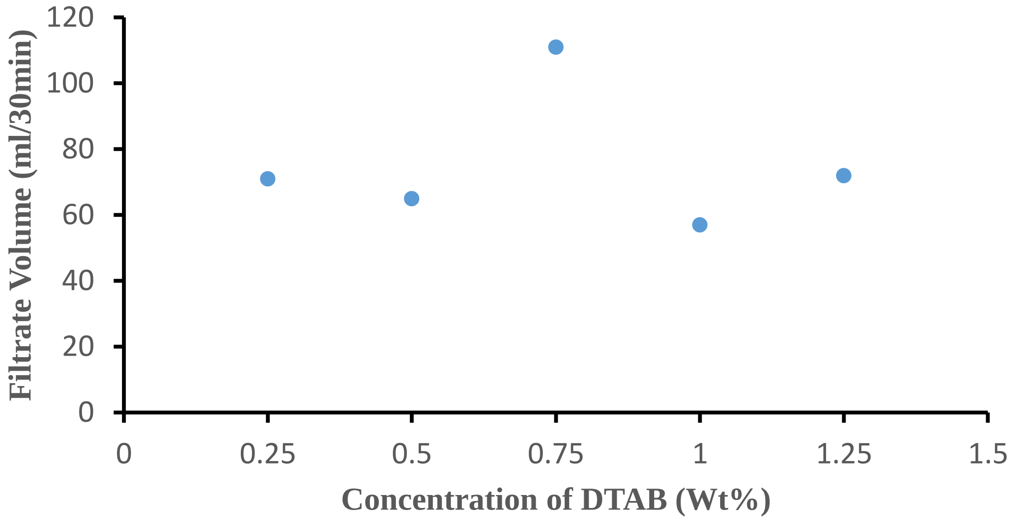

Figure 22: Fluid loss of drilling fluid with nWt% DTAB

The filtrate volume of different surfactant has shown a similar with or without ZnO nanoparticles. According to figure 23, it is notable that fluid loss was less at 1wt% of DTAB surfactant because the filtrate volume was the lowest, being 57 ml; whereas the highest volume was at 0.75wt% whereby the volume is 111 ml. Also, figures 23, 24 and 25; show that at 1wt%, all surfactants have the lowest volume of filtrate (Triton® X-100 = 66 ml, DTAB + ZnO = 53ml and Triton® X-100 + ZnO = 53 ml); and the highest filtrate volume was at 1.25 wt % for Triton® X-100 + ZnO (160 ml), DTAB + ZnO (80 ml) and Triton® X-100 90 ml).

Figure 23 shows the measured API filtrate values for 5 drilling fluids formulated containing different concentration of Triton® X-100. The DF which contains 1%wt of Triton® X-100 shows lower filtrate loss.

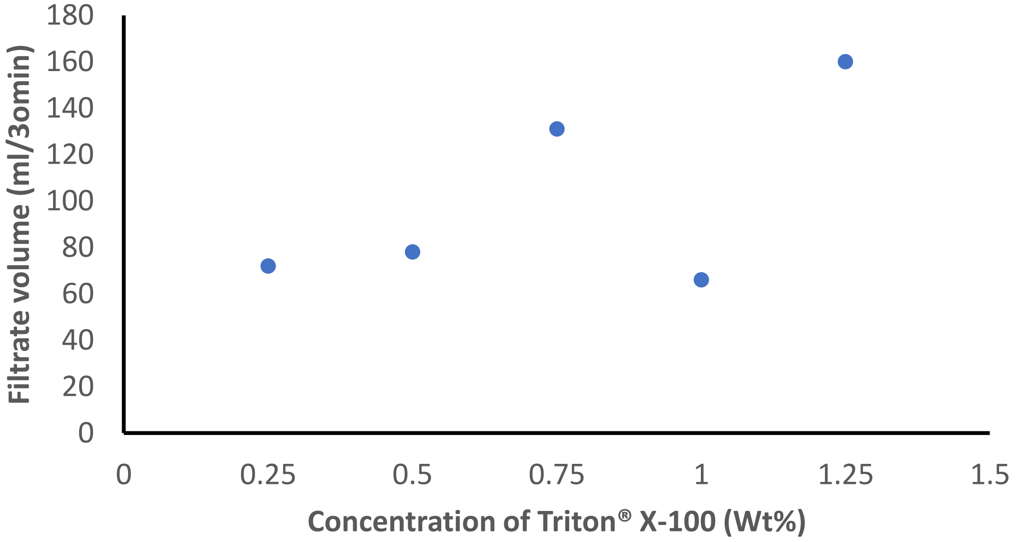

Figure 23: Fluid loss of drilling fluid with nWt% Triton® X-100

Figure 24 shows the measured API filtrate values for 5 drilling fluids formulated containing a different concentration of DTAB + ZnO. The DF which contains 1%wt of DTAB + ZnO shows lower filtrate loss.

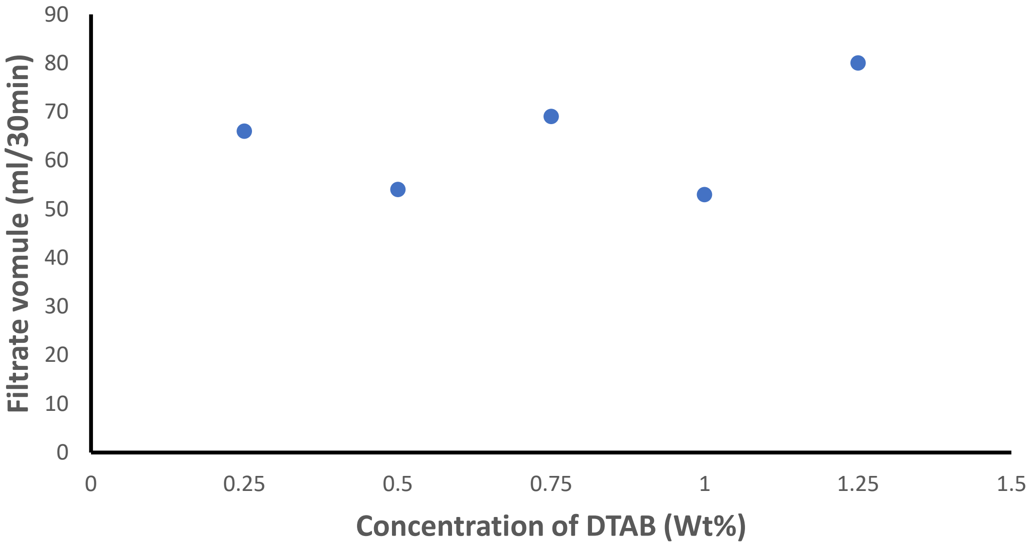

Figure 24: Fluid loss of drilling fluid with 1Wt% DTAB + ZnO

figure 25 shows the measured API filtrate values for 5 drilling fluids formulated containing different concentration of Triton® X-100 + ZnO. The DF which contains 1%wt of Triton® X-100 + ZnO shows lower filtrate loss.

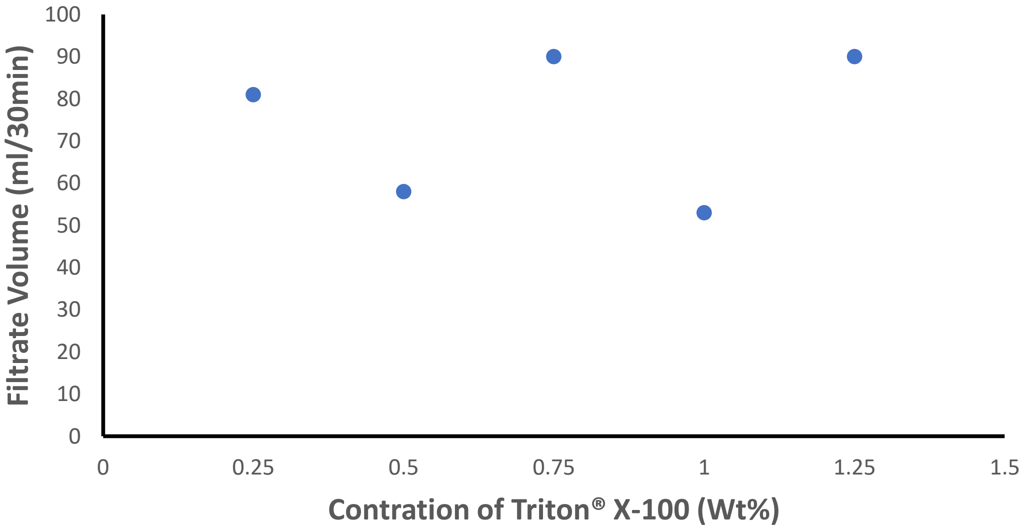

Figure 25: Fluid loss of drilling fluid with 1Wt% Triton® X-100 + ZnO

Figure 26 shows the measured API filtrate values for the 4 drilling fluids formulated which has the lower fluid loss property. The DFs which contains 1%wt in each formulation were the ones which have the lower filtrate loss, among them the one formulated with Triton® X-100 + ZnO and DTAB + ZnO show lowest filtrate loss.

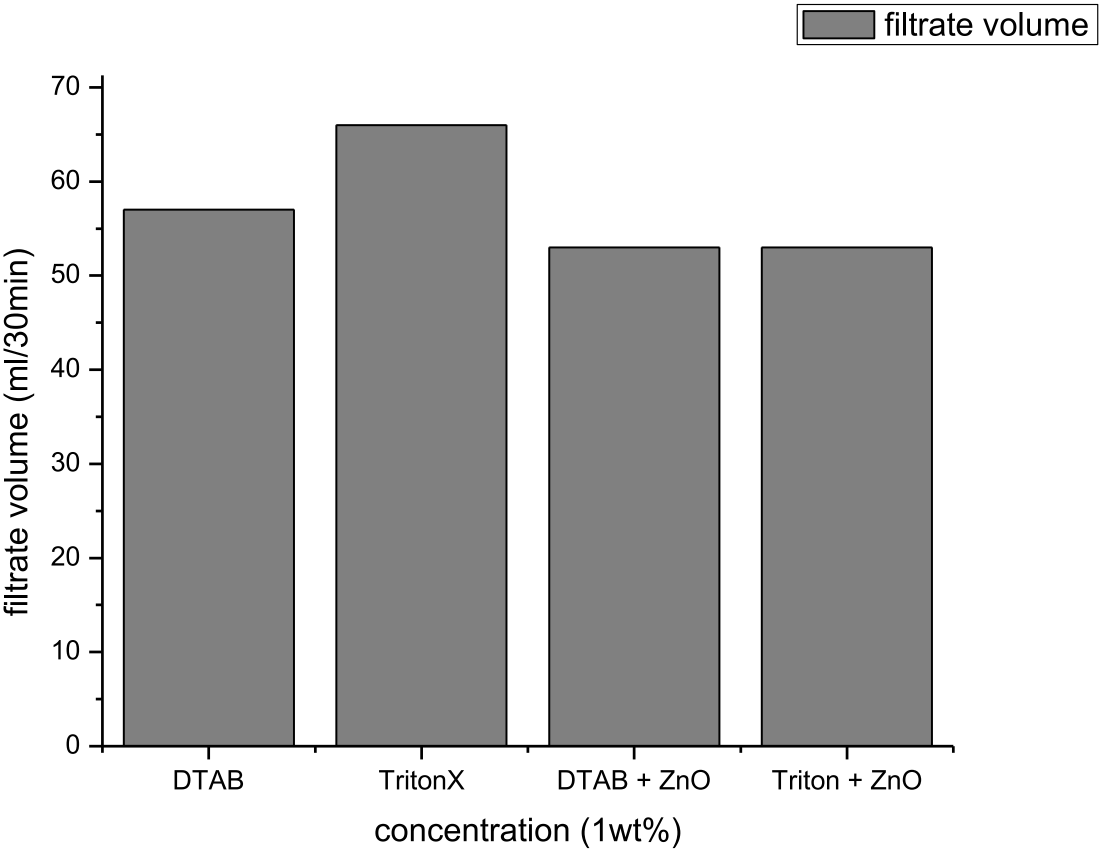

Figure 26: Fluid loss of drilling fluid with different surfactants

It is highly notable that the fluid that consists of both the surfactant and the nanoparticles has the lowest filtrate volume at 1Wt% of the filtrate as seen in figure 26. In this study, the best combination that gave the lowest filtrate was the DF that contained both DTAB (1%wt) and ZnO. For the filtration, it is expected that the emulsion-based drilling fluid should be able to retain more liquid in order to be able to fulfill its functionality of regulating the temperature by cooling and lubricating the bit and drilling string, hence also protecting the drill string and casing from corrosion. If the drilling mud is unable to retain water and/or liquid, there will also be no transportation medium for the drilling cuts and hydraulic pressure cannot be regulated too (Caenn *et al*., 2011). The inability of DFs to retain water means that more pressure will be required, and hence the drilling process becomes even more expensive.

4.3 Effect of CNCs on the rheological and filtration properties of emulsion drilling fluids at variable temperature using attapulgite clay and different oil.

4.3.1 CNCs size characterization

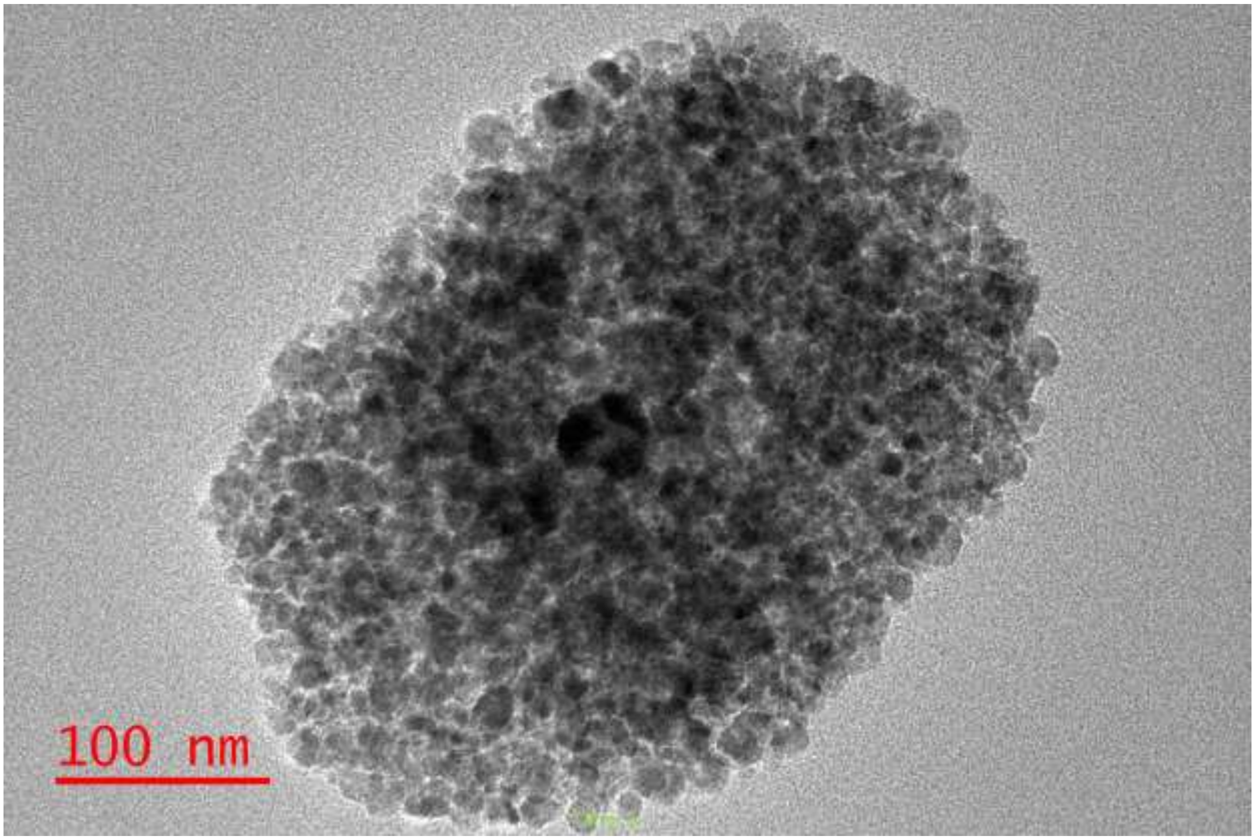

Figure 27: TEM image of synthesized CNCs

Figure 27 shows the TEM results obtained from characterization the produced CNCs, which shows quite small sizes less than 100 nm. The shape of the produced CNCs confirmed the spherical shape found in the literature (Lu and Hsieh, 2010; Li *et al.*, 2001), which showed the CNCs were successfully produced as expected.

4.3.2 Preparation of the emulsion muds

The evaluation of the performance of emulsion based DFs with attapulgite clay, mineral oils and different concentrations of CNCs was investigated. Mud samples were prepared in the same manner as mentioned in Section 3.1.3 (but in this case the CNCs were dispersed into the aqueous phase for 45min), with 100g samples of 6wt% Attapulgite and varying CNCs concentration i.e. 0, 0.8, 1.0 and 1.2wt% CNCs summarized in the table 5. The fluids were prepared and allowed to stand for 15min. The results of the prepared emulsion muds are shown in the different following pictures below.

Table 5: Drilling fluid systems at variable CNCs concentration

Additives	Drilling fluid systems			
	DF 1	DF 2	DF 3	DF 4
water (g)	162.9	162.36	162	161.64
Oil (g)	18.1	18.04	18	17.96
DTAB (g)	2	2	2	2
$CaCl_2$ (g)	2	2	2	2
NaCl (g)	2	2	2	2
Attapulgite (g)	12	12	12	12
CNCs (g)	1	1.6	2	2.4

Figure 28: Emulsion prepared with DTAB as surfactant and crude oil

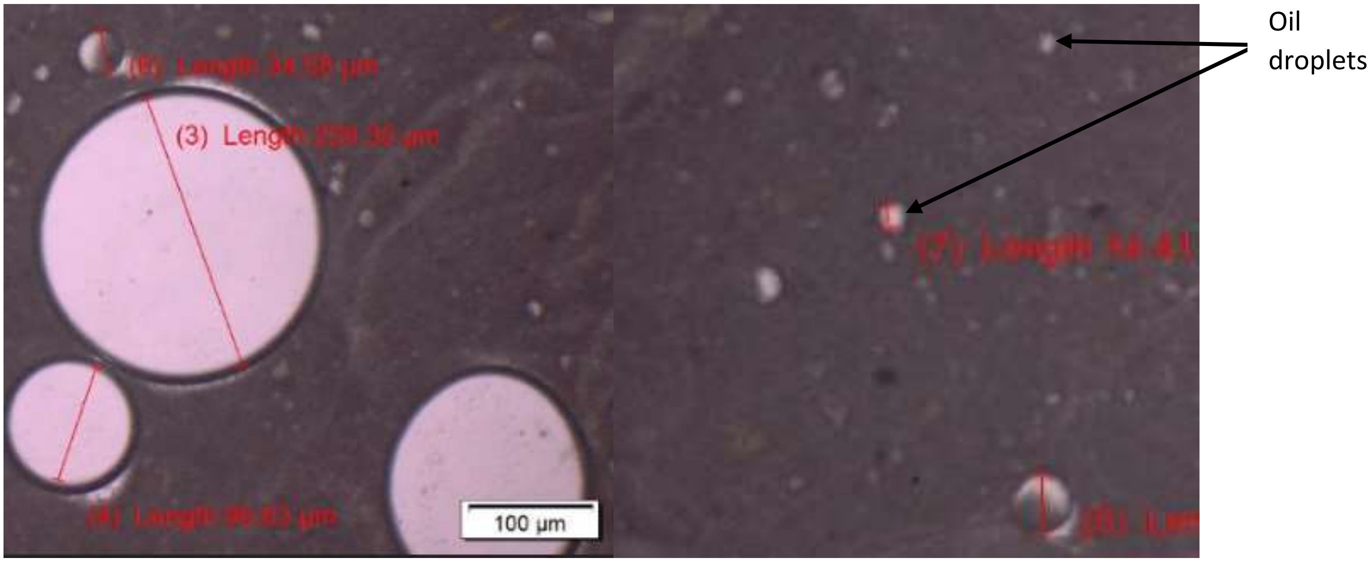

Figure 29: Emulsion’s droplets

Emulsion shows droplets with diameters comprised from microsize to nanosize which was expected for the study. The bigger droplets resulted from the fact that the ultrasonication should have been longer enough to subdivide them into nanosize droplets. The surfactants surrounding the droplets could keep the droplets for few days until the surfactants lose their efficiency and notice separation phase.

4.3.3 Rheological and filtration procedure

Rheology test results have been divided into different sections, namely mud flow behavior (shear stress vs shear rate, viscosity vs shear rate) and 10 sec and 10 minutes gel strength test results adding to that the filtrate fluids has been recorded within 30 minutes to draw corresponding graphs.

Graphical representation of each section is show in Figure 32 to 38 Data obtained from experiments is presented in Appendix (Table A.1 to A.2).

4.3.3.1 Flow behavior curves

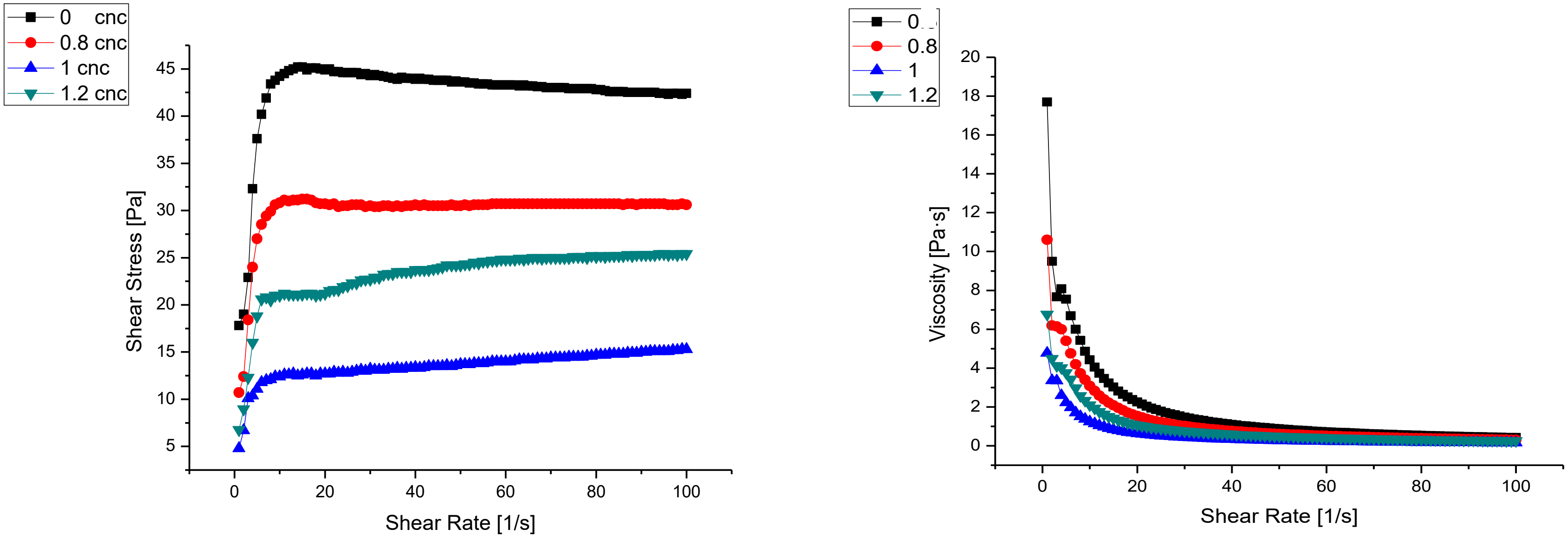

Figure 30 shear rate versus shear stress with DTAB as surfactant and crude oil at different CNCs concentrations (0, 0.8, 1.0, 1.2%wt); (b) Viscosity vs shear rate with DTAB as surfactant and crude oil at different CNCs concentrations (0, 0.8, 1.0, 1.2%wt)

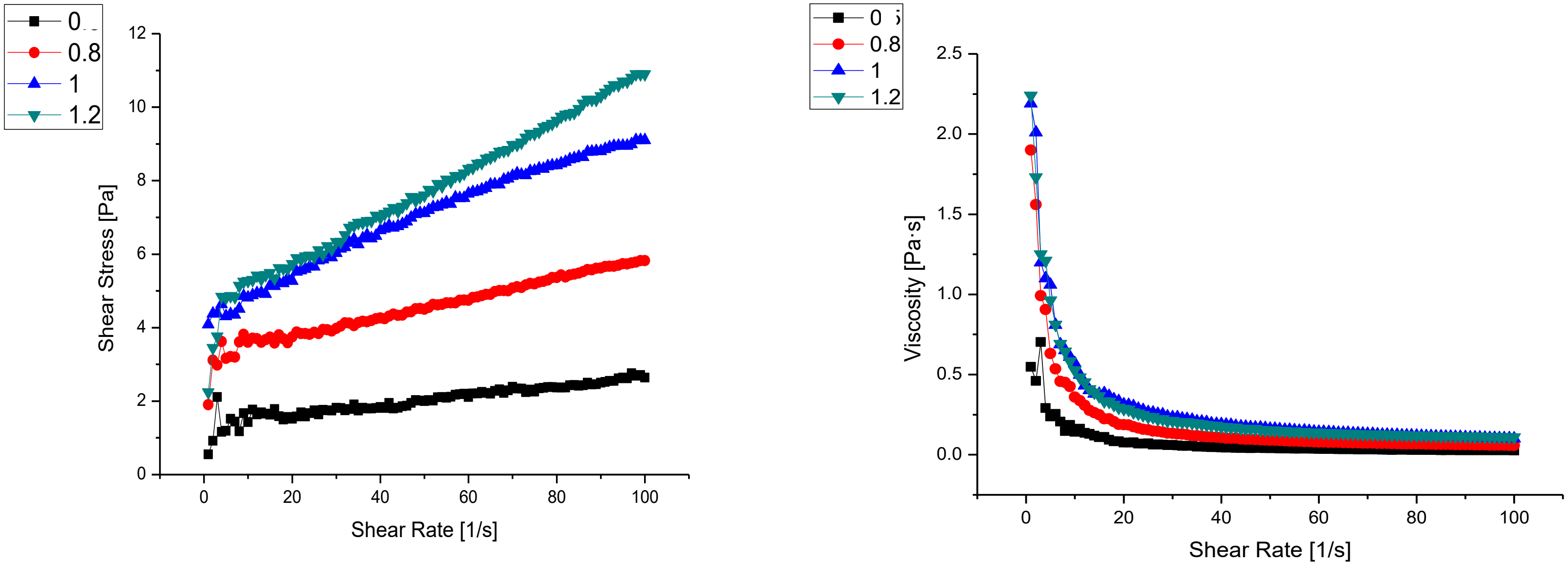

Figure 31 (a) shear rate versus shear stress with DTAB as surfactant and mineral oil at different CNCs concentrations (0, 0.8, 1.0, 1.2%wt); (b) Viscosity vs shear rate with DTAB as surfactant and mineral oil at different CNCs concentrations (0, 0.8, 1.0, 1.2%wt)

4.3.3.2 Flow behaviour curves at different temperatures

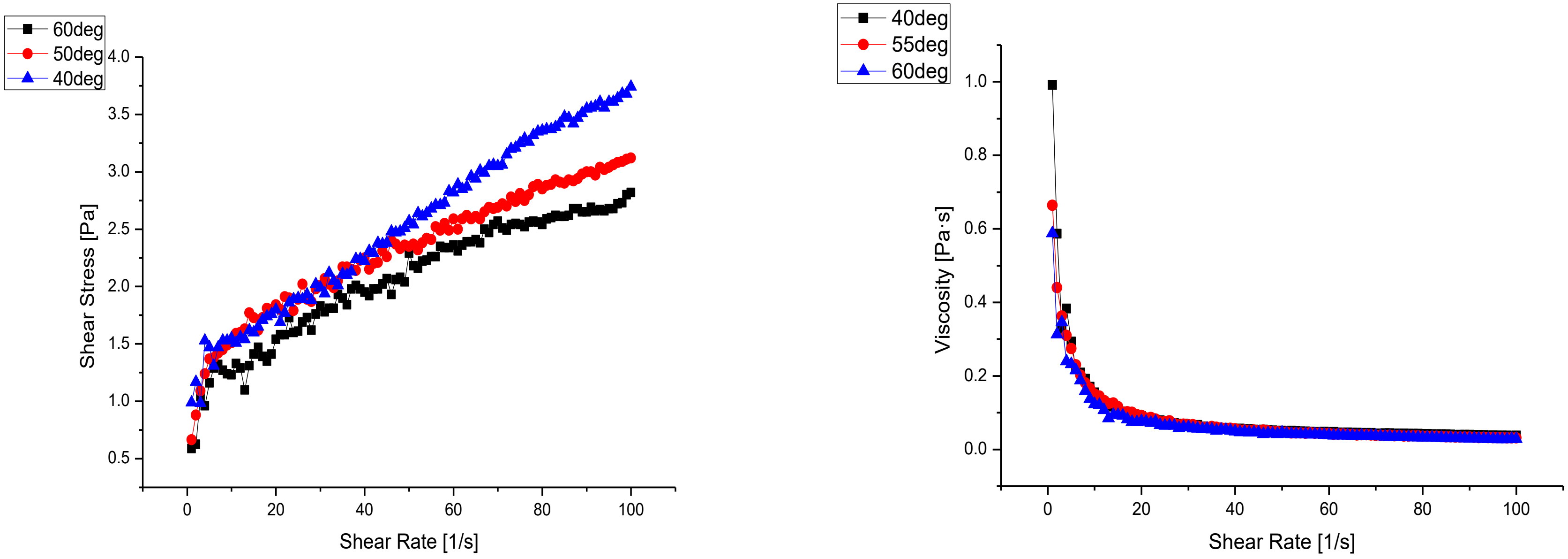

Figure 32 (a) Shear rate vs shear stress 0.5%wt CNCs min oil attapulgite at different temperature (b) Viscosity vs shear rate 0.5%wt CNCs min oil attapulgite at different temperature

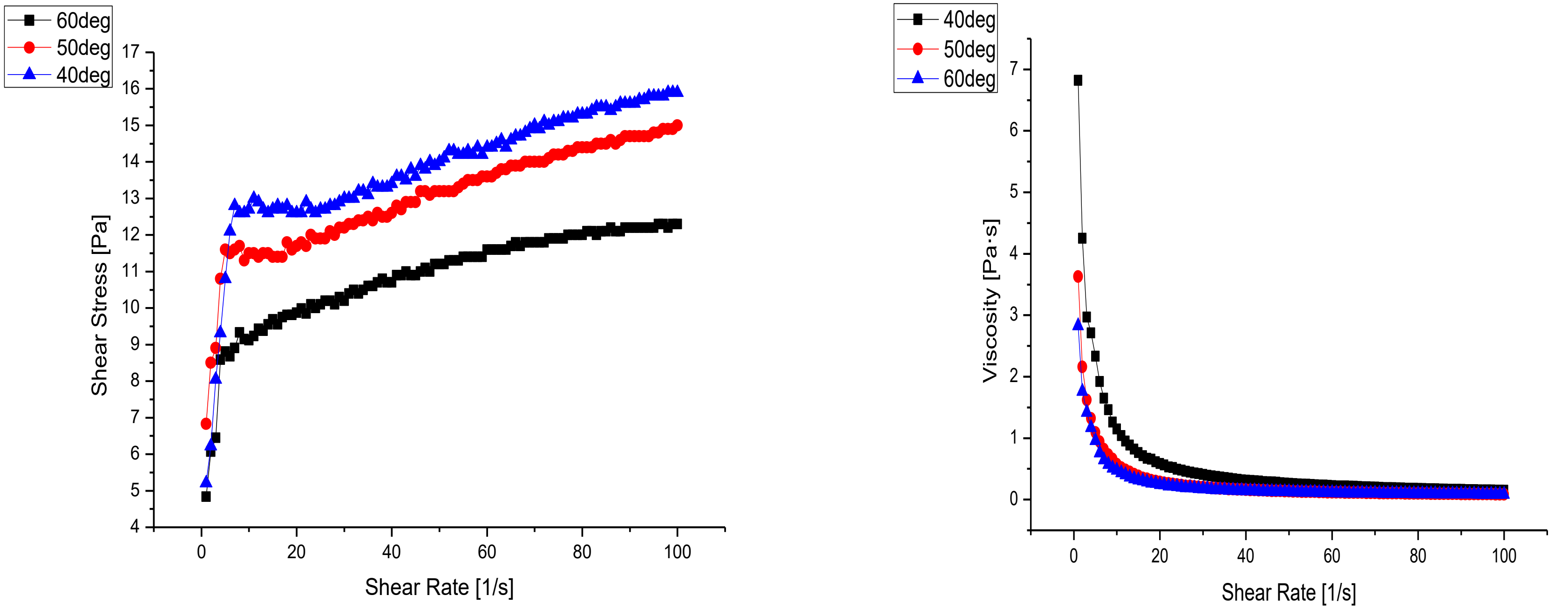

Figure 33(a) Shear rate vs shear stress 0.8%wt CNCs min oil attapulgite at different temperature (b) Viscosity vs shear rate 0.8%wt CNCs min oil attapulgite at different temperature

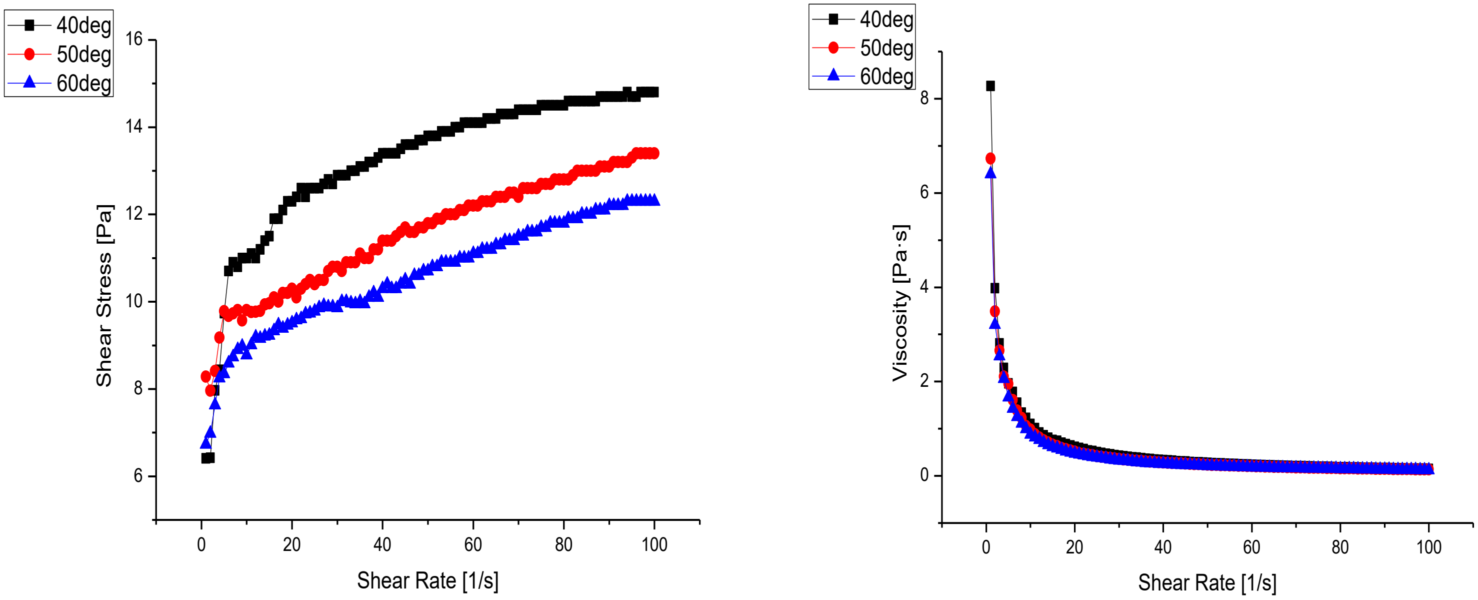

Figure 34 (a) Shear rate vs shear stress 1%wt CNCs min oil attapulgite at different temperature (b) Viscosity vs shear rate 1%wt CNCs min oil attapulgite at different temperature

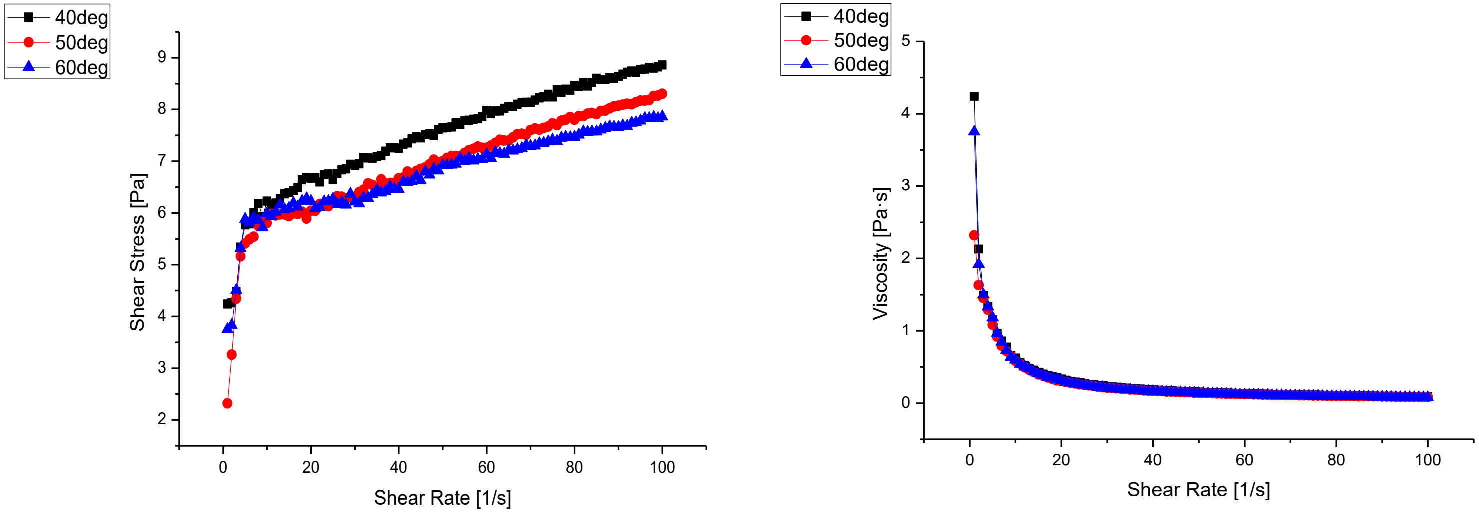

Figure 35 (a) Shear rate vs shear stress 1.2%wt CNCs min oil attapulgite at different temperature (b) Viscosity vs shear rate 1.2%wt CNCs min oil attapulgite at different temperature

4.3.3.3 Fluid loss curves

- **Mineral oil and Crude oil**

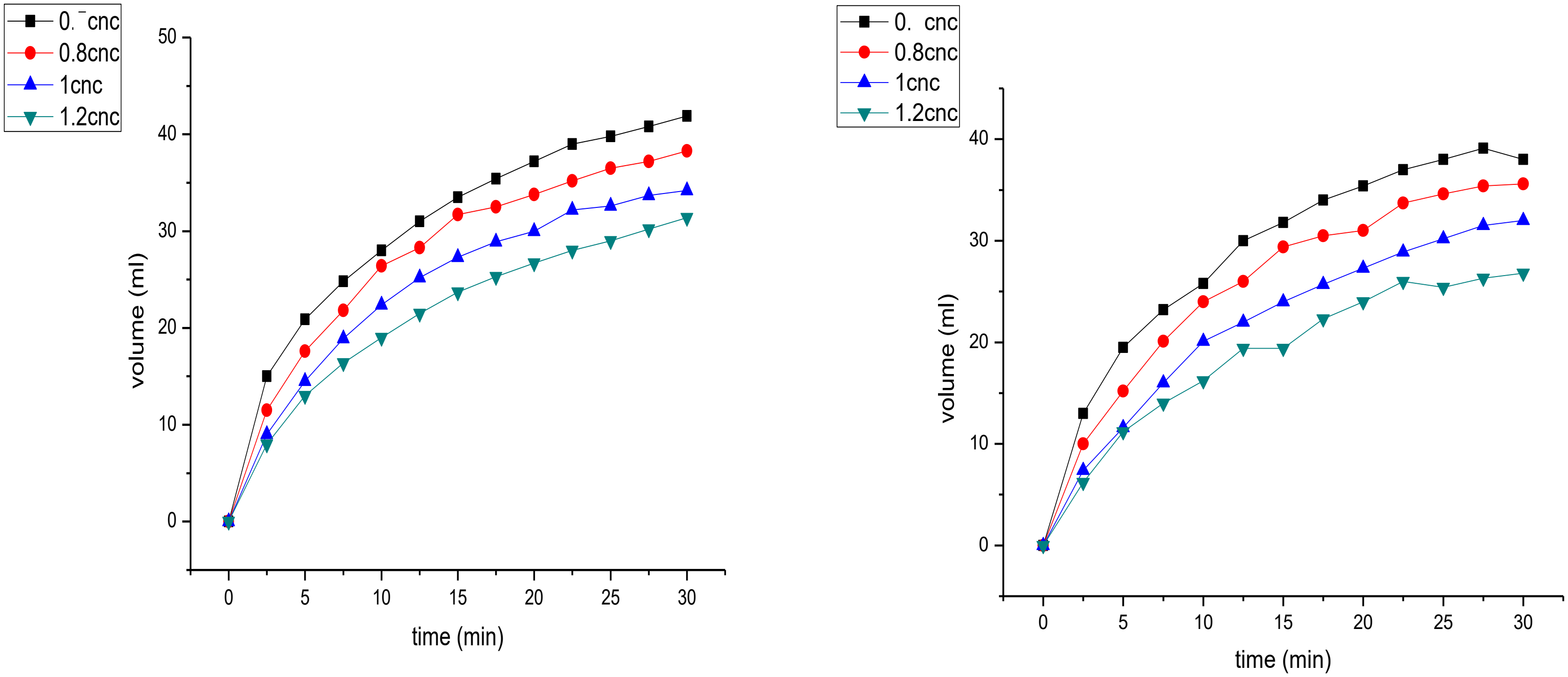

Figure 36: fluid loss properties graphs for different CNCs concentration (a) with mineral oil (b) with crude oil

4.3.3.4 10s and 10min gel strength diagram

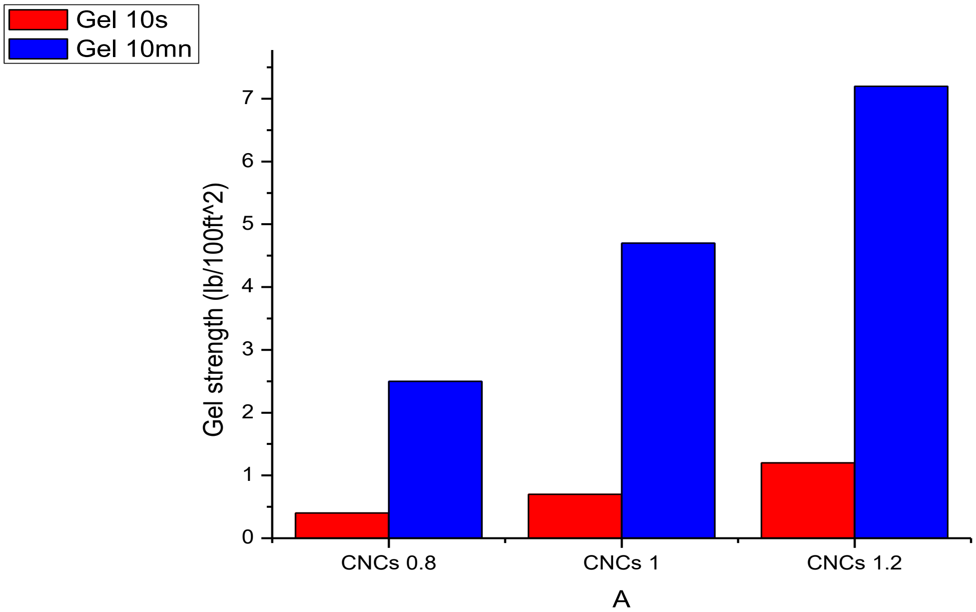

Figure 37 : Gel strength 10s and 10min with varying CNC concentrations i.e. 0.8, 1 and 1.2 wt%.

- **RHEOLOGICAL CARACTERISTICS**

The fluids behaviours were characterized in terms of their rheology, filtrate loss. The desirable properties of polymers for polymer flooding and oil drilling fluids are:

- **SHEAR RATE VS SHEAR STRESS**

The objective was to evaluate the performance of nano-emulsion DFs with various CNCs concentration formulated with different type of oils such as crude oil and mineral oil, in the purpose to evaluate the use and effectiveness of using the latter oil for the rest of this research. Figures 32-36 show the curves, which are the relationship between the Mud shear stress and the CNC concentrations into the prepared DFs. The shape of the curves is slightly the same and all exhibit a non-Newtonian fluid behavior, although the CNCs concentration in each drilling formulation was quite low. Having a look at the figures 31 and 32 it can be seen that an increase of CNC-Attapulgite Mud shear stress is consecutive to an increasing of CNC concentration from 0.5 to 1.2wt% CNCs for both types of oil.

The higher impact on the rheological properties was observed in DF based crude. Similar effect was observed also on the filtrate fluid values. Globally the results varied from oil type to oil type and also from a CNC concentration to the other. However, it is important to remember that increasing the concentration of CNC in the fluid may provide a positive result up to an optimum concentration value. Indeed A high velocity is desirable in such a way that it helps to remove cuttings and this is allowed when the drilling fluid shows a high shear forces. And this characteristic is encountered for crude based DF as well as mineral oil based DF.

- **VISCOSITY VS SHEAR RATE**

Another objectives was also to investigate the performance of CNCs viscosity in various oil in the drilling fluid formulation. The flow behavior curves of O/W emulsion-based drilling fluids are shown in Figures 32-36 with varying concentrations of CNCs. The fluids show enhanced shear thinning profile, so that the higher the velocity the lower the viscosity was recorded. For low velocities the fluid has high viscosity. Indeed high viscosity of the fluids at low rates is mainly required it enables the fluids to suspend drilled cuttings and at the same time carry them out from the wellbore. Furthermore, a low viscosity of a DF at high shear rates confer to the fluid the ability to flow into downhole with less resistance.

This is important for covering all sections of the well, i.e. from riser (low velocity) to through the nozzles (very high velocity). Increasing the flow rate will always improve the hole cleaning, for all sections of the well.

The difference in CNCs concentration does not show any significant impact on the viscosity. Nevertheless, the viscosity profile of the fluid slightly decreased with the increase in CNCs concentration. In the fluids systems, the addition CNCs didn’t show any significant impact on the viscosity. From the figures 31 and 32, it can be seen that at low shear rate, the DF based CNCs mud have a high viscosity compared to the 0% CNC mud but approaching a similar trend which shows how mud viscosity is affected by the presence of CNCs within the fluid system.

- **FILTRATION CARACTERISTICS**

The drilling fluids prepared have an extremely low solid content and relatively small size of CNCs, resulting in a low filtrate after the pressure was applied. It appears that the filtrate volume of CNCs based DF formulations show the same trend with varied concentrations of CNCs. A small difference can be seen between the ones formulated with crude oil and the one formulated with mineral oil showing a better filtrate with crude oil. A low filtrate may be the result of a low porosity of the filter cake due the presence of attapulgite and mainly CNCs in the matrix which form a barrier to close the pores.

The filtrate decreased with increase in CNCs concentration but further increase of CNCs may end up not giving a significant improvement in fluid loss. The progressively improvement of the filtration characteristic may result in a specific structure of the overall ingredients inside the fluid. In fact, the pores seemed to be confined by the surrounding CNC and attapulgite particles, and these pores were sufficiently obstruct. Thus, an optimal amount of CNCs should be used to obtain significant fluid loss control to minimize cost. With the cellulose size reduced to nano-scale all the CNCs have an increased surface area to volume ratio, increasing the contact area between cellulose and water; thus improving its fluid loss control ability.

- **EFFECT OF TEMPERATURE**

To investigate and understand the effect of the increase in temperature on the viscosity and flow behaviour of EDF, the rheology of the prepared fluids has been studied, but also to provide an interpretation to the role of CNCs based DF in high temperature environment. Figure 34-37 presents the graphs of shear stress versus shear rate and viscosity versus shear rate for emulsion based drilling fluid subjected to three different temperatures; 40, 50 and 60 degrees.

It can be observed that the readings of the flow behavior gradually decrease with temperature. At a given shear rate, the values of shear stress decrease as the temperature increases. In addition, the viscous flow behavior of both (crude and mineral) oil drilling fluids drastically changes as temperature increases. This temperature-dependent behavior was reported by Rossi et al. (1999) for water-based muds. This can be explained by the fact that as the temperature is increasing the water and even oil particle start to be more mobile since the increase in temperature leads to a change of state. In fact the increase in temperature leads to a change of the fluid density

Another factor which can explain the change in flow might be the degradation of the CNCs with the increase of temperature. It appears therefore that the increase in temperature tends to break down the internal structure within the matrix fluid very rapidly and irreversibly.

According to Seeton (2006), any increase of temperature is consecutive to a supply of energy to the fluid. This results in a rupture of the binding forces which maintained a better cohesion of the fluid. The above observation has also been reported by Mohammed Sahjan (1990); His study reported that a severe damage carboxyméthylcellulose (CMC) and bentonite clay was consecutive to an increase in temperature and mechanical shear as well. It might be say the forces generated force by the applied stress and the thermal forces tend to balance each other as the latter is increasing.

The drilling fluids viscous flow curves exhibit a well-defined yield stress in the low shear rate region at high temperature. This temperature-dependent behaviour was reported by Rossi et al. (1999) for water-based muds.

Figures 34-37 show the plot of relationship between viscosity of CNCs and temperature at different shear rates. Based on the viscosity's graphs, it is apparent that the viscosity of CNCs seems to be less or not affected by the temperature with the increment of shear rate. The change in viscosity is negligible at high shear rates compare to the one at low shear rate which is more significant; which means that the CNCs viscosities gradually lose their dependency on temperature changes.

Based on the plotted graphs, it is apparent that the graph of viscosity vs shear for that of lowest temperature is on top of the one of 50 degrees which is on top of the one of 60 degrees. At low shear rate the viscosity is high for 40 degrees and lower for 60 degrees which means that the thinning behaviour is more accentuated for lower temperature than high temperature.

Also, Exner and Craft (1933) quoted an author to have stated: "The viscosity of most muds is decreased on heating, this implies that the increment of the force generated from the applied stress at high shear rate works simultaneously with the thermal energy. Based on the results, at low temperatures the CNC concentration has more effect on the mud viscosity as opposed to higher temperatures.

- **GEL STRENGH**

It can be seen from the diagram (figure 38) that an increase in gel strength is the result of an increase in CNC concentrations and the same observation can be noticed for both 10s and 10min gels. Therefore, the drilling fluids based CNCs exhibit progressive gel strength behaviour, as already stated (**2.1.4.3**) this type of gel strength requires increased pressure to break circulation after shutdown.

Moreover, the ability of drilling fluids to form a gel at rest is desirable to suspend cuttings (crushed rocks) and avoid settling out of cuttings to the bottom of the well. It may result in the drill bit being stuck, the synthesized mud-CNC suspensions would have a very promising industrial application. Nevertheless, a too strong gel is not desirable since it will result in reduced penetration rate. But for a fluid with shear thinning characteristics a strong gel is not an issue since it will quickly break as the fluid gets thinner due to shearing resulting in increased penetration rate (Caenn *et al*., 2011).

CHAPTER 5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

WBM is the most used fluid worldwide for drilling operation, this is quite reasonable for the sake of the environment. OBM is also used from different ways namely for deep well, but it suffers from its environmental drastic impact. The better view related to this research was the formulation of a fluid with both characteristics such as environmental friendly and able to perform deeper. For this to be achieved the formulation had to be done with the right ingredients at optimum concentration, reaching a good behavior. Add to that, it is necessary to bring another ingredients such as NPS (at good concentration) aiming to move beyond the current DFs limits in HTHP.

The main aim of this study was to assess the effect of ZnO and synthesized CNCs nanoparticles on prepared EDFs and Characterization by filter press and the rheometer were used to determine basic parameters.

EDFs were successfully prepared containing two surfactants (DTAB and Triton X-100) at different concentration, without and with addition of ZnO NPs to find the better surfactant and the required concentration. The DFs were then place in poly vial bottles and kept at room temperature for 10 days to control the evolution of the emulsion's stability. The DFs based DTAB were still stable after more than a week whereas those based Triton X-100 were showing a separation of phase after just 3 days. Moreover, after comparison of the plotted graphs from the rheometer, the DFs containing DTAB have shown relevant results, proving that DTAB which is a cationic surfactant is better than Triton X-100 a non-ionic surfactant.

The CNCs were produced by the method of oxidation of microfibrillated cellulose through TEMPO-mediated. The nano-size (>100nm) and quasi-spherical shape expected were successfully confirmed by TEM. In addition, EDFs were made with DTAB by adding different concentrations of synthesized CNCs (0.0, 0.8, 1.0 and 1.2 wt %) to find the better NPs concentration.

An ultrasonicator was used to create small droplets size leading to (nano/micro) emuslion (mostly preferred) as well as to improve the homogeneity of the solution.

The addition of CNCs has improved the EDFs in general; principally an increase in viscosity and reduction of fluid loss has been noticed while the concentration of CNCs increased. Furthermore, the EDF based CNCs were suggested to different temperatures and tested evaluating the resistance of the fluids against such condition. The analysis revealed a good behavior of the fluids, even though the fluids were degrading when the temperature increased.

5.2 Recommendations

The following are recommended for further studies

A future work would investigate the optimum amount of CNCs suspension required for a good rheological and fluid loss property.

For future work it would be beneficial to compare the performance of CNCs-ZnO or CNCs-Fe_2O_3 nanoparticle as surfactant instead of polymeric surfactants to overcome the destabilization problem which occurs after a certain resting time.

A further study on the effect of temperature on the formulated mud fluid loss will help assess the performance of those nanoparticles at high pressure and temperature conditions.

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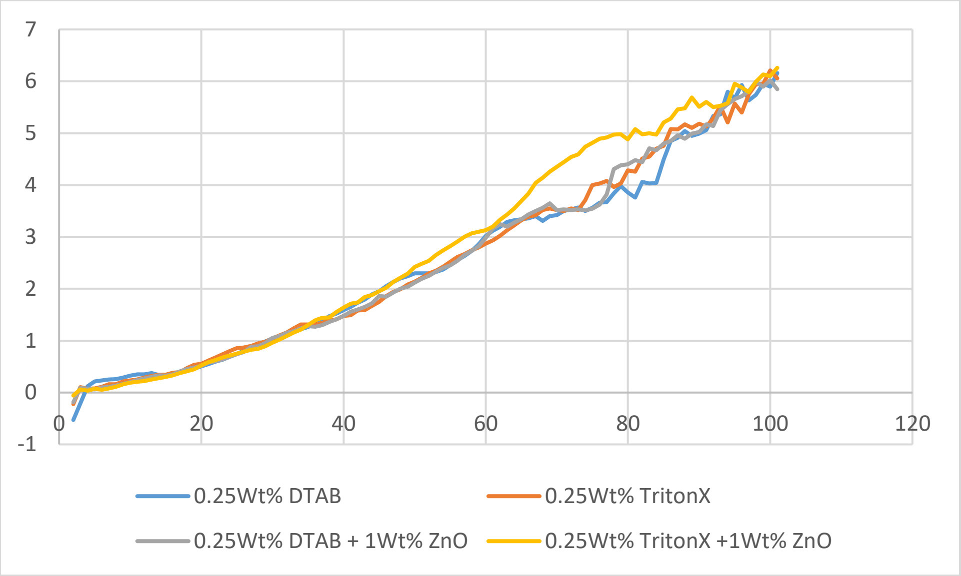
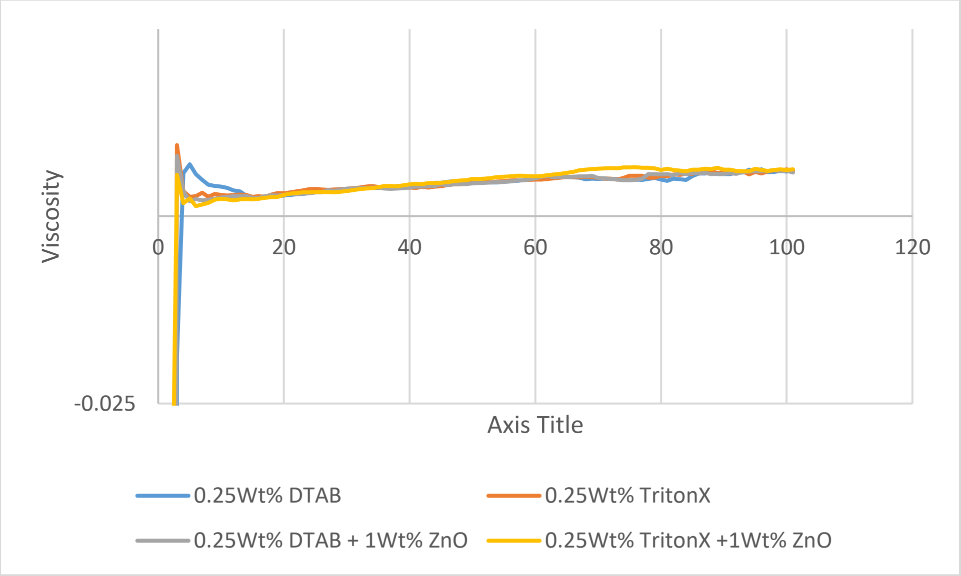
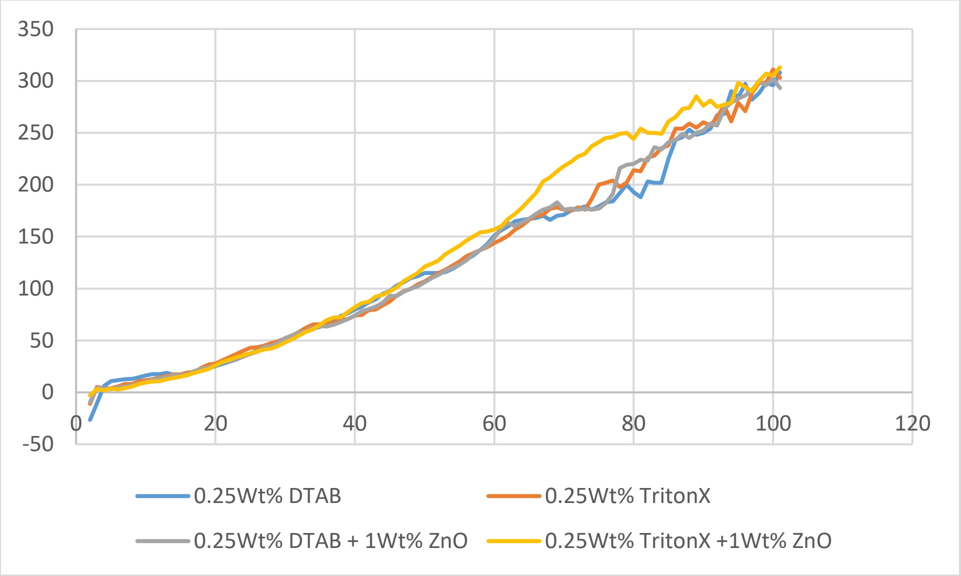
APPENDIX

APPENDIX A: (RHEOLOGY: GRAPHS AND DATA)



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200
150
100
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-50
0
20
40
60
80
100
120
0.25Wt% DTAB
0.25Wt% TritonX
0.25Wt% DTAB + 1Wt% ZnO
0.25Wt% TritonX +1Wt% ZnO


9
8
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6
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-1
-2
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20
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60
80
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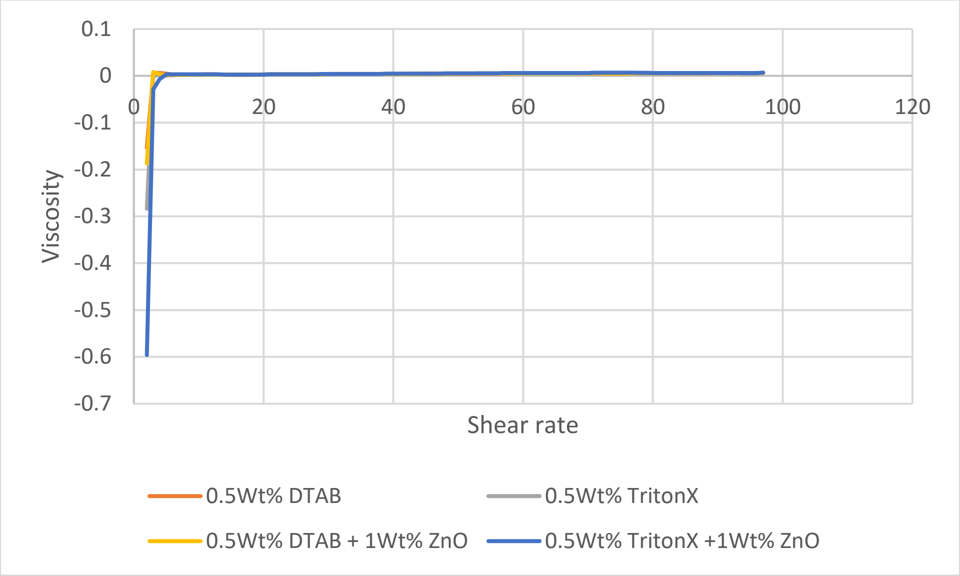
0.5Wt% DTAB
0.5Wt% TritonX
0.5Wt% DTAB + 1Wt% ZnO
0.5Wt% TritonX +1Wt% ZnO



0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Viscosity
0
20
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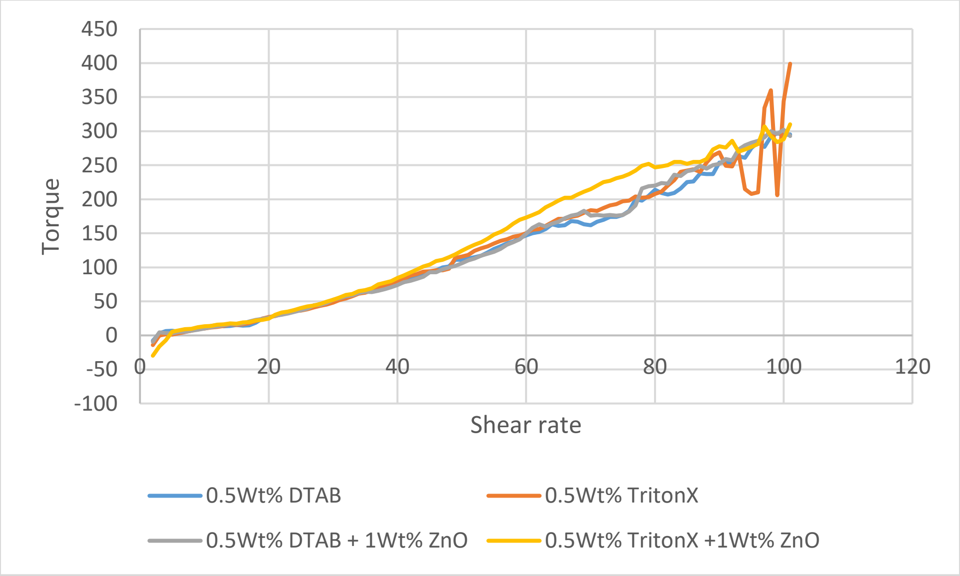
60
80
100
120
Shear rate
0.5Wt% DTAB
0.5Wt% TritonX
0.5Wt% DTAB + 1Wt% ZnO
0.5Wt% TritonX +1Wt% ZnO



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-100
Torque
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80
100
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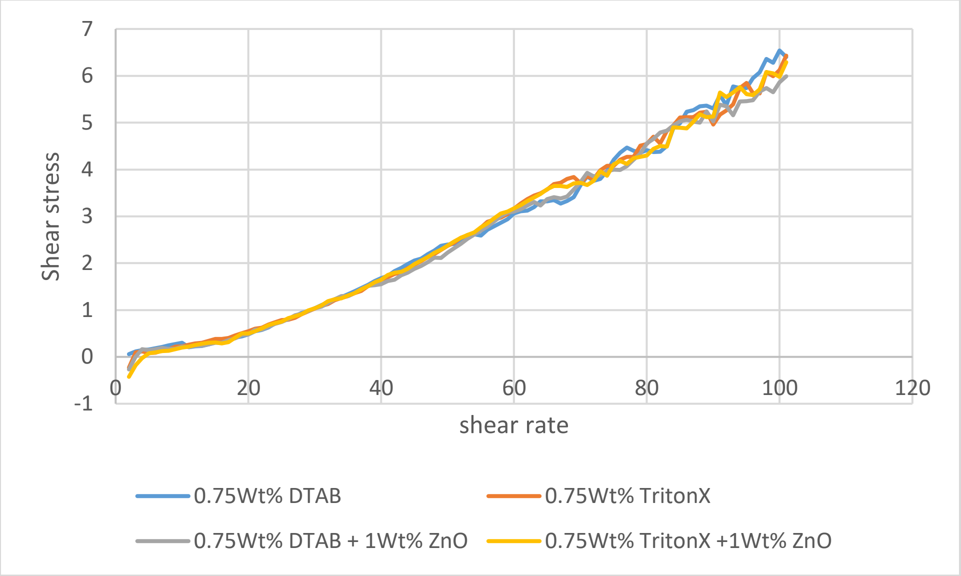
Shear rate
0.5Wt% DTAB
0.5Wt% TritonX
0.5Wt% DTAB + 1Wt% ZnO
0.5Wt% TritonX +1Wt% ZnO


7
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4
3
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Shear stress
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80
100
120
shear rate
0.75Wt% DTAB
0.75Wt% TritonX
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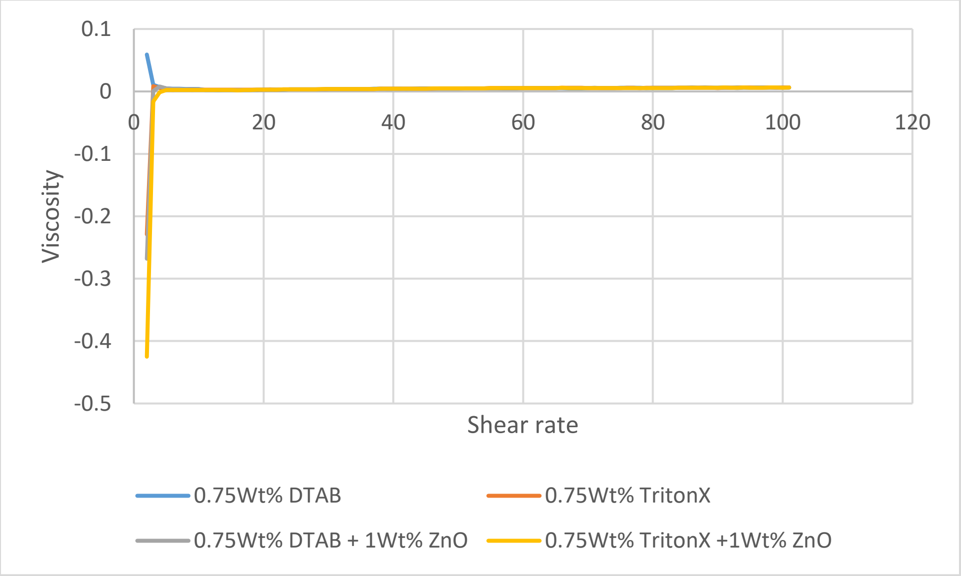
0.75Wt% TritonX +1Wt% ZnO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Viscosity
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Shear rate
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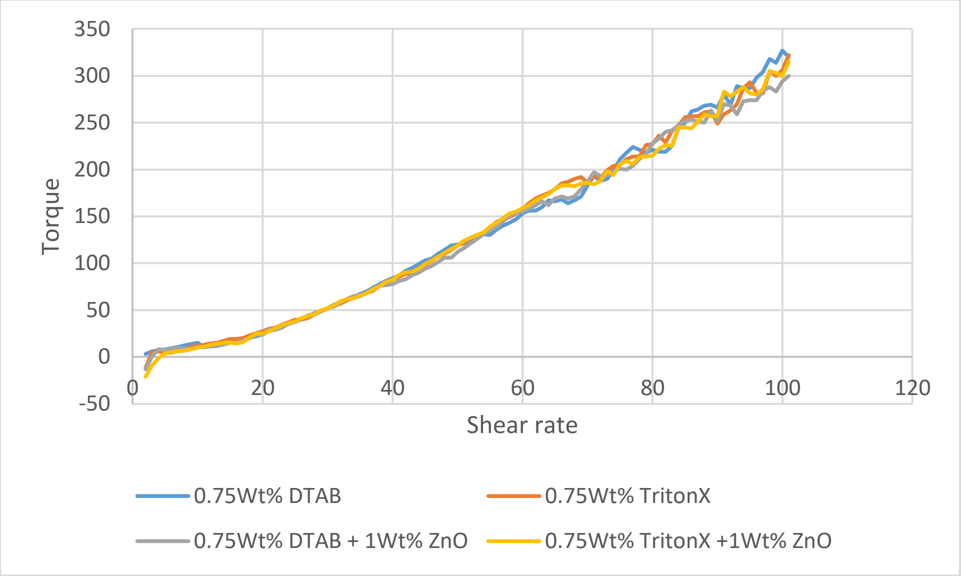
0.75Wt% TritonX
0.75Wt% DTAB + 1Wt% ZnO
0.75Wt% TritonX +1Wt% ZnO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Shear rate
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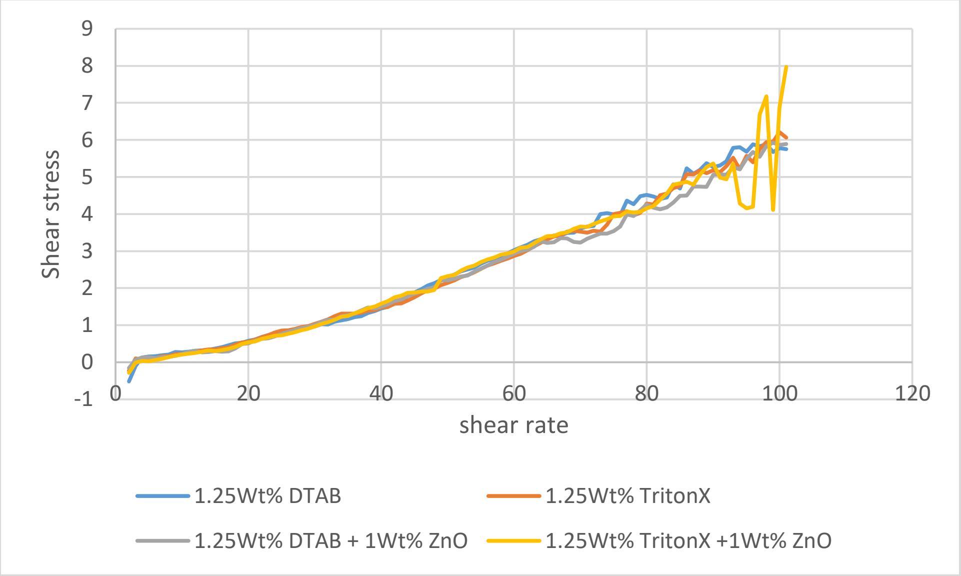
0.75Wt% TritonX
0.75Wt% DTAB + 1Wt% ZnO
0.75Wt% TritonX +1Wt% ZnO


Shear stress
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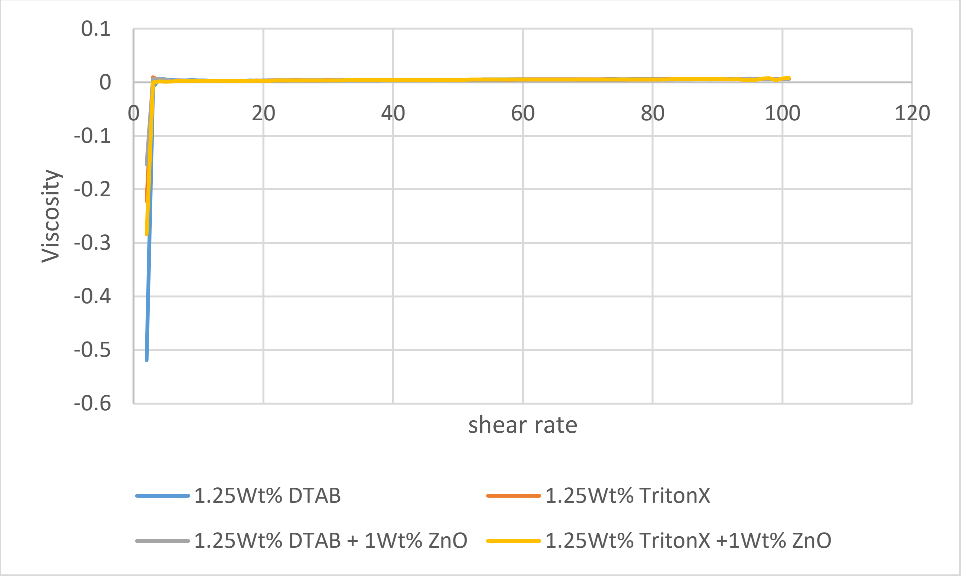
80
100
120
shear rate
1.25Wt% DTAB
1.25Wt% TritonX
1.25Wt% DTAB + 1Wt% ZnO
1.25Wt% TritonX +1Wt% ZnO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-0.5
-0.6
Viscosity
0
20
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80
100
120
shear rate
1.25Wt% DTAB
1.25Wt% TritonX
1.25Wt% DTAB + 1Wt% ZnO
1.25Wt% TritonX +1Wt% ZnO


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Torque
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shear rate
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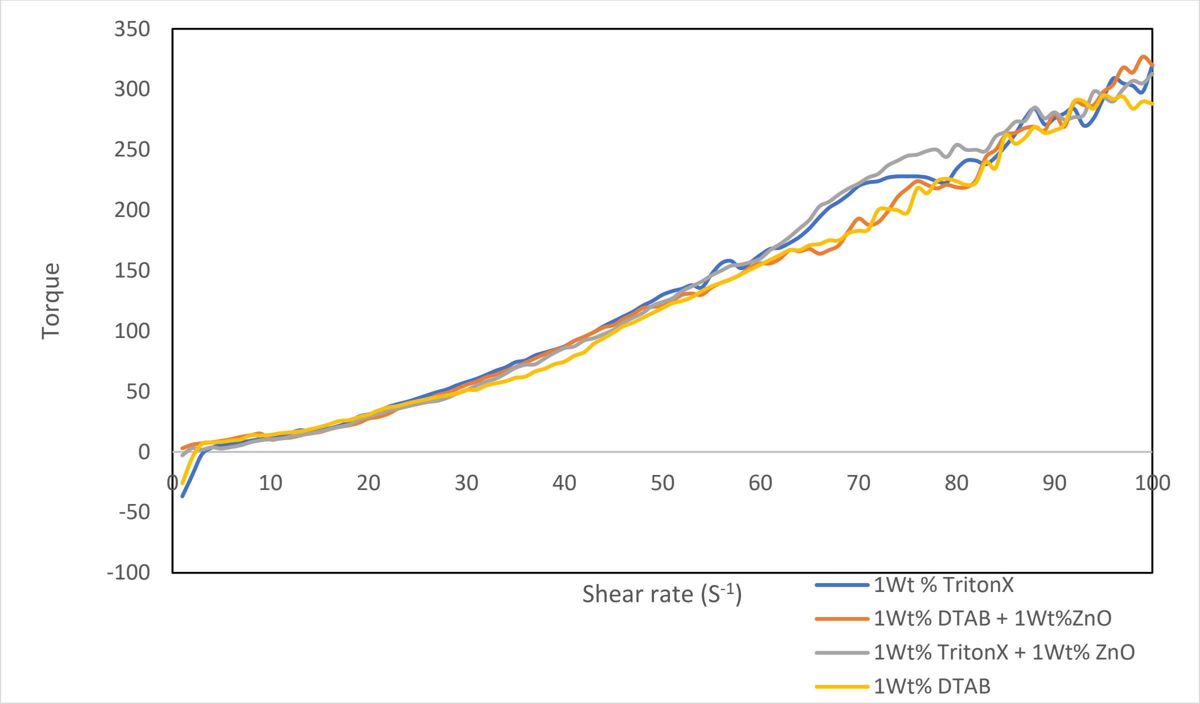
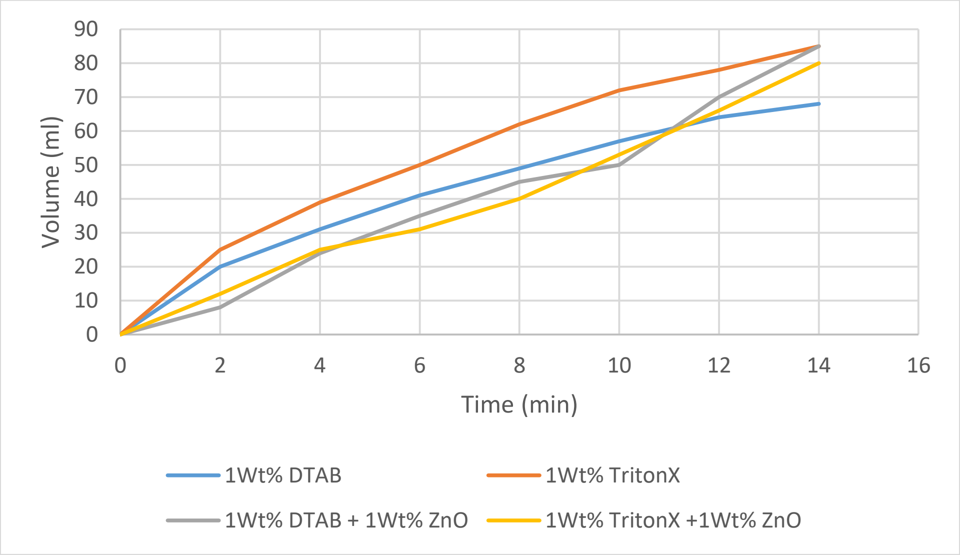
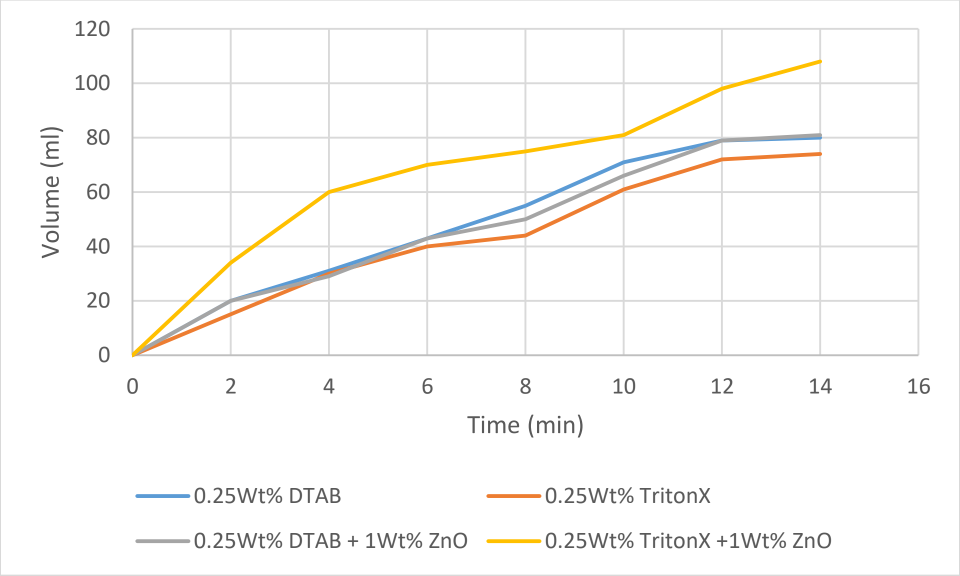
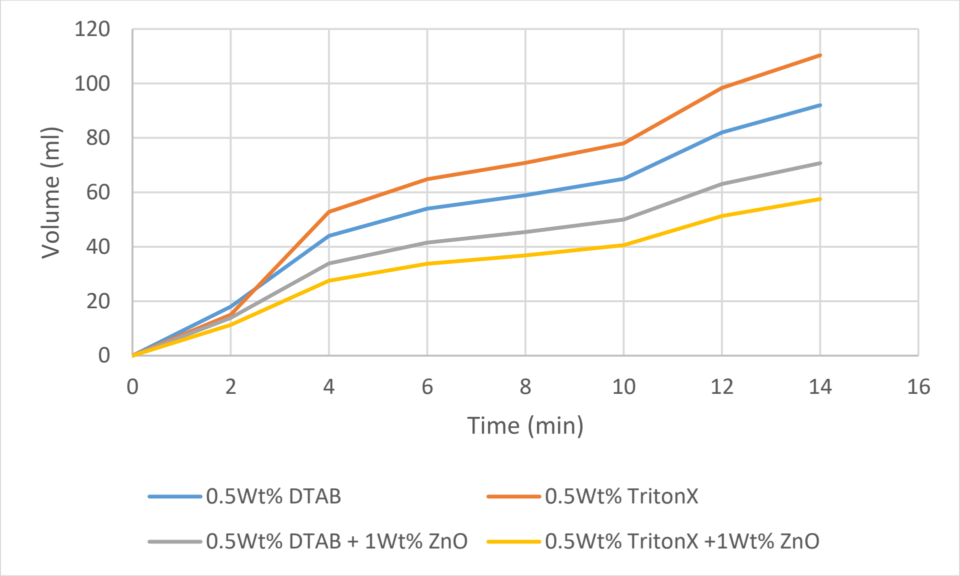
1.25Wt% TritonX
1.25Wt% DTAB + 1Wt% ZnO
1.25Wt% TritonX +1Wt% ZnO

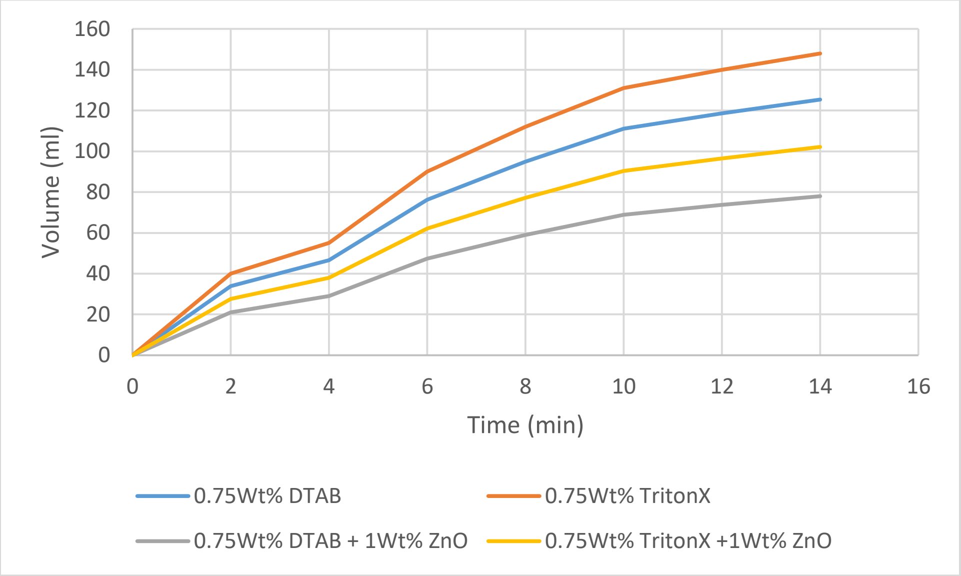


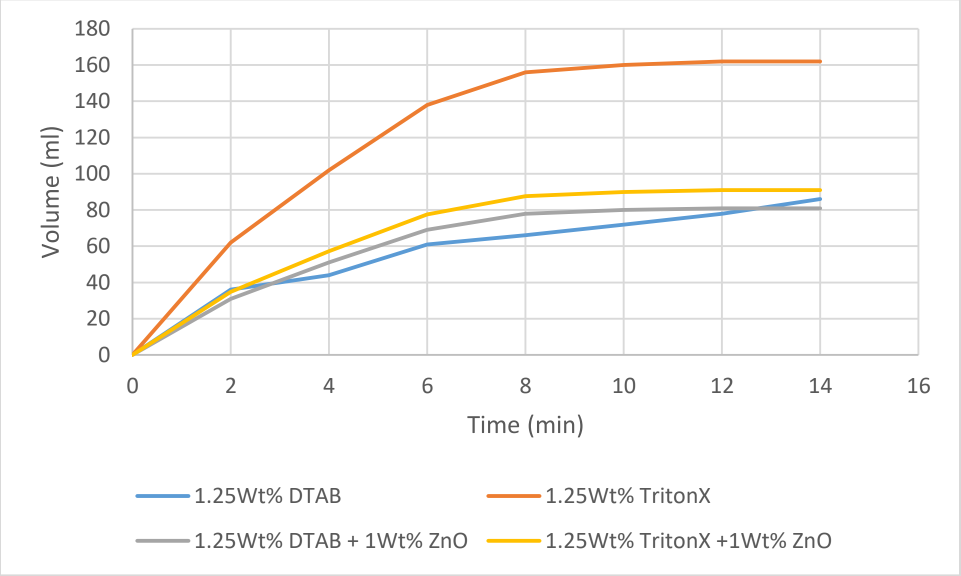
APPENDIX B: (FEED LOSS)




Volume (ml)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
Time (min)
0.25Wt% DTAB
0.25Wt% TritonX
0.25Wt% DTAB + 1Wt% ZnO
0.25Wt% TritonX +1Wt% ZnO


Volume (ml)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
Time (min)
0.5Wt% DTAB
0.5Wt% TritonX
0.5Wt% DTAB + 1Wt% ZnO
0.5Wt% TritonX +1Wt% ZnO





APPENDIX C: (FLUIDS LOSS AND GEL STRENGH)

Measurement(%wt)	DTAB(0.25)	DTAB(0.5)	DTAB(0.75)	DTAB(1)	DTAB(1.25)
Filtrate loss (mL)	71	65	111	57	72

Measurement(%wt)	**triton(0.25)**	**triton(0.5)**	**Triton(0.75)**	**triton(1)**	**triton(1.25)**
Filtrate loss (mL)	72	78	131	66	160

Measurement(%wt)	**DTAB + ZnO (0.25)**	**DTAB + ZnO (0.5)**	**DTAB + ZnO (0.75)**	**DTAB + ZnO (1)**	**DTAB + ZnO (1.25)**
Filtrate loss (mL)	66	54	69	53	80

Measurement(%wt)	**Triton + ZnO (0.25)**	**Triton + ZnO (0.5)**	**Triton + ZnO (0.75)**	**Triton + ZnO (1)**	**Triton + ZnO (1.25)**
Filtrate loss (mL)	81	58	90	53	90

Measurement(1%wt)	**DTAB**	**Triton**	**DTAB + ZnO**	**Triton + ZnO**
Filtrate loss (mL)	57	66	53	53

Gel strength				
	Gel 10sec		Gel 10min	
	crude oil	mineral oil	crude oil	mineral oil
CNCs 0.8	0.4	0.3	2.5	2.4
CNCs 1	0.7	0.5	4.7	4.7
CNCs 1.2	1.2	0.9	7.2	7