Faculty of Engineering and Science

WASM: Minerals, Energy and Chemical Engineering

Improving Rheological and Filtration Properties of Water Based Drilling Fluid using Palm Derived Methyl Ester Sulphonate Surfactant and Waste Polystyrene Nanoparticle

Luke Kennedy Sia Si Lung

This thesis is presented for the Degree of

Master of Philosophy (Chemical Engineering)

of

Curtin University

November 2018

DECLARATION

To the best of my knowledge and belief, this report contains no materials that was previously publish by any other person except where due acknowledgement has been made. This report contains no materials which has been accepted for the award of any other degree or diploma in any other university.

Signature :

Name : Luke Kennedy Sia Si Lung

Date : 1 November 2018

ACKNOWLEDGEMENT

I would like to thank Mr. Henry Elochukwu and the thesis committee for their guidance during this study in the past 19 months. It is a privilege to be under their supervision.

I wish to extend my special appreciation to the Higher Degree by Research Department at the Curtin University, Malaysia for conducting the writing skills workshops and other trainings which helped me to improve my report writing skills.

I also gratefully acknowledge the Faculty of Engineering and Science of Curtin University, Malaysia for their financial support and the Fundamental Research Grant Scheme by the Malaysian's Ministry of Higher Education for funding this research.

ABSTRACT

In drilling operations, the drilling fluids are the main components that cools down the bit, clean the borehole and prevents the wellbore failure by exerting the overbalanced pressure on the wellbore walls. Therefore, a successful drilling operation requires a suitable selection of the mud in terms of rheological properties for circulation and filtration control. Polymers are often used because of their viscosifying properties and molecular size which allow them to act as an encapsulation and reduces the fluid loss from the permeable formation. However, polymers are sensitive to temperature and are degraded during drilling under high pressure and high temperature (HPHT) conditions.

This study focusses on the design of a new water-based mud using polymers, surfactants and polystyrene at different scales. Methyl ester sulphonate, polyanionic cellulose and xanthan gum were also used as part of this study for comparison purposes. Methyl ester sulphonate is an anionic and biodegradable surfactant which is known as the Green Surfactant.

The optimum formulation of the water-based drilling fluid was chosen based on a series of rheological and filtration control tests. The optimized drilling fluid formation were then viewed under the scanning electron microscope to evaluate the nano-pores plugged by the polystyrene nanoparticles. The results obtained showed that the optimized drilling fluid formulation adding the additives of nanopolystyrene as the nanopartlces, polyanionic cellulose as the polymer and methyl ester sulphonate as the surfactant proved to be the better option in the formulation of the water based muds. Specifically the presence of the nanopolystyrene has shown to significantly improved in the rheological behaviors of the drilling fluid. Moreover, it has been indicated that with this drilling fluid formulation, reduces the thickness of the mud cake by and as a result, reducing the filtration loss by 51% and 61% at LPLT and HPHT conditions respectively compared to the base fluid. The results obtained indicated that the rheological properties were improved by the nanomodification proposed. In fact, the plastic viscosity increased from 8 cP to 21 cP while the yield point reached 15 Pa from its initial unfavorable value of 2 Pa.

Table of Contents

CHAPTER ONE - INTRODUCTION

CHAPTER TWO – LITERATURE REVIEW

CHAPTER THREE – METHODOLOGY

CHAPTER FOUR – RESULTS AND DISCUSSIONS

CHAPTER FIVE – CONCLUSIONS AND FUTURE WORKS

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

1.1 Introduction

Fossil fuels are the primary sources of energy in the world that allow us to carry out our daily activities. Oil contributes to at least 31% of total primary energy supply, whereas methane gas, coal, nuclear and sum of all renewable energies contribute 21%, 29%, 4.8% and 10.6% respectively (Aftab et al., 2016). The expertise had also projected that the world's energy demand will continue to grow and will be fulfilled primarily by fossil fuels through 2040 (Aftab et al., 2017). Therefore, the most possible way to overcome the fossil fuels energy crisis is to explore and drill more oil and gas wells by 2020 (Hossain and Al-Majed, 2015). However, the exploration conventional oil and gas reservoirs are exponentially depleting which drives us to drill unconventional reservoirs which are located under high pressure high temperature (HPHT) downhole conditions. The drilling fluid plays a significant role in the drilling operations in the oil and gas industry (Kutlu, 2013). There are generally two types of drilling fluid which are generally known as water-based mud (WBM) and oil-based mud (OBM). However, due to the environmental and operational concerns, researches have been focused on improving the performances of the environmentally friendly WBM (Sadeghalvaad and Sabbaghi, 2015).

WBM is considered as the most inexpensive, widely and environmentally friendly mud (Tehrani et al., 2009). There are various WBM such as fresh water, deionized water, salt water, dispersed mud or non-dispersed mud. The deionized water, which is conventionally used for the mud design, has a lower density and a lower viscosity when compared to other base fluids (Fink, 2015). To resolve these issues, certain additives such as bentonite, barite, surfactant and polymers are employed. These additives alters the density, the rheological properties and the fluid loss properties of the drilling fluid (Nareh'ei et al., 2012).

The primary functions of the drilling fluid are to clean the wellbore, transport the cuttings from the subsurface to the surface, cooling and lubricating the drill bit, maintaining the wellbore stability, controlling the formation pressure and forming a thin and impermeable filter cake around the permeable formations (Sehly et al., 2015). The impermeable filter cake is the one preventing formation damage due to the filtrate invasion that can adversely block the producing channels, thereby reducing the production of oil and gas from the reservoir. Therefore, the formulation of drilling fluids for the appropriate well is crucial for a better production from the oil and gas reservoirs. Furthermore, if the mud cannot perform well in the way that is designed for it, severe drilling problems such as fluid loss, borehole instability, high torque and drag, stuck pipe and partial or total loss of wells may occur (Yarim et al., 2007). If any of these problems occur, a huge financial loss can be experienced due to the loss of additives used to design the mud and induction of non-productive time. These problems will be often more severe in deep water wells and HPHT conditions where deterioration of fluid properties will be induced even faster and in a larger scale.

Polymers have shown a broad application in the oil and gas industry, especially in the drilling operations (Yan et al., 2013). The formulation of drilling fluid with polymers can improve the rheological properties and lubricity (Kania et al., 2015). They can also improve the filtration control of the mud (Chu et al., 2013). However, polymers are often sensitive to extreme thermal conditions and their functionality may significantly changes under HPHT condition. According to (Amanullah et al., 2011), polymers are not stable at high temperature to perform essential operational drilling operations tasks in HPHT conditions. This is mainly because polymers do not have the appropriate thermal, mechanical, chemical and physical stability when temperature goes above certain thresholds (Rodrigues et al., 2006). Some of the common polymers used in the WBM for the improvement of the rheological properties and the filtration loss include carboxymethyl methyl cellulose (CMC), polyanionic cellulose and xanthan gum. These polymers are expensive and cannot be used under the HPHT condition. Therefore, the industry is searching for a new formulation of the mud that can perform well its basics functionality under HPHT conditions and in the meantime can be environmentally friendly and thermally stable.

1.2 Problem Statement

Temperature and pH of the drilling fluid are a major factor that control the functionality of additives including the surfactant and the polymer. As the depth of the well increases, the pressure and the temperature increase according to the geothermal gradient. Thus, HPHT conditions are capable of altering the chemical structure of the additives used to design the WBM (Babatunde et al., 2011). Generally, most of the polymers are sensitive to the temperature above 150^0C and their molecular bonding will be will be deteriorated which is also known as thermal degradation. Polymers are also sensitive to divalent cations such as calcium and magnesium which are often found in the WBMs. Thus, if they get degraded during drilling, the WBM may lose its functionality and severe instability issue may occur. Having said that, MES plays an important in the oil and gas industry where it was shown that it can improve the rheological and the filtration properties of WBMs. However, due to the repulsion forces caused by the electronegativity of MES, the electrostatic forces between the particles in the drilling fluid are often reduced (Faizal Wong et al., 2017).

With the recent development in the nanoparticle technology, a number of studies have evaluated the possibilities of incorporating the nanoparticles in modifying the properties of the drilling fluid in the oil and gas industry (Abduo et al., 2016). The nanoparticles have a high surface area to volume ratio which improves the surface dependent materials properties (Behari, 2010). With this, this initiated the use of nanoparticles in improving the thermal conductivity of the base fluid and it was observed that the addition of the nanoparticles had a positive effect on the rheological properties of the drilling fluid (Agarwal et al., 2013). In addition to the benefit of the rheological properties, the nanoparticles had also significantly improved the filtration property of the drilling whereby the fluid loss is control within the acceptable range and this inhibits the wellbore instabilities. This is due to the pore throat sizes of 100 to 10,000 nm and only nanoparticles with the smaller size distribution would have the possibilities of the plugging the pore throats in the formations (Donnelly, 2010).

Therefore, in this study we used nanopolystyrene and methyl ethyl ester surfactant to formulate the water based drilling fluid. The rheological and filtration loss properties haven been invested with the addition of the additives above in varying concentration.

1.3 Objectives

The main objectives of this study are as follows:

- To formulate a new WBM using a combination of polymers, palm derived methyl ester sulphonate and nano polystyrene to reduce fluid in HPHT wells.
- To investigate the effect of polymers, palm derived methyl ester sulphonate and polystyrene nanoparticles on the rheology and filtration control of water-based drilling fluids.
- To validate the rheological properties using the Bingham Plastic and Power Law model and filtration loss properties by using the calculated permeability and filter paper under scanning electron microscope.

1.4 Scope of Study

The scope of this research revolves around the rheological properties and filtration loss of WBMs once polymers, surfactants and polystyrene are used. In fact, attempts are made to see how theses additives can be mixed with the mud in the presence of clay to resolve the issues of fluid loss under HPHT conditions. To do this, a series of experiments will be conducted as part of this research according to the American Petroleum Institute (API) standards. The rheological and filtration loss characteristics of the WBMs modified by these additives will, therefore, be measured and attempts will be made to propose the best formulated mud for being considered for drilling through deep formations and HPHT conditions (i.e., temperature and pressure of 100^{o}C and 500 psi respectively).

1.5 Thesis Organization

In Chapter 1 explains on the introductory functionality of the drilling fluid and the different types of drilling fluids such as the water based drilling fluid and the oil based drilling fluid and its impact on using either one of them (Sadeghalvaad and Sabbaghi, 2015). In Chapter 2 is a comprehensive literature review on the recent development of the additives added into the water based drilling fluid on evaluating the optimum concentration and type of additives used to enhance the rheological and filtration properties. In Chapter 3 are the detail of the experimental setup and the specific procedures taken following the American Petroleum Institute (API) standards. In Chapter 4, are the detail discussions on the experimental results of the rheological and filtration properties of the variation additive added to formulate the optimized water based drilling fluid. In Chapter 5 are the main conclusions of this study and recommendations that could be done on the formulated water based drilling fluid.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, attempts are made to review many of the studies carried out in the past where polymers, surfactants, nanoparticles and other additives were used to improve the rheological and filtration control properties of water-based drilling fluids. The important role of density should not also be ignored as it helps to maintain the borehole stability and prevent any kick from happening. An ideal drilling mud should also be able to produce a thin and impermeable layer of mud cake around the formations, protecting them from the influx of drilling fluid and mud invasion. These important characteristics are considered in this chapter when recent studies are reviewed for their proposed WBMs formulations protecting them from the influx of drilling fluid and mud invasion.

2.2 Rheological modeling

Rheology is referred to as the study of deformation induced in the materials with the ability to flow because of shear stresses. This stress can be cause changes in the shape or the size of the materials and can be applied externally and internally. During the drilling operation, the shear stress and its rate are the parameters defining the rheological behavior of the drilling fluid (Lu et al., 2017). The shear rate is described as the rate of deformation induced in the drilling fluid once it is gone into circulation around the annulus space. On the other hand, according to (Sundstrom and Cervantes, 2017), the shear stress is the measure of internal forces acting within the distorted body. Having the shear stress and rate obtained, the rheological properties of the drilling fluid such as viscosity can be calculated to ensure that the mud can easily circulate in the borehole without inducing any instability issues.

The drilling fluids generally tend to have a non-Newtonian fluid properties due to the non-linearity of relationship between the shear stress and shear rate (González et al., 2011). Moreover, the viscosity of the drilling mud is not only a function of changes in the pressure and temperature of the wellbore but also has a strong relationship with the velocity at which the mud flows in the borehole. Therefore, the rheology of the mud is one of the most important parameter that must be measured and monitored carefully to have a safe drilling (Hassani and Ghazanfari, 2017). In section 2.2.1, 2.2.2, and 2.2.3, the approaches commonly used in the industry to measure the rheological parameters of the drilling fluid using the API Specification 13A 18th Edition, February 2010, are explained and discussed in detail.

2.2.1 Bingham Plastic Model

Bingham Plastic model is one of the most widely used rheological models in the oil and gas industry due to its linear nature and proven applications. This model is addressed by Eq. (2.1), where the slope represents the plastic viscosity, μ_p, and the intercept gives the yield (point) stress giving the amount of shear stress required to start mud circulation.

$$\tau = \mu_p \dot{\gamma} + \tau_0 \tag{2.1}$$

2.2.2 Power Law Model

Power Law model is used to determine the rheological parameters of the drilling fluids which does not have a significant yield point and any amount of shear stress progressively decreases the viscosity. This model is also often used in the oil and gas industry and is expressed as Eq. (2.2).

$$\tau = K\dot{\gamma}n \tag{2.2}$$

Parameters n and K in the above equation can be determined using Eq. (2.3) and (2.4).

$$n = 0.5\frac{log(\theta_{300})}{\theta_3} \tag{2.3}$$

$$K = \frac{5.11\times\theta_{300}}{511^n} \tag{2.4}$$

It should be noted that the parameter n indicates the degree of the non-Newtonian character of a fluid over a defined shear rate range. This parameter is equal to 1 for the Newtonian fluid and as it decreases, the fluid becomes more pseudoplastic or shear thinner. Reducing the value of n improves the hole cleaning performance due to the increase of the annular viscosity and flattening of the annular velocity (Sayindla et al., 2017). The parameter n is dependent on the type of the viscosifier used to formulate the drilling fluid. Parameter K, on the other hand, is known as the consistency index which is directly linked to the viscosity of the fluid at a low shear rate. As K increases, the effectiveness of the annular viscosity increases and the hole cleaning capacity of the drilling mud enhances.

2.2.3 Filtration Control

The filtration control is to prevent the formation fluid from entering the borehole by maintaining the hydrostatic pressure greater than the formation fluid pressure. The solids of the mud are filtered out onto the wall of the borehole, which forms the filter cake of relatively low permeability. In addition to that the filtrate loss additives are added to the drilling fluid to form an impermeable and thin filter cake to avoid the filtrate loss. The filtration loss properties are usually evaluated and control by the API filter loss tests, which is a static test where the mud is not being circulated and the filter cake is undisturbed. However, there is no standard method currently on evaluating the dynamic filtration.

In the next section, attempts are made to evaluate the efficiency of different WBMs formulated with different additives. Density, rheology and filtration control of the mud are the criteria used to compare the application of these mud designs.

2.3 Water Based Drilling Fluids

In this section, recent studies of different additives including polymers, surfactants, carbon-based nanoparticles and metal oxides nanoparticles which are often used to formulate water-based mud for a better rheology and filtration control are reviewed and their optimum concentration are discussed in more details.

2.3.1 Recent studies on water based mud with surfactants and polymers

Surfactants are commonly used in the oil and gas industry as a friction reducer and rheological changer of the water based drilling fluid (González et al., 2011). There are three main types of surfactants which include non-ionic, anionic and cationic. Many researchers compared the performance of water-based drilling fluid once different types of surfactants were added to them. According to (Yunita et al., 2016), a drilling fluid with surfactant is able to effectively reduce the filtration loss up to 41.3%. Surfactants cause the water-based drilling fluid to have a higher thermal stability with a better rheological and filtration control properties. In their study, they prepared different types of drilling fluids with no surfactant, non-ionic surfactant and anionic surfactant. The non-ionic surfactant used was 2-hexadecyloxyethonol whilst the anionic surfactant was called alkyl benzene sulphonate. The results obtained indicated that the drilling fluid with the surfactants has a higher plastic viscosity as the temperature rises. This could be due to the creation of a long molecular chain by surfactants which increases the plastic viscosity. However, the controlled drilling fluid, which was the one without any surfactants, had a lower plastic viscosity as the temperature increased. This was because mainly due to the breakdown of polymer which decreases the plastic viscosity. The yield point and gel strength measured after 10 sec and 10 min revealed an increase once the surfactants added. Filter cakes with the surfactant were more compact and thinner compared to the drilling fluid without them which might because surfactants are able to decrease the interfacial tension allowing a better dispersion of the molecules for a more homogenous structure in the mud cake (El-Sukkary et al., 2014). However, it was appeared that the anionic surfactant performs better than the non-ionic surfactant when it comes to the filtration loss under LPLT and HPHT condition.

A mixture of an anionic and cationic surfactants was used by (Yingcheng et al., 2016) in their study on the WBMs. They used nonylphenyl ethoxylate carboxylate as the anionic surfactant and quaternary ammonium salt as the cationic surfactant. This combination of surfactants could lead to an electrostatic attraction between the oppositely charged surfactant head groups and the intermolecular attraction between the hydrophobic of hydrocarbon chains which induces a new microstructure in the rod-like micelles and vesicles (Antón et al., 2008). The results obtained showed that the drilling fluid is only able to withstand the temperature of up to 76.5°C which was not even close to the temperatures of HPHT condition which is above 100°C. (González et al., 2011) did a series of experiment where the water drilling fluid was formulated by a mixture of anionic/non-ionic surfactant with two different weighting materials of calcium carbonate and hematite. It was found that in the presence of a surfactant, the zeta potential of the calcium carbonate and hematite-based solutions changes from -23.2 to -99mV and from -25.9 to 62.5mV respectively. They concluded that addition of surfactants has a positive effect on the stability of the colloidal dispersions in the drilling fluid.

Another type of surfactant would be Methyl Ester Sulphonate (MES), which is an anionic surfactant with a very high biodegradable property. MES is used in applications in the oil and gas industry due to its low cost of production. It is also used as a demulsifier, anti-sludging or dispersing. Welton et al., (2007) plotted a graph of viscosity vs temperature for a mixture of 5% MES and 10% NaCl, and showed that as the temperature increases, the viscosity increases. However, when the temperature is raised above the optimum point, the viscosity decreases due to the temperature of the fluid. Therefore, it would be required to use some other additives to withstand improve the drilling performance under high temperature and high salinity conditions.

In conclusion, it was appeared that neither surfactant nor polymer are able to withstand high temperature or high salinity conditions. In addition, biopolymers and surfactants can only seal the micro pore spaces of preamble formations (Zakaria et al., 2012). Thus, (Srivatsa and Ziaja, 2012) suggested a combination of polymers and surfactant to be used with nanoparticles to design the water based drilling fluid. This design might be able to sustain a higher temperature and reduces the fluid loss but such fluids with nanoparticles are not easy to prepare. This will be further discussed in the next section.

2.3.2 Recent studies of metal oxide based nanoparticles

Nano Silica is the commonly used nanoparticle in the oil and gas industry when formulating the water-based drilling fluids. They were firstly implemented in the water based drilling fluid by (Sensoy et al., 2009) which was used to reduce the invasion of water into the clay rich carbonate formation. (Ghanbari and Naderifar, 2016) reviewed the optimization of the size of nano silica when designing the water-based drilling fluids. They used coated nano silica and adjusted the binomial size distribution to 25 nm and 115 nm. The rock sample used to test the experiment was a clay rich carbonate formation with the pore throat of 16 to 61 nm. Different nanoparticle based WBMs were prepared with the mass ratio of 0.25, 0.5, and 0.75 at 10 wt%. It was then found that 0.75 wt% is the optimum ratio to have the best fluid loss control. However, nanoparticles with the size of 25 nm showed much superior results compared to the other size chosen. This could be because they were better in plugging the nano pore spaces in the rock samples as it was a lot easier to disperse them into the mud samples. It was eventually concluded that larger nanoparticles are able to agglomerate and plug the large micro pores whilst the smaller once can plug the nanopores. This supports the theory that nano silica can be a good choice to plug the nano- and micro-fractures in the rock sample if they can be properly dispersed in the WBMs.

In a similar study, nano silica was used to reduce the pore pressure transmission in shale formation (Cai et al., 2012). It was found that 10 wt% nano silica with the sizes of 7 to 15 nm can provide a very good plugging performance. However, although many studies suggested that the smaller the size of the nanoparticles, the more favorable it would be to plug the pore spaces, it seem that very small nanoparticles may not be a great choice always. In fact, when the nanoparticles are too small, they are not able to plug the pore spaces of different formations.

(Elochukwu et al., 2017) run a series of experiment to compare the performance of unmodified and modified nano silica once added to WBMs to improve the filtration control. They modified nanosilica by adding a cationic surfactant and were able to reduce the steric repulsion between the nanosilica and bentonite. As a result, they could increase the yield point by inducing attraction between the positively charged nanosilica and the negatively charged bentonite particles via face to face and edge to face interaction. They tested their mud design for the LPLT and HPHT filtration tests and successfully reduce the filtration loss by as much as -38.9%.

(Vryzas et al., 2015) compared the performance of nanosilica and iron oxide nanoparticles once added to the water-based drilling fluid. They found that the iron oxide gave a better result in terms of rheology and filtrate volume compared to the nanosilica. From the zeta potential measurement results, it was observed that the iron oxides are within the stable region in terms of surface charges and can be easily aligned to create a good bond with other additives of the WBM. Under the HPHT test condition, the iron oxide nanoparticles were able to reduce the filtrate volume by 42.5% which was comparatively much better than that of the nano silica based WBMs which was only 13.0%. Under the SEM micrographs, it was clearly observed that iron oxide nanoparticles have a lesser agglomeration capability compared to nanosilica which would induce a good microstructure with bentonite.

2.3.3 Recent studies on the addition of polymers and surfactants with nanoparticles

In the previous section, it was shown nano particles are able to improve the filtration control of the water-based drilling fluids. However, adding nanoparticles into the drilling fluid may unfavorably chances in the rheology such as reduction in the yield point (Jain and Mahto, 2015). As such, there have been few attempts to improve the results of adding nano particles into the WBMs using other additives such as surfactants and polymers. It should be noted that WBMs must basically have bentonite in their formulation which has a negative surface charge due to substitution of low valence in its lattice structure (Missana and Adell, 2000). The stability of the bentonite particles in the drilling fluid is highly affected by the colloidal suspension and they often aggregate and flocculate in in a HPHT environment resulting in decreasing the yield point of the drilling muds and the fluid control capacity. Thus, once of the best methods to improve the stability of the solutions is to modify the surface charge of bentonite and prevent it from generation of a repulsive force once nano particles are added (Bhagat et al., 2008).

Many of the biopolymers used in the drilling fluid are derived from xanthan gum. The molecular structure of xanthan gum is shown in Figure 2.1. The xanthan gum is a non-ionic biopolymer and has a high molecular weight polysaccharide acting as a viscosifier at a low concentration. The molecule of the xanthan gum conforms is in the form of a simple, double or triple helix which interacts with other molecules to form a complex network. Scleroglucan is another well-known biopolymer which is a fungal polysaccharide. The molecular structure of the Scleroglucan is shown in Figure 2.2. The Scleroglucan is a readily water-soluble biopolymer produced through the fermentation of carbohydrates induced by a fungus. It has a triple helical conformation, which are described as rigid rods giving an excellent cutting carrying capacity to WBMs (Biovis, 2003). These two biopolymers were considered as a viscosifier and fluid-loss additives in the study carried out by (Baba Hamed and Belhadri, 2009). They also had other additives included in their mud including potassium chloride (KCl) for inhibiting shale swelling and dispersion. The results obtained indicated that the drilling fluid with xanthan gum and Scleroglucan exhibit a non-Newtonian behavior. The rheology of the mud was also more consistent in the presence of Scleroglucan once the concentration of KCl increases. This is because Scleroglucan is a non-ionic polymer and is compatible with different types of brine containing monovalent or divalent cations. Xanthan gum, on the other hand, is an anionic polymer and chemically incompatible with brines containing monovalent or divalent ions. The length of the xanthan gum polymer also decreases when salt is added and the macromolecules transform into a more coiled conformation which leads to denaturing (Camesano and Wilkinson, 2001). However, Scleroglucan increases the yield stress much higher than to xanthan gum due to its strong interaction with the brine. In drilling operations, a lower yield stress is often regarded as a better criterion which would ease the drilling fluid circulation in the wellbore. It could then be concluded that Scleroglucan is more effective in the presence of salt compared to xanthan gum but xanthan gum would be a better choice in drilling operation when pH is above 12.5 due to its anionic nature.

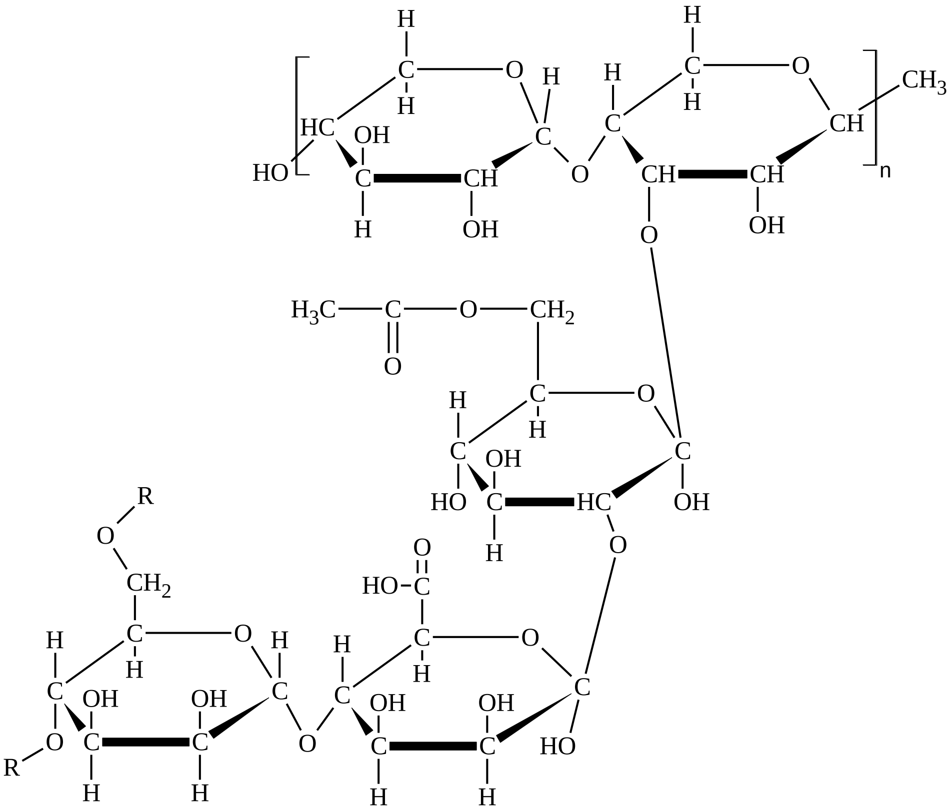


Figure 2.1: Molecular structure of xanthan gum (Rahdar and Almasi-Kashi, 2016)

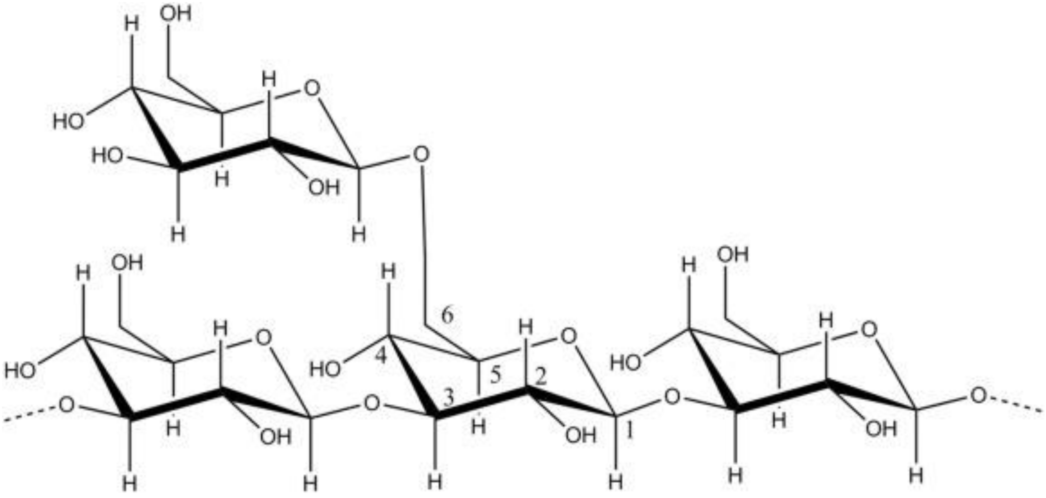


Figure 2.2: Molecular structure of Scleroglucan (Mansa et al., 2016)

Another polymer that is mainly used in the industry is the polyacrylamide to maintain the viscosity in solid free drilling fluid due to its high water-soluble polymer, which is primarily used as an inhibitor by coating or encapsulating formation and cuttings. Also, it helps increases the viscosity of the drilling fluid which helps in better removal of the cuttings in the borehole (Ahmad et al., 2018). Thus, this maintains the borehole stability by preventing wells such as shale from eroding and swelling. (Jain and Mahto, 2015) had recently synthesized a polyacrylamide nanocomposite with clay (PANC) showed to be superior shale encapsulation property than partially hydrolyzed polyacrylamide (PHPA). The nanoclays are nanoparticles which are made up of layered mineral silicates which are made up of montmorillonite. This is the most common material for the synthesis of nanocomposite which is mainly used in rheological modification for mud formulation as montmorillonite are useful in increasing the density of the drilling mud (Abdo and Haneef, 2013). The addition of the nanocomposite into the base fluid were varied from 0.3% to 1.0% with the increment of 0.1% each experiment to test the effect on the drilling fluid. The result showed a trend where the rheological properties and the filtration properties improved as the concentration of the nanocomposite increased comparing to the base fluid, where the optimum result was at 0.7% of nanocomposite. The plastic viscosity, yield point and apparent viscosity had all increased up to 177%, 142% and 200% respectively. Although at 1% concentration of the nanocomposite showed much better results, however it was well above the operating condition. The values for the 0.7% PANC concentration rheological properties values of the plastic viscosity, apparent viscosity, yield point and the 10s gel strength were at 25 cP, 42mPa.s, 17 Pa and 4.5Pa respectively. These values of the developed drilling fluid formulation for this experiment were found to be in the acceptable rage for the drilling operation (Ji et al., 2012). This is due to only requiring moderate range of the viscosity is desired for the circulation of the cuttings, low viscosity inside the pipe where the shear rates are high and consequently, slightly higher viscosity in the annulus to lift out the drilled cuttings prevailing to low shear rate conditions (Mahto and Sharma, 2004).

As drilling fluid are non-Newtonian fluid and is desirable to exhibit a shear thinning or pseudoplasticity behavior, and based on (Mahto and Sharma, 2005), the high yield point to plastic viscosity ratio is an indicative of shear thinning of the property which is shown in (Abdo and Haneef, 2013) results of 0.7% and 1% were at 2.47 and 2.41 respectively.

It is evident that the experimental results showed that the 1% had a better result in filtration loss where 0.7% and 1.0% were at 4.0 ml and 2.7 ml respectively. This is due to the increase in concentration of the PANC into the polyacrylamide matrix. Also, with the effect from the rheological properties the viscosity of the mud affected the dispersion of the PANC and this decreases the diffusion of the filtrate through the porous shale medium. (Kosynkin et al., 2012) stated the acceptable range for the fluid loss volume of the drilling fluid is between 2.8 ml to 9.8 ml for concentration of 0.4 – 0.8% nanocomposite. Therefore, this justifies that the 0.7% is the optimum concentration for the drilling fluid formulation as this concentration takes into account of both the rheological and filtration properties during drilling operation where the drilling fluid has a high viscosity and a minimum filtrate volume for a better inhibition efficiency (Khodja et al., 2010).

Another recent study was made on the polyacrylamide where (Sadeghalvaad and Sabbaghi, 2015) had synthesized a nanoparticles using titanium dioxide (TiO_2) with polyacrylamide (PAM) where the nanoparticles were dispersed by ultra-sonification in distilled water to create a homogenous dispersion in the mixture. Then polymerized solution was added into a glass reactor equipped with a condenser and a mechanical stirrer in a water bath that was conditioned to nitrogen atmosphere to obtain the nanocomposite to be dried at room temperature. The preparation of the nano-enhanced water based mud samples were prepared by adding the synthesized TiO_2/PAM nanocomposite first into 350 mL of distilled water stirred and 10 g of bentonite was then added later on. The concentration of the TiO_2/PAM nanocomposite were varied between 1 – 10 g and 14 g. Based on their results, all of the 11 fluid samples exhibit the shear thinning behavior and the concentration of the TiO_2/PAM nanocomposite showed a steady increase on the plastic viscosity and the yield point. Thus, as the concentration of the TiO_2/PAM was increased, the shear thinning behavior becomes more tangible as the value of the n value decreases and that the value of K goes up, which results in better hole cleaning capacity due to the increase in the annular viscosity (Sayindla et al., 2017).

The concentrations of the TiO_2/PAM nanocomposite between 7 – 9 g showed to be in the range of 20 – 29 cP which are the operating conditions in drilling operations in which the concentration were equivalent to 2.00 wt%, 2.29 wt% and 2.57 wt% respectively. It should be noted that this study was focused on the longevity of the fluid samples and thus the initial results of the rheological and filtration properties were obtained and compared again on the fourth week with one week intervals. Therefore, for concentration below 6 g showed a non-uniform and unstable mixture due to the weakening of the interaction forces between the polymer chain and the bentonite on the fourth week and thus the viscosity measurement was impossible and practically unstable for drilling. The rheological behavior were constant with concentration above 7g, however increasing above 9 g may be detrimental because the plastic viscosity were went above the operating condition and also the longevity of the fluid samples showed a decline with higher concentration of the nanocomposite. The nanocomposite concentration with 14 g showed a decreased of 30% in plastic viscosity whereas 7 – 9 g were able to retained the values and some even improved on the values due to the influence of the TiO_2/PAM nanocomposite. Moreover, the filtration properties showed an improvement too in the fourth week where the fluid loss and the filter cake thickness to about 64%. It was observed that (Sadeghalvaad and Sabbaghi, 2015) DLS measurement experiment that, the particle size distribution were slightly larger on the fourth week with the average size of 79 nm and this was more appropriate than the nanoparticles with the average size of 18 nm due to the better compatibly and interaction with the pore spaces of the filter paper.

Comparing to the study above where (Sadeghalvaad and Sabbaghi, 2015) added the polyacrylamide with the metal oxide of TiO_2, (Aftab et al., 2016) had a different approach of polymerizing the acrylamide (Am) with another type of metal oxide which was zinc oxide (ZnO). It was noted the acrylamide was selected for this study as this polymer provide a better dispersion to the ZnO nanoparticles, as this improved the viscosity, hydrophobicity (Biggs et al., 1992) and the hydrate resistance behavior (Gou et al., 2015) of the drilling fluids. Although there had been some concerns regarding the toxicity and the environmental impact of using metal oxides in the drilling fluid as suggested by (Kim et al., 2014) that ZnO nanoparticles were found to be highly toxic to the environment at a high concentration. In contrast to that statement, (Ryu et al., 2014) and (Wahab et al., 2016) proved that the concentration of ZnO nanoparticles up to 1000 mg/kg body weight showed no toxic behavior and that the environmental aspects of the metal oxides remained to be controversial. However, to ensure that the ZnO nanoparticles are environmentally friendly, the concentration of the nanoparticles must be reduced to an acceptable level. Moreover, the modification of the surface (Aboulaich et al., 2012) and the controlling of the diameter (Zhang et al., 2009) should decrease the toxicity level. From (Aftab et al., 2016) studies, it was noted that the ZnO nanoparticles are cheaper than some of the conventional drilling fluids. The synthesized method on preparing the ZnO-Am nanocomposite was done by the green solvo-hydro thermal technique with concentration varied between 1 – 10 g that was added in the conventional water based mud after barite. This method was able to incorporate the ZnO nanoparticles building block into the polyacrylamide where the force of attraction on the surface of the nanoparticles increases and resulting the inside and outside agglomerates of the nanoparticles equally activated based on their FESEM results. Thus, with this deposition of the ZnO nanoparticles into the polyacrylamide matrix, this enhanced the thermal stability of the polymer.

This is due to the fact that the ZnO-Am nanoparticles were tested with the thermogravimetric analysis (TGA) at three different temperatures that replicated the downhole temperature conditions such as elevated temperature, high temperature and ultra-high temperature which the temperature range were between 0 – 300^{o}F, 300 – 400^{o}F and 500 – 600^{o}F respectively and results showed that the weight loss of the nanocomposite were much less compared to the polyacrylamide. Furthermore, the weight loss for the nanocomposite showed a very slight change in the weight loss at all the different downhole conditions compared to the polyacrylamide. The rheological properties showed that 0.8 g was the superior drilling fluid formulation as it drilling operations whereas in terms of filtration properties 1.0 g was the optimum concentration. The trend for the apparent viscosity was slightly increased as the concentration of the ZnO-Am nanocomposite increased. This is due to the distinctive composition of the ZnO-Am where the metal oxide nanoparticles is a solid material which are good heat transfer particles, thus minimized the effect of the temperature through the drilling fluid system, and the polyacrylamide is considered to the hydrophobic materials and the viscosifier (Biggs et al., 1992). Typically the range for the apparent viscosity is between 33.5 – 49.5 mPa by (Mao et al., 2015) and from (Aftab et al., 2016) results, 0.8 g of the ZnO-Am nanocomposite added into the water based mud showed to be 36 mPa at HPHT condition which was in the operating conditions. It was also observed that at 0.8 g of ZnO – Am, the plastic viscosity and the yield point were well within the operating conditions of 20 – 29 mPa.s and 7 – 12.8 Pa (Ji et al., 2012) respectively. Raising the concentration of the ZnO – Am any further than 0.8 g may be detrimental to the drilling operations due to the fact that high plastic viscosity can exhibit high viscosity at the drill bit which will result in a lower rotation per minute of the drill string. Thus, raising several problems during the drilling operations such as swap pressure and high differential pipe sticking. Also, it was noted that increasing the concentration of the Zn)-Am nanocomposite increased the yield point due to the fact that the ZnO – Am nanocomposite were adsorbed over the surface of the drilling additives and the agglomeration among the particles decline. The yield point for the 0.8 g was maintained in the operating conditions of to ensure that the drill cutting efficiency is better than the lower yield point drilling fluid. The yield point of the drilling fluids are affected as well by the gel strength which is the ability to hold the cutting and debris for a certain period of time during the operation.

The operating range for the 10-s gel strength is between 3 – 5 Pa (Ji et al., 2012) and that at 0.8 g, the 10 –s gel strength was at 4.2 Pa which improved from 3 Pa of the base fluid. This is due to the inorganic materials of the metal oxides nanoparticles were incorporated into the composite of the nanoparticles that the conferred link between the surface of the micro and macro particles of the drilling that might support the gelation behavior of the drilling fluid (Jung et al., 2011). In contrast to the rheological properties, the average filtrate loss below 1.0 g was at 5.5 ml and the best result for the filtrate loss was reduced to 4.7 ml at 1.0 g of the ZnO – Am. (Smith et al., 2018) states that filtrate loss additives minimized the filtrate loss by decreasing the flocculating and coating the solids. (J.J. Azar, 2007) also emphasized that the shape and the size of the nanoparticles were factors in the achieving better filtration properties of the water based mud due and in this study the ZnO nanoparticles plugged the nanopores of the wellbore which improved the fluid stability and the hydrophilicity. Also, in addition to the inorganic material of the addition ZnO nanoparticles for the nanopores, the organic material of the polyacrylamide was better at plugging the macro size pores due to its macro size. This provide better deflocculating of the polymer by coating the solids and the hydrophobic nature due to the long chains resulting of the formation of the hydrate resistance. This is due to the fact the acrylamide is hydrophobic in nature and coats the drill solids. Thus, the combination of adding together with the inorganic metal oxide in this study improved its life span at elevated temperature as the inorganic part act as a good heat transfer agent.

The filter cake which is the deposition over the wall of the wellbore that affects the filtration loss properties and this filter cake is dependent on the solids and base water retained in the filter. The filtration loss decreased with the increase in the solid concentration, however increasing the solid increases the thickness of the filter cake. Therefore, experimental work of using nanoparticles to produce a thin and high solid concentration in the filter cake. In this study, the API filter cake showed a decreasing trend with the increase of the concentration of ZnO – Am nanocomposite. It was found that at 0.6 g, the filter cake thickness was greater than the base fluid. This may be due to the face that the same particle size distribution increases the porosity which resulted in the increased of the filter cake thickness (M. Bo, 1965). Hence in this study by , 0.8 g again showed to be optimized concentration of ZnO – Am where the thickness of the filter cake was reduced to 1.65 mm from 2.54 mm of the base fluid (Aftab et al., 2016).

2.3.4 Recent studies on the carbon-based nanoparticles

Clay nanoparticles were also used in few studies to improve the filtration control of WBMs due to the ability of clay to build up a stable viscosity throughout the drilling operation at a relatively low solids level whilst maintaining the desired viscosity. For instance, (Abdo and Haneef, 2013) used Palygosrkite (Pal) which has very good colloidal properties such as high temperature endurance, salt and alkali resistance and high adsorbing capabilities to design a new WBM. They milled the clay in coarse grains of nano-size particles and disperse it into ethanol by a high frequency of ultra-sonic vibrations. It was then found that clay nanoparticles with the size of 10 nm to 20 nm increase the plastic viscosity from 9 to 12 cp but there was a good improvement in the filtration control when the temperature and pressure went up to 365^{o}C and 16,000 psi respectively.

Another study by (Ismail et al., 2016) which the additives they used Multi-Walled Carbon Nano Tube (MWCNT), nanosilica and 2 different sizes of Glass Beads (GBs) in which there sizes are from 21 nm, 12 nm, 90 – 150 μm and 90 – 150 μm respectively. It was found at 0.01 ppb of MWCNT was the optimized concentration in both aspect of the rheological and filtration properties within the operating conditions. The plastic viscosity was maintained between the operating values of 20 – 29 cP (Guo et al., 2006) when it was enhanced by adding MWCNT and nanosilica. Based on (Ismail et al., 2016) results, the rheological properties of the nanoparticles at 0.01 ppb showed to be the optimized concentrations in the plastic viscosity and yield point parameters. The trend for the MWCNT before 0.1 ppb showed a decreasing trend as compared to the nanosilica which was the increasing trend and henceforth after the 0.1 ppb showed the same trend. This may be due to improve volume of suspended material in the drilling fluid whereby the presence of nanoparticles gives less effect to the drilling fluid by increasing the friction between the suspended in the drilling fluid. Also, it may be that the concentration of the nanoparticles is so small compared to the other base fluid additives to give a significant on the rheological properties of the plastic viscosity. The GBs exhibited a different trend result compared to the nanosilica and MWCNT whereby the plastic viscosity trends increase as the concentration of both the GBs sizes increases up to 30 cP. However, a lower plastic viscosity is favorable as it helps in drilling rapidly because of the lower viscosity of the drilling fluid exiting at the bit and within the operating the condition and therefore, the 0.01 ppb concentration of the MWCNT and nanosilica on attaining the 21 cP. The trend for the yield point showed an increase after the 0.01 ppb which was unfavorable due to inappropriate can affect the equivalent circulation transition point between laminar and turbulent flow and efficiency of the cutting transport. The 10 seconds gel strength trend for the MWCNT was at the typical range of the gel strength value (Jain and Mahto, 2015) and was much higher compared to the nanosilica due stronger attraction forces between MWCNT particles which resulted in a higher gel strength value.

Both the nanoparticles were better in term of the filtration properties where the minimum filtrate volume were below 5 ml and GBs were above 5 ml. This is due to the plugging properties whereby the GBs are in macrosizes and cannot plug the nanopore throat of the wall of the wellbore (Mao et al., 2015). MWNCT was found to be the better material between the nanoparticles, where at 0.01 ppb the MWNT was at 4.5 ml filtrate loss and the 0.01 ppb nanosilica was at 4.8 ml. This may be due to its high surface area and nanotube structure of the MWCNT, and these nanoparticles are able to disperse themselves to the drilling fluid materials and formed a thin and impermeable mud cake. The thickness of the mud cake were less affected with the addition of the nanoparticles when compared to the GBs. With the better dispersion from the MWCNT, the nanotube structure may prevent the movement of the barite particles from passing through the filer paper. Therefore, the mud cake produced from the MCWNT had a thin and a smooth surface texture because the nanoparticles have a good strength and dispersion property. In addition to that, the MCWNT nanoparticles may also form a bridge within the particle which gives a homogenous system which further reduces the porosity of the mud cake and thus conclude to the lower filtrate loss volume when compared to the nanosilica. In contrast to that, the trend for the GBs had a different effect where the thickness of the mud cake increased when the concentration increases which resulted in forming a very thick mud cake.

Another approach to incorporate the clay nanoparticles into the water based mud by (Cheraghian et al., 2018) where they synthesized the SiO_2 with the clay nanoparticles to form a clay/SiO_2 (CS) nanocomposite by the effective hydrothermal method. The results showed that the nanocomposite had a significant improvement in the rheological and filtration loss properties comparing the drilling fluid with SiO_2 nanoparticles, particularly at higher temperature. (Cheraghian et al., 2018) run a series of experiments in comparing the nanocomposite with the SiO_2 nanoparticles at both LPLT and HPHT conditions at varied concentrations. It was found that the CS had enhanced the yield point and the plastic viscosities, from the base fluid at 40 % and 70 % respectively at 25^oC whereas the addition of SiO_2 nanoparticles only enhanced at 22% and 41% respectively. Also, the samples were tested at a higher temperature of 90^oC where the results of the yield point and plastic viscosity for the CS nanocomposite were enhanced by 65% and 82% respectively when compared to the base fluid whereas the SiO_2 nanoparticles only had about 38% and 53% improved compared to the base fluid. Hence, the yield point showed a significant difference which is a clear indication that the CS nanocomposite helped to improve the rheological stability of the water based mud. Moreover, the gel strength results from this study as well was higher in the CS nanocomposite and also had better filtration loss control. Thus, this indicated that the addition of the CS nanocomposite was able to improve on the rheological stability of the drilling fluid. This is due to the CS nanocomposite having a smaller particle size distribution due to the entrapment of the CS nanocomposite within the gel network formed by the polymer molecules in the as seen in the SEM micrographs and the XRD analysis of (Cheraghian et al., 2018). Therefore, the CS nanocomposite could plug the pore throat of the filter paper and form a thin and hard filter cake, which decreases the filtration loss from the mud. Furthermore, the filter cake of the water based mud were much smaller compared to the base fluid filter cake and that as the concentration of the CS nanocomposite increases, the filter cake thickness decreases too.

Evidently, at low concentration of the CS nanocomposite incorporated into the water base fluid would produce a thicker, high permeability and high porosity filter cakes which would lead to a higher fluid loss from the mud. Their test results showed that the total fluid loss with CS nanocomposite and SiO_2 nanoparticles were reduced comparing the base fluid by approximately 60 % and 45% at room temperature and 65% and 10% at 90°C. However, it should be noted that SiO_2 nanoparticles only requires a lower concentration to significantly reduce the fluid loss when compared to the base fluid whilst the CS nanocomposite requires a higher concentration. This is due to the size distribution where it would require more concentration as the particle size distribution is much smaller to fill the pore throat in the filter paper (T.M. Al-Bazali, 2005). Therefore, to conclude in (Cheraghian et al., 2018) study, the filtrate loss for the CS nanocomposite were at 7ml at 25°C and 9ml at 90°C whereas the SiO_2 nanoparticles were at 10ml at 25°C and 21ml at 90°C. The thickness of the filter cake for the CS nanocomposite were at 1.67mm at 25°C and 1.72mm at 90°C whereas the SiO_2 nanoparticles were at 1.83mm at 25°C and 1.90mm at 90°C, where initially the base fluid filter cake thickness were averagely around 3.50mm at 25°C and 3.75mm at 90°C. This is a clear indication that the addition of nanoparticles reduces the thickness of the filter cake as they filled the voids in the mud cake creating a more densely-packed cake hence better control in the permeability to create an efficient filtration system.

(Kazemi-Beydokhti and Hajiabadi, 2018) did a different approach where they synthesized a complex of oxidized multi-walled carbon nanotube wrapped by polyethylene glycol (POCNT). In their study, when the POCNT were added into the base fluids, the plastic viscosity of the mud samples improved due to the larger surface area to volume ratio of the POCNT with the clay particles, this leads to a higher interaction and friction inside the mud samples and increases the viscosity of the mud samples. (Inglefield et al., 2016) suggested the reason of the plastic viscosity improvement was due to the hydrogen bonding where the network in the individual nanoparticles and the interlamellar water molecules, controls the large scale properties of the Carbon-Nanotube solution. As the concentration of the POCNT into the mud samples, the hydrogen bonding becomes denser and leads to a higher plastic viscosity (Medhekar et al., 2010). It should be noted that the polyethylene glycol (PEG) molecules are non-ionic polymers, which cannot interact with the negatively charged clay particles. However, these PEG molecules can attach themselves on the platelets of the mud samples in which they penetrate between the clay layers and this will lead to the swelling of the solution and improving the plastic viscosity. In addition to the hydrogen bonding between the individual nanoparticles, the PEG forms hydrogen bonds with the oxygen molecules on the clay particles and this lead to flocculation in the mud and changing the viscosity during the testing (S. Tunc, 2008). The filtration properties of the POCNT when added into the mud samples showed to be significantly improved on the filtration loss by 82% when compared to the base fluid. The PEG is found to be an efficient polymer which is capable of suppressing the filtration volume (Fereidounpour and Vatani, 2014). The effectiveness of this polymer is due to the attachment of the surface of the bentonite components that blocks the pores partially and clogged the flow medium (Caenn et al., 2011). With these properties supports the reinforced structure of the filter cake, which were made from the rigid nanotubes and covered by the pliable PEGs and this combination was able to develop flexible impermeable plugs on the pores and improved the filtration efficiency. In addition to the filtration efficiency, the ultra-small size POCNT, the high surface area and high aspect ratio of the POCNT, this creates a thin layer of mud cake, leading to a lesser amount of friction during the drilling operations that is necessary to reduce of differential pipe sticking (A.T. Bourgoyne, 1986).

CHAPTER THREE

METHODOLOGY

3.1 Introduction

As it was mentioned before in Chapter 1, this study intends to formulate a WBMs by a combination of polymer, palm derived methyl ester sulphonate surfactant and polystyrene at nanoscale/macroscale which can reduce the fluid loss in permeable formations and improve the rheology. To achieve this, a series of mud samples with different combination of additives are prepared and attempts are made to measure changes in their rheological and flirtation control properties under LPLT and HPHT conditions. The materials used and the procedure followed to make these measurements are discussed in this chapter.

3.2 Materials

3.2.1 Polystyrene

The polystyrene was chosen for this experiment due to low level of hazardous identification and also its high thermal resistance of up to 100^{o}C (Faraguna et al., 2017). This help reduces the environmental waste of the disposed polystyrene from the landfills (Aminudin, 2011). The polystyrene was prepared at both macroscale and nanoscale. The macroscale polystyrene (MP) with the average size of 65 microns were then dispersed in deionized water using the LSP-500 Ultrasonic Liquid Processor for 15 minutes with the varied concentration between 0.01% - 0.05% and the solution was left for 5 minutes to allow the particles to settle down. The weight of the MP was tested at 0.01% - 0.05% and found that after the concentration of 0.01% had no further improvement on the filtration and rheological testing with the base fluid. The nanoscale polystyrene with the average size of 20nm were prepared and dispersed with the same method with concentration between 0.01% - 0.05% and found that were no significance improvement was done as well after 0.01%. Therefore, the concentration for the MP and NP were prepared both at 0.01%.

3.2.2 Polymers and Surfactant

The polymers used to test in the experiment were polyanionic cellulose and xanthan gum. The polymers were selected due to their properties in achieving the ideal rheological properties for low filtrate loss volumes (Villada et al., 2017). The concentrations of the polymer were tested between 0.5g - 1.5g and found that the optimized concentration was at 1g as there were no significance improvement on the rheological and filtration testing with the base fluid. In respect to the benefit to the environment by reducing the polystyrene waste, the surfactant in this experiment used the methyl ester suphonate (MES) which is considered as a green surfactant. Also, an anionic surfactant which are highly compatible with the polymers (Sheng, 2011). Surfactant are water soluble amphiphilic molecules that consist of the polarized hydrophilic head and the non-polarized hydrophobic part which is usually the hydrocarbon chain (Fernandes et al., 2010). The hydrophilic head can be either a nonionic, anionic, cationic or zwitterionic. In this experiment, the MES is an anionic hydrophilic head and the balance between the hydrophobic and the hydrophilic parts allows the surfactant to form micelles. Critical micelle concentration (CMC) is the concentration when the surfactant starts to form micelles in the solution. At low concentrations of below 1g of the MES, only slight change in the surface tension is detected until the CMC where the surface tension becomes fully saturated and no further change in the surface tension when the concentration of MES increased. From Figure 3.1, it was found that the concentration of 0.03% was the CMC solution for this experiment which is equivalent to the 0.1g added into the 350cc of the water-based mud.

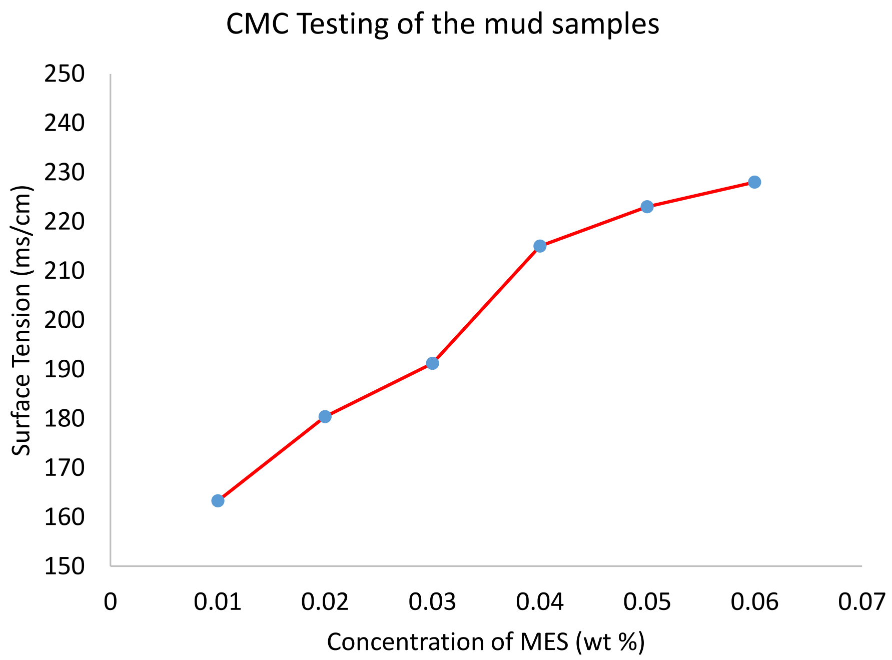


Figure 3.1: Surface tension against the concentration of MES

3.3 Barite

Barite are then added after the addition of the methyl ester surfactant, as the surfactant decreases the density of the water-based mud below the operating conditions. This is due to the formation of microbubbles produced by the MES. The total amount added into the water-based mud was 150g after a series of testing from 100g to 200 g and found that 150g was the minimum required for the water-based mud to acquire the standard operating condition for density which were in between of 9 and 10 ppg.

3.4 Mud Samples

3.4.1 Reference Mud

WBMs prepared for the purpose of this study composed of 15g bentonite and 350 ml deionized water. Bentonite and water were mixed using the FANN Multimixer 9B and the mixture was blended for 10 minutes at a constant rate of 11,500 RPM to ensure that the drilling fluid is very well mixed, and the coagulation of bentonite is prevented. Table 3.1 and 3.2 respectively give the chemical components and the list of apparatuses used for the mud sample preparations.

Table 3.1: Chemical components used for the mud sample preparation

Components	Purity	Brand	Purpose
Deionized Water	-	-	Mud Sample Preparation
Bentonite	60 – 100 %	M-I SWACO	Viscosifier
Sodium Hydroxide (NaOH)	99%	Merck	pH modifier
Xanthan Gum	60 – 100 %	M-I SWACO	Viscosifier and to plug the macrosize pores
Polyanionic Cellulose	60 – 100 %	M-I SWACO	Viscosifier and to plug the macrosize pores.
Methyl Ester Sulphonate	-	Chemithon	For better dispersion of the materials in the mud
Barite	60 – 100 %	M-I SWACO	To increase the density of the mud
Polystyrenes	-	-	To plug the nanosize pores

Table 3.2: List of apparatuses used for the purpose of this study

Equipment	**Purpose**
FANN Multimixer 9B	To blend the bentonite with the solution to prepare the mud samples.
LSP-500 Ultrasonic Liquid Processor	To sonicate the solution to create a well dispersed solution.
Multi Conductivity Meter	To measure the conductivity of the solution for CMC test
pH Meter, Senslon + ph1, Hach, USA	To measure the pH value of the mud samples.
FANN Viscometer 35SA	To examine the rheological properties of the mud samples
FANN Four Cells LPLT Filter Press Series 300	To determine the filtrate volume, and thickness of the mud cake
FANN HPHT Filter Press 175CT	To measure the filtrate volume, and thickness of mud cake formed

Water-based drilling fluids were formulated according to the American Petroleum Institute (API) standards with a combination of bentonite, Xanthan gum (XG), polyanionic cellulose (PAC-L), methyl ester sulphonate (MES) surfactant and polystyrene at macroscale and nanoscale as reported in Table 3.1. A based WBM was also prepared by adding 15g of bentonite to 350 cc deionized water which will be used for the comparison purposes.

Table 3.3: Mud sample mixture

Sample	Mixtures
1	350cc Deionized water + 15g Bentonite
2	350cc Deionized water + 15g Bentonite + MES
3	350cc Deionized water + 15g Bentonite + 0.01% MP
4	350cc Deionized water + 15g Bentonite + 0.01% NP
5	350cc Deionized water + 15g Bentonite + 1g XG
6	350cc Deionized water + 15g Bentonite + 1g PAC-L
7	350cc Deionized water + 15g Bentonite + 1g XG + 0.01% MP
8	350cc Deionized water + 15g Bentonite + 1g XG + 0.01% NP
9	350cc Deionized water + 15g Bentonite + 1g XG + 0.1g MES
10	350cc Deionized water + 15g Bentonite + 1g PACL-L + 0.01% MP
11	350cc Deionized water + 15g Bentonite +1g PAC-L + 0.01% NP
12	350cc Deionized water + 15g Bentonite + 1g PAC-L + 0.1g MES
13	350cc Deionized water + 15g Bentonite + 0.1g MES + 150g Barite + 0.01% MP
14	350cc Deionized water + 15g Bentonite + 0.1g MES + 150g Barite + 0.01% NP
15	350cc Deionized water + 15g Bentonite + 1g XG + 0.1g MES + 150g Barite
16	350cc Deionized water + 15g Bentonite + 1g PAC-L + 0.1g MES + 150g Barite
17	350cc Deionized water + 15g Bentonite + 1g PAC-L + 0.1g MES + 150g Barite + 0.01% MP
18	350cc Deionized water + 15g Bentonite + 1g PAC-L + 0.1g MES + 150g Barite + 0.01% NP
19	350cc Deionized water + 15g Bentonite + 1g XG + 0.1g MES + 150g Barite + 0.01% MP
20	350cc Deionized water + 15g Bentonite + 1g XG + 0.1g MES + 150g Barite + 0.01% NP

In Table 3.3, shows the amount of the each of the materials required to formulate the following samples for this research and there was a total of 20 samples made. The base sample for this research experiment is deionized water and bentonite, where these 2 materials were in all the samples. The variations of the additives such as xanthan gum, polyanionic cellulose, polystyrene at macroscale and nanoscale, and methyl ester sulphonate surfactant were varied to evaluate the effect on the rheological and the filtration loss properties. The samples that were added with methyl ester sulphonate surfactant was added with barite as the weighting agent to maintain the density of the mud between 9 and 10 ppg.

3.5 Measurement Methods

The measurement reported in the following sections were done according to the API Specification 13A.

3.5.1 Plastic Viscosity

Plastic viscosity (PV) is define as the measurement of shear rate against stress of the fluid. These values were derived using the Fann 35SA Viscometer, which is a rotating – sleeve viscometer made up of an outer rotating sleeve and an inner bob, using two speed model at 300 and 600 rpm. The mechanics of the viscometer works in a way that the outer sleeve is rotated at a known speed, then the torque is transmitted through from the mud through the bob. The bob is connected to a spring and dial, where the torque is measured. The shear rate is the rotational speed of the sleeve and the shear stress is the torque applied to the bob, measured as deflection units on the instrument dial. However, these measurements need to be converted to true units. Shear rate is defined as the rate of change as the fluid layers move past another layer per unit distance, and is measured in reciprocal seconds, s^{-1}. Thus, converting the dial reading to shear stress, the dial reading is then multiplied by 1.065 to obtain the units in $lb/100ft^2$.

The water-based muds are classified as Non-Newtonian fluids, where the ratio of shear stress to shear rate is not constant and varies for each of the shear rate. The Bingham plastic fluid, the finite force is required to initiate a constant rate of increase of shear stress with shear rate. Thus, to obtain the plastic viscosity as shown in the Eq. 3.1 and the unit is measured in centipoise, the readings are taken with a viscometer at 300 and 600 pm which are at 511 sec^{-1} and 1022 sec^{-1} respectively.

$$PV = \theta_{600} - \theta_{300} \quad (cP) \qquad (3.1)$$

3.5. Apparent Viscosity

The apparent viscosity is half the dial reading when the shear rate is at 1022 sec^{-1}. This is the measure of the part of resistance flow caused by the mechanical friction between solids in the mud, solids and liquids and the shearing layers of the drilling fluid itself.

$$AV = \frac{\theta_{600}}{2} \quad (cP) \qquad (3.2)$$

3.5.3 Yield Point

The yield point (YP) is also obtained from the Fann 35SA Viscometer. The yield point is defined as the measure of electro-chemical attractive forces within the drilling fluid under the flowing conditions. These forces are caused by the positive and negative charges located around the particle's surface. This makes the yield point as a function of the surface properties of the mud solids, the volume concentrations of the solutions and the concentration and the type of ions within the fluid phase. Based on the Bingham Plastic model, the yield point is the shear stress at the y-axis or can be measured with Eq. 3.2.

$$YP = \theta_{300} - \text{PV} \qquad (\text{lb}/100\text{ft}^2) \tag{3.2}$$

3.5.4 pH

The water-based drilling fluids samples always treated to be more alkaline because the bentonite is least affected when the pH is in between the range of 8 and 9. The pH will affect the rheological properties in terms of the viscosity where keeping them at optimum operating conditions. Moreover, higher pH in the range of 9 to 10 appears to give the best downhole stability and control over the drilling fluid properties (Welton et al., 2007). However, pH higher than 10 shown to cause more shale problems (Gholami et al., 2018). For this research, the water-based drilling fluids was maintaining in between 9 and 10 throughout all the formulation sample mixtures. This was done by the addition of a few drops of diluted Sodium Hydroxide.

3.5.5 Gel strength

This is a measurement of the attractive forces of the drilling fluid under static conditions. Both the yield point and the gel strength are measures of flocculation, thus the results for them will tend to be proportional to each other. Although, a low yield point does not mean that there is no gel formation. The gel strength is measured by the Fann 35SA Viscometer by stirring the mud at 600 rpm for about 15 seconds, then turn off for the drilling fluid to remain static with the desired time frame at 10 seconds or 10 minutes and then turn back on at the speed of 3 rpm. The gels are described as either strong or weak and for a drilling fluid, the weak is more favorable. This type of gel can be easily broken down and would require a lower pump pressure to initiate circulation during operations (Abdo and Haneef, 2013).

3.5.6 Fluid Loss Properties

The fluid loss represents the interaction between the fluids in the wellbore under a simulated pressure and temperature conditions of LPLT, at 25°C and 14.6 psi and HPHT conditions, at 100°C and 500 psi. The ideal formulated drilling fluid should be able to produce a thin and impermeable layer of mud cake. This mud cake is responsible to protect the formation from preventing influx of drilling mud into the formation that would be detrimental to the production later on. The fluid loss measurement are taken every 5 minutes interval for 30 minutes and the mud cake formed is only available at the end during the process of cleaning the filter press carefully as the mud cake is very fragile.

3.5.7 Permeability

The permeability of the mud cake was determined by the rate of filtration through the filter cake as described by the Darcy's Law formula as shown in Eq. 3.3, where the dV/dt is the rate of filtration, A is the cross-sectional area, K is the permeability, ΔP is the differential pressure, μ is the viscosity and h is the thickness of the mud cake. It is worth to note that the cross-sectional area for LPLT and HPHT were at were at 22.06 cm^2 and 46.6 cm^2 respectively.

$$\frac{dV}{dt} = \frac{KA\Delta P}{\mu h} \tag{3.3}$$

3.5.8 Morphological Structure of the Mud Samples

Selected mud samples were then tested using the scanning electron microscope to observe their internal packing structure and distribution of the nanopolystyrene in the mud samples. Figure 3.2 shows the experimental flow chart of this study.

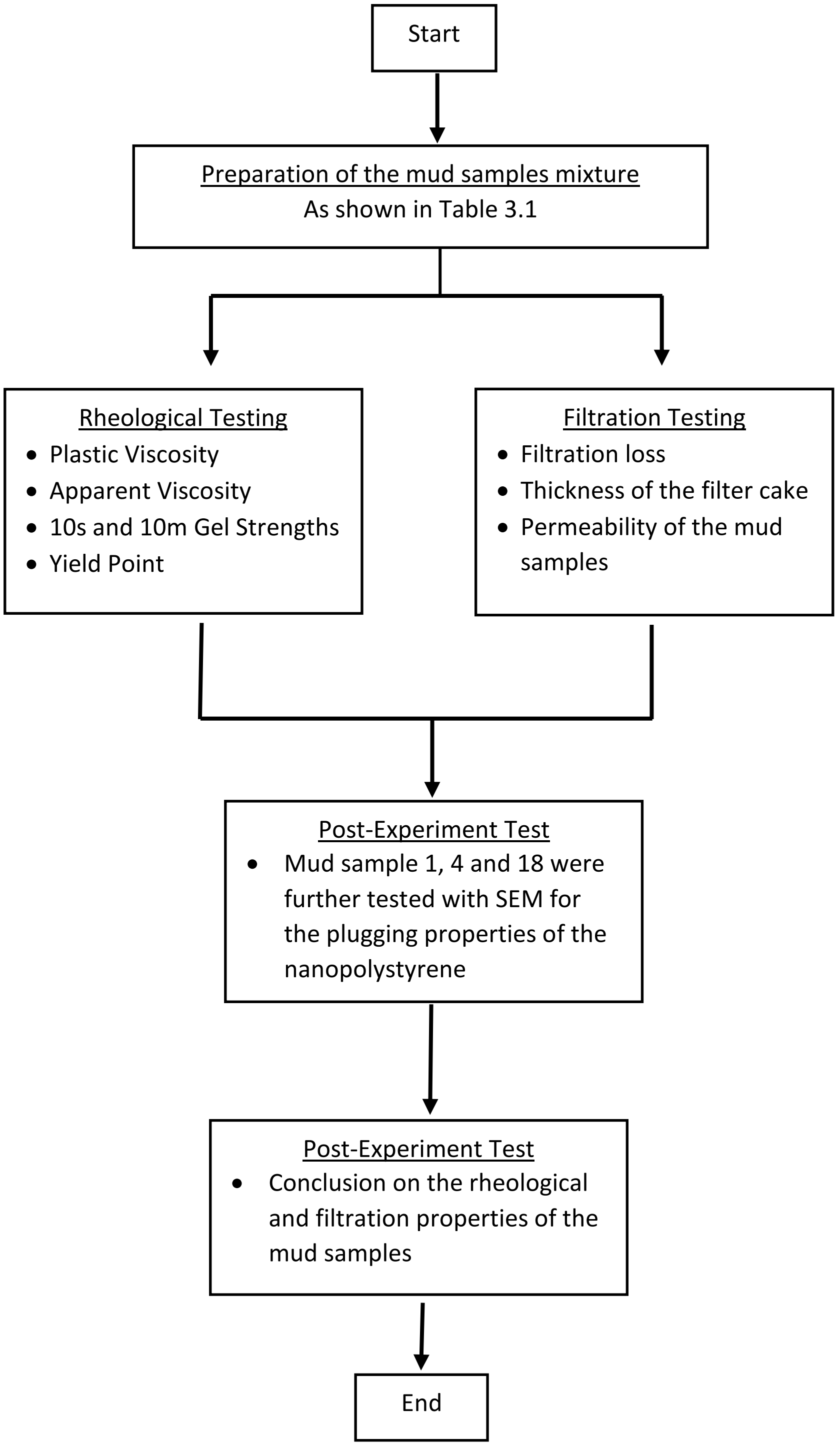


Figure 3.2: Experimental Flow Chart

CHAPTER FOUR

RESULTS & DISCUSSION

In this section shows the results based on the rheological properties of density, plastic viscosity, shear stress and shear rate and the gel strength at 10 seconds and 10 minutes. So once the optimum operating conditions of the rheological properties was determined then the measurement of the fluid loss at LPLT and HPHT conditions was taken to get the best formula of the water-based drilling fluid.

4.1 Density of the mud samples

Based on (Fattah and Lashin, 2016), the optimum condition for density should be in between 9.5 and 10.5 lb/gal and the formulation of the drilling fluid. In Table 4.1, shows the changes in density of the mud sample compared to sample 1 which is the base sample that is formulated with bentonite and deionized water. The base density was at 8.6 lb/gal and does not vary with the addition of the xanthan gum and polyanionic cellulose and the polystyrene at both macroscale and nanoscale. However, the only density that varies was when the base was added with methyl ester sulphonate surfactant, where there was a drastic drop in density of the mud to 6.4 lb/gal and 6 lb/gal as shown in sample 2 and sample 12. This is due to the microbubbles formed when preparing the mud sample. Based on (Kuru et al., 2008) experiments, increasing the concentration of MES, the density when compared to the base fluid decreased drastically. Similarly, the addition of MES with the polymers in sample 9 and 12 showed that the density decrease at least by 25% which made the drilling fluid composition further from the optimum condition for density. Therefore, barite was added into the mud samples from sample 13 to 20 as a weighting agent which showed to be better option in terms of density where the density was well within the optimum density of 9.5 lb/gal with a slight variation from sample 13 and 19 with an average difference of 2% to 3% from the rest of the samples. The role of the surfactant in the mixture is to reduce the interfacial tension between the particles, so this is important for sample 13 to 20 as these samples are with the addition of polymers. The polymers was well dispersed within the drilling fluid which improves the rheological properties which will be discussed further in this chapter.

4.2 Rheology of the mud samples

4.2.1 Plastic Viscosity

In Table 4.1 shows the changes of the plastic viscosity of the mud samples with reference to the base sample 1. The addition of polystyrene at both macroscale and nanoscale illustrated that the plastic viscosities decrease by 37.5% whereas for the methyl ester surfactant plastic viscosity decreased by 12% from sample 1, which is negligible as the dial reading only had a difference by one which caused the plastic viscosity to differ by 12%. Generally, a decrease in plastic viscosities relates to the decrease of the viscosities around the bit which can cause a higher penetration rate. However, increasing too much of the plastic viscosities beyond the operating condition is not suitable for drilling as it can reduce the available flow rate and can change the increase in the ability of lifting the cuttings to the surface.

The plastic viscosities is an indicator capable of describing the behavior of the mud at the drill bit caused the mechanical friction of the particles. Thus, the plastic viscosities is highly dependent on the concentration of the solids and viscosities of the drilling fluid. With the addition of the polymers, it is shown that there is general trend increase in the plastic viscosities by 112% and 37.5% of sample 5 and 6 respectively. This is due to the increase in viscosity of the mud from the production of aphrons (Nareh'ei et al., 2012). Now as mentioned before in section 4.1, the addition of methyl ester sulphonate surfactant helps reduce the interfacial tension between the polymers and causes the polymer to be well dispersed in the drilling fluid which improved the plastic viscosity of sample 15 to 20 by at least 187.5%. Another reason to this would be the addition of barite which is a weighting agent that allows the clay particles to be more flocculated making it denser. As shown in Table 4.1, sample 16 to 20 were also well within the operating conditions of 20 – 29 cP for plastic viscosity (Jain and Mahto, 2015). Although in sample 15, showed the best improvement of 275% increase from the base sample but any further increase to the plastic viscosity beyond the operating conditions would be less efficient for the penetration rate of the drilling fluid as the fluid would be too viscous, where it would require much more energy. The sample 12, 15 and 16 which are without the addition of polystyrenes showed to have similar results with samples added with the polystyrene like in sample 17, 18, 19 and 20, however, in terms of the filtration loss properties there is a purpose for the addition of the polystyrene which will be discuss later in this chapter.

4.2.2 Yield Point

Based on (Ismail et al., 2016), the yield point is define as the ability of the drilling fluid to lift the cuttings from the downhole to the surface of the well. Based on (Ji et al., 2012), the acceptable yield point value for drilling operation is 13.5 to 20.5 lb/100ft^2. Although higher yield point is supposed to have a better flow of the drilling fluids throughout the circulation system but increasing above the operating conditions will hamper the efficiency of the cutting carrying capacity. This is because when the yield point is very high, the gelling characteristics of the fluid may demand a high starting torque which needs to be justified by investigating the shear thinning behavior of the fluid. The addition of nanoparticles shows to have increased the yield point of the drilling fluid samples. As can be seen in sample 7, 8, 10 and 11, there was an increase in the yield point of up to 14% when compared to sample 5 and 6. The only difference between them is that the sample 7, 8, 10 and 11 are added with polystyrenes which confirmed that the addition of polystyrene into the mud samples increases the yield point.

It should be noted that even with addition of polystyrene did increased the yield point but it was not within the optimum drilling operation condition. To top with that, for drilling fluid with the xanthan gum polymers shows to have a much higher yield point compared to polyanionic cellulose which was well above the optimum yield point drilling operation. Therefore, in terms of yield point and plastic viscosity and the filtration loss properties which will be discussed further in this chapter that the superior polymer for this drilling fluid formulation that polyanionic cellulose shows better results in rheological properties and filtration properties. The result from Table 4.1 proves that addition of polyanionic cellulose together with the other additives such as methyl ester sulphonate, barite and polystyrene as shown in sample 17 and 18 with yield point of 14 lb/100ft^2 and 15 lb/100ft^2, well within the optimum drilling operation. This shows that the additions MES does improves the yield point of the mud sample, due to the repulsion forces and causes the reduction in the electrostatic forces between the particles in the mud sample (Faizal Wong et al., 2017).

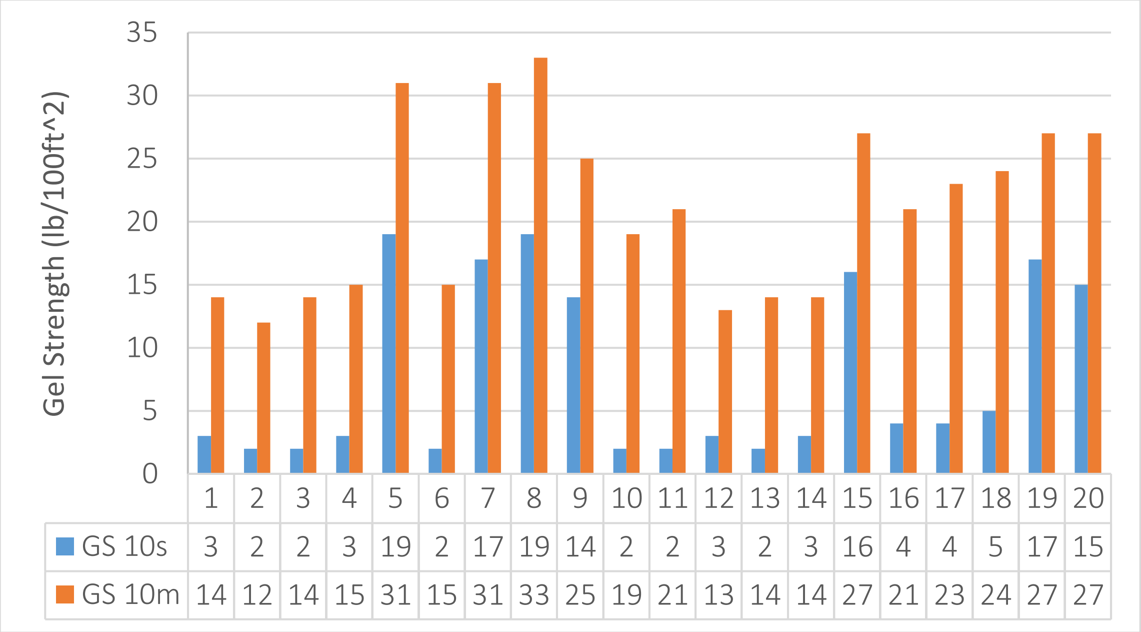
4.2.3 Apparent Viscosity

The Table 4.1 shows the apparent viscosity of the mud samples. The apparent viscosity is the reflection of the combination of plastic viscosity and yield point. An increase or decrease in either both the parameters will have an effect on the apparent viscosity. Based on (Ismail et al., 2016), the operating conditions for apparent viscosity is between 33.5 to 49.5 mPa, which only shows that the addition of xanthan gum to fall in to that category as shown in Figure 4.4 for sample 15 and 20. This is due to the fact that xanthan gum polymer forms a much more viscous dispersion compared to polyanionic cellulose (Villada et al., 2017). However, as discussed in section 4.2.1 and 4.2.2, plastic viscosity and yield point plays a higher role in determining the factors that comes into deciding the drilling fluid formulation for a better rheological property.

4.2.4 Gel Strength

The gel strength of 10 seconds and 10 minute as shown in Figure 4.1 is a measurement of shear stress that is required to initiate the flow of a fluid that was static for a period of time (Wang et al., 2012). This is caused by the electrical charged particles that links them together to form a rigid structure in the fluid. The rigid structure is generally influenced by the additives added so in this experiment would be the surfactants and polymers. The polystyrene does not show much effect in the gel strength of the drilling fluid. It is important that mud samples with the addition of barite, the 10 seconds gel strength needs to be in between 2 to 4 lb/100ft^2 to have enough life to suspend the barite. Otherwise, the barite will settle down to the bottom of the drilling fluid regardless of the viscosities (Jia et al., 2017).

In Figure 4.1, it is shown that the addition of polymers such as the xanthan gum alone in sample 5 had already increased the both the 10 seconds and 10 minutes gel strength result 533% and 106% respectively. As xanthan gum has a higher viscous dispersion, it is shown in Figure 4.1 that sample 5, 7 and 8 had the highest gel strength in both categories of 10 seconds and 10 minutes. When there is an increase in gel strength is due to the flocculation of the particles and having a high yield point do not necessarily means that it is more efficient in terms of drilling fluid as more torque is required to initiate the rotational drilling operations. This can be reduced by the addition of the surfactant as shown in sample 15, 18, 19 and 20 for xanthan gum where the gel strength decreased up to 18%. The surfactant reduces the interfacial tension between the polymers causing the xanthan gum particles to be deflocculated. However, for the polyanionic cellulose polymer and the methyl ester surfactant did not affect much on the gel strength characteristics as these additives particles tend to not flocculate in the drilling fluid mixture and leading to a well dispersed mixture of components as shown in sample 16, 17 and 18. Therefore, sample 17 and 18 shows the best result compared to other samples for both gel strength at 10 seconds and 10 minutes.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
🟦 GS 10s	3	2	2	3	19	2	17	19	14	2	2	3	2	3	16	4	4	5	17	15
🟧 GS 10m	14	12	14	15	31	15	31	33	25	19	21	13	14	14	27	21	23	24	27	27

Figure 4.1: Gel Strengths of mud samples

Table 4.1 Rheological Testing Results of the mud samples

Mud Samples	Density (lb/gal)	Plastic Viscosity (cP)	Yield Point (Pa)	Apparent Viscosity (cP)
1	8.6	8	2	9
2	6.4	7	3	9
3	8.8	5	4	7
4	8.5	5	4	7
5	8.6	17	28	31
6	8.5	11	8	15
7	8.5	17	25	30
8	8.5	13	32	29
9	7.5	19	23	31
10	8.5	11	10	16
11	8.6	11	10	16
12	6	23	3	25
13	9.5	10	4	12
14	9.5	10	5	13
15	9.6	30	19	40
16	9.5	28	7	32
17	9.5	24	14	31
18	9.5	21	15	29
19	9.6	29	23	41
20	9.6	23	31	39

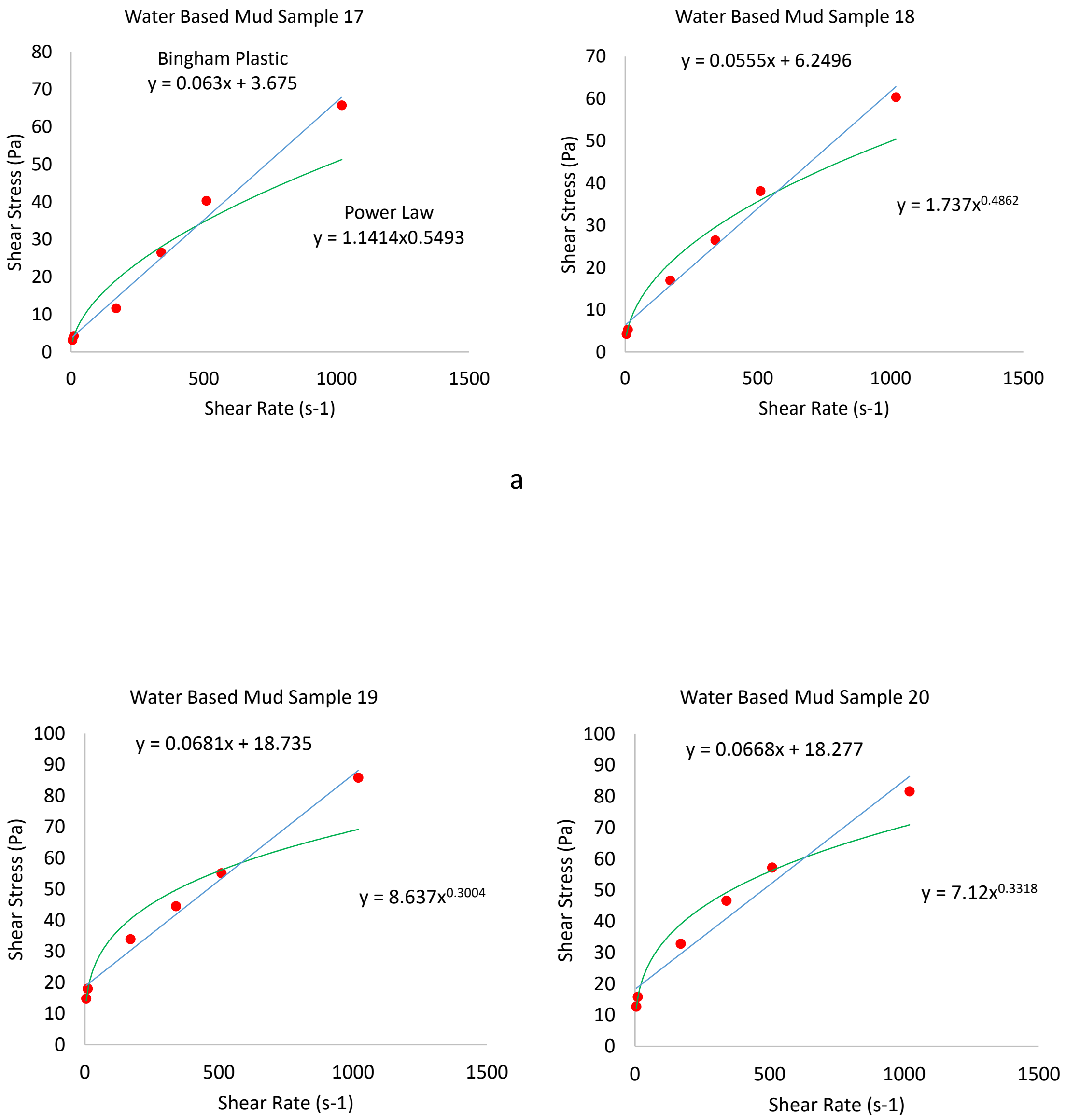
4.3 Shear Stress and Shear Rate

Based on (Welton et al., 2007), the drilling fluid generally behave as a non – Newtonian fluid and as shown in Table 4.2 and Figure 4.2, where the power law index has a value less than 1. The “n” constant indicates the degree of the non-Newtonian character that the fluid exhibits over a defined shear rate change and when the “n” value is equal to one, the fluid exhibits a Newtonian behavior fluid. Lowering the “n” value does improves the hole cleaning performance of the drilling fluid as this increases the effective annular viscosity and flattening the annular velocity profile. This reduces the tuning effect on the cuttings helping to prevent the particles breakage and moves the solids to surface. In Table 4.2, the sample 7, 8, 9, 15, 19 and 20 which all of these consist of xanthan gum shows to be the best option as the “n” value is the lowest and the “K” value the highest which attributes to the hole cleaning capacity. The “K” is the consistency index where the shear stress of the fluid at shear rate of one sec^{-1}. As the “n” value improves the hole cleaning performance by increasing the annular viscosity, the “K” value increases the viscosity of the drilling fluid and reduces the circulating pressure loss. As mentioned in previous section 4.2 and 4.3, the xanthan gum as a higher viscosity composition which contributes to the higher yield point and plastic viscosity compared to the polyanionic cellulose. Through the power law index and the consistency index, this further justifies that the xanthan gum is the better agent in terms of the hole cleaning capacity. However, this does cause the viscosity of the drilling fluid to increase and leads to higher torque and to be less efficient in drilling operation.

The sample 4 which is the base and nano-polystyrene mixture shows the lowest shear stress whereas the sample 15, 19 and 20 which consist of the base, xanthan gum, barite, MES and polystyrene shows the highest shear stress. Generally adding the surfactant to the mixture causes the number of bubbles to be present in the mud and this increases the intermolecular forces and subsequently increases the viscosity (Bjorndalen et al., 2014). Thus, there is a general increase in shear stress when there is the addition of MES and xanthan gum as shown in Table 4.2 and Figure 4.2. Also, addition of PAC-L do not have much effect on the rheological properties as xanthan gum as this is due to the fact that xanthan gum viscosifier that provides the lowest “n” constant. The results shows that the addition of MES and xanthan gum polymer do play a role in affecting the rheological properties. This is mainly due to the microbubble formed from the addition of MES that causes the intermolecular forces. More samples have to be conducted to understand the relation between the microbubbles and the addition of MES. Therefore, as shown in Table 4.3, it can be seen that the addition xanthan gum and polyanionic cellulose with the polystyrene had siginificantly improved on the rheological properties when compared to the base fluid. However, when we are comparing closely between which of the polymer would better fit optimized drilling fluid conditions is the polyanionic cellulose. This is due to the fact that the plastic viscosity and the yield point were well within the operating conditions for polyanionic cellulose.

Table 4.2: The Bingham plastic and Power Law and Consistency Index of the mud samples

Mud Samples	μ (cP)	τ_y (Pa)	n	K
1	7.95	2.84	0.35	5.78
2	7.60	2.73	0.35	5.78
3	6.05	2.93	0.33	6.00
4	6.05	2.93	0.33	6.00
5	23.05	21.67	0.21	61.54
6	14.35	4.12	0.49	4.60
7	21.45	21.58	0.20	63.06
8	20.50	23.41	0.20	66.49
9	25.10	16.38	0.27	39.34
10	14.95	5.13	0.42	7.69
11	14.95	5.12	0.42	7.69
12	24.15	3.07	0.56	4.12
13	11.25	2.91	0.42	5.13
14	11.35	3.70	0.35	8.67
15	32.95	17.87	0.26	50.40
16	31.15	4.10	0.53	6.42
17	31.50	3.68	0.55	6.24
18	27.75	6.25	0.48	9.39
19	34.05	18.74	0.28	44.95
20	33.40	18.28	0.33	35.99



a

b

Figure 4.2: The shear stress-strain rate plot of the water based mud having (a) polyanionic cellulose with polystyrene and (b) xanthan gum with polystyrene

Table 4.3: Rheological properties of the base fluid with the additive water-based mud of having polyanionic cellulose with polystyrene and xanthan gum with polystyrene

Mud	**Bingham Plastic**		**Power Law**		**Gel Strength**	
Samples	YP (Pa)	PV (cP)	K	n	10s (Pa)	10m (Pa)
1	2.84	7.95	5.78	0.35	3	14
17	3.68	31.50	6.24	0.55	4	23
18	6.25	27.75	9.39	0.48	5	24
19	18.74	34.05	44.95	0.28	17	27
20	18.28	33.40	35.99	0.33	15	27

4.4 Fluid Loss

Filtration characteristics of the water-based drilling fluid is dependent on the nature of the quantity of colloidal materials included. Thus, an effective fluid loss additive that controls and limits the filtration loss is achieved by adding substantial amount of certain colloidal materials (Zhang et al., 2016). In Figure 4.3, the LPLT filtration loss measurement shows a general improvement when the addition of both polymers are added into the mixture. However, the addition of either MES or polystyrenes individually shows no improvement on the filtration loss at LPLT condition. This is due to the absence of polymers to form the cross-linking between the bentonite particles to have a higher water retention in the drilling fluid (Chen et al., 2015). Even the sample 13 and 14, when there is the addition of surfactant to reduce the interfacial tension between the bentonite particles and barite to maintain the density at the appropriate level, did not show any improvement on the filtration loss at both LPLT and HPHT conditions. The sample 18 shows to be the best drilling fluid formulation that had the least amount of filtration loss in at 7.5 ml at LPLT conditions and 7 ml at HPHT conditions whereby the sample consist of PAC-L as the polymer in the mixture. Therefore, when considering the formulation of the mud samples, the better polymers would be PAC-L compared to xanthan gum that consider both aspect of the rheological properties and the filtration properties.

When comparing sample 17 and 18 where the only difference between those two samples would be that sample 17 consist of the macroscale polystyrene and sample 18 consist of the nanoscale polystyrene as their additive. From Figure 4.3 and 4.3, it can be seen that the conditions of LPLT and HPHT, the sample 17 was at 8 ml and 7.5 ml and sample 18 had a 7.5 ml and 7 ml respectively. This shows that the nanoparticles would be the better option in terms of the plugging properties as the smaller surface area are able to plug in between the pore spaces after the PAC-L polymers had plug the macroscale pores. Samples that only consist either surfactant or polystyrene individually in the drilling fluid formulation such as sample 1, 2, 3 and 4 shows no improvement in the filtration loss control. This is because that the surfactant reduces the interfacial tension between the bentonite particles which allows the water to flow out form the drilling fluid then this leads to fluid loss into the formation (Welton et al., 2007). For the polystyrene at both the nanoscale and macroscale was due to the size of the particles that was not able to enter the pore spaces as shown in sample 3 and 4.

The addition of polystyrene did improve the filtration loss properties when it was added with polystyrene and even better with the MES and barite. This is due the fact that the addition of the surfactant reduces the interfacial tension between the bentonite particles, allowing a better dispersion of the polymers to plug into the macro scale of the pore spaces whilst the nano-polystyrene plugs the nanoscale pore spaces. In Figure 4.3 and 4.3, when comparing sample 17, 18, 19 and 20 where these are the complete drilling fluid formulation with polymers, surfactant, barite and polystyrenes whereas comparing to their base formulation of sample 5 and 6 where it only consists of the polymer additive, the filtration loss properties at both LPLT and HPHT conditions improved up to 16%.

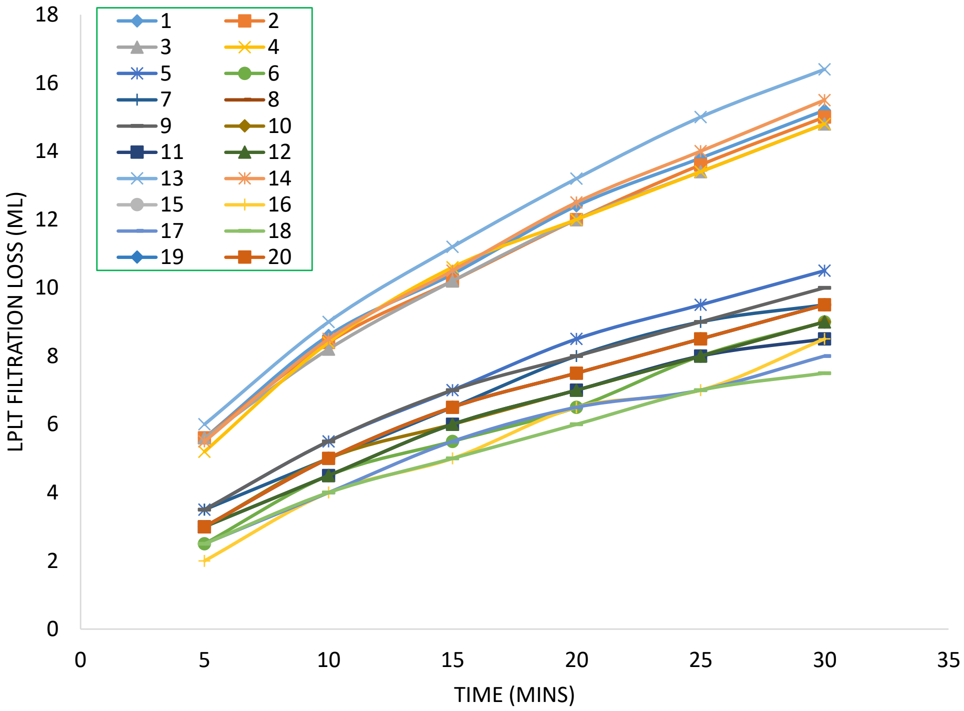


Figure 4.3: Filtration Loss measurement at Low Pressure Low Temperature

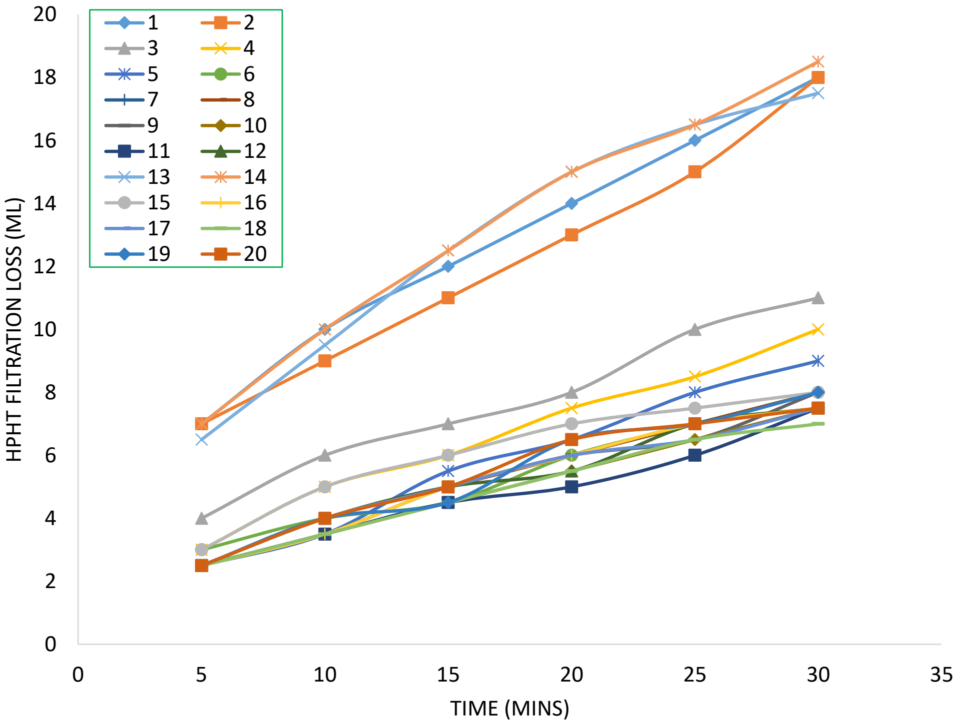
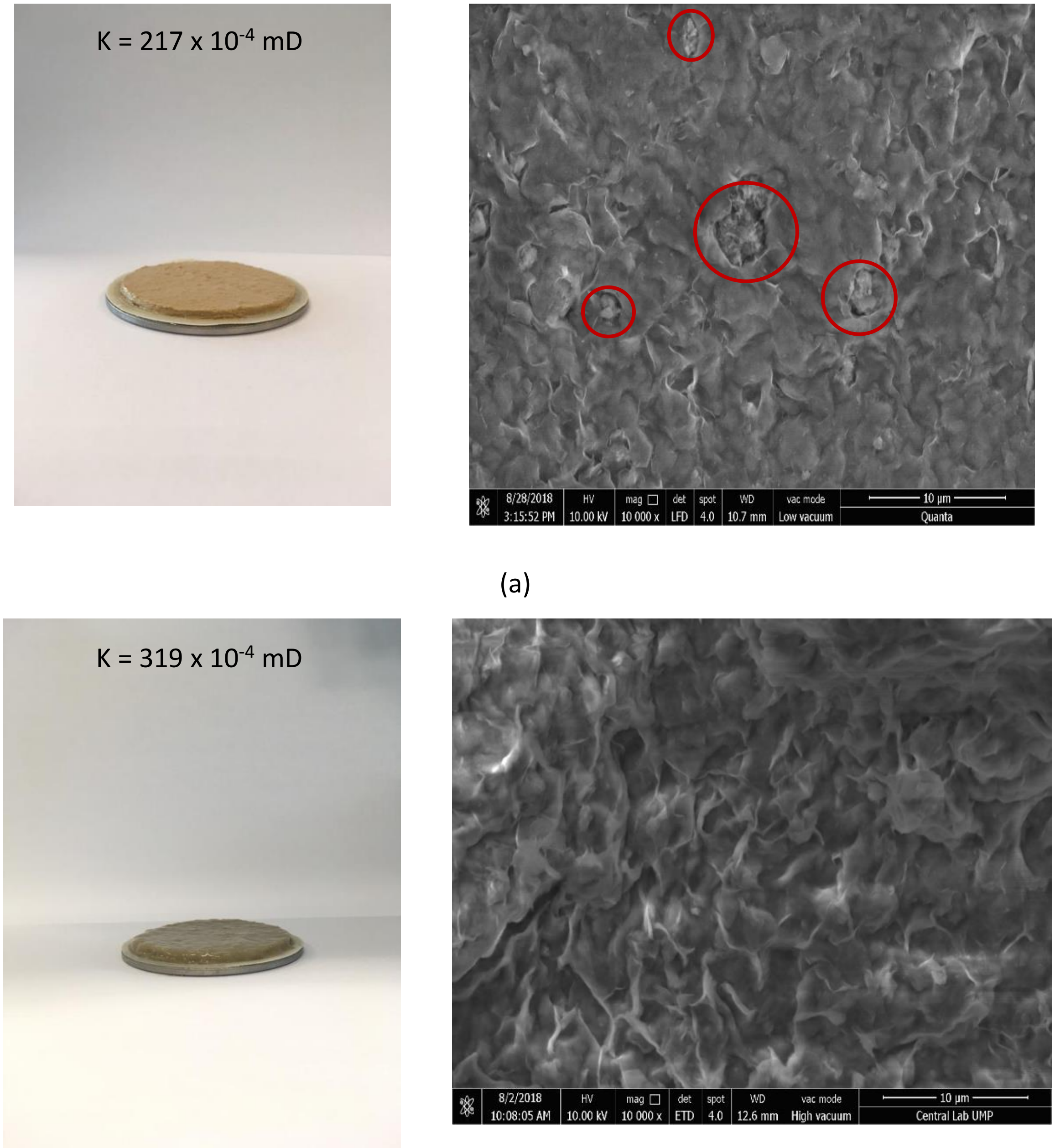


Figure 4.4: Filtration Loss measurement at High Pressure High Temperature

4.5 Thickness of the mud cake

The mud cake is an important parameter in drilling industry as this associates with the differential pipe sticking, torque and circulation loss which leads to formation damage and kick (Cai et al., 2012). In the ideal drilling operation, the ideal mud cake should be thin and form an impermeable filter cake layer. In Table 4.4 and 4.5, the sample 18 which had been proven in previous sections showed to be the ideal drilling fluid formulation was at 2 mm at both LPLT and HPHT conditions. This is ideal because the mud cake should be thin and impermeable filter cake layer. As seen in Table 4.5 and Figure 4.5, the sample 18 was able to reduce the thickness of the mud cake and permeability by 33% respectively from the base sample 1 at HPHT conditions. This is due to the microbubbles formed on top of the filter paper which reduces the formation of mud cake from the addition of MES (Kuru et al., 2008). However, in terms of filtration loss at both LPLT and HPHT, the MES alone do not show any improvement but it does show improvement when the addition of other additives such as polymer and barite. This is because the surfactants allow the polymer particles to be well dispersed in the drilling fluid.

The morphological state of the filter cake of the base fluid and the sample 18 was viewed under a scanning electron microscope as shown in Figure 4.5. In Figure 4.5(a) shows the accumulation of the nanopolystyrene in the filter cake indicating the internal packing of the nanopolystyrene which supports the low permeability of sample 18. However, when compared to the base fluid, this internal packing is absent for the base fluid filter cake as shown in Figure 4.5 (b). The texture of the filter cake from Figure 4.5(a) is different from Figure 4.5 (b) which indicates that the MES gave a better dispersion of additives and forms a rigid filter cake. Therefore, it can be concluded that, based on this data from this experiment that methyl ester sulphonate (MES) which dispersed the drilling fluid additives improved the rheology of the drilling fluid formation for sample 18. Meanwhile, the addition of the nanopolystyrene effectively reduced the drilling fluid filtrate loss and resulted to a thin non-erodible and low permeability filter cake. This filtration data was validated by SEM images of filter cake.



(a)

(b)

Figure 4.5: Filter cake filtration under HPHT conditions (a) mud sample 18 and (b) base fluid

Table 4.4: LPLT Permeability, thickness and other characteristics of the mud samples prepared

Sample	Filtrate Volume (ml)	Filtration Change (%)	Mud Cake Thickness (/32in)	Mud Cake Permeability (x10^{-4} mD)
1	15.2	-	2	85.3
2	15	+1.3	3	110.4
3	14.8	+2.6	2	51.90
4	14.8	+2.6	2	51.90
5	10.5	+30.9	3	187.78
6	9	+59.2	2	69.43
7	9.5	+37.5	3	169.90
8	9.5	+37.5	2	86.61
9	10	+34.2	3	199.88
10	9	+40.7	2	69.43
11	8.5	+44.1	2	65.57
12	9	+40.7	2	145.18
13	16.4	-7.9	2	115.01
14	15.5	-1.9	4	217.41
15	9.5	+37.5	2	199.88
16	8.5	+44.1	2	166.97
17	8	+47.4	2	164.65
18	7.5	+50.7	2	110.45
19	9.5	+37.5	2	110.46
20	9.5	+37.5	2	193.21

Table 4.5: HPHT Permeability, thickness and other characteristics of the mud samples prepared

Sample	Filtrate Volume (ml)	Filtration Change (%)	Mud Cake Thickness (/32in)	Mud Cake Permeability (x10^{-4} mD)
1	18	-	3	319.7
2	18	+0.0	2	186.51
3	11	+38.9	2	81.42
4	10	+44.4	2	74.01
5	9	+50.0	2	226.49
6	8	+55.6	2	130.27
7	8	+55.6	2	201.32
8	8	+55.6	3	230.93
9	8	+55.6	2	225.00
10	7.5	+58.3	2	122.13
11	7.5	+58.3	2	122.13
12	7.5	+58.3	2	255.35
13	17.5	+2.8	2	259.05
14	18.5	-2.8	2	273.86
15	8	+55.6	2	355.28
16	7.5	+58.3	2	310.87
17	7.5	+58.3	2	266.46
18	7	+61.1	2	217.61
19	8	+55.6	2	343.43
20	7.5	+58.3	2	255.35

CHAPTER FIVE

CONCLUSION & FUTURE WORKS

5.1 Conclusion

In this study, an experimental investigation was done to formulate the drilling fluid formula with the additives of polymers, surfactant, barite and polystyrene to improve on the rheological and filtration characteristics of water-based muds. The major applications of analyzing the rheological properties and filtration loss properties are to avoid occurrence of unfortunate drilling event such as suspension, hydraulic calculations, erosions in the downhole, filtrate migration into the formation and solids control. This research objectives is to formulate a combination of polymers, surfactant and polystyrene water based drilling fluid to reduce the fluid loss by sealing the pore throats of the permeable formations. The additives added such as the surfactant and the polymers are biodegradable and has been frequently used in the oil and gas industry for the development of the enhanced oil recovery (Welton et al., 2007). The rheological properties of the mud samples were tested using the 35SA Fann Viscometer, which provides six different dial readings accordingly to the speeds at RPM of 3, 6, 100, 200, 300 and 600. These data acquired from the viscometer allow us to analyze the rheology based on the Bingham Plastic and Power Law model. The filtration loss properties were measured using the filter press at both LPLT and HPHT conditions. From both the rheological and filtration loss properties, it was shown that the sample 18 shows to be the better option of the formulation of the drilling fluid. It can be concluded that the sample 18 showed to be the better results that compensate for both properties, where the fluid shows an improvement in the filtration loss at both LPLT and HPHT conditions by 50% and 61% respectively. Moreover, the sample 18 was well within the operating conditions for plastic viscosity, yield point and gel strengths (Ji et al., 2012).

5.2 Future Works

Some of the future works that would be recommended in further evaluating the rheological and filtration results of this experiment would be using a rheometer in evaluating the change in the rheological properties under different temperature conditions. Another would be to run a series of testing that could be done to further validate the internal packing structure by studying the nature of the plugging properties of the drilling fluid on a sandstone formation to evaluate the nanopolystyrene pore plugging abilities.

REFERENCES

A.T. BOURGOYNE, K. K. M., M.E. CHENEVERT, F.S. YOUNG 1986. Applied Drilling Engineering.

ABDO, J. & HANEEF, M. D. 2013. Clay nanoparticles modified drilling fluids for drilling of deep hydrocarbon wells. *Applied Clay Science,* 86**,** 76-82.

ABDUO, M. I., DAHAB, A. S., ABUSEDA, H., ABDULAZIZ, A. M. & ELHOSSIENY, M. S. 2016. Comparative study of using Water-Based mud containing Multiwall Carbon Nanotubes versus Oil-Based mud in HPHT fields. *Egyptian Journal of Petroleum,* 25**,** 459-464.

ABOULAICH, A., TILMACIU, C. M., MERLIN, C., MERCIER, C., GUILLOTEAU, H., MEDJAHDI, G. & SCHNEIDER, R. 2012. Physicochemical properties and cellular toxicity of (poly) aminoalkoxysilanes-functionalized ZnO quantum dots. *Nanotechnology,* 23.

AFTAB, A., ISMAIL, A. R., IBUPOTO, Z. H., AKEIBER, H. & MALGHANI, M. G. K. 2017. Nanoparticles based drilling muds a solution to drill elevated temperature wells: A review. *Renewable and Sustainable Energy Reviews,* 76**,** 1301-1313.

AFTAB, A., ISMAIL, A. R., KHOKHAR, S. & IBUPOTO, Z. H. 2016. Novel zinc oxide nanoparticles deposited acrylamide composite used for enhancing the performance of water-based drilling fluids at elevated temperature conditions. *Journal of Petroleum Science and Engineering,* 146**,** 1142-1157.

AGARWAL, S., PHUOC, T. X., SOONG, Y., MARTELLO, D. & GUPTA, R. K. 2013. Nanoparticle-stabilised invert emulsion drilling fluids for deep-hole drilling of oil and gas. *Canadian Journal of Chemical Engineering,* 91**,** 1641-1649.

AHMAD, H. M., KAMAL, M. S. & AL-HARTHI, M. A. 2018. High molecular weight copolymers as rheology modifier and fluid loss additive for water-based drilling fluids. *Journal of Molecular Liquids,* 252**,** 133-143.

AMANULLAH, M., ALARFAJ, M. K. & AL-ABDULLATIF, Z. A. 2011. Preliminary Test Results of Nano-based Drilling Fluids for Oil and Gas Field Application. Society of Petroleum Engineers.

ANTÓN, R. E., ANDÉREZ, J. M., BRACHO, C., VEJAR, F. & SALAGER, J. L. 2008. Practical surfactant mixing rules based on the attainment of microemulsion-oil-water three-phase behavior systems. *Advances in Polymer Science.*

BABA HAMED, S. & BELHADRI, M. 2009. plRheological properties of biopolymers drilling fluids. *Journal of Petroleum Science and Engineering,* 67**,** 84-90.

BABATUNDE, Y., BUTT, S., MOLGAARD, J. & ARVANI, F. 2011. Investigation of the Effects of Vibration Frequency On Rotary Drilling Penetration Rate Using Diamond Drag Bit. American Rock Mechanics Association.

BARRY, M. M., JUNG, Y., LEE, J.-K., PHUOC, T. X. & CHYU, M. K. 2015. Fluid filtration and rheological properties of nanoparticle additive and intercalated clay hybrid bentonite drilling fluids. *Journal of Petroleum Science and Engineering,* 127**,** 338-346.

BEHARI, J. 2010. Principles of nanoscience: An overview. *Indian Journal of Experimental Biology,* 48**,** 1008-1019.

BHAGAT, S. D., KIM, Y. H., SUH, K. H., AHN, Y. S., YEO, J. G. & HAN, J. H. 2008. Superhydrophobic silica aerogel powders with simultaneous surface modification, solvent exchange and sodium ion removal from hydrogels. *Microporous and Mesoporous Materials,* 112**,** 504-509.

BIGGS, S., SELB, J. & CANDAU, F. 1992. Effect of Surfactant on the Solution Properties of Hydrophobically Modified Polyacrylamide. *Langmuir,* 8**,** 838-847.

BIOVIS 2003. *Oilfield Polymers-Construction chemicals-Degussa Edition August*.

BJORNDALEN, H. N., JOSSY, W. E., ALVAREZ, J. M. & KURU, E. 2014. A laboratory investigation of the factors controlling the filtration loss when drilling with colloidal gas aphron (CGA) fluids. *Journal of Petroleum Science and Engineering,* 117**,** 1-7.

CAENN, R., DARLEY, H. C. H. & GRAY, G. R. 2011. *Composition and Properties of Drilling and Completion Fluids*.

CAI, J., CHENEVERT, M. E., SHARMA, M. M. & FRIEDHEIM, J. 2012. Decreasing water invasion into Atoka shale using nonmodified silica nanoparticles. *SPE Drilling and Completion,* 27**,** 103-112.

CAMESANO, T. A. & WILKINSON, K. J. 2001. Single molecule study of Xanthan conformation using atomic force microscopy. *Biomacromolecules,* 2**,** 1184-1191.

CHEN, L., ZHANG, G., GE, J., JIANG, P., ZHU, X., RAN, Y. & HAN, S. 2015. Ultrastable Hydrogel for Enhanced Oil Recovery Based on Double-Groups Cross-Linking. *Energy and Fuels,* 29**,** 7196-7203.

CHERAGHIAN, G., WU, Q., MOSTOFI, M., LI, M.-C., AFRAND, M. & S.SANGWAI, J. 2018. Effect of a novel clay/silica nanocomposite on water-based drilling fluids: Improvements in rheological and filtration properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 555**,** 339-350.

CHU, Q., LUO, P., ZHAO, Q., FENG, J., KUANG, X. & WANG, D. 2013. Application of a new family of organosilicon quadripolymer as a fluid loss additive for drilling fluid at high temperature. *Journal of Applied Polymer Science,* 128**,** 28-40.

DONNELLY, J. 2010. SPE Annual Conference Makes History. *Journal of Petroleum Technology,* 62**,** 36-41.

EL-SUKKARY, M. M. A., GHUIBA, F. M., SAYED, G. H., ABDOU, M. I., BADR, E. A., TAWFIK, S. M. & NEGM, N. A. 2014. Evaluation of some vanillin-modified polyoxyethylene surfactants as additives for water based mud. *Egyptian Journal of Petroleum,* 23**,** 7-14.

ELOCHUKWU, H., GHOLAMI, R. & SHAM DOL, S. 2017. An approach to improve the cuttings carrying capacity of nanosilica based muds. *Journal of Petroleum Science and Engineering,* 152**,** 309-316.

FAIZAL WONG, F. W., ARIFF, A. B. & STUCKEY, D. C. 2017. A biocompatible surfactant, methyl ester sulphonate (MES), as a precipitating ligand for protein purification. *Biochemical Engineering Journal,* 117**,** 30-40.

FATTAH, K. A. & LASHIN, A. 2016. Investigation of mud density and weighting materials effect on drilling fluid filter cake properties and formation damage. *Journal of African Earth Sciences,* 117**,** 345-357.

FEREIDOUNPOUR, A. & VATANI, A. 2014. An investigation of interaction of drilling fluids with gas hydrates indrilling hydrate bearing sediments. *Journal of Natural Gas Science and Engineering,* 20**,** 422-427.

FINK, J. K. 2015. *Water-Based Chemicals and Technology for Drilling, Completion, and Workover Fluids*.

GHANBARI, S. & NADERIFAR, A. 2016. Enhancing the physical plugging behavior of colloidal silica nanoparticles using binomial size distribution. *Journal of Natural Gas Science and Engineering,* 30**,** 213-220.

GHOLAMI, R., ELOCHUKWU, H., FAKHARI, N. & SARMADIVALEH, M. 2018. A review on borehole instability in active shale formations: Interactions, mechanisms and inhibitors. *Earth-Science Reviews,* 177**,** 2-13.

GONZÁLEZ, J. M., QUINTERO, F., ARELLANO, J. E., MÁRQUEZ, R. L., SÁNCHEZ, C. & PERNÍA, D. 2011. Effects of interactions between solids and surfactants on the tribological properties of water-based drilling fluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 391**,** 216-223.

GOU, S., YIN, T., LIU, K. & GUO, Q. 2015. Water-soluble complexes of an acrylamide copolymer and ionic liquids for inhibiting shale hydration. *New Journal of Chemistry,* 39**,** 2155-2161.

GUO, J., YAN, J., FAN, W. & ZHANG, H. 2006. Applications of strongly inhibitive silicate-based drilling fluids in troublesome shale formations in Sudan. *Journal of Petroleum Science and Engineering,* 50**,** 195-203.

HASSANI, A. H. & GHAZANFARI, M. H. 2017. Improvement of non-aqueous colloidal gas aphron-based drilling fluids properties: Role of hydrophobic nanoparticles. *Journal of Natural Gas Science and Engineering,* 42**,** 1-12.

HOSSAIN, M. E. & AL-MAJED, A. A. 2015. *Fundamentals of Sustainable Drilling Engineering*.

INGLEFIELD, D., JR., BODNAR, R. J. & LONG, T. E. 2016. Hydrogen bond containing multiwalled carbon nanotubes in polyurethane composites. *Polymer Composites,* 37**,** 1425-1434.

ISMAIL, A. R., AFTAB, A., IBUPOTO, Z. H. & ZOLKIFILE, N. 2016. The novel approach for the enhancement of rheological properties of water-based drilling fluids by using multi-walled carbon nanotube, nanosilica and glass beads. *Journal of Petroleum Science and Engineering,* 139**,** 264-275.

J.J. AZAR, G. R. S. 2007. Drilling Engineering. *PennWell Books, Oklahoma, USA (2007)*.

JAIN, R. & MAHTO, V. 2015. Evaluation of polyacrylamide/clay composite as a potential drilling fluid additive in inhibitive water based drilling fluid system. *Journal of Petroleum Science and Engineering,* 133**,** 612-621.

JI, L., GUO, Q., FRIEDHEIM, J. E., ZHANG, R., CHENEVERT, M. E. & SHARMA, M. M. 2012. Laboratory evaluation and analysis of physical shale inhibition of an innovative water-based drilling fluid with nanoparticles for drilling unconventional shales. In: Proceedings of the SPE Asia Pacific Oil and Gas Conference and Exhibition. Society of Petroleum Engineers.

JIA, H., CHEN, H. & GUO, S. 2017. Fluid loss control mechanism of using polymer gel pill based on multi-crosslinking during overbalanced well workover and completion. *Fuel,* 210**,** 207-216.

JUNG, Y., SON, Y. H., LEE, J. K., PHUOC, T. X., SOONG, Y. & CHYU, M. K. 2011. Rheological behavior of clay-nanoparticle hybrid-added bentonite suspensions: Specific role of hybrid additives on the gelation of clay-based fluids. *ACS Applied Materials and Interfaces,* 3**,** 3515-3522.

KANIA, D., YUNUS, R., OMAR, R., ABDUL RASHID, S. & MOHAMAD JAN, B. 2015. A review of biolubricants in drilling fluids: Recent research, performance, and applications. *Journal of Petroleum Science and Engineering,* 135**,** 177-184.

KAZEMI-BEYDOKHTI, A. & HAJIABADI, S. H. 2018. Rheological investigation of smart polymer/carbon nanotube complex on properties of water-based drilling fluids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 556**,** 23-29.

KHODJA, M., CANSELIER, J. P., BERGAYA, F., FOURAR, K., KHODJA, M., COHAUT, N. & BENMOUNAH, A. 2010. Shale problems and water-based drilling fluid optimisation in the Hassi Messaoud Algerian oil field. *Applied Clay Science,* 49**,** 383-393.

KIM, Y. R., PARK, J. I., LEE, E. J., PARK, S. H., SEONG, N. W., KIM, J. H., KIM, G. Y., MEANG, E. H., HONG, J. S., KIM, S. H., KOH, S. B., KIM, M. S., KIM, C. S., KIM, S. K., SON, S. W., SEO, Y. R., KANG, B. H., HAN, B. S., AN, S. S. A., YUN, H. I. & KIM, M. K. 2014. Toxicity of 100 nm zinc oxide nanoparticles: A report of 90-day repeated oral administration in Sprague Dawley rats. *International Journal of Nanomedicine,* 9**,** 109-126.

KOSYNKIN, D. V., CERIOTTI, G., WILSON, K. C., LOMEDA, J. R., SCORSONE, J. T., PATEL, A. D., FRIEDHEIM, J. E. & TOUR, J. M. 2012. Graphene oxide as a high-performance fluid-loss-control additive in water-based drilling fluids. *ACS Applied Materials and Interfaces,* 4**,** 222-227.

KURU, E., BJORNDALEN, N., JOSSY, E. & ALVAREZ, J. M. 2008. Reducing Formation Damage with Microbubble-Based Drilling Fluid: Understanding the Blocking Ability.

KUTLU, B. 2013. Rheological Properties of Drilling Fluids Mixed with Lightweight Solid. Society of Petroleum Engineers.

LU, Y., YANG, F., GE, Z., WANG, Q. & WANG, S. 2017. Influence of viscoelastic surfactant fracturing fluid on permeability of coal seams. *Fuel,* 194**,** 1-6.

M. BO, D. F., B. SCARLETT 1965. The effect of particle size distribution on the permeability of filter cakes. *Trans. Inst. Chem. Eng., 43 (2) (1965), pp. 228-232*.

MAHTO, V. & SHARMA, V. P. 2004. Rheological study of a water based oil well drilling fluid. *Journal of Petroleum Science and Engineering,* 45**,** 123-128.

MAHTO, V. & SHARMA, V. P. 2005. Tragacanth gum: An effective oil well drilling fluid additive. *Energy Sources,* 27**,** 299-308.

MANSA, R., DZENE, L., QUINTELA, A., ROCHA, F. & DETELLIER, C. 2016. Preparation and characterization of novel clay/scleroglucan nanocomposites. *Applied Clay Science,* 126**,** 235-244.

MAO, H., QIU, Z., SHEN, Z. & HUANG, W. 2015. Hydrophobic associated polymer based silica nanoparticles composite with core-shell structure as a filtrate reducer for drilling fluid at ultra-high temperature. *Journal of Petroleum Science and Engineering,* 129**,** 1-14.

MEDHEKAR, N. V., RAMASUBRAMANIAM, A., RUOFF, R. S. & SHENOY, V. B. 2010. Hydrogen bond networks in graphene oxide composite paper: Structure and mechanical properties. *ACS Nano,* 4**,** 2300-2306.

MISSANA, T. & ADELL, A. 2000. On the applicability of DLVO theory to the prediction of clay colloids stability. *Journal of Colloid and Interface Science,* 230**,** 150-156.

NAREH'EI, M. A., SHAHRI, M. P. & ZAMANI, M. 2012. Rheological and filtration loss characteristics of colloidal gas aphron based drilling fluids. *Journal of the Japan Petroleum Institute,* 55**,** 182-190.

RAHDAR, A. & ALMASI-KASHI, M. 2016. Dynamic light scattering of nano-gels of xanthan gum biopolymer in colloidal dispersion. *Journal of Advanced Research,* 7**,** 635-641.

RODRIGUES, J. D. A., LACHTER, E. R., DE SÁ, C. H., DE MELLO, M. & NASCIMENTO, R. S. V. 2006. New Multifunctional Polymeric Additives for Water-Based Muds. Society of Petroleum Engineers.

RYU, H. J., SEO, M. Y., JUNG, S. K., MAENG, E. H., LEE, S. Y., JANG, D. H., LEE, T. J., JO, K. Y., KIM, Y. R., CHO, K. B., KIM, M. K., LEE, B. J. & SON, S. W. 2014. Zinc oxide nanoparticles: A 90-day repeated-dose dermal toxicity study in rats. *International Journal of Nanomedicine,* 9**,** 137-144.

S. TUNC, O. D. 2008. The effect of different molecular weight of poly (ethylene glycol) on the electrokinetic and rheological properties of Na-bentonite suspensions. *Colloids Surf. A Physicochem. Eng. Asp., 317***,** pp. 93-99.

SADEGHALVAAD, M. & SABBAGHI, S. 2015. The effect of the TiO2/polyacrylamide nanocomposite on water-based drilling fluid properties. *Powder Technology,* 272**,** 113-119.

SAYINDLA, S., LUND, B., YTREHUS, J. D. & SAASEN, A. 2017. Hole-cleaning performance comparison of oil-based and water-based drilling fluids. *Journal of Petroleum Science and Engineering,* 159**,** 49-57.

SEHLY, K., CHIEW, H.-L., LI, H., SONG, A., LEONG, Y.-K. & HUANG, W. 2015. Stability and ageing behaviour and the formulation of potassium-based drilling muds. *Applied Clay Science,* 104**,** 309-317.

SENSOY, T., CHENEVERT, M. E. & SHARMA, M. M. 2009. Minimizing Water Invasion in Shales Using Nanoparticles. Society of Petroleum Engineers.

SMITH, S. R., RAFATI, R., SHARIFI HADDAD, A., COOPER, A. & HAMIDI, H. 2018. Application of aluminium oxide nanoparticles to enhance rheological and filtration properties of water based muds at HPHT conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 537**,** 361-371.

SRIVATSA, J. T. & ZIAJA, M. B. An experimental investigation on use of nanoparticles as fluid loss additives in a surfactant - Polymer based drilling fluid. Society of Petroleum Engineers - International Petroleum Technology Conference 2012, IPTC 2012, 2012. 2436-2454.

SUNDSTROM, L. R. J. & CERVANTES, M. J. 2017. Transient wall shear stress measurements and estimates at high Reynolds numbers. *Flow Measurement and Instrumentation,* 58**,** 112-119.

T.M. AL-BAZALI, J. Z., M.E. CHENEVERT, M.M. SHARMA 2005. Measurement of the sealing capacity of shale caprocks Dallas, 9–12 October. *Paper SPE 96100 Presented at the SPE Annual Technical Conference and Exhibition*.

TEHRANI, A., YOUNG, S., GERRARD, D. & FERNANDEZ, J. 2009. Environmentally Friendly Water Based Fluid for HT/HP Drilling. Society of Petroleum Engineers.

VILLADA, Y., GALLARDO, F., ERDMANN, E., CASIS, N., OLIVARES, L. & ESTENOZ, D. 2017. Functional characterization on colloidal suspensions containing xanthan gum

(XGD) and polyanionic cellulose (PAC) used in drilling fluids for a shale formation. *Applied Clay Science,* 149**,** 59-66.

VRYZAS, Z., MAHMOUD, O., NASR-EL-DIN, H. A. & KELESSIDIS, V. C. 2015. Development and Testing of Novel Drilling Fluids Using Fe2O3 and SiO2 Nanoparticles for Enhanced Drilling Operations. International Petroleum Technology Conference.

WAHAB, R., KAUSHIK, N., KHAN, F., KAUSHIK, N. K., CHOI, E. H., MUSARRAT, J. & AL-KHEDHAIRY, A. A. 2016. Self-Styled ZnO Nanostructures Promotes the Cancer Cell Damage and Supresses the Epithelial Phenotype of Glioblastoma. *Scientific Reports,* 6.

WANG, M., SUN, M., SHANG, H., FAN, S., LIU, M. & LIU, F. 2012. Biodiesel-based Drilling Fluids. *IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition.* Tianjin, China: Society of Petroleum Engineers.

WELTON, T. D., BRYANT, J. & FUNKHOUSER, G. P. 2007. Anionic Surfactant Gel Treatment Fluid. Society of Petroleum Engineers.

YAN, L., WANG, C., XU, B., SUN, J., YUE, W. & YANG, Z. 2013. Preparation of a novel amphiphilic comb-like terpolymer as viscosifying additive in low-solid drilling fluid. *Materials Letters,* 105**,** 232-235.

YARIM, G., UCHYTIL, R. J., MAY, R. B., TREJO, A. & CHURCH, P. 2007. Stuck Pipe Prevention--A Proactive Solution to an Old Problem. Society of Petroleum Engineers.

YINGCHENG, L., WEIDONG, Z., BAILING, K., MAURA, P., XINNING, B., OU, S., ZHIQIN, S., YIQING, Y., YANHUA, L., SONGYUAN, G., CLARENCE, M. & HIRASAKI GEORGE, J. 2016. Mixtures of anionic/cationic surfactants: A new approach for enhanced oil recovery in low-salinity, high-temperature sandstone reservoir. *SPE Journal,* 21**,** 1164-1177.

YUNITA, P., IRAWAN, S. & KANIA, D. 2016. Optimization of Water-based Drilling Fluid Using Non-ionic and Anionic Surfactant Additives. *Procedia Engineering,* 148**,** 1184-1190.

ZAKARIA, M. F., HUSEIN, M. & HARELAND, G. Novel nanoparticle-based drilling fluid with improved characteristics. Society of Petroleum Engineers - SPE International Oilfield Nanotechnology Conference 2012, 2012. 232-237.

ZHANG, S., LI, J., LYKOTRAFITIS, G., BAO, G. & SURESH, S. 2009. Size-dependent endocytosis of nanoparticles. *Advanced Materials,* 21**,** 419-424.

ZHANG, W., SHEN, H., WANG, Y. & DONG, Y. 2016. Grafting lignite with sulformethal phenoldehy resin and their performance in controlling rheological and filtration properties of water-bentonite suspensions at high temperatures. *Journal of Petroleum Science and Engineering,* 144**,** 84-90.