Water-Based Drilling Fluids for High Temperature and Dispersible Shale Formation Applications

By

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Declaration

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

Signed………………………………………….

EMMANUEL UDOFIA AKPAN

Supervisors (Joint)

Signed……………………….	Signed………………………
Dr Godpower Enyi	Prof. G.G. Nasr

List of Publications

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Nomenclature

θ_{300}	300 RPM Dial Reading
θ_{600}	600 RPM Dial Reading
AHR	After Hot Rolling
API	American Petroleum institute
AV	Apparent Viscosity
BHR	Before Hot Rolling
CEC	Cation Exchange Capacity
CMC	Carboxymethyl cellulose
ECD	Equivalent Circulating Density
EPA	Environmental Protection Agency
FR-SBM	Flat-Rheology Synthetic Based Mud
GBF	Gas Based Fluid
GoM	Gulf of Mexico
HPHT	High Pressure High Temperature
HPWBM	High Performance Water Based Mud
IEM	Invert Emulsion Mud
IPA	3-Indolepropionic Acid
K	Fluid Consistency Index
KGM	Konjac Glucomannan Gum
LSRV	Low Shear Rate Viscosity
n	Flow Behaviour Index
OBM	Oil Based Mud

OHS	Occupational Health and Safety
PAC R	Polyanionic Cellulose Regular
PAO	Polyalpha olefin
PCF	Pounds Per Cubic Feet
PEG	Polyethylene glycol
PHPA	Partially-Hydrolysed Polyacrylamide
PPE	Personal Protective Equipment
PPG	Pounds Per Gallon
PV	Plastic Viscosity
ROP	Rate of Penetration
RPM	Revolutions per Minute
S. G	Specific Gravity
SBM	Synthetic Based Mud
SI	SI Unit
TD	Total Depth
T_m	Transition Temperature
WBM	Water based Mud
XC	Xanthan Gum
YP	Yield Point
YP/PV	Ratio of Yield Point to Plastic Viscosity

Unit Conversion Factors

Viscosity

1 Centipoise = 0.01 Poise

= 0.001 Pascal Seconds

Shear Stress

Ib/100 ft2 = 0. 4788Pascal

= 0.4788 N/m^2

Shear Rate

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

Abstract

The negative impacts of drilling fluids, most especially oil-based muds, on the environment are a source of concern to regulators and governments all over the world. Consequently, regulations on the discharge and disposal of drilling fluids worldwide have become stricter. The recent research in drilling fluids formulation is focussed on the design of high-performance water-based drilling fluids, which are environmentally friendly, remain stable when exposed to high temperatures, and prevent problems associated with reactive shale. Even though water-based fluid systems are environmentally-friendly, their instabilities when exposed to high temperatures remain a big challenge. Biopolymers are commonly used in water-based muds to provide viscosity but degrade at high temperatures.

In this study, an attempt has been made to investigate whether the combination of anti-oxidants, formate salts, pH control agents, and polyethylene glycol could increase the stability temperatures of biopolymers in water-based drilling fluids and inhibit shale dispersion at high temperatures. The rheological properties of the drilling fluid formulations with pH 8-10 were measured using Models 800 and 1100 viscometers before and after aging dynamically in a roller oven for sixteen hours. The stability temperature of drilling fluid formulation was defined as the temperature at which it retains 50% of its original viscosity after aging for 16-hours. Shale rock samples were characterised using scanning electron microscope photos; X-ray diffraction analysis was used to identify the mineral contents of the shale samples. Shale dispersion tests were carried out by aging shale cuttings in drilling fluid formulation and in freshwater, dynamically in a roller oven for 16 hours at 120°C. The percentage recovery of shale rocks after dynamic aging was determined. Experimental data indicated that the stability temperatures of diutan gum, konjac gum, and xanthan gum in bentonite water-suspension after aging for 16 hours were 115°C, 65°C, and 100°C respectively. The mud formulations with the additives - sodium erythorbate, potassium formate, and polyethylene glycol – retained at least 50% of their viscosities up to 232°C. The additives, therefore, significantly retarded the degradation of the biopolymers and other mud additives up to 232°C. The result from the shale dispersion test showed that the shale cuttings recovered from freshwater was 78%; with drilling fluids formulated with the additives, the shale cuttings recovered were 100%. When a shale plug (14.99g) was exposed to freshwater, it was found that 79% of the shale plug was recovered. When another shale plug (13.77g) interacted with an inhibitive mud formulation, it was found that 100% of the shale rock was recovered. This new fluid systems which are stable at high temperatures and inhibits shale dispersion can meet high temperature and shale formation drilling requirements.

Chapter 1: Introduction

1.1 Introduction

As the demand for energy increases, harsh and extreme environments are explored for hydrocarbon; and deeper wells have been drilled to reach targets in formations with very high temperatures and pressures. To drill successfully, safely, and economically in such harsh environments, a drilling fluid whose properties remain stable when exposed to high temperatures and that can retard shale problems is required. Regarding their technical performance, oil-based mud (OBM) systems can be used successfully in such environments (Bland et al., 2006). However, oil-based drilling mud has its limitations: It is susceptible to contamination by water; there are fire risks; the rate of bit penetration is low; and most importantly, there is the risk of environmental impact. Arising from stringent environmental legislation, the current effort in the oil industry is geared towards the development of environmentally friendly fluids that could perform like oil-based muds (Apaleke et al.,2012). More so, industrial regulators are becoming stricter on the use of environmentally friendly drilling fluids. For example, the Environmental Protection Agency in the United States of America prohibited any discharge of OBMs or their cuttings from offshore platforms (Amanullah, 2005). In addition, the attendant high cost of a litigation action and fines from man-made environmental pollution, have engendered the search for environmentally friendly additives in the formulation of drilling fluids (Amanullah, 2007). Even though water-based fluid systems are environmentally friendly, their instabilities when exposed to high temperatures remain a big challenge (Tehrani et al., 2007). High temperature affects the hydration of components, fluid loss, clay dispersion, and the degradation of additives in water-based fluids (Wenjun et al., 2014). One of the additives used in drilling fluids is polymer. The function of polymers in drilling muds is to provide viscosity, shale inhibition and fluid-loss control, and to prevent clay dispersion (Galindo et al., 2015). Polymers are used in almost all water-based muds and classified into natural, synthetic, and modified natural polymers. They are selected for use based on the following: classification, strengths, weaknesses, molecular weight, and functionality (Strickland,1994). Synthetic polymers are stable at high temperatures (Strickland,1994; Plank, 1992) but are expensive, cause formation damage and generate high plastic viscosity (Tehrani et al.,2007). Conversely, biopolymers are non-toxic and less expensive and have less effect on formation damage (Mahto et al.,2004; Mahto et al., 2005). In addition, biopolymers are environmentally friendly (Dayawant,1999) and enhance the properties of water-based muds even at very low concentrations (Darley and Gray,1988). They are either used separately or mixed together to improve bentonite performance (Darley and Gray,1988). Any drilling mud systems that are made up of soluble polymers can be referred to as polymer muds.

1.2 Problem statement

Biopolymer-based muds have some limitations: High solid contents (Amoco Production comapnay,1994) and high temperatures pose a major challenge to running biopolymer-based muds successfully (Tehrani et al.2007; Galindo et al., 2015). High temperatures cause the degradation of biopolymers in drilling muds (Wenjun et al., 2014, Tehrani et al., 2007); Zhang et al.,2016), thus leading to the decrease or total loss in viscosity and fluid loss control properties of a drilling fluid (Weaver et al.,2003). The degradation of a biopolymer in water-based muds when subjected to elevated temperatures for a long period remains a big challenge (Bradshaw et al.,2006). The low stability temperatures of biopolymers, therefore, make them unsuitable for high-temperature drilling operations. It is challenging to select additives that can give water-based muds the rheological and fluid-loss properties required in a formation with temperatures exceeding 300°F (150°C) (Bradshaw et al.,2006). Consequently, most water-based fluids formulated with biopolymers can only be deployed in formations with temperatures lower than 300°F (150°C) (Galindo et al.,2015). To stabilise biopolymers in drilling fluids, the mechanisms through which biopolymers degrade at elevated temperatures, therefore, must be understood. The degradation mechanisms of thermally labile biopolymers, therefore, include acid-catalysed hydrolysis at the acetal linkages present in the biopolymer backbone (Weaver et al.,2003) as well as oxidation-reduction (redox) reactions and early onset of the helix-coil conformation transition (Seright and Henrici, 1990). These mechanisms can be exploited to stabilise biopolymers in water-based fluids at high-temperatures, by deploying additives that can counteract, neutralise, or retard the degradation processes (Seright and Henrici, 1990; Wellington, 1983; Downs,1993). These mechanisms are, therefore, exploited in this work to stabilise water-based drilling fluids at high temperatures by screening additives (formate salts, antioxidants, and polyglycols) that can counteract, neutralise, or retard these processes. Antioxidants protect biopolymers, increase their thermal stability at high temperatures, and inhibit oxidative reactions and reacts with hydroxyl free radicals that contribute to the degradation of polymers; the stability temperature of a biopolymer is the temperature at which it maintains 50% of its viscosity when aged for 16-hours (Howard et al.,2015). In addition, formate brines are used in high-temperature drilling operations to stabilise biopolymers as they act as antioxidants (Downs, 1993; Howard, 1995; Clarke-Sturmanet al., 1986, 1988; Howard et al., 2015; Bungert et al., 2000). They stabilise biopolymers at high temperatures by raising their melting (transition) temperatures (T_m) and providing free-radical properties, which retard oxidative processes (Clarke-Sturmanet al., 1986). At the transition temperature (T_m), a biopolymer undergoes an order-disorder conformational change; the order-disorder conformational change is followed by a loss in viscosity and by an increase in the rate of hydrolytic degradation by two orders of magnitude (Clarke-Sturman and

Sturla, 1988). Formate brines, therefore, increase the thermal stability of biopolymers by increasing their Tm, are potent antioxidants, and can prevent biopolymers from thermal degradation up to a temperature of at least 150°C (Downs, 1993; Howard et al., 2015). It is, therefore, not recommended to use formate salts alone to stabilise water-based fluids above 150°C.

Dissolved oxygen in drilling fluid is not only responsible for thermal degradation of biopolymer at high temperatures (Seright and Henrici, 1990), but it is also responsible for corrosion of drill pipes. In addition, polyglycols are used to stabilise biopolymers in water-based fluids above 150°C (Howard et al.,2015). Biopolymers and polyglycols in solutions associate by intermolecular hydrogen bonding and hydrophobic interactions. These associations and complexation stabilised biopolymers at high temperatures (Oort et al.,1997). Apart from being environmentally friendly, polyglycol muds inhibited sensitive shale formations, lubricated drill pipe, and cleaned and deposited a thin and impermeable mud cake on well-bore (Saki et al., 2010). Polyglycols are also deployed to stabilise reactive shale formations. They absorb strongly on clay rock, thereby reducing clay hydration, but are not very effective in salt-free or low-salt fluids (Brady et al., 1998).

Some users of biopolymers also used buffering agents and antioxidants to prevent their degradation at high temperatures. This method is not very successful as changes in molecular conformation in biopolymer at elevated temperature are not taken into consideration (Downs,1992). In addition, oxidation-reduction reactions which involve free radicals are the probable cause of biopolymer degradation in drilling muds and its associated viscosity loss (Wellington,1983). Without the presence of dissolved oxygen and based on pH, acid-catalysed hydrolysis and base-catalysed formation reactions have significant effects on biopolymer degradation at high temperatures (Seright and Henrici, 1990).

Apart from the detrimental effects of high temperatures on the rheological properties of drilling fluids, suspension, and fluid-loss control, there are also well bore instability problems associated with fluid interaction with reactive shale formations. About 70% of well-bore instability problems is caused by shale (Aftab et al., 2017). During drilling operations, drilling fluid replaces shale in the wellbore, thereby causing mechanical stress changes, changes in capillary pressure in the shale, swelling pressure in the shale, changes in pressure around the wellbore, and fluid movement due to differential pressure. These changes lead to hole instability (Lal, 1999). As shale is made of kaolinite, illite, smectite, and montmorillonite, it has an affinity for water. Therefore, if a shale formation is drilled with a non-inhibitive water-based mud, the shale instability problems occur (Wilcox et al., 1987; Soric et al., 2004; Reid et al., 1992). Consequently, water-based fluids are formulated with organic or inorganic additives to improve shale inhibition properties (Sandra and Arvid, 2013; Pinya et al., 1995; Clark et al., 1976). The organic inhibitors are classified into three categories (Sandra and Arvid, 2013): (1) monomeric amine shale inhibitors (they have a low level of inhibition and high ammonia odour), (2) oligomeric amine shale inhibitors (they provide a more permanent shale stabilisation), and (3) polyamine shale inhibitors (they are a more permanent shale inhibitor and less attractive due to their incompatibility with other anionic additives). The inorganic shale inhibitors are salts such as sodium chloride, calcium chloride, and potassium chloride. Potassium chloride is a commonly used inorganic additive for shale inhibition. However, high concentrations of potassium chloride in drilling fluids are an environmental concern (Bloyset al., 1994). Another inorganic shale inhibitor are silicate additives (Soric et al., 2004). Silicate additives have the potential to damage formation, and the control of rheological properties is a major problem with the use of a silicate-based mud system (Vikas and Rajat, 2015). A lot of attempts have been made to stabilise water-based fluids at high temperatures and in inhibiting shale hydration and dispersion in reactive shale formations. None has, however, considered the combination of additives used in this work. The additives were used to formulate high-performance water-based drilling muds (HPWBMs). HPWBMs are environmentally friendly and cost-effective regarding cuttings and fluids disposal, remain stable when exposed to high temperatures, and retard problems associated with reactive shale. Their technical performance approaches that of oil-based mud systems.

1.2 Research contribution

This experimental study provides a detailed procedure on water-based fluid formulations for high temperature drilling operations and findings on the effects of anti-oxidants, formate salts and polyglycols on biopolymers in water-based drilling fluids and on reactive shale formations at high temperatures. Since water-based fluids degrade at high temperatures, the findings of this study will contribute greatly to knowledge as this present study seeks to develop biopolymer water-based drilling fluids that are stable and inhibit shale dispersion. In addition, the use of sodium erythorbate, potassium formate, buffering agents, and polyethylene glycol (8000) to stabilise water-based polymer fluids and to inhibit shale dispersion at high temperatures has never been investigated before. This study, therefore, would help to uncover critical areas with respect to the use of anti-oxidants, formate salts, pH control agents, and polyglycols to raise the stability temperatures of biopolymers in water-based drilling fluids and to inhibit shale dispersion.

1.3 Overall aims

The aims of the research are to:

- Develop an experimental procedure for the formulation of high-performance water-based drilling muds.
- Design water-based drilling fluids for high temperature formation applications.
- Design water-based drilling fluids for dispersible shale formation applications.

1.4 Objectives

The objectives of the research are to:

- Devise an experimental method by pressurizing drilling fluid formulations in aging cells and aging them dynamically in a roller oven at different temperatures for 16 hours to mimic the interaction between drilled cuttings and drilling fluids in a well-bore annulus.
- To measure the rheological properties of drilling fluid formulations using Models 800 and 1100 viscometers to determine 16-hour stability temperatures of biopolymers in drilling fluids.
- To determine which combination of antioxidants, pH control agents, buffering agents, polyglycol, and formate salts raises the stability temperatures of biopolymers in water-based drilling fluids at high temperatures.
- To investigate the effects of antioxidants, formate salts, polyglycol, and pH control agents on reactive shale formations at high temperatures.

1.5 Thesis outline

This thesis comprises six chapters, each of which discusses the relevant aspects of the research:

- It begins with a brief introduction of the research background, including the aim and objectives.
- Chapter 2 gives a brief description of the types of drilling fluids, classification of drilling fluids, drilling fluid properties, aging of drilling fluids, and classification of drilling fluid additives. The effects of drilling fluid on the environment are also covered.
- Chapter 3 examines relevant literature on drilling fluids with emphasis on biopolymers in water-based drilling fluids and on shale-fluid interactions. The effects of high temperatures

on water-based fluids containing biopolymers are presented. In addition, previous works including problems associated with the use of biopolymers as drilling fluids additives are also reviewed.

- In chapter 4, the methodology used in the research work is outlined. The laboratory equipment and test procedures used in the research work are described in detail.
- In Chapter 5, the results of the laboratory test are presented and analysed. It also discusses the significance of the experimental data.
- Chapter 6 covers the conclusions and the recommendations in the research. It discusses the future direction in the research.

Chapter 2: Theoretical Background

2.1 Introduction

In this Chapter, water-based fluids are considered as it is relevant to the present study. The types of drilling muds, classification of water-based fluids, and additives used in drilling fluids are presented. The properties of drilling fluids which are relevant to present study are also presented. In addition, drilling fluid aging and the effects of drilling fluids on the environment are also highlighted briefly in this chapter.

2.2 Drilling fluids

A drilling fluid is used in the drilling of water, crude oil, and natural gas wells. It is pumped from the surface through the drill string and back to the surface through the annulus (ASME Shale Shaker Committee,2005). In the oil industry, there are nine categories of drilling fluids: five categories are freshwater systems, one category, saltwater systems; two categories, oil or synthetic based systems; and the last category, pneumatic fluid systems (Mitchel and Miska, 2011). Drilling muds, oil or water-based, are made up of clays, water, and chemical additives. In addition, drilling fluids are an essential part of any drilling operations and make up a substantial portion of drilling cost (Mitchel and Miska, 2011). In water-based muds**,** the solid materials are mixed in water or brine without chemicals or with chemicals with some percentages of oil. The solids materials are usually clays, weighting agents, and organic materials. When oil is dispersed in water, the water in the mud is called the continuous phase. When water or brine is dispersed in the oil, the continuous phase is the oil. Oil-based muds (OBMs) are made up of mineral oils, chemical additives, and barite; and are not environmentally friendly (Amanullah, 2005). In the oil based-mud, diesel, kerosene, and fuel oils are used as based fluid; but in synthetic-based muds (SBMs), an oil like substance is used as the based fluid (Bourgogne et al., 1986; Darley and Gray, 1988). For the pneumatic (gas) fluids, high velocity air or natural gas is used to carry cuttings out of the well bore. Foaming agents are used to remove formation water that flows into the well bore. For any drilling operation, the following factors are considered in the selection of drilling fluid: the type of formation to be drilled; the water used in preparing the drilling mud; and effect on the environment (Mitchel and Miska, 2011).

2.3 Water based drilling fluids

Most wells are drilled with water-based drilling muds (WBMs). WBMs are made up of minerals, salts, and organic compounds. The base fluid is water. The additives in water-based muds include alkalis, salts, surfactants, organic polymers, barite, and clay. In addition, water-based drilling muds are also made of several metals. The toxic metals found in water-based muds include arsenic, nickel, chromium, barite, cadmium, copper, iron, lead, mercury and zinc (Neff et al., 1987). They also contain a substantial quantity of organic matter such as biopolymers, which are highly degradable and less toxic (Schaaning et al.,2008). The composition of water-based muds is as shown in Figure 2.1) (Neff, 2005). The mud additives are selected based on the type of formation to be drilled, formation lithologies, and cost (Apaleke et al. 2012).

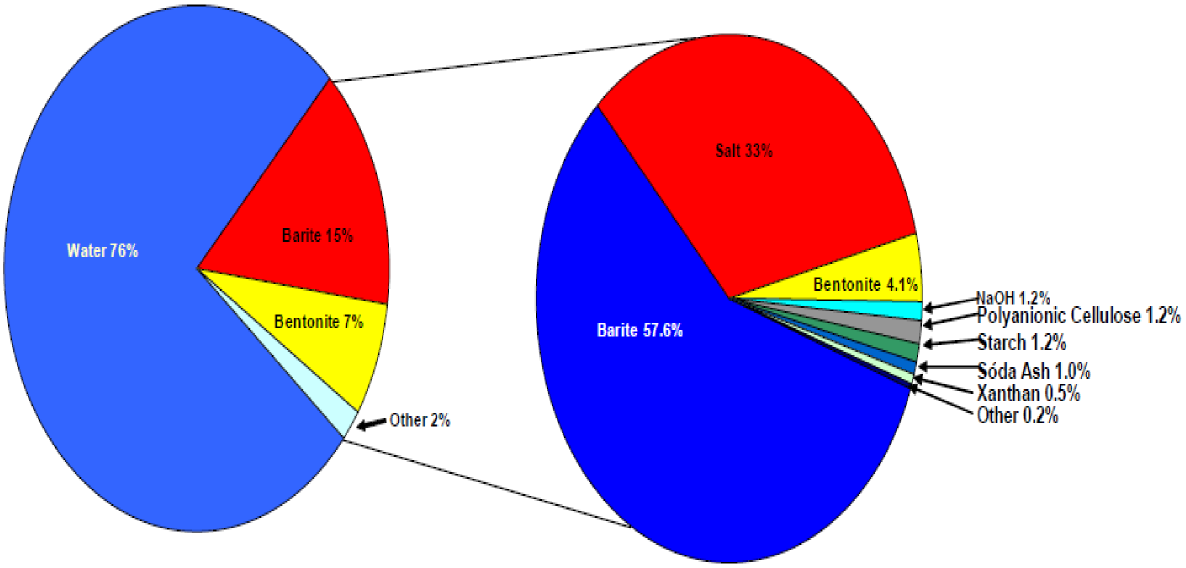


Figure 2.1: A typical composition of water-based drilling mud (Neff, 2005)

2.3.1 Types of water-based muds

Water-based muds are categorised into dispersed and non-dispersed muds. The main difference between dispersed and non-dispersed muds is the lack of a dispersant. In the dispersed muds, chemical dispersant is used to disperse mud solids. Dispersants such as lignite and lignosulfonate are in use. Since the dispersants are acidic, they required an alkaline environment to function properly. The dispersants make it possible for clay to deflocculate to control fluid losses. In the non-dispersed mud, dispersants are not added. One of the viscosifiers and fluid loss agents used in water-based muds is bentonite. The pH of water-based mud is controlled with caustic soda (NaOH) while the density is controlled with weighting agents. There are two categories of dispersed muds: calcium-based and seawater muds. Since the non-dispersed drilling muds do not need high pH, a dispersant is not needed, but they are not as tolerant of solids and contamination as the dispersed muds. Polymers are usually used for fluid loss control and for viscosity. The polymers and other mud additives are very susceptible to contaminations from produced gases and fluids (Young, 1993). Water-based fluids are classified as follows (Mitchel and Miska, 2011):

- Inhibitive
- Non-inhibitive
- Polymer

There are no specific ions - sodium, calcium, and potassium - in non-inhibitive fluids, but inhibitive fluids have these ions (Mitchel and Miska, 2011). Since non-inhibitive fluids do not have these ions, they do not significantly inhibit clay swelling. Non-inhibitive fluids are made up of clay from the formation to be drilled or bentonite and caustic soda or lime. Deflocculant or dispersants or both are also added to non-inhibitive fluids. Lignites, lignosulfonates, or phosphates are the dispersants usually used in non-inhibitive fluids, which are generally spud muds (Amoco Production Company,1994). Inhibited water-based systems minimise water wetting of the rock pores (Young, 1993), and do not contain chemical dispersants (thinners) as well as inhibitive ions. But they are made up of native water. The cations such as (Na^+), (Ca^{++}) and (K^+) in inhibited water-based systems reduce clay swelling. The inhibitive drilling fluid system are usually used to drill reactive shale formation and sandstone formations containing reactive clays. High cost of disposal is a major disadvantage of using an inhibitive fluid since the source of the cation is usually a salt (Amoco Production Company,1994)**.** Polymers are used to provide viscosity, to control fluid loss, and to deflocculate or encapsulate solids in drilling fluids. Polymers can remain stable up to 400^{o}F, and the presence of solids poses a big challenge to the use of polymer mud systems (Amoco Production Company,1994)**.** To enhance shale inhibition, potassium chloride is used as the brine for polymer mud system. The inhibitive properties of polymer fluids can further be improved by using glycol and amine-based inhibitors (PetroWiki, 2015). In this present study, polymer-based muds are designed for high temperature operations and for shale inhibition.

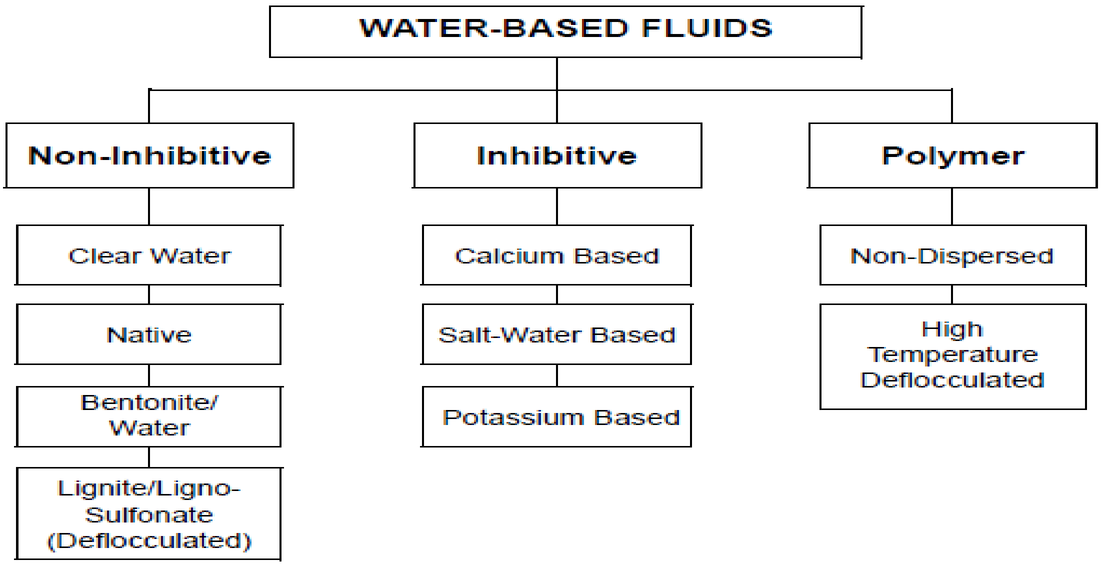


Figure 2.2: Water-Based Fluids (Amoco Production Company,1994)

2.3.2 Disadvantages of Water- based mud

According to Mellot, the major disadvantages of WBMs are as follows (Mellot, 2008):

1. Unwanted increase in density from salt in a formation
2. Causes formation damage.
3. Causes clay disintegration and dispersion
4. Not effective in sensitive shale formation
5. Causes corrosion

The present study seeks to address the problems associated with the use of water-based fluids.

2.3.3 The Advantages of WBMs

The major advantages of WBMs are as follows (Apaleke, 2012):

1. It is easy to handle, inexpensive, and cost effective.
2. Low toxicity on the environment.
3. It is readily available.
4. High rate of penetration.

2.3.4 Drilling fluid additives

The additives mostly used in water-based muds are clays, lost-circulation materials, polymers, weighting agents, fluid loss control additives, dispersant or thinners, inorganic chemicals, and surfactants. The additives list for water-based mud is divided into eighteen categories (Neff,2005):

weighting materials, viscosifiers, thinners, dispersants, alkalinity, pH-control additives, bactericides, filtrate reducers, flocculants, foaming agents, lost circulation materials, pipe-freeing agents, calcium reducers, corrosion inhibitors, emulsifiers, defoamers, shale control inhibitors, surface-active agents, temperature stability agents, and lubricants. As the present study seeks to develop water-based muds for high temperature operations and for shale inhibition and dispersion, the additives investigated are viscosifiers, pH-control additives, filtrate reducers, shale control additives, and temperature stability agents.

2.3.5 Clay minerals, freshwater, and polymers

In this Sub-section, the materials used in this study are considered.

2.3.5.1 Freshwater

Water, the continuous phase of any water-based mud, provides the initial viscosity and serves as the base fluid and as a means for conditioning the bentonite and other additives used in the drilling fluid preparations Another function of water is to suspend solids in drilling fluids and serves as the medium for transferring the surface available hydraulic horsepower to the bit on the bottom of the well-bore. Other additives and clays are mixed in the water to create a homogenous mixture (Neff, 2005). Clay and other additives are added to improve the properties of drilling mud.

2.3.5.2 Clay minerals

Clay minerals, hydrous alumina silicates, are found in soils and sedimentary rocks (Moore and Reynolds, 1997). Their surface properties make them very important; clay minerals are reactive, thereby making them very important in industrial applications and environmental controls (Hall,1987). The properties of clay include acidity, high surface area, and cation exchange capacity (CEC). These properties make them play the important roles of a catalysts and adsorbents for toxic substances (Hall,1987). The functions of clay in water-based muds are to provide density, viscosity, gel strength, and yield point. Clay in water-based muds also control fluid loss. There are three groups of clays used in water-based drilling muds:

- Montmorillonites (bentonite)
- Kaolinites
- Illites

Montmorillonite is used in this present study.

2.3.5.3 Montmorillonites (bentonite)

Bentonites are made up of clay of the smectite group. Its unique properties are due to its structure, chemical composition, exchangeable ion type, and a small crystal size of smectite (Odom, 1984). Calcium bentonite are non-swelling; sodium bentonite is swelling bentonite. Calcium and magnesium cations displace part of sodium from the clay platelets in a bentonite suspension. Figure 2.3 shows the approximate dry bentonite requirements in various salinities (Annis and Smith, 1996).

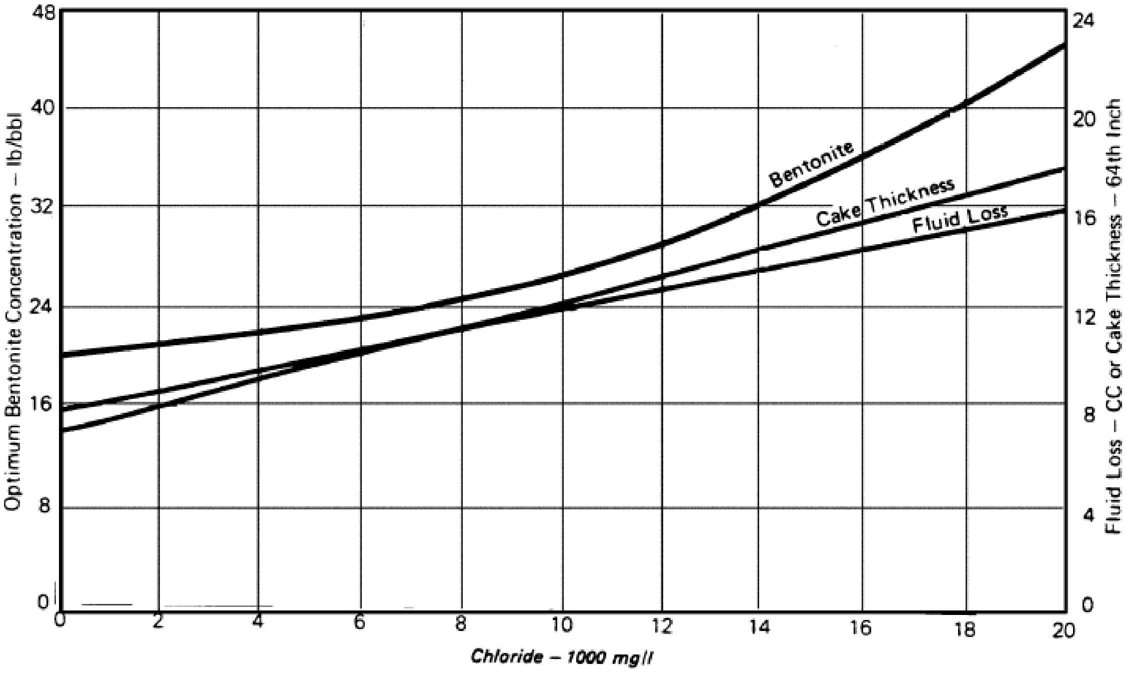


Figure 2.3: Approximate dry bentonite requirements in various salinities (Annis and Smith, 1996)

The calcium or magnesium ions influences the performance of clays. In drilling muds, an increase in calcium or magnesium concentration causes drastic changes. The clay in the drilling mud dehydrates and flocculates. Flocculation leads to a decrease in plastic viscosity. It also causes an increase in fluid loss, yield point, and gel strength (Annis and Smith, 1996).

The selection of clays for use in drilling fluids are based on the following:

- Yield
- Suspension capacity in salt water
- Plastic viscosity
- Apparent viscosity
- Yield strength
- Thixotropic properties

- Wall building properties
- Thickness of filter cake produced

2.3.5.4 Polymers in drilling fluid

The function of polymers in drilling muds is to provide viscosity, shale inhibition and fluid-loss control, and to prevent clay dispersion (Galindo et al., 2015). Polymers are used in almost all water-based muds. Synthetic polymers are stable at high temperatures (Strickland,1994; Plank, 1992). Conversely, high temperatures cause the degradation of biopolymers in drilling muds (Wenjun et al., 2014, Tehrani et al., 2009); Zhang et al.,2016). The biopolymers investigated in this work were konjac gum, xanthan gum, and diutan gum and selected because they degrade when exposed to elevated temperatures.

2.4 Properties of drilling fluids

Drilling fluids properties, physical or chemical, are observed frequently to optimise drilling operations. The physical properties help to prevent fluid loss, stabilise the well-bore, supply hydraulic energy to the bit, help in cutting removal, suspend cuttings during quiescence, and help separate solid and gas at the surface. The chemical properties cause problems such as formation damage, changes in rheological properties, and problems of cuttings transport. (Mitchel and Miska, 2011). The properties of drilling fluids are as follows (Darley and Gray,1988):

- Density
- Viscosity
- Filtration
- pH
- Alkalinity
- Cation Exchange capacity: Methylene Blue test
- Electrical conductivity
- Lubricity
- Corrosivity

In this chapter, the properties of the drilling fluid relevant to this present study are considered.

2.4.1 PH of drilling fluids

PH value of drilling mud is measured using different methods; pH measurement is important in drilling fluid control. Clay interactions and effectiveness of additives depend on pH. In addition, solubility of components and contaminants in drilling mud also depends on the pH. By monitoring the pH values, the corrosion of drilling and well equipment caused by the acidic and sulphide contents in a drilling fluid can be easily controlled. Fluids with a pH value less than 7 are acidic, and fluids with pH values greater than 7 are basic or alkaline. Fluid with pH equal to 7 is termed neutral. The concentration of (H^+) ion in drilling fluid gives an indication of its acidity and alkalinity.

2.4.2 Viscosity

A fluid's viscosity is a measure of its resistance to flow. It plays a very important role in rotary-drilling operations and is controlled for optimal fluid performance (Darley and Gray,1988). In the oil industry, the terms used to describe viscosity are as follows:

- Funnel viscosity,
- Apparent viscosity,
- Plastic viscosity, and
- Effective viscosity

Figure 2.4 shows the viscosity of a bentonite suspension at different shear rates (Annis and Smith,1996).

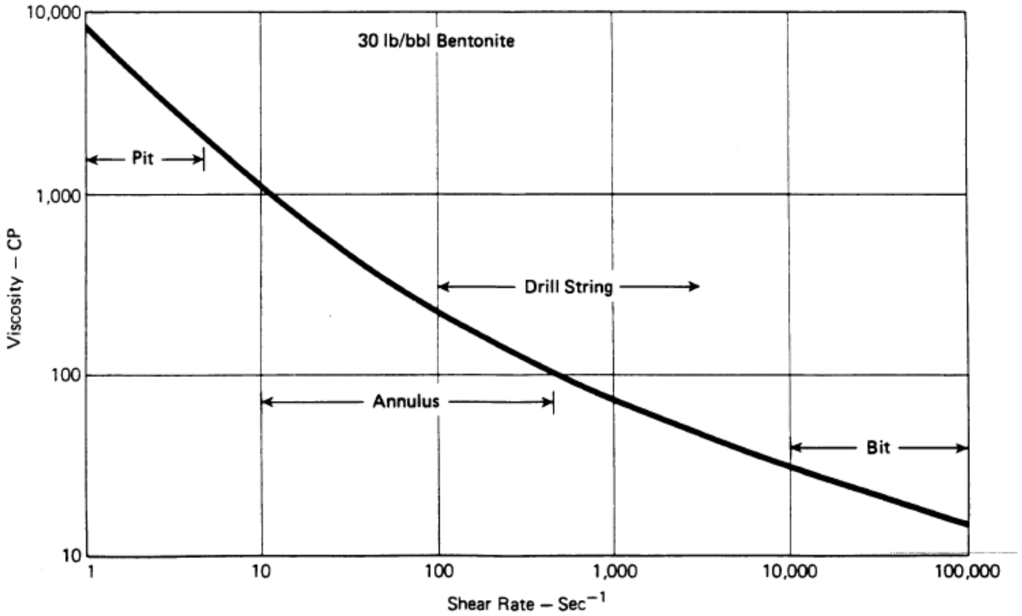


Figure 2.4: Viscosity of bentonite-water suspension at different shear rates (Annis and Smith,1996)

Viscosity, a rheological property of the drilling mud, is defined as the ratio of shear stress to shear rate (Mitchel and Miska, 2011):

$$\mu = \frac{\tau}{\gamma} \tag{2.1}$$

Where, τ is the shear stress, γ is the shear rate, and μ is the viscosity. It is expressed in centipoise (cP) in the oil industry. Viscosity must be measured at a known shear rate to acquire reliable value and at a specific temperature and pressure. At the well site, the Marsh-funnel is used to test for viscosity. Viscosity of a drilling mud is measured using concentric viscometer. The viscosity of Newtonian fluid is independent of share rate while the viscosity of a non-Newtonian fluid is shear rate dependent. Many drilling muds are non-Newtonian fluid. For Newtonian fluids, the plot of shear stress against shear rate on a Cartesian graph (green lines) is linear; for the non-Newtonian fluids, the plot of shear stress against shear rate on a Cartesian graph (red curve) is nonlinear, as seen in Figure 2.5 and Figure 2.6 shows the viscosity comparison of a Newtonian fluid with a non-Newtonian fluid (Overas,2011).

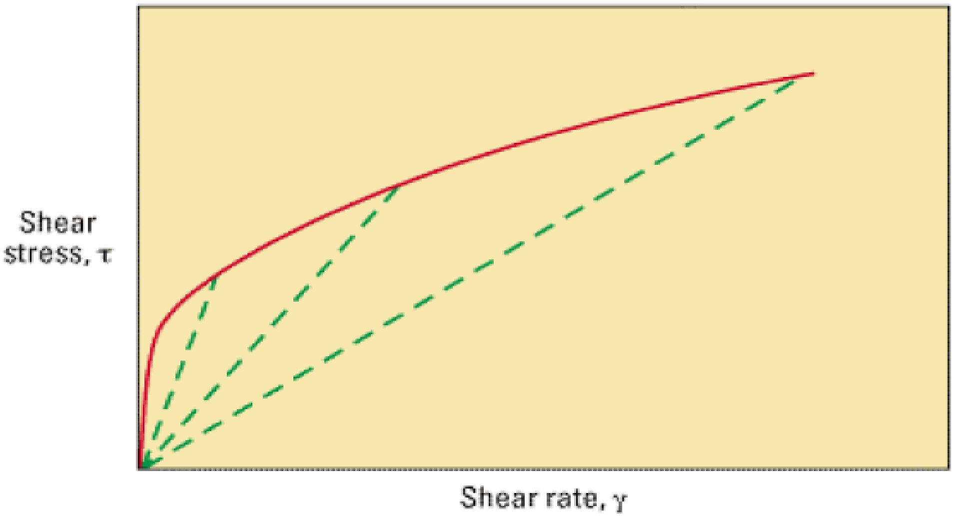


Figure 2.5: Non-Newtonian and Newtonian fluid (Overas,2011)

In addition, the red curve shows that the viscosities of non-Newtonian fluids are shear rate dependent.

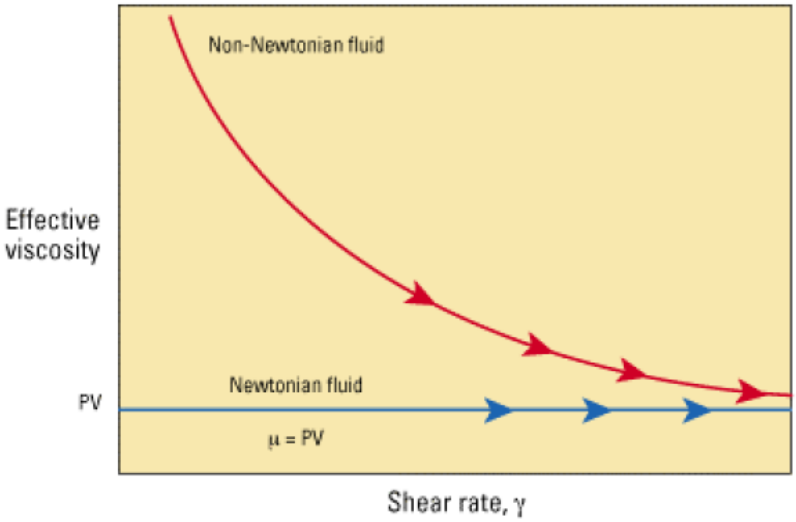


Figure 2.6: The viscosity comparison of a Newtonian fluid with a non-Newtonian fluid (Overas,2011)

As temperature increases, the viscosity of Newtonian liquids decreases. The Arrhenius relationship defined the viscosity of Newtonian liquids (Mitchel and Miska, 2011):

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

Where, the absolute temperature is T, and A and B are constants of a liquid.

There are different types of non-Newtonian fluids, each with different characteristics: pseudo plastic fluids, dilatant fluids, thixotropic fluids, anti-thixotropic fluids, rheomalactic fluids, and plastic fluids. The viscosity of pseudo plastic fluid is shear rate dependent. Emulsions and gums are an example of pseudo plastic fluids. Thixotropic fluids viscosity decreases with time under shear conditions. Most drilling fluid muds are thixotropic fluids. The viscosity of dilatant fluids increases as shear rate increases. In most drilling fluids, viscosity decreases with an increase in shear rate. This phenomenon is called shear-thinning. In other words, it can be called temporary viscosity loss and pseudo plasticity (Ochoa, 2006).

2.4.3 Rheological models

Newtonian model, the Bingham plastic model, the Power-Law or Ostwalde-de Waele model, and the Herschel-Bulkley model are used to approximate fluid behaviour (Mitchel and Miska, 2011). Figure 2.7 shows the rheological models (Ochoa, 2006).

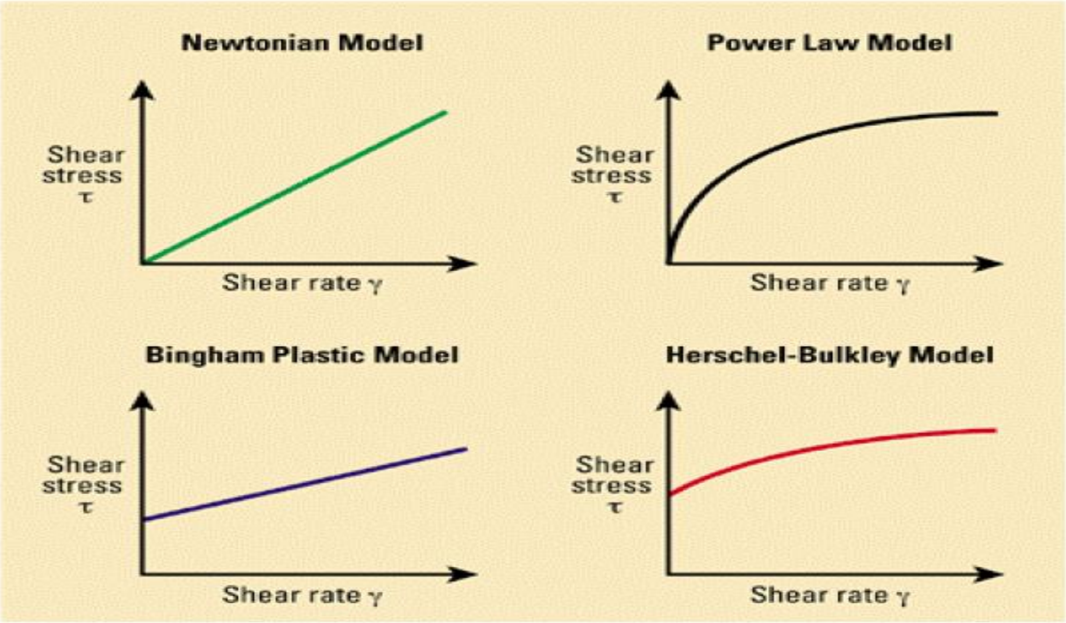


Figure 2.7: Rheological Models (Ochoa, 2006)

2.4.3.1 Newtonian fluid model

The viscosity of a Newtonian fluid is constant at all shear rates at a temperature and pressure. A one-parameter rheological model is used to described Newtonian fluid. For the Newtonian fluid model, the shear stress, τ is directly proportional to the shear rate γ (Mitchel and Miska, 2011):

$$\tau = \mu\gamma \tag{2.3}$$

Where μ is known as the apparent viscosity.

2.4.3.2 Bingham plastic fluid model

In the oil industry, the Bingham plastic model is widely used to describe flow behaviour of drilling muds, and it is a two-parameter rheological model (Mitchel and Miska, 2011):

$$\tau = \tau_y + \mu_p\gamma \tag{2.4}$$

The shear stress is τ; γ is the shear rate.

For the Bingham model, there is no flow for shear stresses below τ_y, called the yield point. It behaves like a Newtonian fluid for shear stresses above the yield point with viscosity μ_p, called the plastic viscosity. The yield point is a very important property of drilling mud. The two functions of a drilling mud associated with yield points are (1) to clean a drilled hole and (2) to control pressure. A high yield point enhances the solids carrying characteristics of a drilling fluid (Annis and Smith, 1996); and it must be high enough to enable the carrying of drilled cuttings and weighting materials out of a well-bore, but not be too high to create excessive pump pressure when the pump starts to pump mud.

2.4.3.3 The Power Law model

The Power-law model defines a fluid by two parameters (Mitchel and Miska, 2011):

$$\tau = K\,\gamma^{n} \tag{2.5}$$

Where the fluid consistency index is K, and the flow behaviour index is n. K is the viscosity at a shear rate of $1s^{-1}$ and is expressed in $Ib/100ft^{2}$, while n shows the extent of shear thinning. The smaller the value of n, the higher the shear thinning behaviour. Its equation is suitable for modelling water-based polymer muds, most especially the polymer mud containing xanthan gum and is better than any other two-parameter model, including Bingham plastic model (Chilingarian and Vorabutr, 1981). It is effective under low-shear-rate condition but ineffective at high shear rates (Hemphill et al.,1993).

2.4.3.4 The Herschel-Bulkley model

The Herschel-Bulkley is a three parameters model (Mitchel and Miska, 2011):

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

Where the fluid consistency index is K; the flow behaviour index is n.

The Herschel-Bulkley model can represent a yield-pseudo plastic fluid ($n < 1$), a dilatant fluid ($n>1$), a pseudo-plastic fluid ($\tau_y = 0$, $n < 1$), a plastic fluid ($n=1$), or a Newtonian fluid ($\tau_y = 0$, $n=1$) (Mitchel and Miska, 2011). It gives the best fit of the viscometer measurements when compared with the other rheological models (Merlo et al.,1995). The Power-law model defines a fluid by two parameters (Mitchel and Miska, 2011):

2.4.3.5 Plastic viscosity

Plastic viscosity (PV) is the viscosity of drilling fluid contributed by the solid phase and the liquid phase (IMCO Services,1981). It is measured by a viscometer. PV is the difference between readings at 600rev/min and that at 300rev/min. It is a function of the number of solid particles in a drilling fluid. Figure 2.8 shows suggested ranges of plastic viscosity.

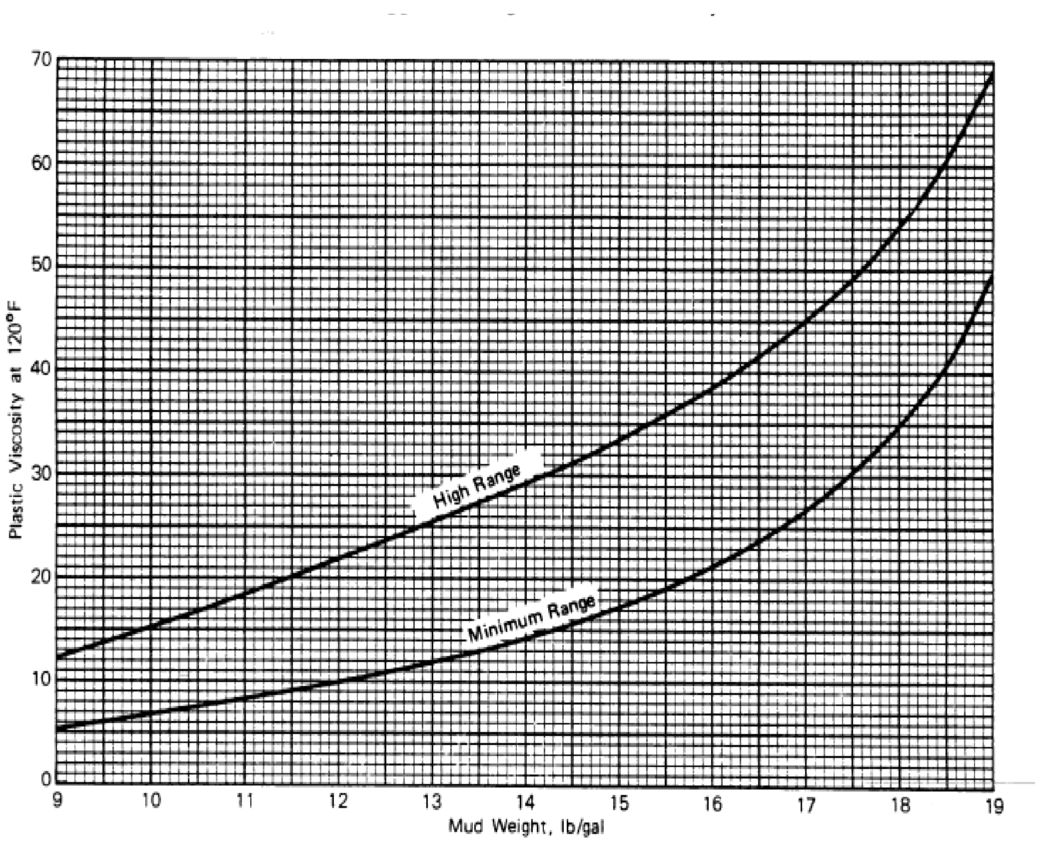


Figure 2.8: Suggested Ranges of Plastic Viscosity (Annis and Smith, 1996)

If the solid content in drilling mud increases, PV also increases. The plastic viscosity of drilling fluid decreases as its temperature increases since the viscosity of the base fluid decreases. High plastic viscosity is not desirable: PV causes an increase in pressure drop, which reduces flow rate. Therefore, in drilling fluids, the plastic viscosity must be kept as low as practical. Figure 2.9 shows the effect of inert drilled solids on plastic viscosity (Annis and Smith, 1996).

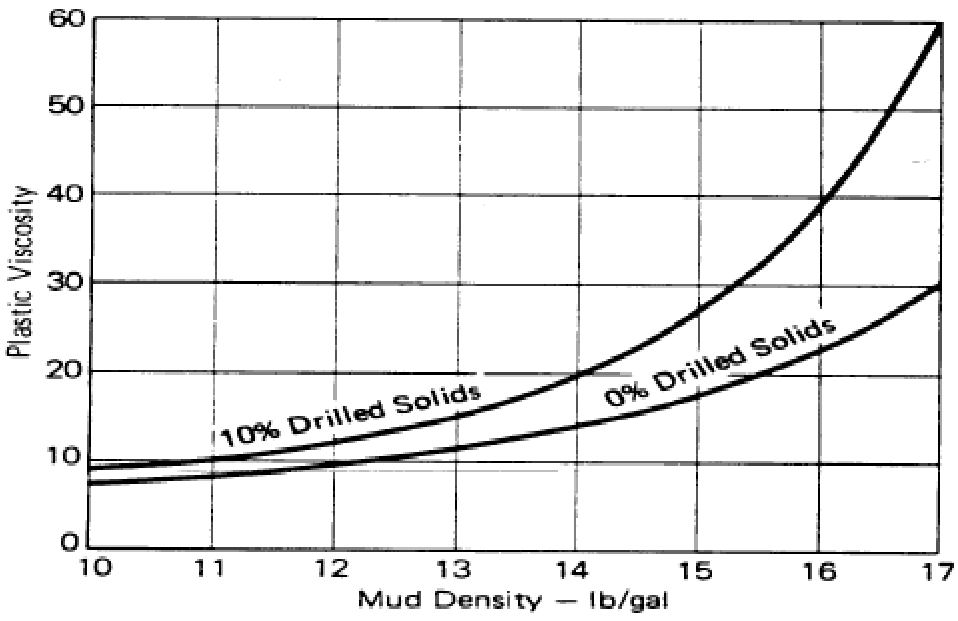


Figure 2.9: Effect of inert drilled solid on plastic viscosity (Annis and Smith, 1996)

Many water-soluble polymers increase plastic viscosity. If a drilling mud is kept free of drilled solids, a minimum plastic viscosity can be attained (Annis R. M. and Smith, 1996).

2.4.3.6 Yield point

The measure of the electro-chemical attractive forces within a drilling mud in motion is the yield point. Yield point is a function of the concentration of the solids, the surface properties of the mud solids, and the concentration and type of ions in a drilling fluid. Viscometer is used to measure yield point. The yield point calculated from the Bingham equation is less than the true yield stress, which is required to maintain flow (Annis R. M. and Smith, 1996). The large molecules such as a polymer or colloidal particles collide with one another, thereby increasing the resistance to flow. Chemical treatment is used to control electrical interaction of solids; the mechanical interaction is controlled by solids adjustment. Figure 2.10 shows the suggested range of yield point (Annis R. M. and Smith, 1996).

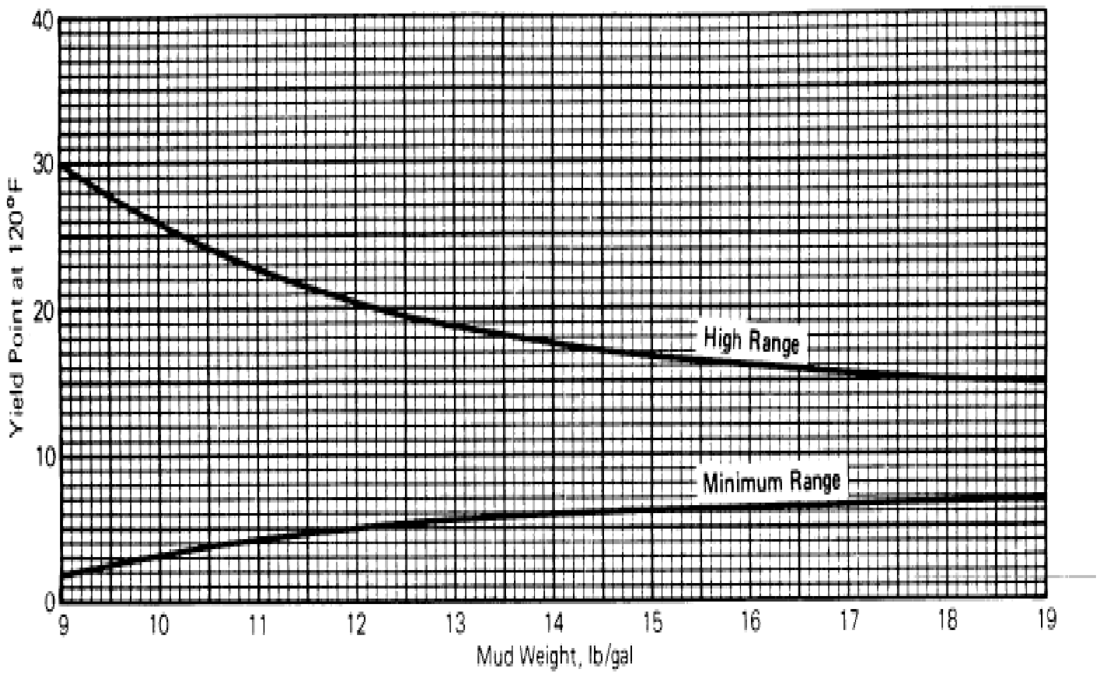


Figure 2.10: Suggested range of yield point (Annis and Smith, 1996)

The presence of high concentrations of colloidal solids and the flocculation of clay solids cause high yield points. Flocculation is caused by the lack of enough deflocculant, high temperature, or the presence of salt, calcium, carbonates, and bicarbonate, which are contaminants. In addition, the presence of a high solids' concentration aggravates flocculation. There are two functions of yield points: hole cleaning and the pressure control. Furthermore, a high yield point implies that a drilling mud is non-Newtonian and can carry cutting better than any mud with a lower yield point.

2.4.3.7 Gel strength

The measurement of the attractive forces in a mud while at rest is the gel strength. The unit is expressed in lbs/100 ft^2. Gel strength represents the thixotropic properties of drilling mud, measured by a viscometer. In other words, it is a measurement of the shear stress required to initiate flow of a fluid that has been static for some time (Mitchel and Miska, 2011). Electrically charged particles in a drilling mud linking together to create a firm structure cause gel strength. Gel strength is a function of the quantity and kind of solids in solution, time, temperature, and chemical environment. It is increased by any anything that helps link particles in suspension together and decreases by anything which prevents the linking of particles together (Annis R. M. and Smith, 1996). Gel strength is increased by flocculation while deflocculation decreases the gel strength. Dispersant is added to mud to reduce gel strength. If the dispersant fails to reduce the gel strength, it means that the problem is caused by colloidal solids or a chemical contamination. The problem can be solved temporarily by water-dilution, which is expensive. In addition, there may be insufficient hydroxyl ion to activate the dispersant; and a high concentration of carbonate or bicarbonate could be causing flocculation (Annis R. M. and Smith, 1996).

2.5 Aging of drilling muds

The aging of drilling fluids is the process whereby a drilling mud freshly formulated can more fully develop its rheological and filtration properties. In this study, some drilling fluid formulations were aged dynamically to mimic the interaction between a drilling fluid and well-bore annulus. The aging time varies from 16 hours to as much as several days. There are two types of drilling muds aging at either ambient or elevated temperatures: static and dynamic aging. The viscosity, yield point, and gel strength of drilling fluid aged at a temperature increase as the aging time increases, and the effects of aging diminishes with increasing aging time. The reason for this could be that as the particle numbers are increasing due to the aging of the mud, inter-particle forces increase leading to an increase in the yield point and gel strengths (Ali and Al-Marhoun ,1990).

2.6 Environmental impact

The activities of hydrocarbon exploration and production impacts negatively on the environment (Odiete,1999). Drilling muds and cuttings are the wastes generated during oil well drilling (Ferrari et al., 2000). In addition, some additives used in drilling fluids are toxic (Reis, 1988). The heavy metals and hydrocarbon present in drilling wastes can pollute the environment, based on the type, nature and their concentrations (Hastings, 1984) and by extension, the degree of exposure (American petroleum institute,1978). There are different proportions of hydrocarbons and heavy metals in drilling muds. The oil-based drilling muds (OBM) are formulated with saturated and unsaturated hydrocarbons and according to Darley and Gray (1988) the saturated and unsaturated hydrocarbons in the OBM could be as high as 60% and 45% respectively. Consequently, the OBMs are more toxic than the water-based muds (WBMs). In the US, the discharge of OBMs and WBMs containing free oil and the accompanying cuttings is prohibited; and based on the level of toxicity, most water-based muds, synthetic based fluids, and mineral-oil-type oil-based muds are non-toxic (Burke and Veil, 1995).

Chapter 3: Literature Review

3.1 Introduction

This literature survey considers the effects of high temperature on the performance of water-based drilling fluids. It is challenging to come up with additives capable of giving water-based muds the properties required for high temperature drilling operations. For these reasons, a detailed understanding of water-based mud formulations that perform like oil-based muds is vitally important for further improvement in the performance of water-based drilling fluids. The literature survey is, therefore, divided into four sections. The first section considers the effects of water-based muds on the environment. The second section of this chapter is focused on high-performance water-based muds. The third section considers the performance of biopolymer in water-based muds. The fourth section is focused on the stabilisation of biopolymer in water-based muds and inhibition of shale dispersion using anti-oxidants, pH control agents, buffering agents, and polyglycols.

Even though the main objective of this study is to investigate the effects of antioxidants, pH control agents, formate salts, and shale stabilisers on biopolymers and on reactive shale in water-based bentonite muds, it is reasonable to identify other additives that stabilise water-based muds and inhibit shale dispersion. Attention is given to the additives that contribute to the technical performance of water-based drilling fluids at high temperatures. The literature survey is mostly focused on studies carried out experimentally, which are relevant to this present study.

3.2 Effects of water-based muds on the environment

Despite its technical performance, oil-based drilling mud has its limitations: It is susceptible to contamination by water; there are fire risks; the rate of bit penetration is low; and most importantly, there is the risk of environmental impact. Arising from stringent environmental legislation, the current effort in the oil industry is geared towards the development of environmentally friendly fluids that could perform like oil muds with respect to toxicity, performance, efficiency, and cost (Apaleke et al.,2012). Consequently, various studies have been undertaken to design high performance water-based muds. One of the drilling fluid additives that make the performance of water-based muds approach that of oil-based muds are salts. In the present study the salts used for drilling mud formulation are potassium formate and sodium erythorbate. Soluble silicates, which are salts, are commonly used to improve the properties of water-based muds. Oort et al. (1996) experimentally investigated a water-based mud formulated with silicates. The materials used in a silicate-based mud were as shown in Table 3.1, and they compared potassium chloride-based mud with silicate-based mud as shown in Table 3.2. According to Oort et al. (1996), the mud formulation performed much better than conventional water-based muds (WBMs) and demonstrated excellent cuttings and well-bore stabilising capacity. They noted that OBMs and synthetics should be replaced by improved WBMs. However, the rheological properties of the mud system were adversely affected by temperature. In addition, silicates can cause formation damage, and it is difficult to control the rheological properties of drilling mud when using silicate-based mud system (Vikas and Rajat ,2015).

Table 3.1: Additives used in silicate-based mud formulations (Oort et al., 1996)

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

Table 3.2: Properties of KCl/Polymer/and KCl/polymer/sodium silicate muds before and after aging at different temperatures (Oort et al., 1996)

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

Zuvo et al. (2005) considered the effects of cuttings discharged in the Barents Sea after drilling with water-based mud formulated with potassium and sodium formate. An environmental survey was conducted on the physical, chemical and biological conditions of the sediments in the Barents Sea. The survey was done to verify the findings in a life cycle assessment (LCA) for formate brine. They reported that the discharge of moderate amounts of formate brines would not have an adverse effect on marine environment significantly. It is to be noted that potassium formate is one of the additives used in this present study. Gilbert et al. (2007) compared the regulatory approaches for different regions and nations on environmental protection with respect to chemicals. They used formate-based drilling fluids as an example in their discussion. They noted that the level of toxicity of formate brine on the environment is low. This finding supports the conclusion drawn by Zuvo et al. (2005)

Ramirez et al. (2005) formulated a water-based mud, which was used to drill through a troublesome shale formation up to the top of a reservoir. The mud was made up of clay, shale stabilisers, an ROP enhancer, and scaling agents. It was noted that the mud formulation prevented hole problem and was tolerant with carbon dioxide and hydrate contaminations. It was also noted that the mud formulation prevented bit balling and improved the rate of bit penetration. They concluded that water-based muds, when properly designed, can be a suitable alternative to oil-based mud systems where environmental impacts and formation damage are a concern. This conclusion drawn by Ramirez et al. (2005) is supported by Oort et al. (1996) who stated that water-based muds are environmentally friendly. The additives used in the mud formulated by Ramirez et al. (2005) was as shown in Table 3.3.

Table 3.3: The additives used in the mud formulation (Ramirez et al.,2005)

Component	Concentration (Ib/bbl)
Bentonite	9.0
PHPA	1.5
Aluminum complex	3.5
Amine	5.0
Low Vis PAC	1.0
Regular PAC	0.7
Blown Asphalt	4.0 I

Oswald et al. (2006) experimentally investigated water-based drilling fluids, which were used in formation with a temperature less than 300°F because of their limitations in very high temperature formations. In the study, the Miano and Sawan fields in Pakistan had a high temperature of up to 340˚F; and in consideration of environmental impacts, water-based muds were used in all drilling operations in the fields. They concluded that based on laboratory results, a formate-based drilling fluid was selected for the fields. This conclusion supports the finding by Oort et al. (1996) and Ramirez et al. (2005), who suggested that water-based muds could replace oil-based muds.

On environmental impacts of formate brines, Downs et al. (1993) subjected formate brines to hazard identification and procedure before its application in the field with respect to regulatory requirements. They noted that formate salts pose a slight hazard to the environment and users. They concluded that regulators would not object to the use of formate-based drilling and completion fluids for offshore and onshore operations. This finding supports the findings by Gilbert et al. (2007) and Zuvo et al. (2005).

3.3 The performance of high-performance water-based muds

High-performance water-based drilling muds (HPWBMs) are cost effective, stable, inhibitive, and environmentally-friendly. Their technical performance approaches that of oil-based mud systems. Therefore, most of the discussion here is on high performance water-based muds with attention given to additives and procedure involved in their formulations. The knowledge of the compositions of HPWBMs is important in their design. Numerous studies have been undertaken to develop HPWBMs. Al-Ansari et al. (2005) developed a water-based mud with partially hydrolysed polyacrylamide and polyamide derivatives. The mud formulation was used to drill several wells successfully and performed like OBMs. However, hydrolysed polyacrylamide and polyamide derivatives are synthetic polymers. Synthetic polymers are stable at high temperatures (Strickland,1994; Plank, 1992), but generate high plastic viscosity (Tehrani et al.,2007). Sawdon et al. (1995) formulated a water-based mud to perform like an OBM in all applications except in high temperature application. The mud formulation was designed to work in synergy with other additives. They found out that the mud formulation was environmentally friendly. However, the effects of high temperature were not considered. Galindo et al. (2015) developed a thermally and rheologically stable water-based drilling fluid at 400˚F. The fluid was aged dynamically at 150˚F for 16 hours before testing. The fluids were also aged under static or dynamic conditions at temperatures between 300 and 400˚F. Viscometer and pH meter were used to measure the viscosity and pH values respectively. HP/HT filter press was used to measure the fluid loss properties of the fluids at 350˚F. Figure 3.1 shows the effects of increasing temperatures on the viscosity of the drilling fluid formulation after 16 hours static aging.

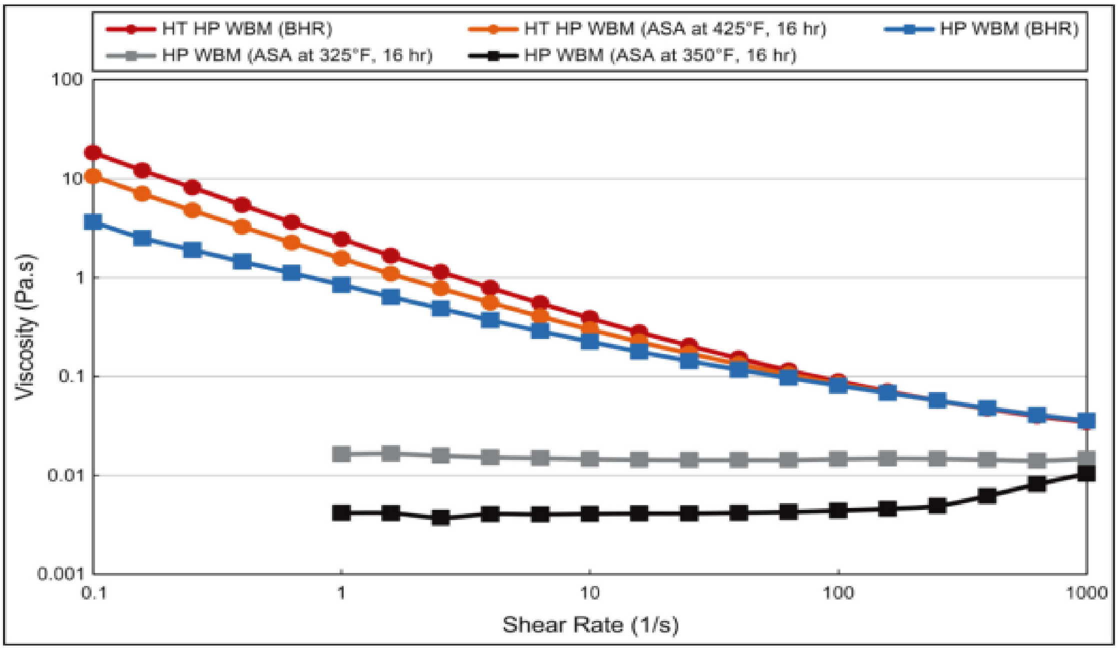


Figure 3.1: Effect of temperature on the mud viscosity after 16 hours static aging (Galindo et al. 2015)

Results showed that the drilling fluid formulation maintained its properties up to 400˚F and was tolerant with contamination. In addition, the mud formulation was environmentally acceptable for use in onshore and offshore drilling. The composition of the water-based mud is shown in Table 3.4. They concluded that the water-based drilling fluid formulation was thermally stable and could be suitable for extremely high temperature formations, while maintaining the benefits of high-performance water-based drilling muds. However, the effects of temperature above 425˚F were not considered, and the mud viscosities collapsed sharply at higher temperatures.

Table 3.4: Representative HTHP WBM formulation (Galindo et al., 2015)

Sample	14.0 Ibm/gal
Water (bbl)	0.79
pH buffer (Ibm/bbl)	4.5
KCl (Ibm/bbl)	8.0
Rheology modifier (Ibm/bbl)	1.0
High temperature polymer (Ibm/bbl)	7.0
Thinner (Ibm/bbl)	3.0
Barite (Ibm/bbl)	311.0

Abdon et al. (1989) experimentally investigated a high solid deflocculated polymer (HSDP) with a density as high as 20.9ppg (156pcf) and used in a field with temperature above 300^{o}F. The mud was formulated with three polymers. They found out that in the field, the mud formulation was tolerant to monovalent and divalent cations (Na^{+}, Mg^{++}, Ca^{++}) contamination, carbonates (CO$_3^{--}$, HCO$_3^{--}$), water, oil, gases and drilled solids. The effects of high temperature above 300^{o}F on the mud system were not considered. This finding by Abdon et al. supports the findings by Al-Ansari et al. (2005) and Galindo et al. (2015) who noted that HPWBMs performed like oil-based muds. Pinya et al. (1995) investigated the design and the field application of an amphoteric polymer mud system. The mud formulation solved problems caused by conventional polymers in mud containing high reactive shale and was used to drill formations with different lithologies, with high salinity, and with high temperature in China. They found out that the mud system was effective against shale, stabilised well bore, enhance rheological properties, improved rate of penetration, and protected the pay zone. The performance of the drilling fluid formulation was like that developed by Galindo et al. (2015). However, synthetic polymers create high plastic viscosity and cause formation damage. Young and Ramses (2006) formulated a water-based mud. The additives used included a hydration suppressant, a dispersion suppressant, a viscosifier (xanthan gum), a filtration controller, and an accretion suppressant. They concluded that the mud formulation performed like an invert emulsion-mud. The additives used in the mud systems were as shown in Tables 3.6 -3.9.

Table 3.5: Typical composition HPWBM (Young and Ramses, 2006)

Seawater (ml)	293.0
NaCl (g)	80.4
Filtration controller (g)	4.0
Polymer viscosifier (g)	0.8
Dispersion suppressant (g)	2.0
Hydration suppressant (g)	10.5
Accretion Suppressant (g)	7.5

Table 3.6: Typical composition of silicate mud (Young and Ramses, 2006)

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

Table 3.7: Typical composition of NaCl/Polymer mud (Young and Ramses, 2006)

Freshwater (ml)	323.0
NaCl (g)	73.2
NaOH (g)	0.5
Bentonite (g)	5.0
Fluid loss agent (g)	3.0
PHPA (g)	1.0
Polymer viscosifier	0.5

Table 3.8: Typical composition of oil based mud (Young and Ramses, 2006)

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

Table 3.9: Typical field composition of HPWBM (Young and Ramses, 2006)

Product/Formulation	#1	#2	#3
Freshwater (ml)			320
Seawater (ml)	290	315	
NaCl (g)	80		
KCl (g)		20	
Filtration controller (g)	3	4	3
Polymer viscosifier	1.25	1	1.25
Dispersion suppressant (g)	2	2	2
Hydration suppressant (g)	10	8	10
Accretion suppressant (g)	8	6	
# - Gulf of Mexico deepwater well			
# - South China Sea shelf well			
# - Western USA land well			

Kjosnes et al. (2003) formulated a water-based drilling fluid using potassium chloride, polyanionic cellulose and xanthan gum. They concluded that the mud formulated improved hole cleaning and stability. The effect of high temperatures on the mud system were not considered. Samaei and Tahmasbi (2007) experimentally investigated a water-based glycol drilling mud. The rheological properties of OBM and the glycol mud were tested. The test was done on the cuttings from an oil field in Iran. The Mud formulation significantly reduced the dispersion of shale and hydration of cuttings and was considered a good alternative to oil-based fluid and other water-based mud systems. This finding supports the finding by Reid et al. (1992), Pinya et al. (1995), and Young and Rames (2006) that water-based mud can perform like oil-based mud. The properties of the glycol mud were compared with those of oil-based mud (Figures 3.2 – 3.5). It should be noted that the effects of high temperature on the mud formulation was not considered.

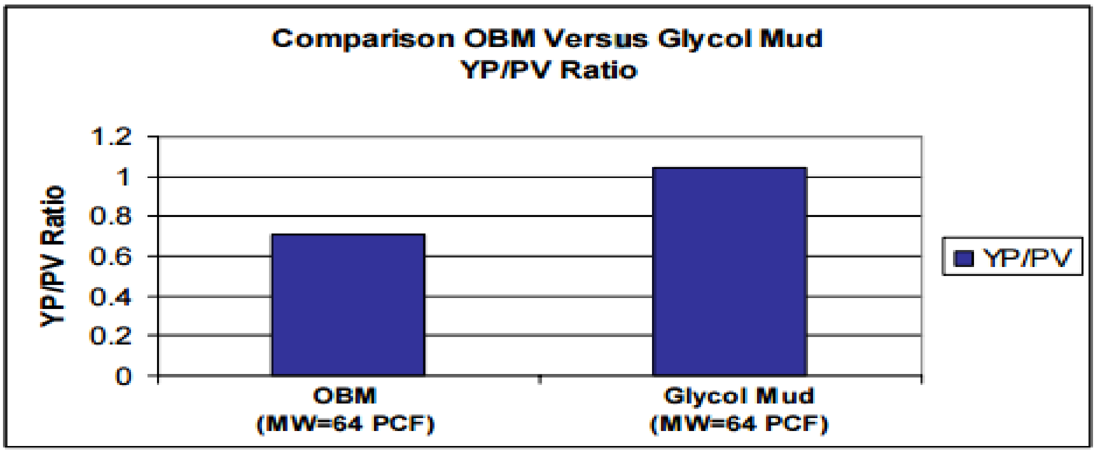


Figure 3.2: Comparison of OBM versus glycol mud YP/PV ratio (Rames, 2006)

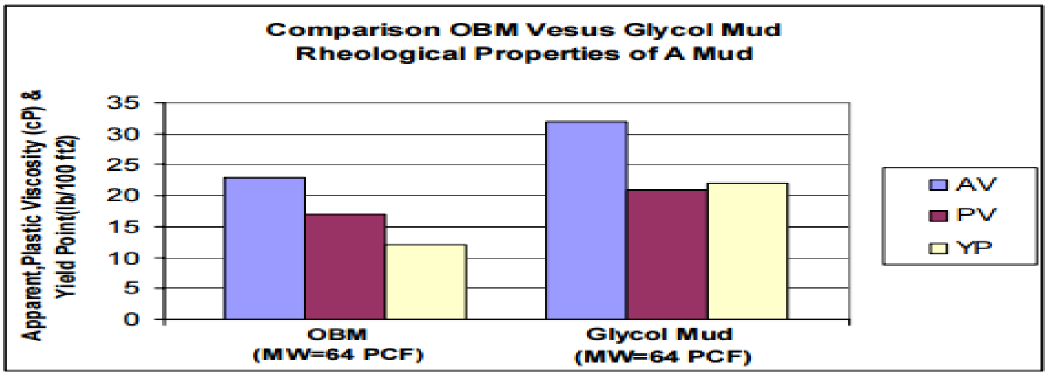


Figure 3.3: Comparison of OBM versus glycol mud rheological properties (Rames ,2006)

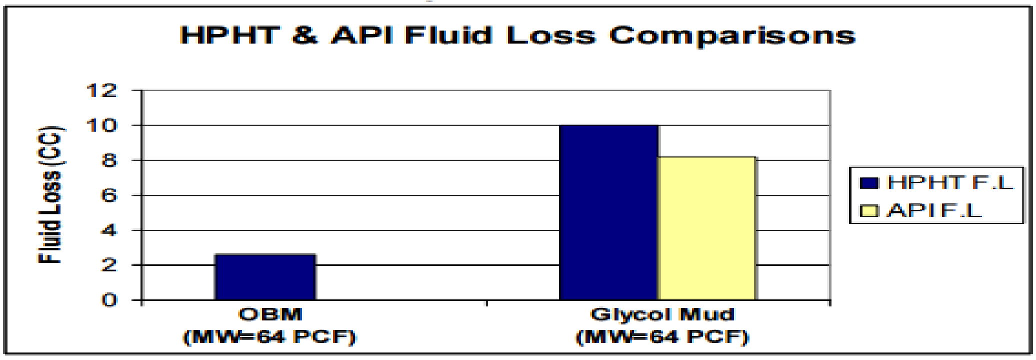


Figure 3.4: Comparison of OBM versus glycol mud HPHT & API fluid loss (Rames, 2006)

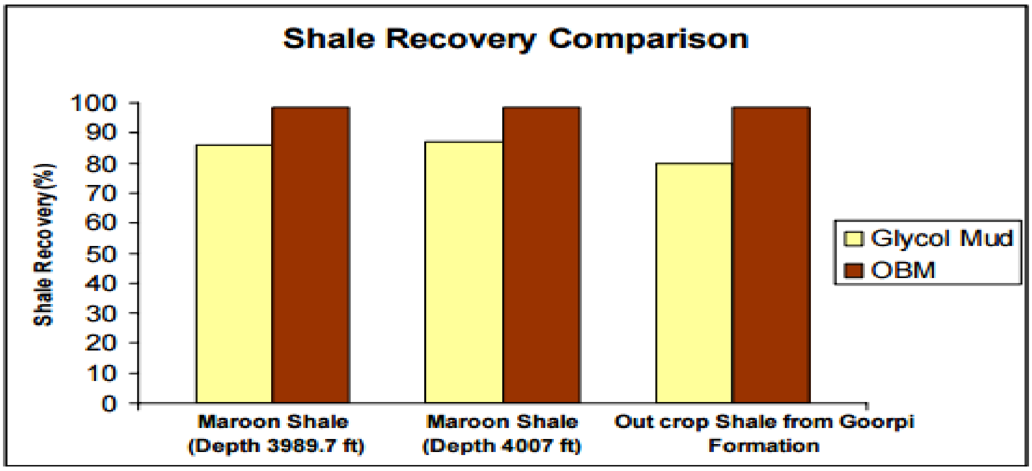
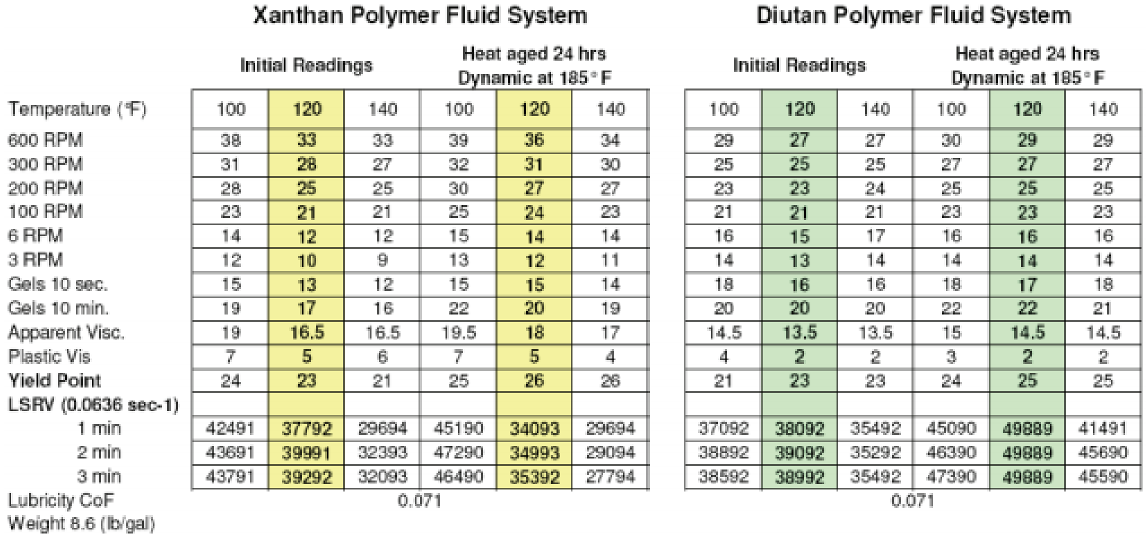


Figure 3.5: Comparison of OBM Versus Glycol Mud shale recovery test (Rames, 2006)

3.4 The Performance of biopolymers in water-based muds

Any drilling mud systems that are made up of soluble polymers can be referred to as polymer muds. Biopolymer are commonly used in water-based muds to provide viscosity, shale inhibition and fluid-loss control, and to prevent clay dispersion (Galindo et al., 2015). In addition, biopolymers are environmentally friendly (Dayawant,1999) and enhance the properties of water-based muds even at very low concentrations (Darley and Gray,1988). They are either used separately or mixed together to improve bentonite performance (Darley and Gray,1988). In this section, attention is focused on the performance of water-based mud containing biopolymers. Sarber et al. (2010) compared the performance of drilling fluid formulated with diutan gum with that of the mud formulated with xanthan gum. Table 3.10 shows the comparison between the xanthan gum mud and diutan gum mud, and Table 3.11 shows the effect of high temperature on xanthan gum and diutan gum. They found out that the diutan based solids free mud perform better than xanthan gum-based solids free mud. However, the mud formulations were sensitive to increasing temperatures. The effects of high temperatures on the mud systems were not considered, and mud formulations were solid free.

Table 3.10: Rheological difference exhibited between xanthan gum and diutan gum before and after aging (Sarber et al., 2010)



	Xanthan Polymer Fluid System						Diutan Polymer Fluid System					
	Initial Readings			Heat aged 24 hrs Dynamic at 185° F			Initial Readings			Heat aged 24 hrs Dynamic at 185° F		
Temperature (°F)	100	120	140	100	120	140	100	120	140	100	120	140
600 RPM	38	33	33	39	36	34	29	27	27	30	29	29
300 RPM	31	28	27	32	31	30	25	25	25	27	27	27
200 RPM	28	25	25	30	27	27	23	23	24	25	25	25
100 RPM	23	21	21	25	24	23	21	21	21	23	23	23
6 RPM	14	12	12	15	14	14	16	15	17	16	16	16
3 RPM	12	10	9	13	12	11	14	13	14	14	14	14
Gels 10 sec.	15	13	12	15	15	14	18	16	16	18	17	18
Gels 10 min.	19	17	16	22	20	19	20	20	20	22	22	21
Apparent Visc.	19	16.5	16.5	19.5	18	17	14.5	13.5	13.5	15	14.5	14.5
Plastic Vis	7	5	6	7	5	4	4	2	2	3	2	2
Yield Point	24	23	21	25	26	26	21	23	23	24	25	25
LSRV (0.0636 sec-1)												
1 min	42491	37792	29694	45190	34093	29694	37092	38092	35492	45090	49889	41491
2 min	43691	39991	32393	47290	34993	29094	38892	39092	35292	46390	49889	45690
3 min	43791	39292	32093	46490	35392	27794	38592	38992	35492	47390	49889	45590
Lubricity CoF	0.071						0.071					
Weight 8.6 (lb/gal)												

Table 3.11: The breakdown of biopolymer after aging at high temperatures (Sarber et al., 2010)

Time	Xanthan-based Fluid LSRV (cP@0.06sec $^{-1}$)	Diutan-based Fluid LSRV (cP@0.06 sec $^{-1}$)
Initial	47,000	42,000
24 hours	21,400	38,000
48 hours	3,900	25,000
72 hours	200	10,600
96 hours	0	600

Ezell et al. (2010) evaluated a water-based drilling fluid formulation designed to perform efficiently during drilling operation. The additives used in the mud formulation include starches, derivatised starches, gums, derivatised gums, and cellulosic. According to Ezell et al. (2010), cross-linked starches degrade when subjected to temperatures above 300˚F for a long time. They concluded that bio-polymers cannot be successfully deployed at temperatures exceeding 300˚F.

Gallino et al. (1996) noted that xanthan gum is normally used in water-based drilling fluids for hole cleaning and solids suspension. However, they stated that xanthan presented some limitations with respect to tolerance with field contaminants and temperature. The finding by Gallino et al. is supported by Ezell et al. (2010), who reported that biopolymers degrade at elevated temperatures.

Ujma et al. (1989) observed that the fluid loss polymers for drilling fluids compactible with German Zechstein formation wells tolerated up to 140,000 ppm of Ca/Mg and were stable up to a temperature exceeding 350^{o}F [l77°C]. They noted that high contents of Ca/Mg have a negative effect on the polymers and clays in water-based mud (Figure 3.6). As water-based muds degrade at elevated temperatures, it loses more fluid to the formation. Excessive fluid loss is not desirable. Ujma et al.

pointed out that the carboxymethylcellulose (CMC) and polyanionic cellulose (PAC) used in the field were not effective but combining a new sulfonated polymer with starch improve the performance of the mud and reduced drilling cost. They concluded that the starch in combination with the new polymer showed excellent filtration control, hardness tolerance, and temperature stability and led to a cost saving of 20 to 50% on fluid-loss polymer costs. The mud system, however, was not stable above 375^{o}F. Sharma and Mahto (2006) developed water-based drilling fluids using tamarind gum and polyanionic cellulose. They investigated the rheological properties of mud formulations and their effects on formation damage. Three different bentonite clays samples and tamarind gum were used in the experiment. The experiment showed that the mud formulations had favourable rheological and fluid loss properties for optimal oil well drilling and that the muds filtrates showed minimal formation damage on sandstone cores. However, the effects of high temperatures and field contaminants on the biopolymers were not considered.

3.5 Effects of antioxidants, formate salt, and polyglycol on biopolymers

Biopolymer is used in water-based muds and degrade at high temperatures, thereby leading to the reduction or complete loss of drilling fluid rheological properties, and fluid loss and suspension properties (Weaver et al.,2003). To avoid the problem associated with the use of biopolymer at high temperatures, they are used in formations with temperatures not higher than 300°F (150^{o}C) (Galindo et al.,2015). The degradation mechanisms of biopolymer include acid-catalysed hydrolysis, oxidation-reduction (redox) reactions and early onset of the helix-coil conformation transition. These mechanisms can be counteracted, neutralised, or retarded to stabilise water-based drilling muds at high temperatures (Downs,1992; Seright and Henrici,1990; Wellington, 1983). These processes are, therefore, exploited in this present study to stabilise water-based drilling fluids at high temperatures by screening additives (formate salts, antioxidants, and polyglycol) that can counteract, neutralise, or retard them. Numerous research works have been done to stabilise water-based fluids and to retard problems associated with reactive shales in high-temperature drilling operations using formate salts, antioxidants, and polyglycol (Sections 3.5.1 – 3.5.3).

3.5.1 Stabilisation of water-based muds with formate salts

Formate brines are usually used in water-based drilling muds in high-temperature drilling operations as they act as an anti-oxidant, which preserves biopolymers (Downs,1993; Howard,1995; Clarke-Sturman et al.,1986; Clarke-Sturman and Sturla,1988). Various studies have shown that formate brines do not affect the environment negatively and are anti-oxidants, which stabilises polymer in water-based muds. To determine the effects of formate brines on water-based fluids at high temperatures, Bungert et al. (2000) reviewed the performance of formate brine-based drilling fluids. They reported that formate-based systems exhibited fast rates of penetration, eliminated solids sag problems, and improved well productivity. Figure 3.6 showed the effect of CO_2 on buffered and un-buffered formate brine. In this present study, drilling fluid formulations are buffered with sodium carbonate and sodium bicarbonate.

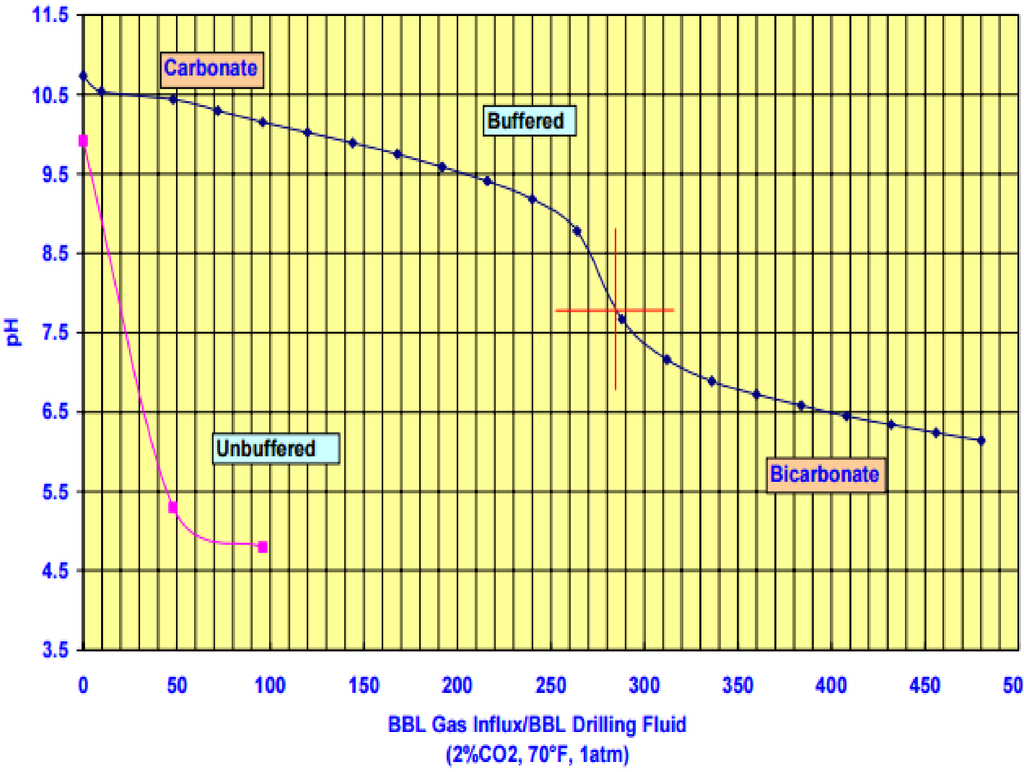
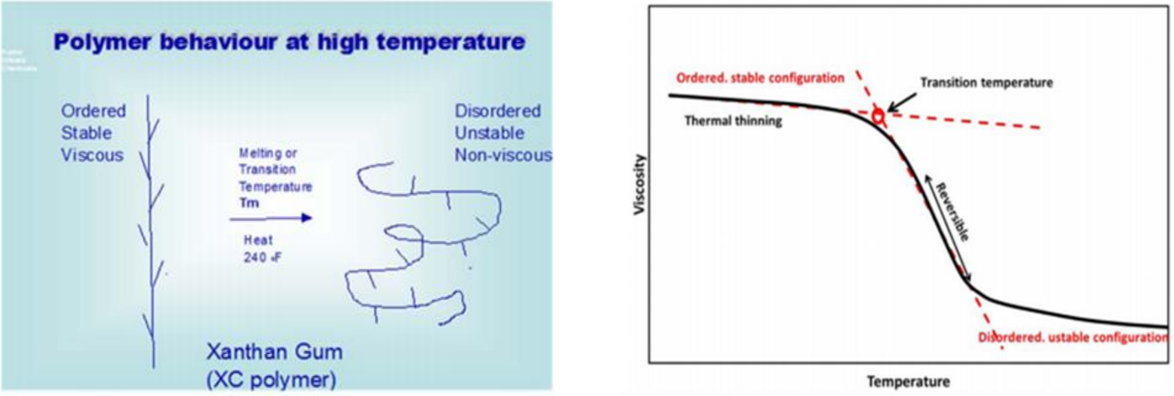


Figure 3.6: Effect of CO_2 on buffered and unbuffered formate systems (Bungert et al., 2000)

Gallino et al. (1997) investigated the performance of innovative polymer mud formulations that Agip S.P.A used to drill plastic shale in Southern Italy. The muds were formulated with K-acetate and K-formate polymers. The result showed an increase in rate of penetration (ROP) and a reduction in bit balling or reaming time as well as in the volume of wastes generated per hole. However, potassium salts present in the mud caused an increase in mixing costs per hole capacity. They noted that the environmentally friendly formate salts in the mud formulation, instead of KCL, limit the mud disposal costs when compared with the use of KCl in mud formulation. They also noted that potassium formate (KCOOH) are biodegradable, and its toxicity level to aquatic life is low. They concluded that formate salts reduce the rate of the biopolymer degradation processes - hydrolytic and oxidative mechanisms at high temperatures. This finding supports the findings by Oort et al.

(1996) and Zuvo et al. (2005) on formate fluids. Formate brines stabilise water-based fluid systems by raising the Tm (transition temperature) of a biopolymer and by providing free-radical properties, capable of retarding the oxidative process (Clarke-Sturman et al.,1986). Consequently, formate brines increase the thermal stability of biopolymers by increasing their T_m. The transition temperature (T_m) is the temperature at which a polymer can undergo an order-disorder conformational change, and the order-disorder conformational change is followed by a loss in viscosity and by an increase in the rate of hydrolytic degradation by two orders of magnitude (Clarke-Sturman and Sturla,1988). For xanthan gum, the xanthan molecules undergo an order-disorder conformational change from a long rigid helical rod structure to a collapsed random coil at its transition or melting temperature. Figs. 3.7 (a) and (b) show a biopolymer behaviour at high temperatures and the loss in polymer viscosity in a solution at melting (transition) temperature respectively (Howard et al., 2015). It is clear, therefore, that at high temperature, biopolymers can lose their viscosities through hydrolytic and oxidation mechanisms if they are not protected by temperature stabilising agents.



(a) **(b)**

Figure 3.7: Effects of temperature on biopolymer (Howard et al., 2015): (a) Xanthan gum's behaviour when heated to its transition (melting temperature, T_m); (b) The effects of temperature on the viscosity of a typical biopolymer

Bradshaw et al. (2006) observed that stabilising the temperature of polymers in conventional water-based fluids with formate salts had made the use of synthetic polymers or oil-based fluids to drill through a long section of open hole unnecessary. This finding supports the conclusion drawn by Panya et al. (1995) on the use of water-based mud systems instead of oil-based mud systems. Bradshaw J.R. et al. found out that with formate-brine muds, the mud cake formed could be easily removed with a breaker solution, which is less-aggressive and non-corrosive and that $CaCO_3$ had no effects on the quality of the mud cake and fluid-loss characteristics of the drilling mud adversely. Table 3.12 shows the additives used in the low-solid formate salt mud.

Table 3.12: Additives used in formate brine-based muds (Bradshaw et al., 2006)

Additive	Conc. (1 barrel)
Water (bbl)	0.888
Xanthan Polymer (Ib/bbl)	1.5
High Temperature Starch (Ib/bbl)	5.0
Organic Temp. Stabiliser (Ib/bbl)	2.0
Shale stabiliser (Ib/bbl)	4.0
Sodium carbonate (Ib/bbl)	1.5
Sodium formate (Ib/bbl)	38.0
Calcium carbonate (Ib/bbl)	45
Glycol (Ib/bbl)	2.0

Powell et al. (1993) reported that oil-based muds were used to drill wells in Prudhoe Bay, Alaska. According to Powell et al., the environmental risks associated with the use of the oil mud was significant and handling of the muds was also an issue. Consequent upon the challenge posed by using oil-based muds, they stated that formate brine-based drilling fluid was used to drill over sixty wells in Prudhoe Bay, Alaska.

Al-Harbi et al. (2005) reported that a water-based drilling fluid formulated with sodium and potassium formate improved the drilling and completion of HT/HP wells. They noted that as formate based drilling fluids have low solid’s contents; they minimised reservoir formation damage. This finding is supported by Bungert et al. (2000). Ezell et al. (2011) investigated a drilling fluid formulation designed for oil fields in Saudi Arabia. The fluid additives included potassium formate and manganese tetra oxide as a weighting agent. They found out that the fluid formulation minimised formation damage, improved thermal stability, and lower drilling costs. These properties of the drilling muds were maintained at temperatures above 155°C. With the formate brines, the vertical well in the oil field was completed without any problems.

Downs et al. (1994) reviewed oilfield literature about well production rates after drilling and/or completing with formate fluids. He observed that formate fluids are ideal fluids for drilling and completion of challenging well construction projects where drilling fluids are essential for profitability. They concluded that formate fluids perform well when formulated with a low level of solids and degrade when formulated with weighty solids.

Simpson et al. (2009) examined the significance and relevance of formate brine drilling muds used in the drilling of 44 deep gas reservoir sections in Saudi Arabia. The primary purpose for the use of the mud formulation was to prevent reservoir damage. In addition, other benefits for the use of the formate brine drilling fluids included prevention of stuck pipe, improvement of bit performance, better well productivity, and reduction of pump pressures. They concluded that the drilling fluids were used to drill through a sandstone formation with a bottom hole temperature up to 323°F, and that the non-damaging properties of the drilling fluid were proved while drilling through the sandstone.

Simpson et al. (2005) examined formate brine muds used to drill wells in an oil field in Saudi Arabia. These formations, it was observed, required unique drilling fluid density. The formate mud formulation and its properties were as shown in Tables 3.8 -3.9. It was noted that formate brine drilling & completion fluids met the requirements for drilling through the formation and were selected for field trials. They concluded as follows:

- The formate brine drilling fluids were lubricious, improved the performance of bit, and reduced torque, drag, equivalent circulating density, and pump pressures.
- The formate brine muds prevented differential pipe sticking

Table 3.13: Additives used in Na/K formate drilling mud

Formulation & order of addition	Concentration	Unit
Fresh water	As required	Bbl
Sodium formate	As required	Lb
Potassium formate	As required	Bbl
Defoamer	0.1	Gal
XC-Polymer	0.5 – 1.25	Lb
PAC	1.0 – 2.0	Lb
Soda Ash	0.2 – 0.3	Lb
Sodium Bicarbonate	0.2 – 0.5	Lb
$CaCO_3$ ‘sized’	As required	Lb
Oxygen scavenger	0.2 - 0.3	Lb

Downs et al. (2005) in their investigation observed that formate salts provide high-density brines mud that are not hazardous, are compatible with oil field hard ware, and are readily biodegradable. They noted that formate salts are powerful antioxidants (this is supported by Gallino et al. (1997)) and stabilised polymers up to a temperature of at least 150°C and are compatible with formation water containing sulphates and carbonates. They concluded that formate brines muds would be effective in drilling and completion fluids in several demanding operational environments in which conventional fluids had difficulties.

Bradshaw et al. (2006) commented that it is difficult to select additives that can give water-based mud the rheological and fluid-loss properties required to drill and complete horizontal wells in formation with a temperature exceeding 300°F (150°C) as some additives degrade at elevated temperatures. They noted that remote drilling locations could pose logistical challenge in supplying additives, thereby leading to compromise in mud formulations. They indicated that the field reservoir temperature of a field in Indonesia was high (315°F) and that the fluid selected for the field was based on sodium formate.

3.5.2 Effects of polyglycols on biopolymers in water-based fluids

Several researchers have come up with mud formulations using polyglycols to stabilise water-based mud systems at high temperatures. To stabilise water-based fluids at temperatures above 150°C, Howard et al. (2015) screened numerous additives to formulate water-based drilling fluids. The best mud formulation that increased the temperature stability of xanthan in potassium formate was made up of magnesium oxide and 5% v/v of polyethylene glycol. They pointed out that the polyethylene glycol likely acted as a sacrificial scavenger which mopped up free radicals before they could attack the biopolymer. However, high temperatures above 210°C were not considered in their investigation, and the mud formulations were clay-free. Saki et al. (2010) developed water-based glycol mud for use in an oil fields in Iran, which were previously drilled with oil-based muds. They reported that the water-based muds approached the performance of oil-based muds, was environmentally friendly and lubricious, and inhibited reactive shale, cleaned the well-bore, and formed a thin, non-permeable filter cake on the well-bore. The results showed that glycol mud was an excellent alternative to oil-based muds (Tables 3.14 and 3.15). However, the water-based glycol mud caused more formation damage than the oil-based mud.

Table 3.14: Typical additive used in oil-based mud (Saki et al., 2010)

Additives	Density 64pcf	Density 75pcf	Mixing Time (min)
Diesel (cc)	187.5	243.5	-
Primary Emulsifier (cc)	10.5	7.2	10
Lime (g)	12	14	10
F.L. C (g)	13	7	15
Calcium Chloride Brine (cc)	140	56.5	15
Secondary Emulsifier (cc)	3.5	7	15
Viscofier (g)	0.5	8.0	15
Limestone	-	132.2	15

Table 3.15: Additives used in glycol mud (Saki et al., 2010)

Additives	Applications	Mixing Time (min)
Water	Aqueous	-
Soda Ash	Hardness Control	5
XC-Polymer	Viscosity	20
PHPA	Encapsulation, Shale Inhibition	20
PAC-LV	Fluid Loss Control	20
NaOH	pH Control	5
NaCl	Decrease Water Activity, Control Cloud Point	10
KCl	Shale Inhibition, Control Cloud Point	10
Starch	Fluid Loss Control	20
Limestone	Weighting agent	10
Glycol	Shale Inhibition	10
Defoamer	Decrease Foam	-

Oort et al. (1997) investigated a technique used to improve the thermal stability of conventional polymers in water-based drilling muds. The interactions of biopolymers with polyglycols were exploited. It was observed that the biopolymer and polyglycols associate by intermolecular hydrogen bonding and hydrophobic interactions. The biopolymers were stabilised at high temperature by this association and complexation. Laboratory findings were confirmed by field results in a field in Indonesia. They concluded that using polyglycols in water-based drilling fluid formulations improved the thermal stability of biopolymers (Table 3.16).

Table 3.16: Effect of polyglycol on rheology (Oort et al., 1997)

	Base Fluid		+5% V/V PG-A		+5% V/V PG-B		+5% V/V PG-B	
Property	BH	AH	BH	AH	BH	AH	BH	AH
600(Ib/100ft^2)	40	8	38	30	39	35	43	42
300(Ib/100ft^2)	32	4	30	24	31	27	33	33
200(Ib/100ft^2)	27	3	26	21	26	24	28	28
100(Ib/100ft^2)	22	1	21	17	21	20	22	23
6 (Ib/100ft^2)	11	0	11	7	11	11	11	11
3 (Ib/100ft^2)	9	0	9	5	10	9	9	9
PV (cP)	8	4	8	6	8	8	10	9
YP (Ib/100ft^2)	24	0	22	18	23	19	24	23
YZ (Ib/100ft^2)	7	0	7	3	6	7	7	7

3.5.3 Effects of antioxidants and oxygen scavengers on polymers in water-based fluids

To stabilise biopolymers in drilling fluids, the mechanisms through which biopolymers degrade at elevated temperatures, therefore, must be understood. Oxidation-reduction (redox) reaction is one of the mechanisms through which biopolymers degrade at high temperatures. This mechanism can be exploited to stabilise biopolymers in water-based drilling fluids at high temperatures by deploying antioxidants and oxygen scavengers to retard the degradation process. Dissolved oxygen in drilling fluid is not only responsible for thermal degradation of biopolymer at high temperatures but also responsible for corrosion of drill pipes. Consequently, in the industry, oxygen scavengers are used to remove dissolved oxygen from drilling fluids. According to Downs (1992), to protect xanthan from degradation at high temperature, some users used pH preserving agents and antioxidants to prevent polymer degradation processes. This method was not very successful as changes in molecular conformation in biopolymer at elevated temperature were not taken into consideration. Other mechanisms are also involved in the degradation of biopolymers at high temperatures: acid-catalysed hydrolysis and early onset of the helix-coil conformation transition. Seright and Henrici (1990) investigated the relative importance of hydrolysis, oxidation, and helix-coil transition in xanthan degradation. They found out that without the presence of oxidising agents, the dominant degradation processes for xanthan gum are not free-radicals and oxidation/reduction reactions. They reported that based on the pH, the mechanisms that play an important role in xanthan degradation were acid-catalysed hydrolysis and base-catalysed formation reactions. They concluded that with no dissolved oxygen, pH 7 to 8, and moderate to high salinities, a solution containing xanthan gum could maintain at least half of its viscosity for a period of 5 years if the temperature is not above 75 to 80°C (167 to 176˚F). However, high temperatures were not considered in this investigation. Wellington (1983) investigated the chemical stability of polymers. They reported that polymer degradation and attendant viscosity loss are likely caused by oxidation/reduction (redox) reactions involving free radicals. The major disadvantages of biopolymers were stated to be as follows:

- It is difficult to formulate muds that do not impair production zone (This can, however, be overcome by proper mixing equipment, chemical addition, and filtration technique).
- It is difficult to prevent viscosity loss from biochemical and chemical reaction

They pointed out that biopolymers form good viscosity and have good shear stability in high salinity fluids and that synergistic formulations using known anti-oxidants retarded free-radical reactions and prevent the loss of viscosity of a solution containing a biopolymer at high temperatures. The effective mud formulation was found to contain:

- a radical transfer agent;
- a sacrificial, easily oxidisable alcohol;
- a compatible oxygen scavenger; and
- enough brine concentration.

They reported that formulations prepared using the additives mentioned above had not lost viscosity after a one-year storage at 97°C. However, high temperatures were not considered in this investigation. Figure 3.8 shows the positive synergistic antioxidant effect of thiourea and IPA on polymer solution stability. Table 3.17 shows the Effect of antioxidants on polymer in water-based mud (Wellington,1983).

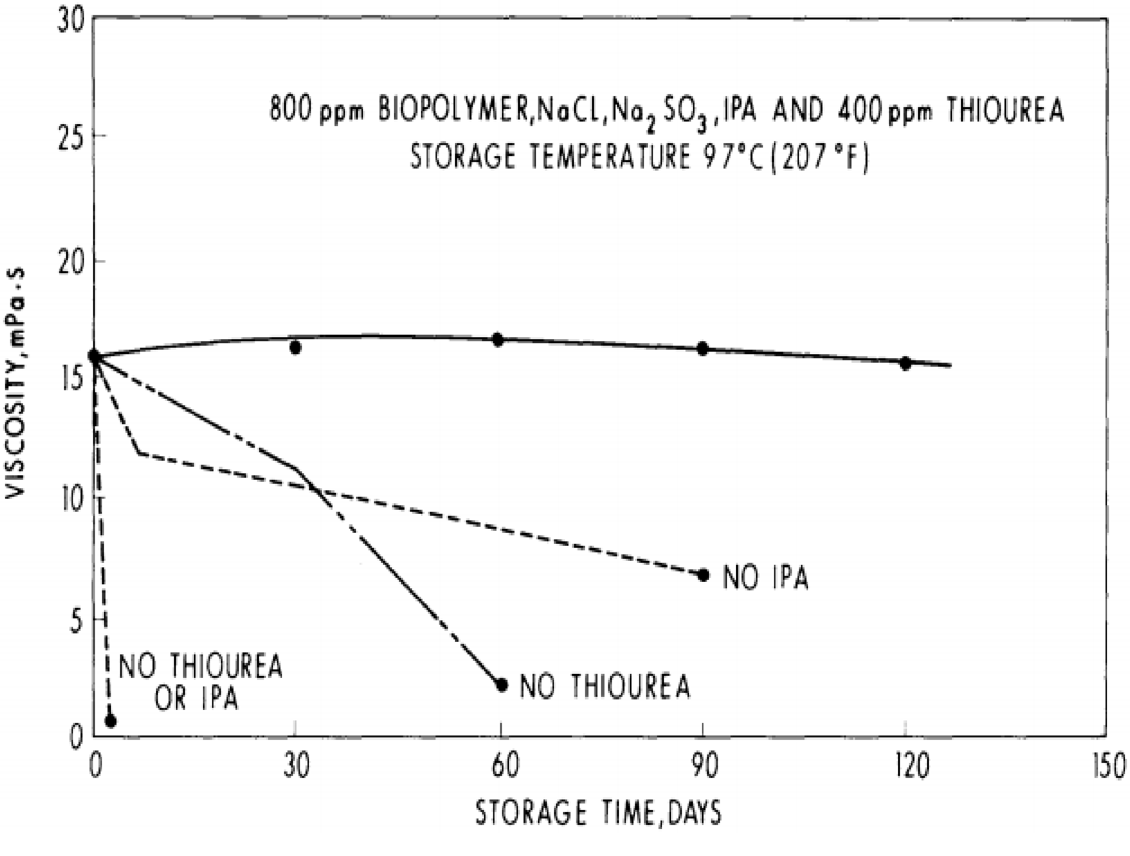


Figure 3.8: Positive synergistic antioxidant effect of thiourea and IPA on polymer solution stability (Wellington,1983)

Table 3.17: Effect of antioxidants on polymer in water-based mud (Wellington,1983)

Sample	Oxgen Scavenger	Other Additives	Initial		Stored at 97°C for		
			Ŋ	pH	Days	ŋ	pH
1	1,000 ppm Na_2SO_3	-	12.1	6.0	3	1.1	5.6
2	1,000ppm Na2SO$_3$	$NaHCO_3$	12.7	8.3	3	1.0	7.6
3	-	$NaHCO_3$	14.1	8.6	3	1.0	7.6
4	1,000ppm Na2SO$_3$	3% IPA	15.4	8.4	3	12.4	8.6
5	-	NaHCO3, 3% IPA	14.6	8.5	3	5.2	9.2
6**	1,000ppm Na2SO3	500ppm thiourea,1000pmm IPA	20.0	8.4	210	15.6	9.6
7	1,000 ppm $Na_2S_2O_4$	-	14.2	3.0	3	1.6	4.0
8	1,000 ppm $Na_2S_2O_4$	$NaHCO_3$	12.4	8.2	3	1.2	7.4
9	1,000 ppm $Na_2S_2O_4$	NaHCO3, 3% IPA	12.7	8.0	3	10.9	9.4
10	1,000 ppm $Na_2S_2O_4$	NaHCO3,500ppm thiourea, 1% IPA	13.4	8.3	14	5.6	8.0
120	800ppm, Na_2SO_3	1,000ppm NaHCO3	12.7	8.3	32	1.0	7.6
100	800ppm, Na2SO3	3,000 ppm NaHCO3, 1% IPA	12.8	8.6	10	4.5	9.1
121	800ppm, Na2SO3	1,000ppm NaHCO3, 3% IPA	14.6	8.5	32	5.2	9.2
122	-	1,000ppm $NaHCO_3$	14.1	8.6	3	1.0	7.6
123	800ppm, Na_2SO_3	1,000 ppm NH_4OH and NH_4Cl	12.4	9.1	4	4.0	9.2
124	800ppm, Na2SO3	5,000 ppm NH_4OH and NH_4Cl	10.7	9.2	4	1.1	9.3
101	800ppm, Na_2SO_3	3,000ppm $NaHCO_{3,}$ 1% IPA	13.1	7.8	35	3.4	9.3
125	800ppm, Na_2SO_3	1,000ppmNaOH and NH_4Cl	9.2	11.4	4	1.4	11.1
127	-	800ppm paraformaldehyde and $NaHCO_3$	14.2	8.3	23	1.4	7.2
131	-	2,000ppm paraformaldehyde,1,000ppm $NaHCO_3$	12.6	8.5	23	1.2	5.9
132	-	1,000ppm paraformaldehyde, and formalin,1,000ppm $NaHCO_3$	12.8	8.4	22	1.6	6.5
151	-	400ppm hypophosphorous acid and 1000ppm $NaHCO_3$	13.4	7.5	34	1.0	9.4
11	Deionized water under vacuum +						

*Biopolymer concentration was 800ppm in 800ppm NaCl

**This sample had 1000ppm biopolymer

+This sample was prepared in a vacuum prepared in a vacuum line and transferred under oxygen-free nitrogen into storage bottles

Glass et al. (1983) examined the effects of thermal-oxidative, mechanical and acid-catalysed hydrolysis on the viscosities of carbohydrate polymers and on that of a synthetic water-soluble polymer, hydrolysed (30%) poly (acrylamide) (HPAM). They reported that HPAM was the most stable polymer under thermal-oxidative conditions when compared with the carbohydrate polymers and that under the same oxidative conditions, the carbohydrate polymers such as xanthan gum prepared by fermentation synthesis were more stable than non-fermentation polysaccharides such as guar gum. They reported further that under acid catalysed hydrolysis, the carbohydrate polymers prepared by fermentation synthesis and non-fermentation polysaccharide showed the same differential performance. The polymer degradation was not dependent on molecular weight under either thermal-oxidative or acid-catalysed condition, but under mechanical condition, the degradation was dependent on molecular weight. It was noted that lower-molecular-weight polymers were more stable. They also noted that the key to successful drilling was for a polymer to maintain its viscosity for over a 50 to 72-hour time at temperatures exceeding 135^{o}C (275^{o}F). The polymers commonly used in the petroleum processes were classified into three stability groups:

- synthetic polymers which are more stable than any of the carbohydrate polymers
- Fermentation polysaccharides, which are more stable than non-fermentation polymers.
- Non-fermentation polysaccharides exhibited the poorest thermal-oxidative stability

The effect of oxygen on polymer stability in the presence of magnesium oxide (MgO) and tetraethylenepentamine (TEPA) were also investigated. It was observed that in a solution containing oxygen and non-fermentation carbohydrate polymers, the two additives, the magnesium oxide (MgO) and tetra-ethylene penta-amine (TEPA), were very effective in preventing hydro peroxide groups formation. However, MgO was ineffective in aqueous systems containing oxygen scavengers; but TEPA remained effective. It was found out that the use of either magnesium oxide (MgO) or tetra-ethylene penta-amine (TEPA) in the field can be problematic.

3.6 Stabilisation of shale formations using inhibitive water-based fluids

For successful drilling operations in high pressure/high temperature (HPHT) formations, the drilling mud systems used must remain stable, be environmentally safe, and retard shale problems. About 70% of well-bore instability problems is caused by shale (Aftab and Ibupoto, 2017). As shale is made of kaolinite, illite, smectite, and montmorillonite, it has an affinity for water. The degree of shale affinity to water depends on the type and amount of clay minerals in it; shale with a high amount of smectite has the stronger affinity to water than shale which contains a substantial amount of kaolinite or illite (Lal,1999). The shale-fluid interaction causes shale instability. During drilling operations, drilling fluid replaces shale in the well-bore, thereby causing mechanical stress changes, changes in capillary pressure in the shale, swelling pressure in the shale, changes in pressure around the well-bore, and fluid movement due to differential pressure. These changes lead to hole instability (Lal,1999). In addition, if a shale formation is drilled with a non-inhibitive water-based mud, the shale instability problems occur (Wilcox et al.,1987; Reid et al.; Soric et al.,2004). Extensive works have been done to design water-based drilling fluid formulations that can reduce or control the drilling fluid interaction with reactive shale formations. Water-based fluids are formulated with organic or inorganic additives to improve shale inhibition properties (Sandra and Arvid,2013; Pinya et al.,1995; Clark et al.,1976). The organic inhibitors are classified into three categories (Sandra and Arvid,2013): (1) monomeric amine shale inhibitors (they have a low level of inhibition and high ammonia odour), (2) oligomeric amine shale inhibitors (they provide a more permanent shale stabilisation), and (3) polyamine shale inhibitors (they are a more permanent shale inhibitor and less attractive due to their incompatibility with other anionic additives). The inorganic shale inhibitors are salts such as sodium chloride, calcium chloride, and potassium chloride. Potassium chloride is a commonly used inorganic additive for shale inhibition. Another inorganic shale inhibitor is silicate additives. To study the effects of silicate-based drilling fluid on shale formations, Soric et al. (2004) examined the design of a silicate-based fluid. Silicate mud system is known to be inhibitive. Inhibitive muds are designed to inhibit water sensitive rocks. Table 3.18 shows the basis formulation of silicate-based mud systems. The aim was to inhibit water-sensitive, reactive shale, and dispersible chalk and illite formations. They found out that the silicate mud system performed much better than other water-based mud systems in terms of their inhibition properties and that the mud performance was similar to that of oil-based mud systems. They also found out that the mud was stable even in the presence of high contents of anhydrites of salts. Polymers and other additives used in the silicate mud system to provide rheological properties and fluid loss control were as shown in Table 3.18.

Table 3.18: Basis formulation of silicate-based drill fluid (Soric et al. (2004)

The silicate mud formulation	
Potassium carbonate	40 kg/m^3
Sodium Chloride	To saturation at 35^{o}C
Sodium Silicate Liquid	8% by Volume
Xanthan Gum	YP 25 Ib/100ft^2
Polyanionic Cellulose	8 kg/m^3
Starch	API-PL<5ml/30min
Biocide	1kg/m^3
Calcium Carbonate Fine	25 kg/m^3 (for bridging)
Calcium Carbonate Med.	25 kg/m^3 (for bridging)

The mud was used to drill through anhydrite, claystone, dolomite and salt formation, and six wells on the Hayane Block in Syria. However, the mud rheological properties increased slightly, and the fluid loss increased significantly while drilling through anhydrite. In addition, silicates have the potential to damage formation, and the control of rheological properties is a major problem with the use of a silicate-based mud system (Vikas and Rajat, 2015). Reid et al. (1992) investigated an inhibitive water-based fluid formulated from tetra-potassium pyrophosphate for drilling through tertiary shale. They observed that the formulated mud level of inhibition was closer to that of oil-based muds (Figures 3.9 and 3.10). Inhibitive muds prevent shale hydration. The effects of high temperature on the mud system were not considered.

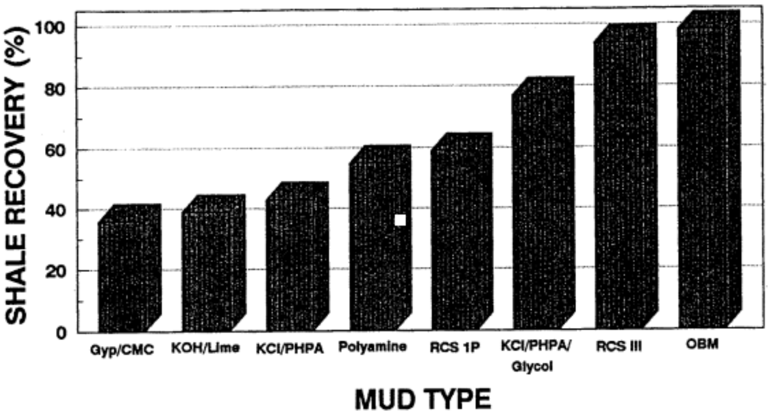


Figure 3.9: Shale dispersion inhibition of tertiary shale (Reid et al., 1992)

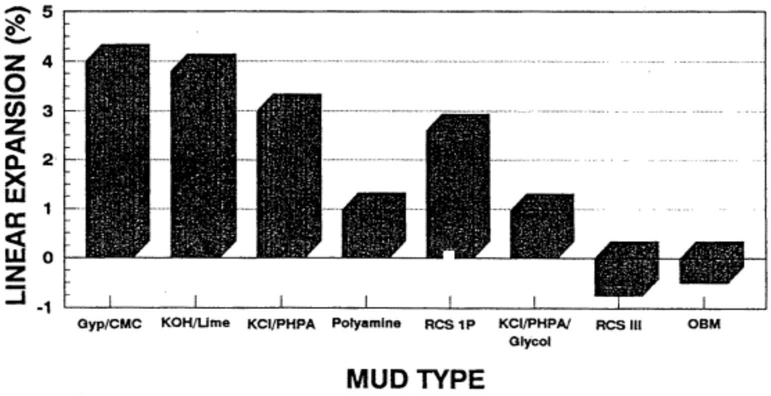


Figure 3.10: Shale swelling inhibition (Reid et al., 1992)

Nevertheless, the tetra-potassium pyrophosphate caused mud accretion problems. Another mechanism through which drilling fluids inhibit shale hydration is polyol chemistry. Polyol reduces water activity and form a membrane on the well-bore. Polyglycols are also used in drilling fluid to stabilise sensitive shale formations. Brady et al. (1998) developed water-based drilling fluids that were highly inhibitive. The polyglycol in the fluid formulations was found to absorb strongly on clay rock, thereby preventing clay-fluid interaction. Commonly used polyglycol for shale inhibition are not very effective in salt-free or low-salt fluids. Other muds additives used for shale inhibition are nanoparticle materials (Ji et al. 2012) and copolymers (Mehtar,2010). Polymeric materials are also used in drilling fluids to control the dispersion by shale encapsulation, thereby preventing the invasion of water in the clay structure. Pinya et al. (1995) investigated the design and application of the amphoteric polymer drilling fluids. The drilling fluid was used in oil fields with different lithologies, with high salinity, and with a high temperature in China. The fluid formulation was effective against shale, stabilised well-bore, enhanced rheological properties, improved rate of penetration, and protected the pay zone. Clark et al. (1976) investigated the performance of a potassium-based polymer mud that has been successful in controlling troublesome shale in many wells around the world. The field application of polyacrylamide and potassium-chloride mud proved successful in stabilising hard, sloughing shale in Canada and in reducing shale-related hole problems in several offshore areas. They concluded that the shale stability results by combining potassium chloride with a high molecular-weight, partially hydrolysis polyacrylamide. However, high concentrations of potassium chloride in drilling fluids are an environmental concern (Bloys et al., 1994). All these efforts of researcher have brought to the fore the attempt made in stabilising water-based fluids at high temperatures and in inhibiting shale hydration in reactive shale formations. Nevertheless, none has considered the combination of additives used in this work.

3.7 Chapter summary

The effects of additives in water-based muds appear to be well understood in the literature. However, the selection of additives that can make water-based muds perform like oil-based muds under high temperature conditions remains a big challenge. In addition, biopolymers are additives used in almost all water-based muds; however, high temperatures pose a major challenge to running biopolymer-based muds successfully. The low stability temperatures of biopolymers, therefore, make them unsuitable for high-temperature drilling operations. The researchers, therefore, identified biopolymer as one of the drilling fluid additives that are sensitive to high temperatures and field contaminants.

The mechanisms identified as responsible for biopolymers' degradation at high temperature were as follows:

- Oxidation-reduction reaction
- Acid-catalysed hydrolysis (dependent on the pH)
- Base-catalysed hydrolysis
- Early onset of the helix-coil conformation transition

Oxidation-reduction reaction and acid-catalysed hydrolysis are, therefore, exploited in this present research to stabilise biopolymers in water-based muds at elevated temperatures. Antioxidants, formate salts, polyglycol, and soluble silicates have been identified as additives used in stabilising biopolymers in water-based muds at high temperatures. However, high concentrations of some of these salts are environmental concern. Researchers have investigated high performance water-based muds and observed that these mud systems' performance approaches that of oil-based muds. In order words, no water-based mud formulations have yet replicated the technical performance of oil-based muds at elevated temperatures. In addition, the techniques for the inhibition of shale hydration and dispersion are well understood in the literature, and researchers have identified shale-fluid interaction as the cause of shale instability. Consequently, shale formations are drilled with inhibitive water-based mud systems to retard shale hydration and dispersion; and water-based fluids are formulated with organic or inorganic additives to improve shale inhibition properties. However, some of these additives have their limitations.

In view of the above, it was felt that a combination of additives that have not been considered in literature would stabilize biopolymers in water-based bentonite muds and inhibit shale hydration and dispersion at elevated temperatures. It was also expected that the use of sodium erythorbate, potassium formate, buffering agents, and polyethylene glycol (8000) to stabilise water-based biopolymer drilling fluids and to inhibit shale dispersion at high temperatures would help to uncover critical areas with respect to the stabilization of water-based muds at high temperatures and the inhibition of shale dispersion. The mud formulations in the present research are expected to be used for high temperature and shale formations drilling operations in the oil industry.

Chapter 4: Apparatus, Materials, Procedures, Mud formulations, Shale Characterisation, and Dispersion test

4.1 Introduction

This chapter describes the apparatuses, the materials (additives), and the procedures for carrying out this research work. In the oil industry, mud formulations are tested to determine their rheological and other properties. If the values of mud properties measured are not suitable for any drilling operation, the concentrations of materials in the mud are varied until the desired values of mud properties are obtained. The mud properties obtained are used to predict the characteristics of drilling fluid during drilling operations. In this investigation, the rheological properties of mud formulations are measured with Models 800 and 1100 viscometers. The materials investigated include bio-polymers: xanthan gum, konjac gum, and diutan gum. The stability temperatures of biopolymers in water-based bentonite muds and the effects of inhibitive mud formulations on reactive shale rock were investigated using aging cells and roller oven. The experimental and mud formulation procedures needed to obtain precise and accurate results are presented in this chapter. This study was conducted in two phases. Phase 1 considers the stability temperatures of biopolymer in water-based bentonite muds. Figure 4.1 shows the methodology flow chart of the Phase1 of this study. Phase 2 considers the effects of mud formulations on shale dispersion. Figure 4.2 shows the methodology flow chart of the Phase 2 of this present study.

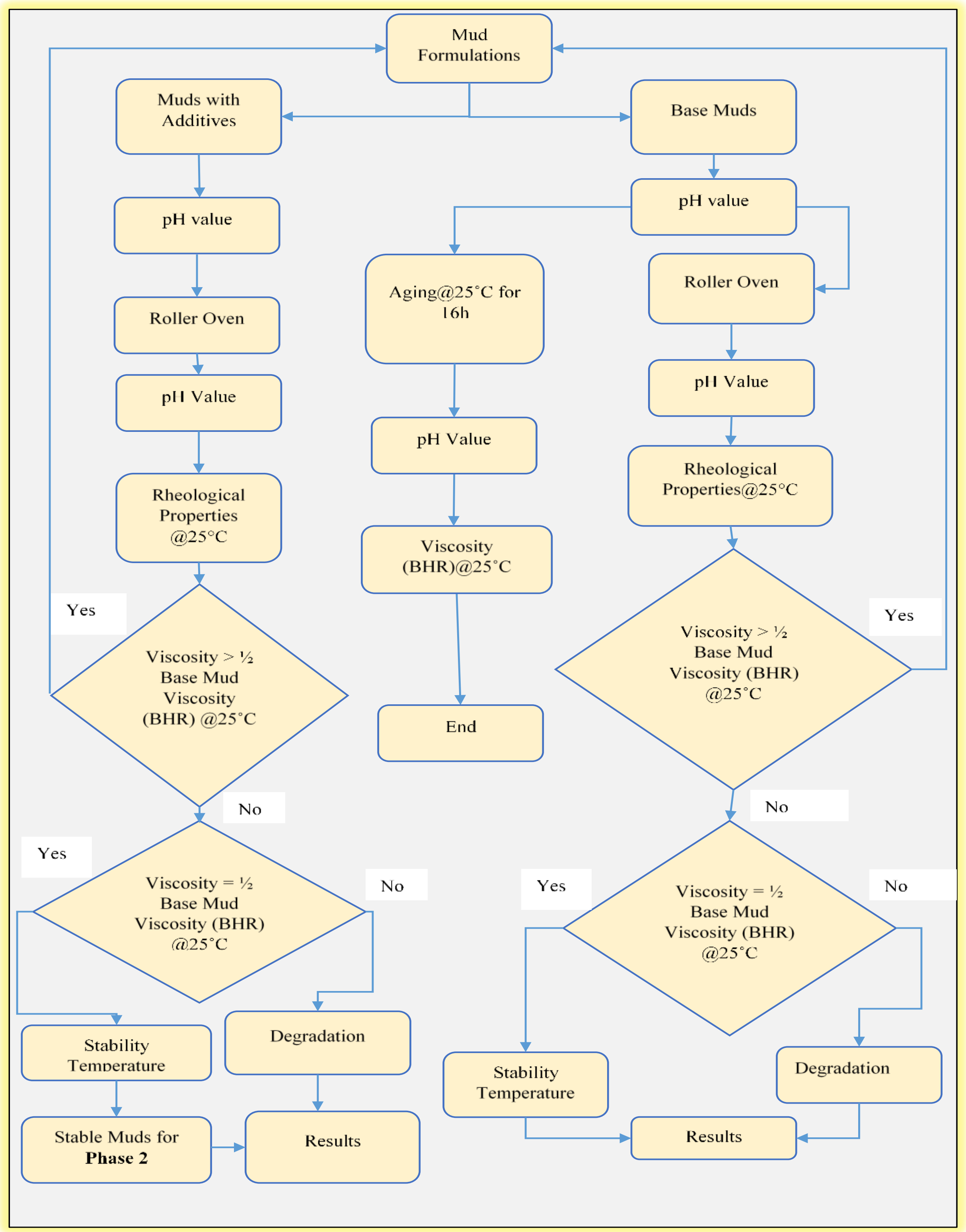


Figure 4.1: Methodology flow chart: Phase 1

As shown in Figure 4.1 above, the control samples were aged at 25°C (room temperature) for 16 hours. A stable mud indicates that its rheological parameters are almost the same as those measured at room temperature after aging tests. In addition, a mud is said to be stable if it does not lose more than half of its initial viscosity (room temperature) after aging for sixteen hours at a temperature (Howard et al. ,2015).

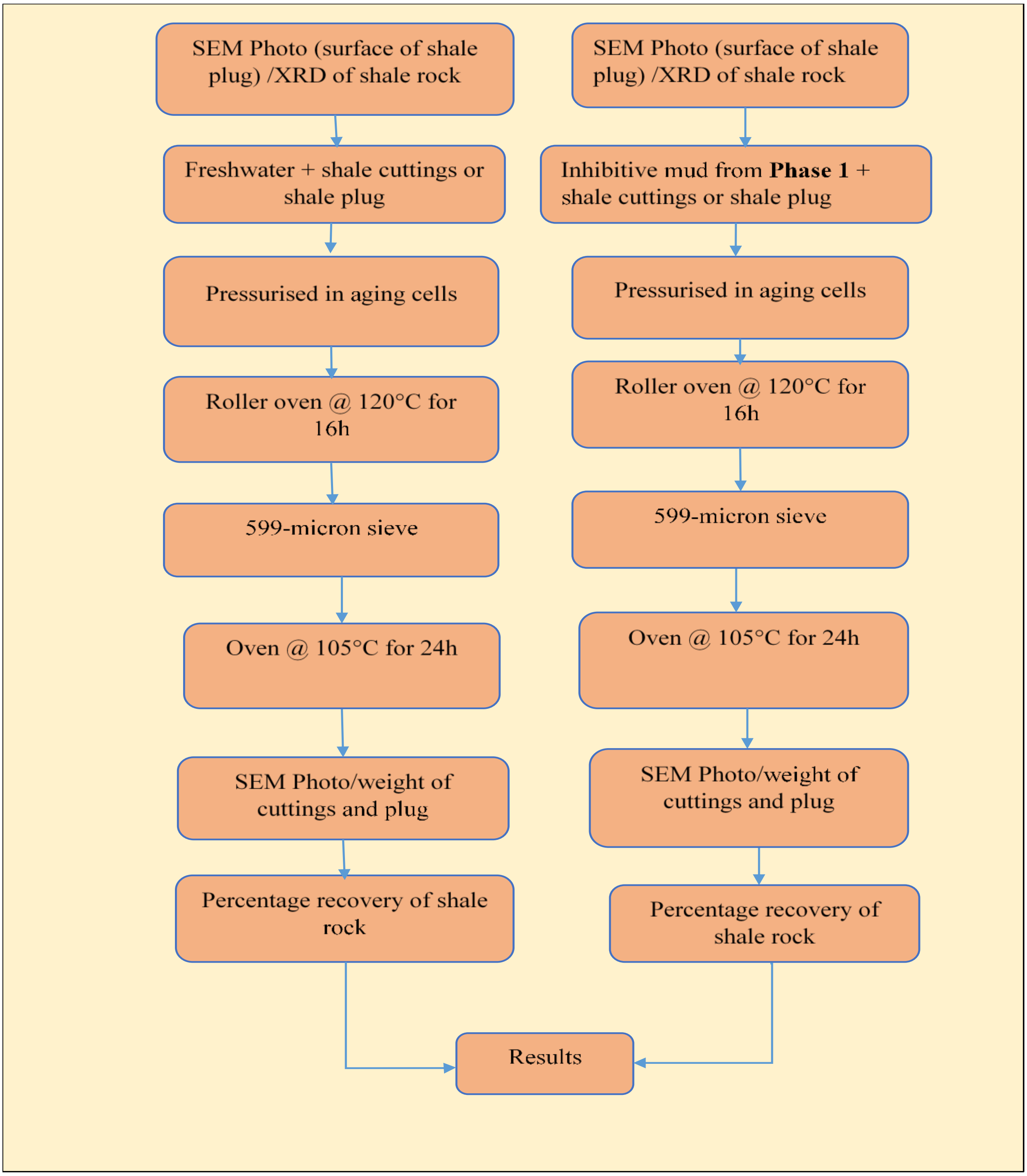


Figure 4.2: Methodology flow chart: Phase 2

As shown in Figure 4.2 above, the tests were intended to simulate the transportation of drilled cuttings in drilling fluids to the surface from a wellbore annulus. Shale cuttings were immersed in freshwater and in inhibitive water-based muds (Sandra and Arvid,2013; Al-Arfaj et al., 2018).

4.2 Materials used in this study

This sub-section describes the drilling fluid materials used in this study. The materials used in the mud formulations were freshwater, bentonite, xanthan gum, konjac gum, potassium formate, sodium erythorbate, polyethylene glycol 8000(PEG), sodium carbonate, sodium bicarbonate, and defoamer. Bentonite was purchased from Hilton Instrument, Aberdeen; xanthan gum powder and diutan gum were provided by CP Kelco, USA. Konjac gum powder was purchased from Aromatic Natural Skin Care, Moray, Scotland. Potassium formate, sodium erythorbate, polyethylene glycol 8000(PEG), sodium carbonate and sodium bicarbonate were purchased from Fisher Scientific, United Kingdom. The defoamer, Dispelair Se574, was provided by Blackburn Chemicals Limited, Blackburn, United Kingdom. Marcellus shale rock was purchased from Kocurek Industries INC.

The freshwater served as the base fluid and as a means for conditioning the bentonite and other additives used in the drilling fluid preparations. The sodium bentonite provided the initial viscosity, suspension, and fluid loss control. The concentration of the bentonite was kept very low as high solid contents in drilling muds could cause problems such as pipe sticking (Darley and Gray,1998). The quantity of bentonite used was 10.5 lbm (3% w/v concentration). 2-3% bentonite concentration is used in polymer mud systems in oil fields (Dayawant,1999; Sharma et al.,2003). The function of the biopolymers, diutan gum and xanthan gum, was to provide viscosity and fluid-loss control. Sodium carbonate and sodium bicarbonate were added to the drilling fluid samples to counteract acid-catalysed hydrolysis. Potassium formate was deployed as an antioxidant and temperature stabiliser. Sodium erythorbate served as an antioxidant and oxygen scavenger. An antioxidant protects a biopolymer at high temperatures from thermal degradation, by preventing oxidative processes and reacting with hydroxyl free radicals (Howard et al., 2015). Polyethylene glycol served as shale stabiliser.

4.3 Equipment description, procedures, calibration, sources of error, accuracies and safety measures

This section describes the key equipment used in this study and their standard operating procedures, calibration, sources of error, accuracies, and safety measures for operation. The key equipment used were as follows:

- Hamilton beach mixer,
- Model 800 viscometer,
- Model 1100 viscometer,

- pH meter,
- Roller oven
- Aging cells

4.3.1 The Hamilton beach mixer

The Hamilton beach mixer (Figure 4.3) was used in this study for drilling fluid mixing. It was used to shear water and other mud additives mechanically to produce a consistent drilling mud. There are two models of Hamilton beach mixer: Single and three-Speed Models. The three-speed model was used in this study. The low speed is 10,000rpm. The medium speed is 14,000rpm while the high speed is 17,000rpm.

Figure 4.3: Hamilton beach mixer

4.3.1.1 Safety measures for operating the Hamilton beach mixer

- Manufacturer's operating instruction on electrical shock was adhered to
- Its cord was unplugged from outlet after use.
- The spindle was not touched while stirring.
- Clothes were kept away from the spindle while stirring.
- Personal protective equipment was worn.

4.3.1.2 Procedure for mud mixing (Hamilton beach mixer)

The weighing balance was used to measure the specified amount of solid and powdered additives. Graduated cylinder was used to measure specified volume of water and defoamer. The drilling mud additives were added to 350 ml (one lab barrel) of freshwater in the mud cup. Thereafter, the mud cup was placed under the spindle of the Hamilton beach mixer and its contents were stirred at room temperature for 30 minutes. After about 25 minutes of stirring, lump materials adhering to the mud cup were scraped down. After that, the mud cup content was stirred again for two minutes.

4.3.2 Model 800 viscometer

OFITE Model 800 viscometer (Figure 4.4) was used to measure the viscosities and gel strengths of drilling mud formulations in terms of shear rate and shear stress for a period and at 25°C and atmospheric pressure. The equipment uses the principle that the force, which turns an object in a fluid, can indicate the viscosity of the fluid (Mitchel and Miska, 2011). On top of the instrument is a knob that is used to control speeds, and the shear stress values are displayed on a lighted magnified dial on the top of the instrument as well. It has the following speeds: 3 (Gel), 6, 30, 60,100,200,300, 600, and a higher stirring speed, called STIR. Test starts with 600RPM, which is the highest speed and ends with the lowest speed, 3RPM. The instrument's speed accuracy (RPM) is 0.1 (OFI Testing Equipment, 2019).

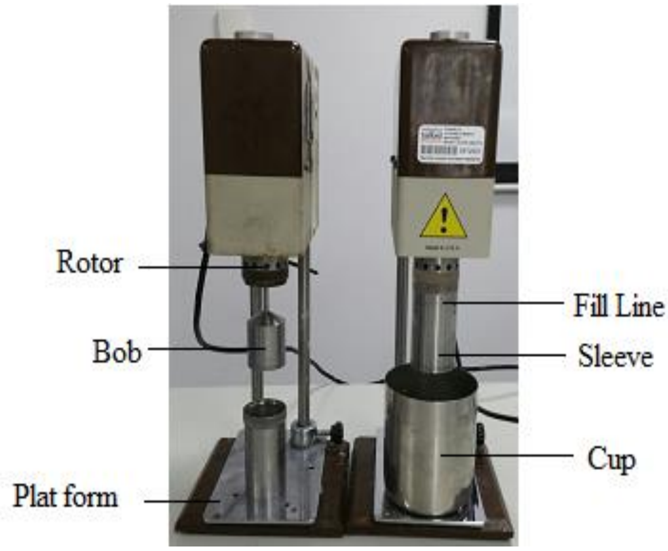


Figure 4.4: OFITE rotational viscometers

4.3.2.1 Sources of error

- Test mud in the cup being above or below the fill line
- Excessive wobbling of the rotor sleeve
- Exposure of the cup to the atmosphere

4.3.2.2 Safety measures

- Manufacturer's operating instructions were adhered to
- Personal protective equipment was worn when running tests

4.3.2.3 Calibration of Model 800 viscometer

The Model 800 viscometer is calibrated because of the following):

- Contaminated bob shaft bearings
- Bent bob shaft.
- Dial not returning to zero
- If the dial deflection is excessive when the main shaft is turning,

The instrument is calibrated in accordance with API Recommended Practice 13B-1 and 13B-2 which recommends monthly checking of viscometers used for testing drilling fluids. A dead-weight method of calibration is used to calibrate this unit.

4.3.2.4 Procedure for calibration of Model 800 viscometer (OFI Testing Equipment, 2019)

- Before calibration, the appropriate calibration fluid was selected via temperature-viscosity chart.
- The viscometer bob, sleeve, and cup were first cleaned and dried.
- The viscometer and the calibration fluid were placed side-by-side on a table in the laboratory and left for at least two hours to equilibrate. The viscometer was then run in air for about four minutes to relax the bearings and gears, and the rotor sleeve was then observed for excessive wobbling.
- The calibration fluid was then poured into the cup up to the scribed line. The cup was placed on the viscometer stage, which was moved until the fluid level in the cup reached the scribed line on the sleeve.
- A thermometer was then placed into the fluid in the cup and taped to prevent breakage. The viscometer was switched on and operated at a low speed until the reading on the thermometer was stable to within ± 0.2˚F (0.1°C) per 30 seconds.
- Thereafter, the temperature reading was noted and recorded. When the temperature stabilised, the viscometer was operated at two speeds, 600 RPM and 300 RPM. The readings on the dial were noted and recorded to the nearest 0.5 dial unit.
- From the temperature-viscosity chart, the certified viscosity was determined to the nearest 0.5cP. Thereafter, the 300 RPM reading was compared to standard viscosity and the deviation plus or minus was recorded. The 600 RPM dial reading was then divided by 1.98

and the value derived was compared to standard viscosity. the deviation plus or minus was recorded. A deviation exceeding 1.5 dial units are not acceptable and a deviation within 1.5 dial unit is acceptable.

- Calibration date was then marked on the viscometer.

4.3.2.5 Testing procedure for rheological properties of formulated muds using Model 800 viscometer (OFI Testing Equipment, 2019)

The drilling fluid formulation was poured in the sample cup which was placed on the platform of the viscometer. The platform was then raised until the rotor immersed in the fluid up to the scribed line. Thereafter, the lock nut on the platform was tightened. The drilling fluid formulation was stirred on the ‘’STIR’’ setting for 10 seconds and the test temperature was recorded with a thermometer. After the 10 seconds, the knob was rotated to the speed of interest. When the dial reading stabilised, the reading was recorded. From the dial readings, plastic viscosity, yield point, apparent viscosity and effective viscosity were calculated. The plastic viscosity (PV) and yield point (YP) were calculated from two dial readings at 600rev/min and 300rev/min respectively as (Mitchel and Miska, 2011):

$$PV = \theta_{600} - \theta_{300} \tag{4.1}$$

$$YP = \theta_{300} - PV \tag{4.2}$$

Apparent viscosity μ_a was calculated as follows:

$$\mu_a = \frac{600RPM}{2} \tag{4.3}$$

Where θ is the dial reading at ω rev/min. It is usually reported at the 600 rev/min reading. The effective viscosity was calculated by the equation below:

$$\mu_e = \frac{300\theta(at\ any\ RPM)}{RPM} \tag{4.4}$$

All the tests were carried at six distinctive speeds of 600, 300, 200, 100 and 60 RPM, and Gel at 25°C.

4.3.3 The Model 1100 viscometer

The Model 1100 viscometer, which is fully automated, was used to measure the shear stress, shear rate, apparent viscosity, low shear viscosity (LSRV), yield point (YP), plastic viscosity (PV) and gel strength of drilling muds at 25°C. The Model 1100 pressurised viscometer is fully automated (Figure 4.5). The instrument is operated with ORCADA® software portable. Its speed (RPM) accuracy is 0.001 and shear rate range (s^{-1}) is 0.01 – 1.002.; the accuracy of instrument calibration is the r^2C value equal to or greater than 0.9990 (OFI Testing Equipment, 2015).

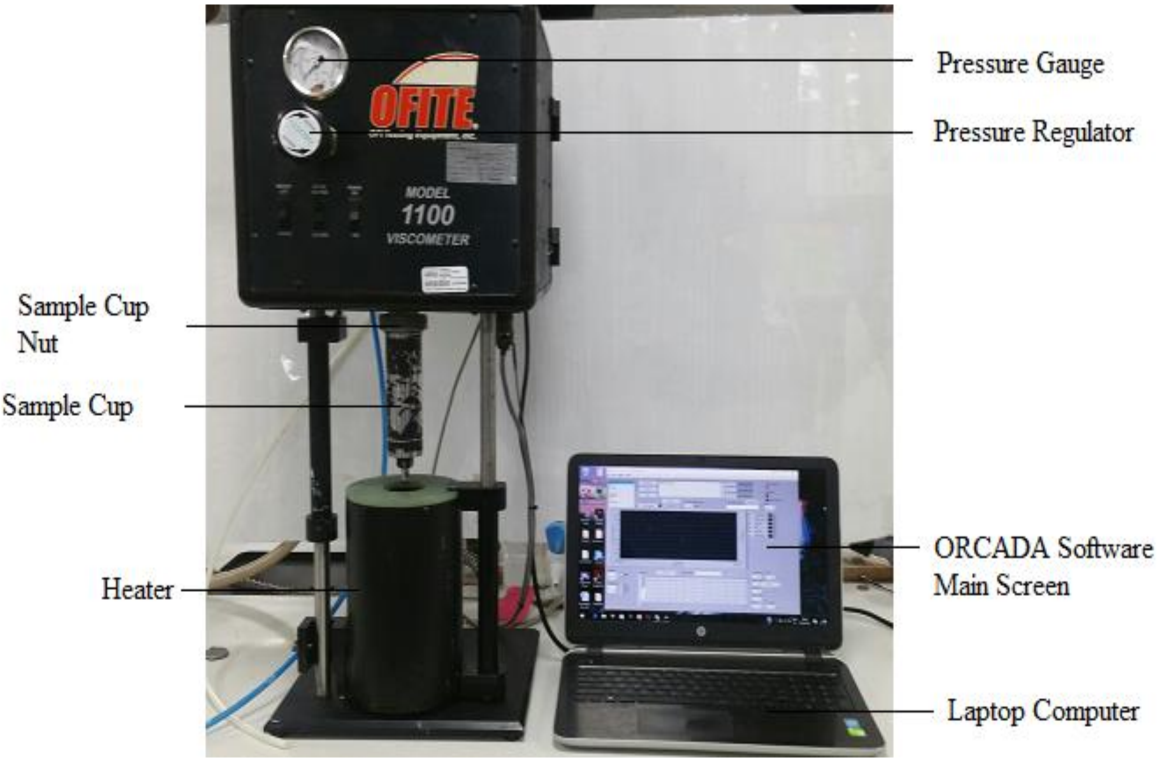


Figure 4.5: Model 1100 Viscometer and laptop computer

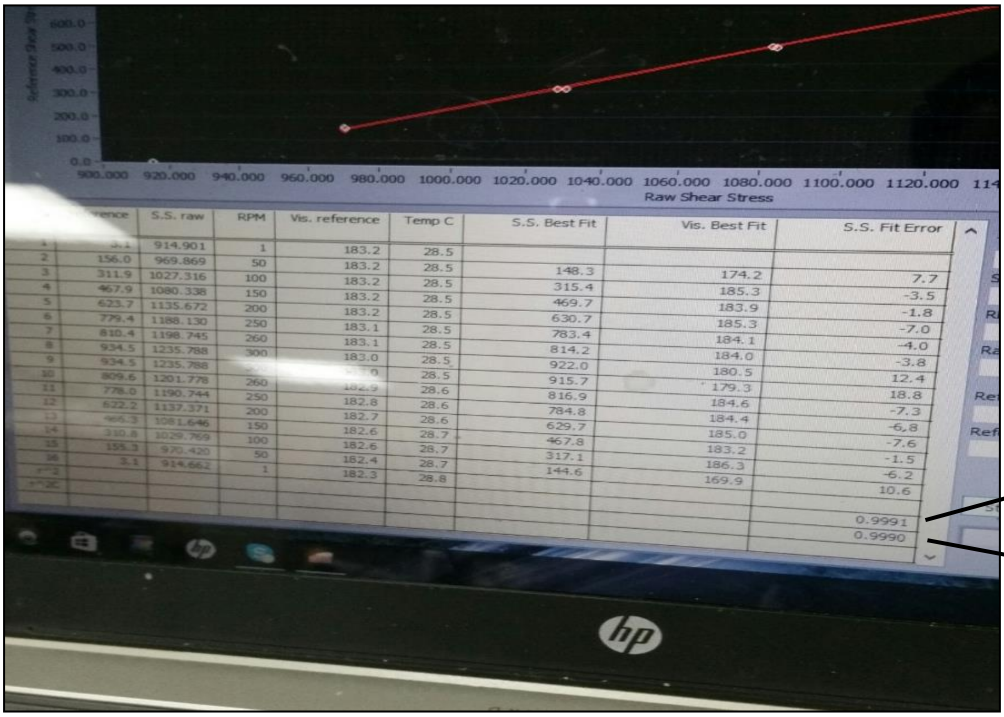
On the back panel of the instrument is located A three ¼" (6.35mm) NPT fittings. A water source, nitrogen source, and drain hose are connected to the appropriate fittings. Nitrogen is used to pressurise the drilling fluid sample to prevent boiling at temperatures above 212˚F (100°C) while water is used to raise and lower the heater. The viscometer is connected to a computer via either a 9-pin RS232 cable, a Local Area Network connection with an Ethernet cable, or Bluetooth (OFI Testing Equipment, 2015).

4.3.3.1 Calibration of Model 1100 (OFI Testing Equipment, 2015a).

The ORCADA® calibration program is calibrated before performing the first test. In addition, calibration is required based on the following reasons:

- The bob is changed
- The instrument is not used for many days,
- The instrument has been serviced
- The “r^2” value below 0.99 during a sweep.
- If operated for two weeks.
- If used for testing drilling fluids, it should be checked monthly.

To start to calibrate, the ORCADA® software on the computer was opened. “Utilities” was selected on the menu bar and thereafter “Calibrate Shear Stress” was selected. The “Shear Stress Raw” value was observed and recorded while the unit was at 0 RPM. Before calibration, the calibration fluid was heated or cooled to within the acceptable range. A 200cP fluid was used for the calibrations as the unit uses a B5 bob. Calibration speeds were set to be greater than 0 and less than or equal to 300. The “Start Calibration” button was clicked to start the calibration. At the end of the calibration, the “r^2C” value was noted. This value measures the accuracy of the calibration. When its value is less than 0.9990, the unit is recalibrated. When the r^2C value was equal to or greater than 0.9990, the calibration was completed. Figure 3.9 shows the calibration of the unit before tests were run.



	rence	S.S. raw	RPM	Vis. reference	Temp C	S.S. Best Fit	Vis. Best Fit	S.S. Fit Error
1	3.1	914.901	1	183.2	28.5			
2	156.0	969.869	50	183.2	28.5	148.3	174.2	7.7
3	311.9	1027.316	100	183.2	28.5	315.4	185.3	-3.5
4	467.9	1080.338	150	183.2	28.5	469.7	183.9	-1.8
5	623.7	1135.672	200	183.2	28.5	630.7	185.3	-7.0
6	779.4	1188.130	250	183.1	28.5	783.4	184.1	-4.0
7	810.4	1198.745	260	183.1	28.5	814.2	184.0	-3.8
8	934.5	1235.788	300	183.0	28.5	922.0	180.5	12.4
9	934.5	1235.788	[illegible]	[illegible]	28.5	915.7	179.3	18.8
10	809.6	1201.778	260	182.9	28.5	816.9	184.6	-7.3
11	778.0	1190.744	250	182.8	28.6	784.8	184.4	-6,8
12	622.2	1137.371	200	182.7	28.6	629.7	185.0	-7.6
13	466.3	1081.646	150	182.6	28.6	467.8	183.2	-1.5
14	310.8	1029.769	100	182.6	28.7	317.1	186.3	-6.2
15	155.3	970.420	50	182.4	28.7	144.6	169.9	10.6
16	3.1	914.662	1	182.3	28.8			
r^2								0.9991
r^2C								0.9990

r^2 Value

r^2C Value

Figure 4.6: Calibration of ORCADA® software

4.3.3.2 Test accuracy of Modell 1100 viscometer

- The speed (RPM) accuracy is 0.001
- Calibration accuracy: r^2C ≥ 0.9990; r^2 ≥ 0.99

4.3.3.3 Sources of error

- The software not calibrated before use
- Test not carried at a specified temperature
- Test carried out with “Shear Stress Raw” value drifting more than 2 or 3 units
- Calibrating the software at speeds above 300RPM
- Using contaminated and expired calibration fluids

- Bent thermocouple

4.3.3.4 Safety measures

- Manufacturer’s operating instructions was adhered to
- Pressure was reduced when the mud temperature dropped below 120˚F (49°C).
- The mud cup was removed when the pressure read 0.

4.3.3.5 Procedure for operation of Modell 1100 viscometer (OFI Testing Equipment, 2015).

The instrument and the computer were first turned on. After booting up the computer completely, the ORCADA® icon on the computer desktop was clicked to open. Thereafter, “Utilities” on the menu bar was clicked and “Calibrate Shear Stress” was selected. The temperature field was checked to ensure that it read room temperature while “Shear Stress Raw” was checked to confirm it was fluctuating when the bob was tuned gently by hand. The sample cup was filled with the proper amount of drilling mud on the bob used (Table 4.1). An R1B1 bob and rotor are used in the Model 1100 Viscometer used in this study.

Table 4.1: Fluid sample volume based on bob type (OFI Testing Equipment, 2015).

Bob Type	Sample Amount (ml)
BI	42
B3	78
B3	96
B4	104
B5	52
XB1	32
XB2	73
XB5	44

The sample cup was held by hand while the bob was positioned in the centre. The sample cup was pushed beyond the O-ring. The mud cup was then screwed into place. The heat bath was raised up to heat the sample cup whenever necessary, manually or automatically.

The sample was pressurized by gradually rotating the regulator knob clockwise and depressurised gradually rotating the regulator knob counterclockwise. The sample was only pressurised when the target test temperature above 200˚F (95°C). Table 4.2 shows the test temperature and corresponding pressure.

Table 4.2: Test samples temperatures and specified pressures

Temperature		Pressure	
Ambient -200°F	(Ambient - 93.3°C)	0Psi	(0 kPa)
201° -295°F	(93.9° - 146.1°C)	100Psi	(690kPa)
296° - 355°F	(146,7° - 179.6°C)	200Psi	(1,380kPa)
356° - 395 °F	(180.1°- 201.8°C)	300Psi	(2,070kPa)
396°- 445°F	(202.4° - 229.6°C)	500psi	(3,450kPa)
446°-500°F	(230.2° - 260.2°C)	800Psi	(5,520kPa)

From the Main Screen of ORCADA® software, the Test Builder from the Edit menu was chosen. Any test was created based on the “RP 10B”, “RP 13D”, or “RP 39” analysis models by clicking the appropriate button. The test name was entered in “Test Name” field. The analysis models were based on the following: “RP 39” - Power Law Model (records the Power Law calculations (n and k); “RP 13D” - Bingham Plastic Analysis Model (records plastic viscosity (PV) and yield point (YP)) and; “RP 10B” - Power Law and Bingham Plastic Models combined. In this investigation, the ‘’RP 13D” - Bingham Plastic Analysis Model was selected for this study.

4.3.4 PH test

The pH meter (Figure 4.7), which consists of a glass electrode and a large screen, was used in this study. The glass electrode measures the pH of a fluid. Before it was used, the electrode was first immersed in electrode storage solution or tap water to condition it for at least 30 minutes. When not in use, the electrode was immersed in its electrode storage solution or tap water using its cap. The pH measurement range for this instrument is from -1.0 to 15.0. Its resolution is 0.1 pH. The pH measurement accuracy is ± 0.1pH (Eutech Instruments Pte Ltd, 2005). The pH meter was calibrated before use.

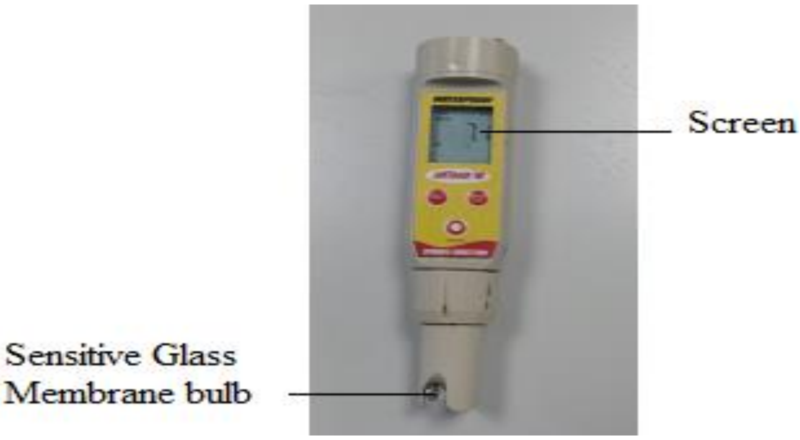


Figure 4.7: PH meter (Eutech Instruments Pte Ltd, 2005)

4.3.4.1 Sources of error

- pH meter not calibrated before use
- Electrode not conditions for at least 30 minutes before use
- Electrode not stored in electrode solution or water after use

4.3.4.2 Testing procedure of PH of formulated muds

The ON/OFF button was first pressed to switch the tester on. The electrode was dipped about 2 to 3cm into the formulated muds. The mud was then stirred with the tester. When the pH value displayed on the screen stabilised, it was recorded as the formulated mud pH value.

4.3.5 Roller oven

The roller oven is used to determine the effects of temperature and pressure on drilling fluids in the wellbore (OFI Testing Equipment, 2015). It was used to hot-roll mud formulations pressurized in aging cells at a constant temperature. There are two types of drilling muds aging: static and dynamic aging. In this study, drilling fluid formulations were aged dynamically for 16 hours in the roller oven to mimic the interaction between a drilling fluid and wellbore annulus. There are different designs of roller oven: the 4-roller oven and the 5-roller oven. Figure 4.8 shows the 4-roller oven and the 5-roller oven used in this study. The roller ovens operated between 100˚F and 450˚F (38°C - 232.2°C).

Figure 4.8: The 4-roller oven and the 5-roller oven

4.3.5.1 Procedure of operation of the roller oven (OFI Testing Equipment, 2015).

The day of the week was selected for each the ON/off operation. The “h” and “min” buttons were then pressed to set the correct time for the “ON” or beginning cycle to begin. Consequently, the “UP” arrow blinked. The “WRITE” botton was then pressed to activate the turn off time. After pressing “WRITE” botton, the down arrow blinked. The day of the week for each on/ OFF operation was then selected. The “h” and “min” buttons were pressed to set the correct time for the “OFF” cycle to an end. Thereafter, the “DOWN” arrow blinked. The “WRITE” button was pressed again. For the oven to start running, the switch was set to “P2” to the right of the display. Finally, the bar (-) displayed the day(s) of operation.

4.3.6 Aging cell

The aging cell is used to subject drilling muds to temperatures higher than the boiling point of water and to keep them in a liquid state. Figure 4.9 shows the aging cells. The cells are used for both static and dynamic aging in a roller oven for at least 16 hours. There are two types of aging cells: the 260 ml and 500 ml sizes seals. The 260 ml and 500 ml aging cells were used in this study. Table shows the mud volume and pressure for aging at high temperatures (OFI Testing Equipment, 2017).

Table 4.3: Mud volume and pressure for aging at high temperatures.

Aging Temp.(˚F/˚C)	Water Vapour Pressure (psi)	Coefficient of Expansion of Water	Suggested Applied Pressure (psi/kPa)	Mud Volume in 260 ml Cell(ml)	Volume with Teflon Liner	Mud Volume in 500ml cell(ml)	Volume with Teflon Liner
212/100	14.7	1.04	25/172	225	130	450	326
250/121	30	1.06	50/345	225	130	450	326
300/149	67	1.09	100/690	200	116	425	308
350/176	135	1.12	150/1,034	200	116	400	289
400/204	247	1.16	250/1,724	-	-	375	271
450/232	423	1.20	300/2,069	-	-	375	253
500/260	680	1.27	375/2,586	-	-	325	235

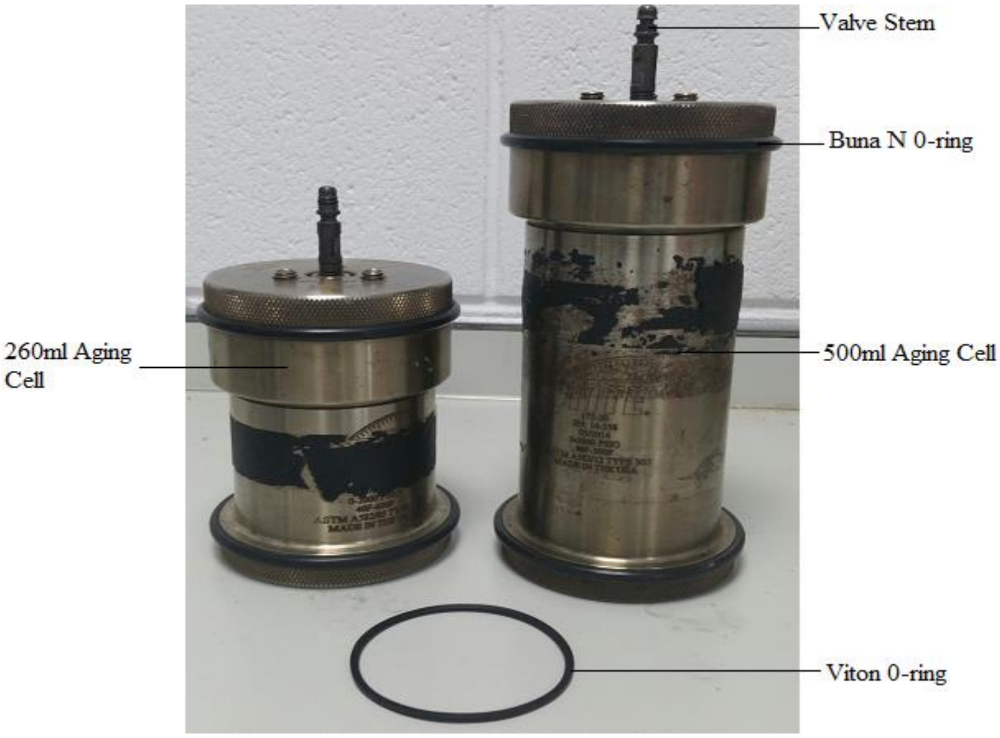


Figure 4.9: Aging cells

4.3.6.1 Sources of error

- Defective O-ring
- Overfilling the cell
- Drilling mud not pressurised with a specified pressure
- Leaking valve stem

4.3.6.2 Safety measures

- Manufacturer's operating instructions were adhered to
- Eye protection was worn
- The aging cells were cooled to room temperature before they were opened.
- The cells were not overfilled.
- Personal protective equipment was worn

4.3.6.3 Procedure for mud aging (OFI Testing Equipment, 2017).

- The 0-ring was carefully inspected for defects, changed if it was hard or had cuts and nicks, and placed in the groove in the cell body. Air was blown through the valve stem to ensure it was not blocked.
- The appropriate safe volume and safe initial pressure for the test temperature was determined from Table 4.3. The appropriate volume of mud was placed in the aging cell; and the cell was not overfilled. Any drop of mud on the edge of the cell was cleaned up and the inner cap

was placed on top of the cell body 0-ring so that it sat in place. The outer cap was, then, hand-tightened in place.

- With an Allen wrench, the set screws in the outer cap were tightened. The valve stem with the 0-rings was inserted in place into the inner cap and tightened completely; the valve stem was loosened about one-half turn before pressurizing and closed and tightened when the desired pressure was reached by tightening it with a wrench. The cell was immersed in water to ensure there were no leaks. Thereafter, the aging cell was placed on the rollers in the oven and the oven temperature was adjusted to the desired temperature.
- After 16 hours, the cell was removed from the oven and allowed to air cool until the drilling mud temperature was 300˚F (149°C) or less. The cell was, then, water-cooled to ambient temperature before the pressure was released; after releasing the pressure, the aging cell was opened. The set screws were loosened, and the outer cap was unscrewed to remove the inner cap.
- Thereafter, the valve stem was cleaned out with water. The drilling mud formulations were then tested for their rheological properties.

4.4 Phase 1 of the research

In this phase of the study, drilling fluids were formulated and their rheological properties were measured at different temperatures. The experimental apparatuses and their standard operating procedures, calibration, sources of error, accuracies, and safety measures are described in Sub-sections 4.3.1 – 4.3.6. The objective of this phase was to determine whether the combination of anti-oxidants, formate salts, and polyglycol can stabilise biopolymers in water-based drilling fluid at high temperatures. The thermal stabilities of mud formulations at high temperatures were investigated through aging tests. The rheological properties of drilling mud formulations were measured using Model 800 and 1100 viscometers. The results obtained were analysed to determine the stable drilling fluid formulations at high temperatures. The stable drilling fluid formulations were, therefore, used for shale dispersion tests in Phase 2.

4.4.1 Drilling fluid formulations

Twenty-three unweighted drilling muds were formulated in total to measure their rheological properties and to determine their shale inhibitive characteristics. Bentonite was first added to 350 ml (one lab barrel) of freshwater in a mud cup. The cup contents were placed under the Hamilton Beach mixer spindle and stirred for 30 minutes at room temperature. After 30 minutes of stirring, the bentonite-water suspension was aged for 16 hours at room temperature to hydrate fully. The control mud formulations were prepared by adding diutan gum, konjac gum, and xanthan gum separately to the pre-hydrated bentonite-water suspension and aged at room temperature for sixteen hours. After that, the mud formulation was stirred again for 15 minutes at room temperature before their rheological properties were measured at 25°C, using Model 800 and Model 1100 viscometers. Nine more control mud samples were also prepared but pressurised in aging cells to prevent them from boiling at 100°C and above and aged dynamically in a roller oven at different temperatures for sixteen hours. After aging, the mud samples were cooled and stirred again for 15 minutes at room temperature; subsequently, the rheological properties of the mud samples were measured at 25°C, using Models 800 and 1100 viscometers.

The other mud formulations were prepared by mixing each of the biopolymers with the mud additives as shown in Table 4.4. The mud formulations were prepared by adding the additives and each of the biopolymers to the pre-hydrated bentonite-water suspension and stirring for 30 minutes at room temperature using the Hamilton Beach mixer. The additives and each of the biopolymer were gradually added to the pre-hydrated bentonite-water suspension while mixing. After 30 minutes of stirring, the mud formulations were pressurised in aging cells to prevent them from boiling at 100°C and above.

The pressurised muds were after that aged dynamically at different temperatures for 16 hours in a roller oven to mimic the interaction between drilled cuttings and well-bore fluids in a wellbore annulus. After aging for 16 hours at different temperatures, the mud formulations were cooled and stirred again for 15 minutes at room temperature before testing. The rheological properties of the mud samples were measured at 25°C, using Model 1100 viscometer. Tables 4.4 – 4.7 show drilling fluid formulation with the biopolymers and the additive package.

Table 4.4: Additives tested for their effects on the temperature stability of biopolymers and reactive shale rock

Additives	Primary function	Amount
Potassium formate (Ibm)	Temperature stabiliser/Anti-oxidant	1 – 3
Sodium erythorbate (Ibm)	Antioxidant/ Oxygen scavenger	1 –3
Polyethylene glycol 8000(PEG) (Ibm)	Shale stabiliser	1 –3
Sodium carbonate (Ibm)	Buffer	1 – 3
Sodium bicarbonate (Ibm)	Buffer	0.1-1.2
Dispelair Se574 (bbl)	Defoamer	0.003-0.03

Table 4.5: Mud formulations with diutan gum and the additives.

Mud Name	Mud 1	Mud 2	Mud 3	Mud 4	Mud5	Mud6	Mud 7	Mud 8	Mud9	Mud 10	Mud 11
Additives											
Water(bbl)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Bentonite (Pre-hydrated) (Ibm)	10.5	10.5	10.5	10.5	10.50	10.5	10.5	10.5	10.5	10.5	10.5
Diutan gum (Ibm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
K-Formate (Ibm)	-	-	-	-	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sodium Erythorbate (Ibm)	-	-	-	-	-	-	1.0	1.5	1.5	3.0	1.5
Na carbonate (Ibm)	-	-	-	-	0.5	0.5	1.0	1.5	1.5	1.5	1.5
Na Bicarbonate (Ibm)	-	-	-	-	-	-	0.8	1.2	1.2	1.2	1.2
DispelairSE 574(bbl)	-	-	-	-	-	-	0.01	0.01	0.01	0.01	0.03
PEG (8000) (Ibm)	-	-	-	-	-	-	1.0	1.0	1.0	1.0	2.0

Table 4.6: Drilling fluid formulations with xanthan gum and other additives

Mud Name	Mud 1	Mud 2	Mud 3	Mud 4	Mud 5
Additives					
Water(bbl)	1.0	1.0	1.0	1.0	1.0
Bentonite (Pre-hydrated) (Ibm)	10.5	10.5	10.5	10.5	10.5
Xanthan Gum (Ibm)	1.0	1.0	1.0	1.0	1.0
K-Formate (Ibm)	-	-	-	3.0	3.0
Sodium Erythorbate (Ibm)	-	-	-	1.5	1.5
Na carbonate (Ibm)	-	-	-	1.5	0.7
Na Bicarbonate	-	-	-	1.2	1.2
DispelairSE 574(bbl)	-	-	-	0.01	0.01
PEG (8000) (Ibm)	-	-	-	1.0	1.5

Table 4.7: Drilling fluid formulations with konjac gum and other additives

Mud Name	Mud 1	Mud 2	Mud 3	Mud 4	Mud 5	Mud 6	Mud 7
Additives							
Water(bbl)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Bentonite (Pre-hydrated) (Ibm)	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Konjac gum	1.0	1.0	1.0	1.0	1.0	1.0	1.0
K-Formate (Ibm)	-	-	-	-	3.0	3.0	3.0
Sodium Erythorbate (Ibm)	-	-	-	-	1.0	1.0	1.5
Na carbonate (Ibm)	-	-	-	-	1.0	1.5	1.2
Na Bicarbonate	-	-	-	-	0.8	1.2	0.7
DispelairSE 574(bbl)	-	-	-	-	0.01	0.01	0.02
PEG (8000) (Ibm)	-	-	-	-	1.0	1.0	2.5

4.5 Phase 2 of the research

In this phase, the effects of an inhibitive fluid formulation and freshwater on reactive shale rock were investigated. For the dispersion test, shale cuttings were aged in freshwater and in an inhibitive mud formulation. The shale rock used in this study was Marcellus shale; the dispersion test procedure is presented in Section 4.5.2. The objective of this phase was to investigate whether the drilling mud additives used in this present study can inhibit shale dispersion. Figure 4.2 shows the methodology flow chart of the Phase 2 of this present study.

4.5.1 Shale characterisation

The Marcellus shale sample was characterised using a scanning electron microscope (SEM) photos and X-ray diffraction to determine its mineral and elemental contents. XRD analysis was carried out at Salford Analytical Services, University of Salford, United Kingdom. SEM photos of dry samples and samples immersed in fluids were taken. XRD was recorded at 15KV. Table 4.8 summarises the mineral contents of a typical Marcellus shale rock. Marcellus shale is a Middle Devonian, carbonaceous black shale. It is less swelling since it contains more illite clay than smectite clay. It is suitable for hardness testing as it is less swelling and dispersible. **Figure 4.10** shows the photo images of Marcellus shale samples and Table 4.8 shows the XRD of Marcellus shale rock (Hosterman and Whitlow, 1983).

Table 4.8: XRD of Marcellus shale rock

Mineral	Average mineral content %
Quartz silt	20
Clay	50
Pyrite	5
Calcite	25
Clay mineral Content %	
Chlorite	15
Illite	70
Illite-smectite	15 (mixed layered clay)
Illite-chlorite	tr
Kaolinite	-

4.5.2 Dispersion tests

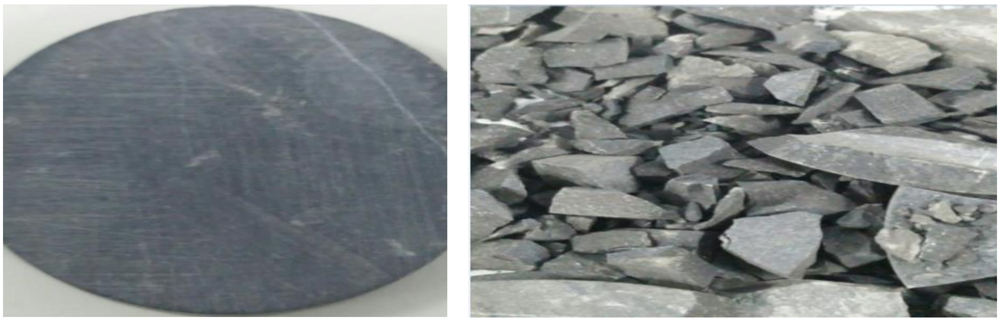
The test was intended to simulate the transportation of drilled cuttings in drilling fluids to the surface from a wellbore annulus (the cuttings were hot rolled dynamically in a roller oven). The shale samples (Figure 4.10 (a)) were broken to sizes less than 8mm with a hammer. A sieve shaker, and

8 mm and 599-micron sieve sizes were used to prepare the shale cuttings for dispersion test tests. 6.0 g of shale cuttings (Figure4.10 (b)) and the formulated inhibitive mud were added to an aging cell. Another 6.0 g of shale cuttings and fresh water were added to another ageing cell. The aging cells were pressurised to prevent the drilling fluids from boiling at 100°C and above. After that, the aging cells were hot rolled dynamically in a roller oven at 120°C for 16 hours. After 16 hours, the aging cells were cooled, and their contents were poured into a 599-micron sieve. The sieve contents were washed with running water to remove all the shale cuttings less than 599 microns. The retained shale cutting in the drilling mud and fresh water were placed in an oven at 105ºC for 24hrs. After being dried, the shale cuttings were weighed. The same procedure above was followed for the dispersion test on shale plugs. However, 14.99g of shale plug and 14.77g of another shale plug were immersed in freshwater and drilling fluid formulation respectively and were aged dynamically in a roller oven at 120°C for 16 hours. The shale recovery rate from water (%RW) and shale recovery rate from muds (%RM) were calculated on a dry mass basis as follows:

$$\%RW = \frac{W_W}{W_{IC}} \times 100\ \% \tag{4.9}$$

$$\%RM = \frac{W_M}{W_{IC}} \times 100\ \% \tag{4.10}$$

Where W_W is the weight of dried shale cuttings recovered from freshwater (g); W_M is the weight of dried shale cuttings recovered from drilling fluid (g), and W_{IC} is the initial weight of dried shale cuttings (g).



(a)

(b)

Figure 4.10: Photo images of Marcellus shale samples: (a) Surface of dried shale plug; (b) Dried shale cuttings

4.6 Chapter summary

In this section, the experimental work carried in this study is summarised. The experimental apparatuses and their accuracies, procedures of operations, safety measures, sources of error, and calibration were described in detail in this chapter. The materials (additives) used in this study are presented. The procedures for drilling fluid formulations and for dispersion test on Marcellus shale rock are described in detail. In addition, the drilling fluids formulated in this study and their compositions are also presented. The rheological properties of drilling fluid formulations are measured before and after dynamic aging at different temperatures. The effects of drilling fluid interaction with a reactive shale rock were carried out through dispersion test. The shale samples were scanned before and after the dispersion test using a scanning electron microscope. X-ray diffraction was used to determine the mineral and elemental contents of the shale samples. The results obtained from this chapter are presented and discussed in detail in the next chapter.

Chapter 5: Results and Discussion

5.1 Introduction

In this chapter, the results obtained from the experimental study undertaken in accordance with the scheme outlined in the methodology flow charts of Figures 4.1 and 4.2 are presented. The rheological properties of drilling fluid formulations were measured using the instruments described in Chapter 4 to determine the optimum combination of drilling fluid additives that could raise the stability temperatures of biopolymers in water-based drilling fluid systems. The biopolymers screened in this study were konjac gum, xanthan gum, and diutan gum. When exposed to high temperatures, biopolymers in water-based drilling fluids degrade. This degradation of the biopolymer can lead to total failure of a water-based drilling fluid under high temperature conditions. Stabilising biopolymers in drilling fluids requires the understanding of the mechanisms through which they degrade at elevated temperatures. The degradation mechanisms of biopolymers in solutions at high temperatures, therefore, include acid-catalysed hydrolysis and oxidation-reduction (redox) reaction. These mechanisms were exploited in this study to stabilise biopolymers in water-based drilling fluids by deploying additives to retard the degradation processes. As discussed in Chapter 3, antioxidants, formate salts, and polyglycol enhances the performance of water-based fluid systems. However, it is difficult to select the optimum combination of additives that can improve the thermal stability of biopolymers in the water-based mud system.

5.2 Phase 1 of the research: Stability temperatures of biopolymer in water-based bentonite muds

The experimental results are presented to determine the additives that optimise the performance of water-based mud systems in high temperature formations. Tables 5.1 – 5.7 present the measured rheological properties – PV, YP, AV, low shear rate viscosity and 10-sec and 10- min gel strengths – of the mud formulations with konjac gum, diutan gum, and xanthan gum. Mud 1 from the mud formulations containing each of the biopolymers was the control mud formulation. The stability temperature was defined as the temperature that a fluid can be exposed to for 16 hours without losing more than half of its viscosity (Howard et al., 2015). The viscosities of drilling fluids formulated with the additives were compared with the control fluid formulations comprising each of the biopolymer in water-based bentonite muds to evaluate the fluids stability and performance. Based on the results of the thermal stability investigation, the stable drilling fluid formulations were, therefore, selected for shale dispersion tests.

Table 5.1: Properties of Muds 1,2,3,4,5,6 and 7 formulated with diutan gum before and after dynamic aging

Muds	1 (BHR @25°C)	2 (AHR@ 115°C)	3 (AHR@ 120°C)	4 (AHR@ 130°C)	5 (AHR@ 150°C)	6 (AHR@ 170°C)	7 (AHR@ 170°C)
Properties							
300RPM	32.0	16.0	12.0	6.0	27.0	12.0	`16.0
600RPM	48.0	24.0	19.0	10.0	34.0	16.0	23.0
Effective Viscosity (cP)@300RPM	30.0	15.0	14.0	6.0	25.0	12.0	15.0
10-sec Gel	18.0	10.0	5.0	1.0	23.0	11.0	9.0
10-min	21.0	11.0	5.0	1.0	24.0	17.0	10.0
Plastic viscosity (PV)(cP)	10.0	5.0	4.0	2.0	5.0	5.0	4.0
Yield Point (YP) (Ib/100ft^2)	24.0	11.0	8.0	4.0	22.0	7.0	12.0
pH (BHR)	9.7	9.7	9.7	9.7	10.9	10.9	10.4
pH (AHR)		8.1	8.0	7.8	8.5	8.4	9.1

Table 5.2: Properties of Muds 8,9,10, and 11 formulated with diutan gum before and after dynamic aging

Muds	**8 (AHR@200°C)**	**9 (AHR@210°C)**	**10 (AHR@232°C)**	**11 (AHR@232°C)**
Properties				
300RPM	24.0	17.0	10.0	21.0
600RPM	25.0	20.0	15.0	27.0
Effective Viscosity (cP)@511s^{-1}	18.0	15.0	10.0	19.0
10-sec Gel	11.0	5.0	4.0	5.0
10-min	15.0	6.0	4.0	6.0
Plastic viscosity (PV)(cP)	3.0	3.0	2.0	4.0
Yield Point (YP) (Ib/100ft^2)	17.0	7.0	4.0	8.0
pH (BHR)	9.9	10.0	9.7	10.0
pH(AHR)	9.1	9.1	9.2	9.3

Table 5.3: Experimental measurement of viscosities of mud formulations with diutan gum before and after dynamic aging

	Shear stress (s^{-1})	1021	511	341	170	102	51	10
Viscosity (cP)	Mud 1 BHR @25°C	23.0	30.0	28.0	68.0	109.0	212.0	990.0
	Mud 2 AHR @115°C	12.0	19.0	25.0	40.0	58.0	96.0	300.0
	Mud 3 AHR@120°C	9.0	12.0	14.0	20.0	27.0	40.0	80.0
	Mud 4 AHR @130°C	4.5	6.0	7.0	10.0	12.0	17.0	70.0
	Mud 5 AHR@150°C	17.0	25.0	36.0	70.0	112.0	234.0	1110.0
	Mud 6 AHR@170°C	8.0	12.0	14.0	25.0	42.0	94.0	442.0
	Mud 7 AHR@170°C	11.0	15.0	20.0	36.0	60.0	100.0	570.0
	Mud 8 AHR@200°C	12.0	19.0	28.0	54.0	90.0	200.0	700.0
	Mud 9 AHR@210°C	17.0	27.0	38.0	74.0	123.0	243.0	800.0
	Mud 10 AHR@232°C	6.0	10.0	12.0	22.0	40.0	98.0	400.0
	Mud 11 AHR@232°C	12.0	19.0	27.0	51.0	86.0	174.0	642.0

Table 5.4: Properties of muds formulated with xanthan gum before and after dynamic aging

Muds	1 (BHR@25°C)	2 (AHR@100°C)	3 (AHR@110°C)	4 (AHR@200°C)	5 (AHR@210°C)
Properties					
300RPM	21.0	12.0	8.0	18.0	15.0
600RPM	30.0	16.0	12.0	22.0	20.0
Effective Viscosity (cP)@300RPM	20.0	11.0	8.0	16.0	14.0
10-sec Gel	9.0	4.0	4.0	11.0	4.0
10-min	11.0	4.0	6.0	14.0	5.0
Plastic viscosity (PV)(cp)	6.0	3.0	2.0	2.0	2.0
Yield Point (YP) (Ib/100ft^2)	11.0	9.0	6.0	15.0	5.0
pH (BHR)	9.9	9.9	9.9	9.9	9.9
pH (AHR)	-	8.5	8.3	9.1	9.3

Table 5.5: The viscosities (AVs) of drilling fluid formulations with xanthan gum at different shear rates

Shear rate (s^{-1})		1021	511	341	170	102	51	10
Mud 1 BHR@25°C	Viscosity (cP)	14	20	25	42	65	119	500
Mud 2 AHR @100°C		8	11	15	15	34	62	210
Mud A3AHR@110°C		6	8	9	14	21	37	100
Mud A4 AHR@200°C		10	17	22	44	75	150	700
Mud A5 AHR@210°C		10	15	20	36	60	100	570

Table 5.6: Properties of muds formulated with konjac gum before and after dynamic aging

Muds	1 (BHR@ 25°C)	2 (AHR@ 60°C)	3 (AHR@ 65°C)	4 (AHR@ 70°C)	5 (AHR@ 170°C)	6 (AHR@ 200°C)	7 (AHR@ 232°C)
Properties							
300RPM	30.0	18.0	15.0	12.0	25.0	16.0	29.0
600RPM	47.0	27.0	23.0	20.0	28.0	19.0	32.0
Effective Viscosity (cP)@300RPM	28.0	17.0	15.0	11.0	23.0	15.0	27.0
10-sec Gel	7.0	4.0	3.0	1.0	13.0	9.0	12.0
10-min	9.0	4.0	3.0	2.0	15.0	11.0	16.0
Plastic viscosity (PV)(cP)	7.0	4.0	4.0	4.0	3.0	2.0	4.0
Yield Point (YP) (Ib/100ft^2)	9.0	14.0	11.0	9.0	22.0	14.0	24.0
pH (BHR)	9.7	9.7	9.7	9.7	10.1	10.0	10.0
pH (AHR)	-	9.4	8.7	8.1	9.3	9.2	9.4

Table 5.7: The viscosities of drilling fluid formulations with konjac gum at different shear rates

Shear rate (s^{-1})		1021	511	341	170	102	51	10
Mud B1 BHR@25°C		22	28	32	47	66	110	400
Mud B2AHR@60°C	Viscosity (cP)	13	17	20	30	39	58	200
Mud B3AHR@65°C	AV(cP)	11	15	19	28	37	57	190
Mud B4 AHR@70°C		9	11	13	16	21	30	75
Mud B5 AHR)@170°C		13	23	29	53	86	167	800
Mud B6 AHR@200°C		9	15	20	39	65	130	500
(Mud B7 AHR@232°)		15	27	38	74	123	243	800

5.2.1 Water-based fluid formulations

This section presents the results obtained from the measurement of viscosities of the water-based bentonite muds containing either xanthan gum, konjac gum, or diutan gum with no other additive added. Hot-rolling tests were used to investigate the thermal stabilities of the biopolymers in water-based bentonite muds and to simulate drilling mud circulation in a wellbore annulus. The stability temperature was defined as the temperature that a fluid can be exposed to for 16 hours without losing more than half of its viscosity (Howard et al., 2015). Mud 1, containing either xanthan gum, konjac gum, and diutan gum, was the control mud sample. Figure 5.1 shows the viscosities of water-based bentonite muds containing only diutan gum. The control mud formulations exhibited shear thinning characteristics: The viscosities of the muds decreased as the shear rate increases. As shown in the plot, increasing temperature influenced the viscosity value. The viscosities of the control mud formulations (which was aged as Muds 2,3, and 4) decreased as the aging temperature increased, meaning that diutan gum underwent thermal thinning.

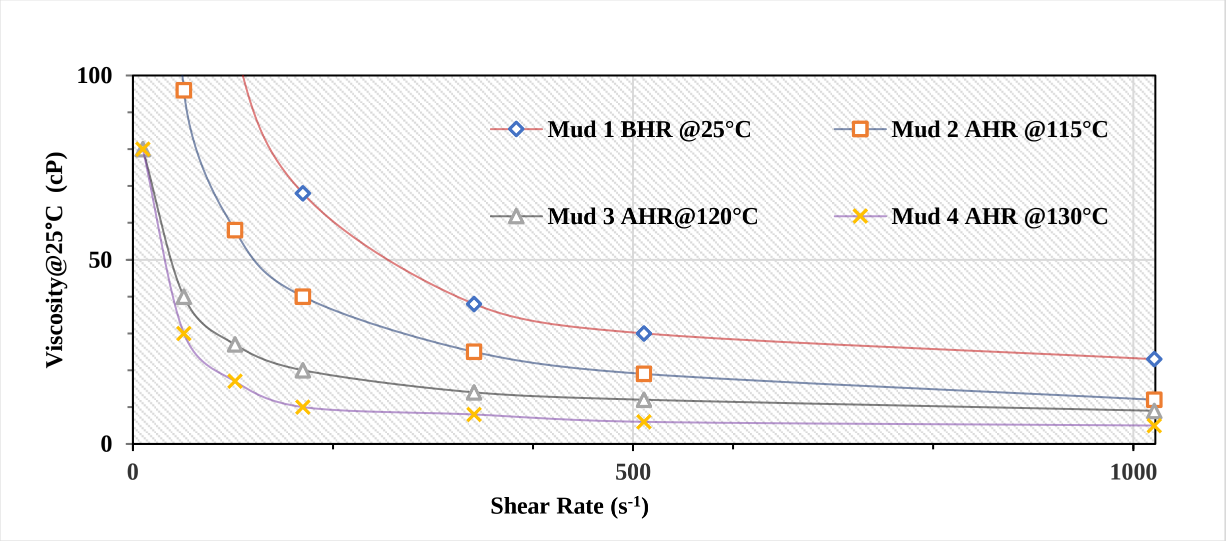


Figure 5.1: The viscosities of the control drilling mud formulated with diutan gum at different shear rates.

Analysis of Figure 5.2 shows that the control mud formulation lost more than half of its viscosity after dynamic aging at 120°C for 16 hours. A stable drilling fluid retains at least half of its viscosity after aging at a temperature for 16 hours (Howard et al., 2015). These results, therefore, indicate drastic thermal degradation of diutan gum in the water-based bentonite mud after aging at 120°C for 16 hours.

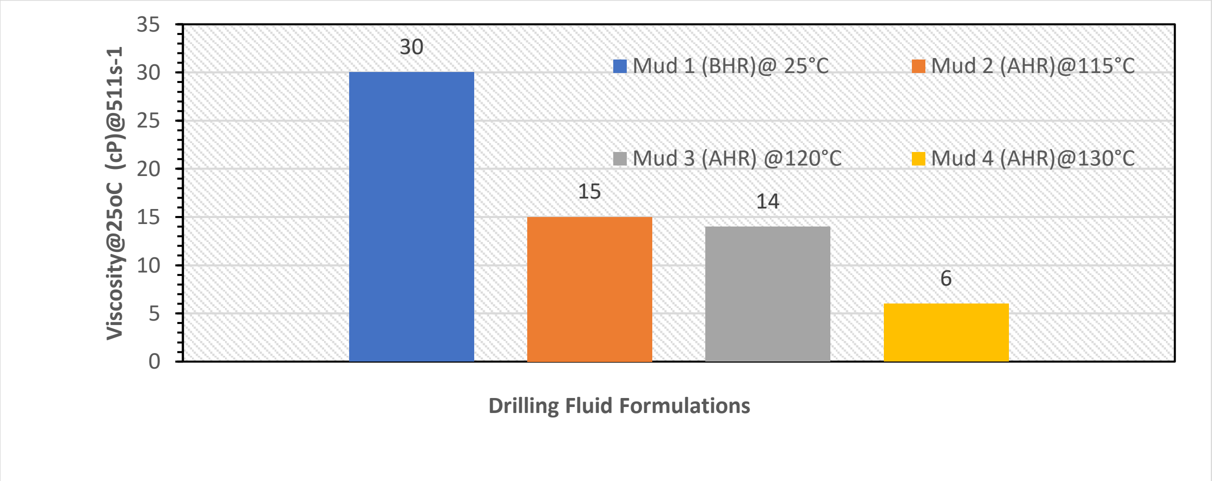


Figure 5.2: Viscosities of the control mud formulation formulated with diutan gum and aged at different temperatures.

As shown in Figure 5.2, after aging at 115°C for 16 hours, Mud 2 lost 50% of its viscosity when compared with the control mud sample, Mud 1; its viscosity measured at 25°C was 15 cP at 511s^{-1} while the viscosity of the control mud sample (Mud 1) measured at 25°C was 30cP at 511s^{-1}. These experimental results, therefore, show that diutan gum stability temperature in water-based bentonite mud after aging for 16 hours is 115°C. Figure 5.3 shows the low shear rate viscosities of the control mud formulations. The low shear rate viscosity of the control mud formulation after aging at 120°C and 130°C for 16 hours was very low. A drilling mud with high viscosity at low shear rate is required for a successful drilling operation (Seeberger et al., 1989).

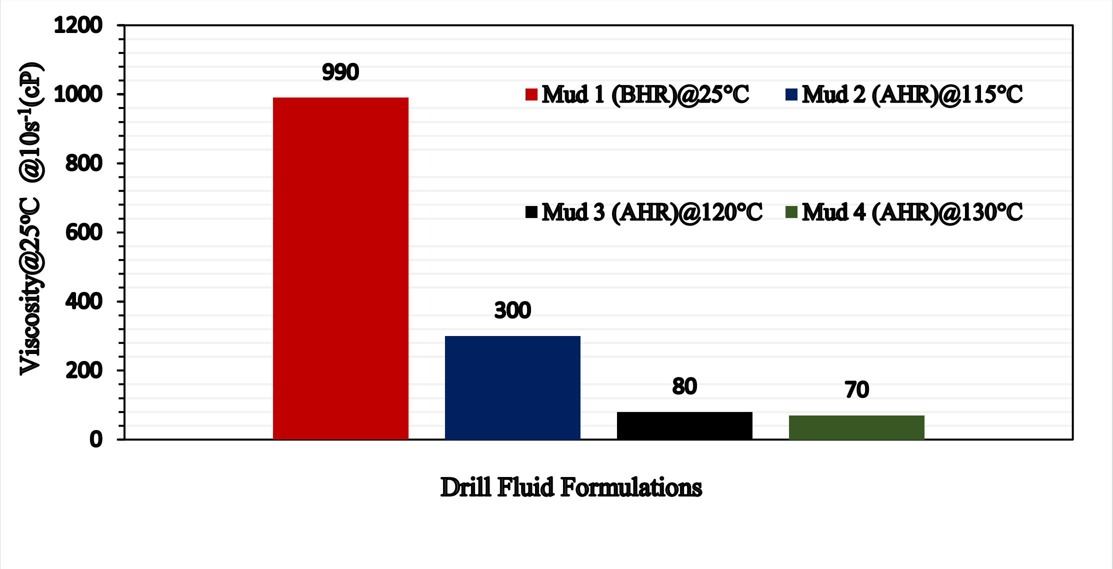


Figure 5.3: Low shear rate viscosities of the control mud formulated with diutan gum and aged at different temperatures

The low viscosities of the control mud formulation - after aging at 120°C and 130°C for 16 hours and measured at low shear rates - indicate its poor cuttings suspension capacity. In addition, the values of the YP and Gel strengths of the control mud formulation measured after aging at 120°C and 130°C were very low (Tables 5.1 and 5.2), thus showing the control fluid instabilities. For this reason, the control mud formulation is not suitable for use in formation with temperatures above 115°C. In order words, when exposed to a temperature above 115°C for 16 hours, diutan gum in a bentonite-water suspension will lose more than 50% of its viscosity through biopolymer degradation processes. To design a water-based drilling fluid containing diutan gum for formations with temperatures above 115°C, the additives that could prevent, counteract, and retard the biopolymer degradation processes as shown in Table 4.4 were deployed.

Figure 5.4 shows the viscosities of water-based bentonite muds containing only xanthan gum aged at different temperatures. The control mud formulation exhibited shear thinning behaviour: The viscosities of the muds decreased as the shear rate increases. As indicated in the plot, increasing temperatures influenced the viscosity values. The viscosities of the control mud formulation (which was aged as Muds 2 and 3,) decreased as the aging temperature increases, meaning that xanthan gum underwent thermal thinning.

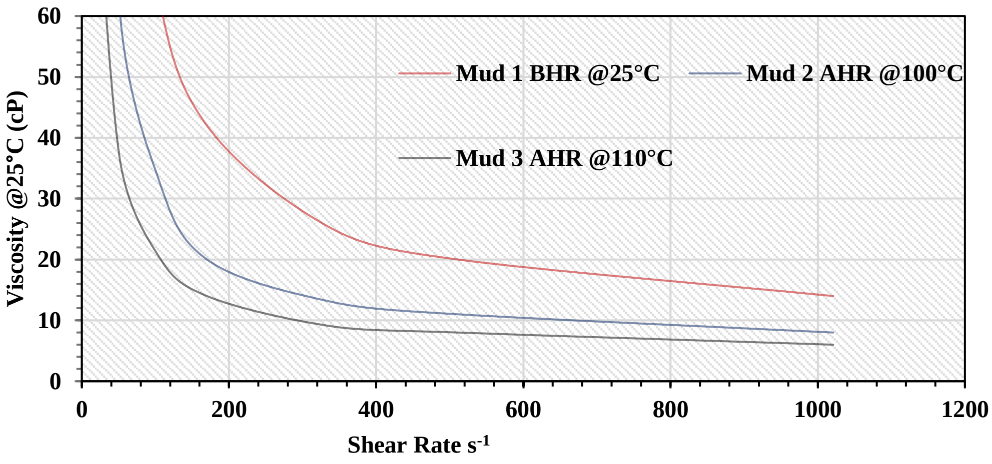


Figure 5.4: The viscosities of the control drilling mud formulated with xanthan gum at different shear rates.

In addition, the reduction in viscosity of drilling muds with increasing temperatures is an indicator of thermal degradation (Howard et al.,2015). After hot rolling at 100°C for 16 hours, Mud 2 lost 50% of its viscosity (Figure 5.5). Consequently, xanthan gum stability temperature in bentonite water-suspension after aging for 16 hours is, therefore, 100°C.

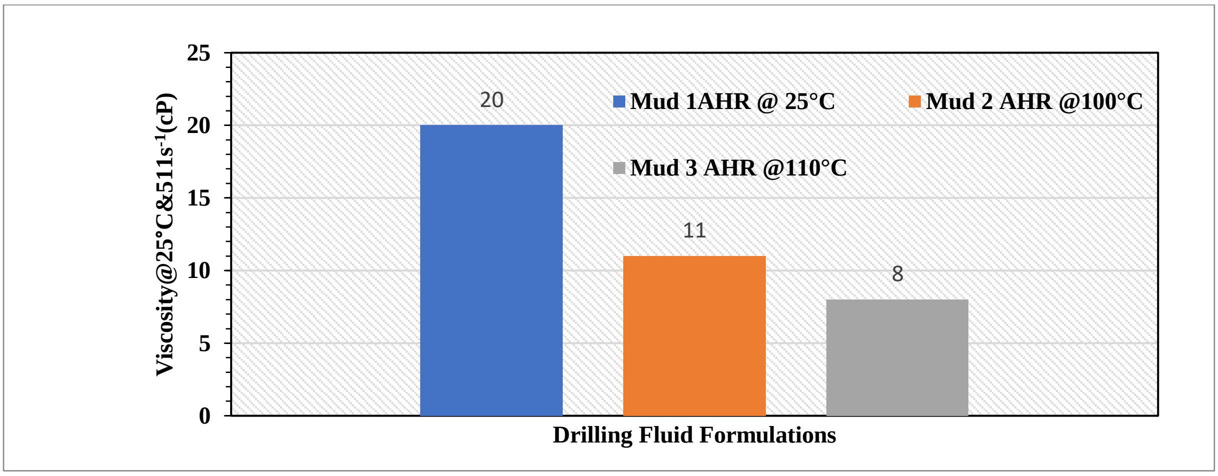


Figure 5.5: Viscosities of the control mud formulation formulated with xanthan gum and aged at different temperatures

In addition, the base fluids low shear rate viscosity after hot-rolling at 110°C for 16 hours was very low (Figure 5.6), thus indicating its inability to suspend cuttings when drilling operations are stopped temporarily.

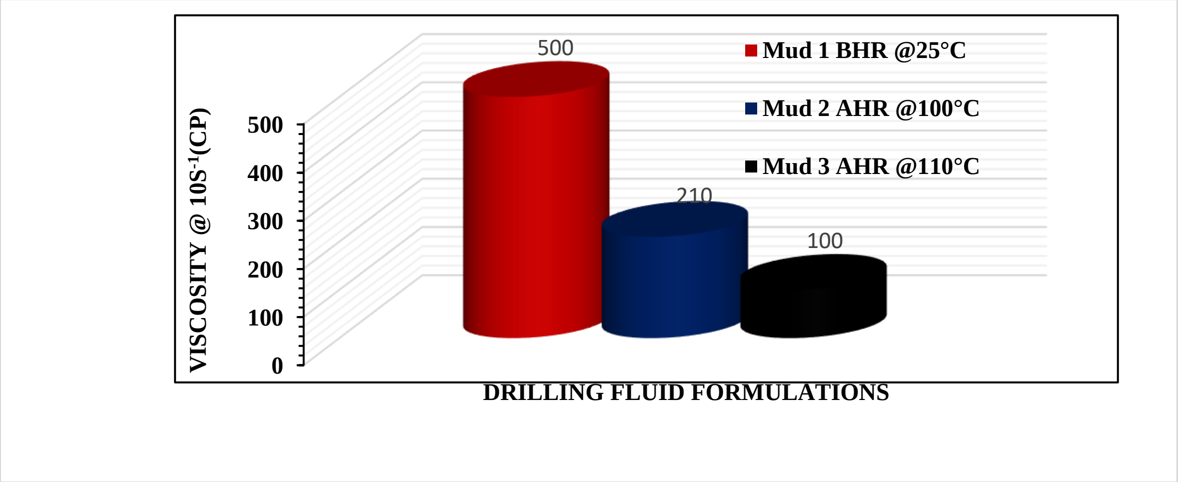


Figure 5.6: Low shear rate viscosities of the control mud formulated with xanthan gum and aged at different temperatures

Figure 5.7 shows the viscosities of water-based bentonite muds containing only konjac gum aged at different temperatures. The control mud formulations exhibited shear thinning behaviour: The viscosities of the muds decreased as the shear rate increases. As indicated in the plot, increasing temperatures influenced the viscosity values. The viscosities of the control mud formulation (which was aged as Muds 2, 3, and 4) decreased as the aging temperature increased, meaning that konjac gum underwent thermal thining.

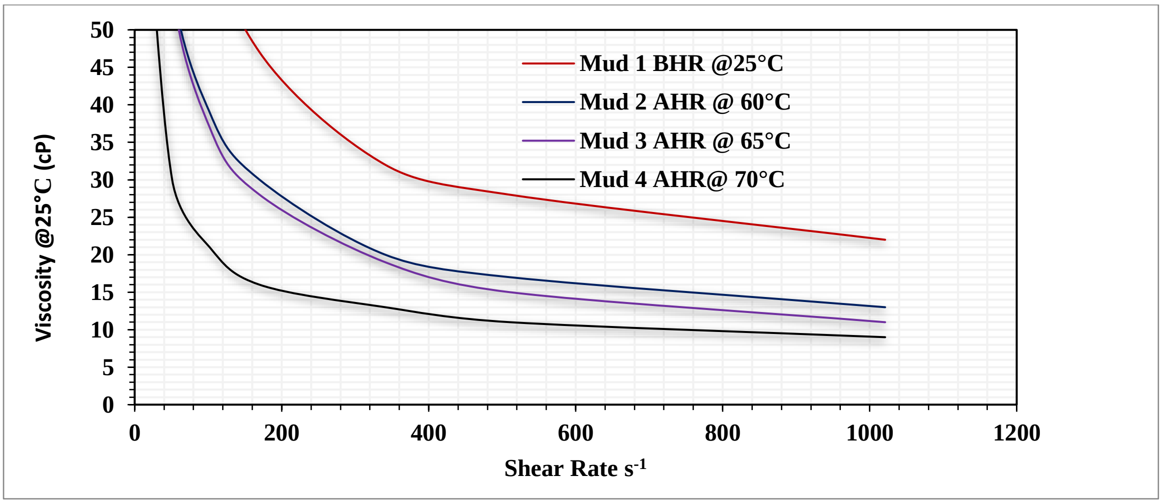


Figure 5.7: The viscosities of the control drilling mud formulated with konjac gum at different shear rates.

The control mud (Mud 1) formulated with konjac gum after hot-rolling up to 70°C lost more than half its viscosity, indicating thermal degradation (Figure 5.8). Mud B1, after hot-rolling at 65°C for 16 hours, lost 50% of its viscosity. However, after being hot-rolled at 70°C, the fluid lost more than half its viscosity, thus indicating thermal degradation. Its apparent viscosity when hot-rolled at 70°C for 16 hours was 11cp at 511s^{-1} while the apparent viscosity of the base fluid before being hot-rolled at 25°C was 28cP at 511s^{-1}. Consequently, the stability temperature of konjac gum in bentonite-water suspension after aging for 16 hours was 65°C.

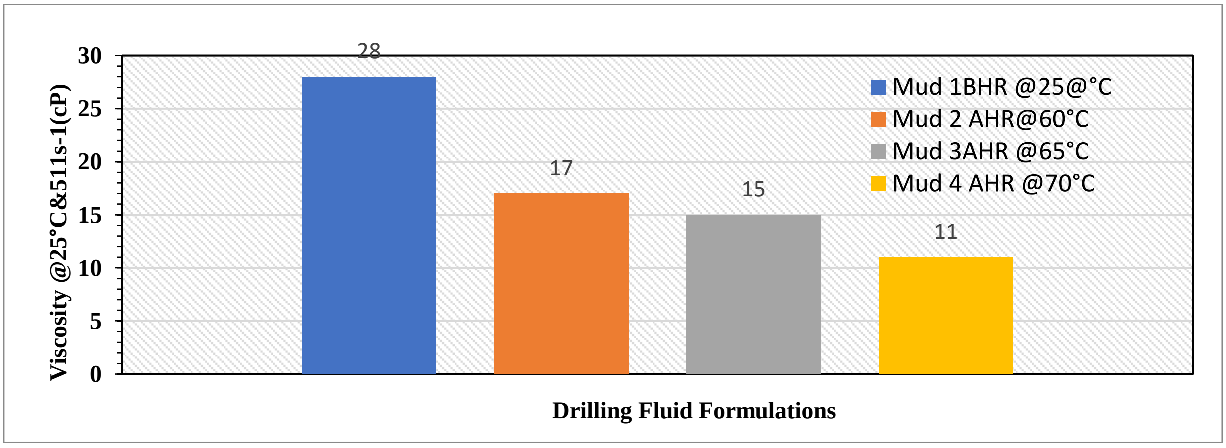


Figure 5.8: Viscosities of the control mud formulation formulated with konjac gum and aged at different temperatures

The control mud's low shear rate viscosity after hot-rolling at 70°C for 16 hours was very low (Figure 5.9). The control mud containing konjac gum will, therefore, degrade when exposed to a temperature of 70°C for 16 hours, thereby losing its capacity to suspend cuttings and weighting materials.

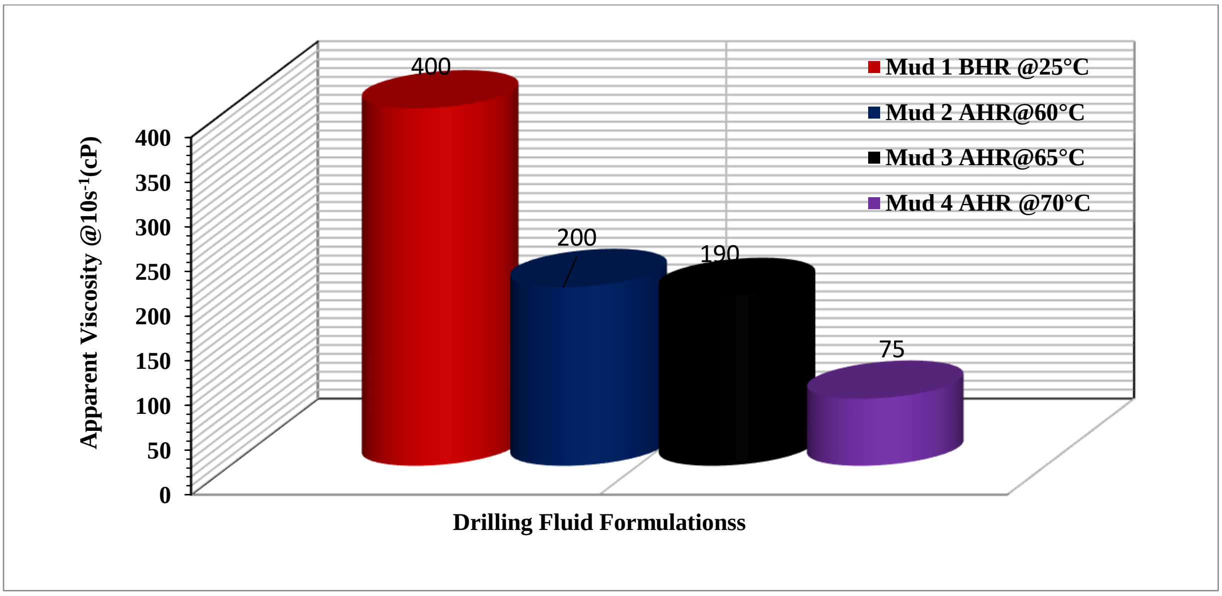


Figure 5.9: Low shear rate viscosities of the control mud formulated with konjac gum and aged at different temperatures

The xanthan gum, diutan gum, and konjac gum developed excellent viscosities in the water-based bentonite muds and underwent thermal thinning as the aging temperatures were increased. It is clear, therefore, that xanthan gum, diutan gum, and konjac gum were in their transition phases from 100°C, 115°C and 65°C respectively. Above the stability temperatures of the biopolymers after sixteen hours of aging, the effects of temperatures on diutan gum, konjac gum, and xanthan gum were irreversible after aging at 120°C, 70°C, and 110°C respectively for 16 hours, regarding the loss in their viscosities.

As the aging temperatures were increased above the stability temperatures, the bonds in the biopolymers chemical structure were damaged. This damage led to the breakage of the side chains of the biopolymers' backbone, hence the reduction in their viscosities (Zhang et al., 2016). It is clear therefore that the control mud samples lost their viscosities at high temperatures as there was no additive to offer them protection from oxidative and hydrolytic degradation. In addition, rheological properties (YP and Gel strengths) of the control mud formulation measured after hot rolling at different temperatures decrease sharply (Tables 5.1, 5.2, 5.4, and 5.6), thus showing the instabilities of the mud formulations at high temperatures. For this reason, the low stability temperatures of the control muds show that they are not suitable for use in high-temperature drilling operations. Above their temperature stabilities, the control muds would experience total failure, regarding the loss of their viscosities, and suspension and fluid loss control capacities. The mud formulations, therefore, require further modification and protection at high temperature, hence the need to deploy additives that can retard oxidative and hydrolytic processes in drilling fluid at high temperatures as shown in Table 4.4. From previous works, the best thermal stabiliser for biopolymers include a solution containing a concentrated salt brine, glycol, and an oxygen scavenger (Howard et al.,2015; Wellington, 1983).

5.2.2 Effects of antioxidants, formate salt, and polyglycol on biopolymers in water-based bentonite muds

5.2.2.1 The viscosities of the mud formulations

The stability temperatures of the mud formulations were investigated through aging tests. Tables 5.1 – 5.7 summaries the measured rheological properties of the drilling mud formulations. Figure 5.10 show the viscosities of drilling muds prepared with the additives and with those of the control mud sample, Mud 1 (containing either xanthan gum, diutan gum or konjac gum). The mud formulations exhibited shear thinning behaviour: The viscosities of the mud formulations decrease as the shear rate increases. At low shear rates, the slopes of the curves were very high and became very small at high shear rates, suggesting that not very high pump pressure will be required to initiate flow with the mud formulations. In addition, the low solids in the mud formulations and the sharp reduction in viscosity as the shear rate is increased show that the mud formulations will flow at high speed through a bit nozzle, thereby cleaning the bit face and carrying drilled solid particles effectively in the wellbore. As shown in Figure 5.10, the low viscosities at high shear rates indicate that not high pump pressure will be needed to pump the mud formulations, thereby preventing formation fracture. In addition, the viscosities of the mud formulations were very high at low shear rates, thus indicating drilled cuttings and weighting material suspension potentials.

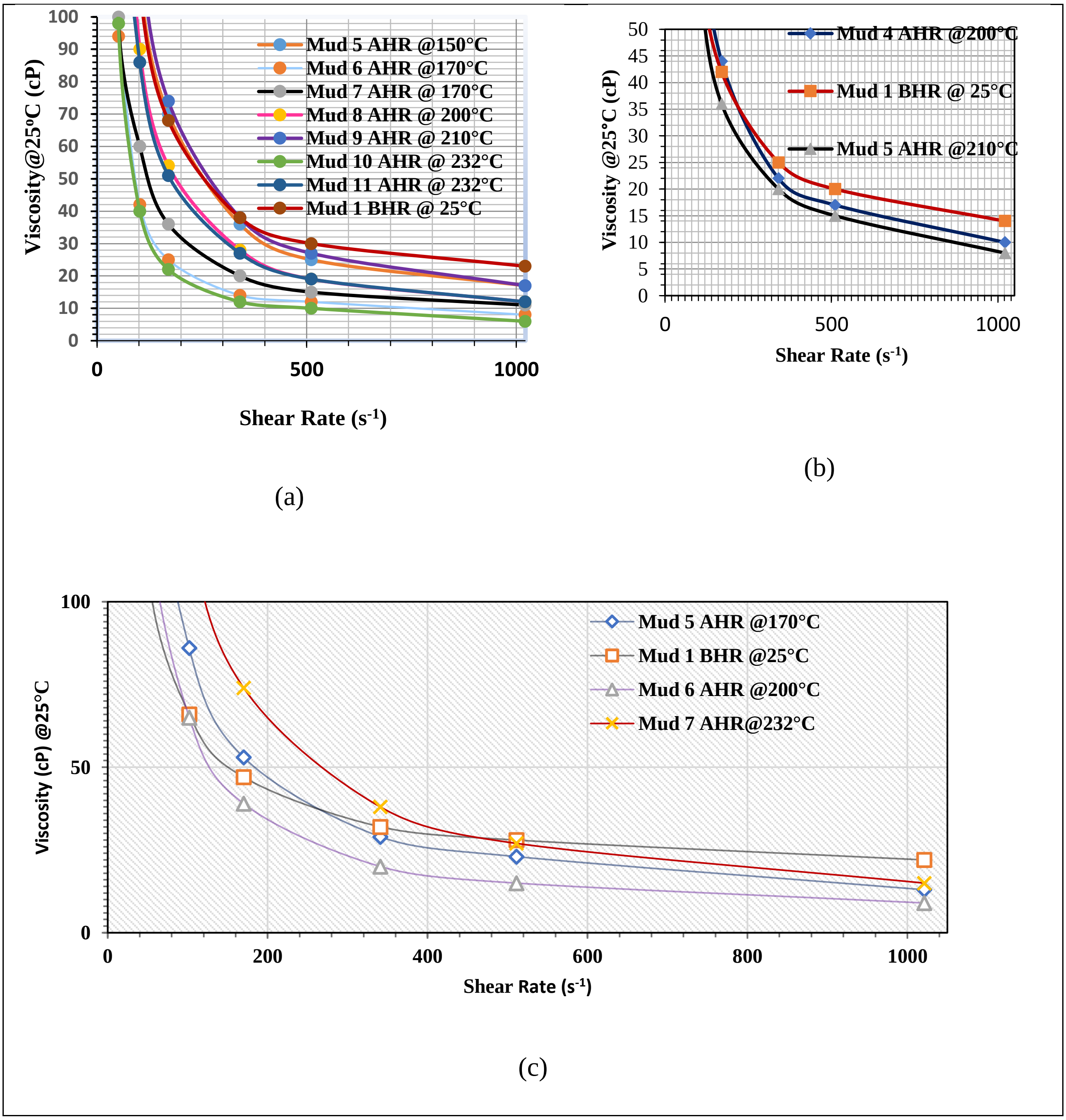
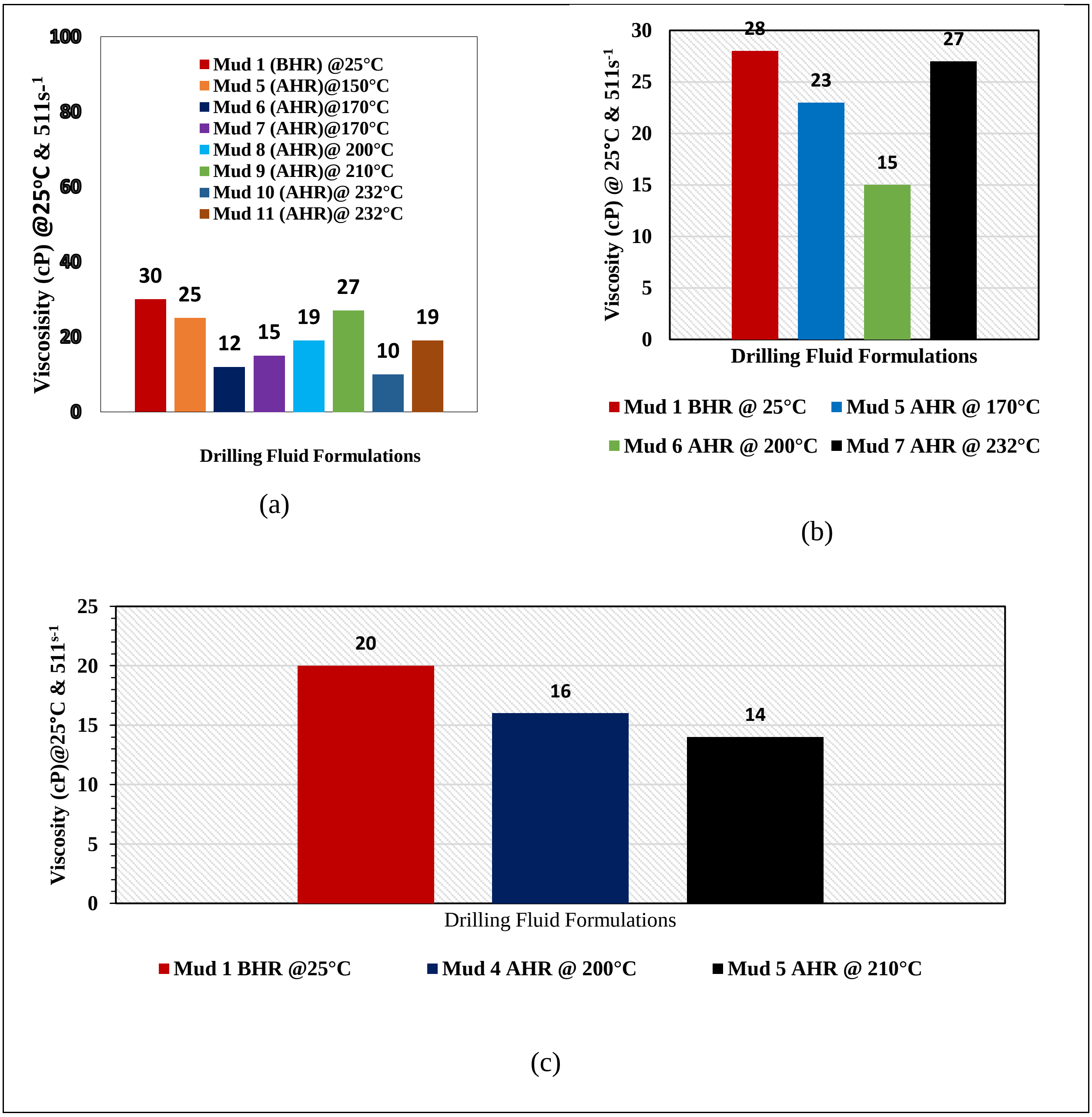


Figure 5.10: The viscosities of drilling fluid formulations and that of the control mud formulation, Mud 1 at different shear rates: (a) Muds formulated with diutan gum; (b) Mud formulated with xanthan gum; (c) Muds formulated with konjac gum.

As shown in Figure 5.11, after aging dynamically for 16 hours at temperatures above 120°C, the viscosities of some mud formulations were more than 50% of the viscosity of the control mud formulation, Mud 1. Howard et al. (2015) showed that a stable mud retained at least 50% of its viscosity after aging at a given temperature for 16 hours. These experimental results, therefore, show that the additives used in this work were very effective in protecting diutan gum, konjac gum, xanthan gum in the mud formulations from thermal degradation at high temperatures.



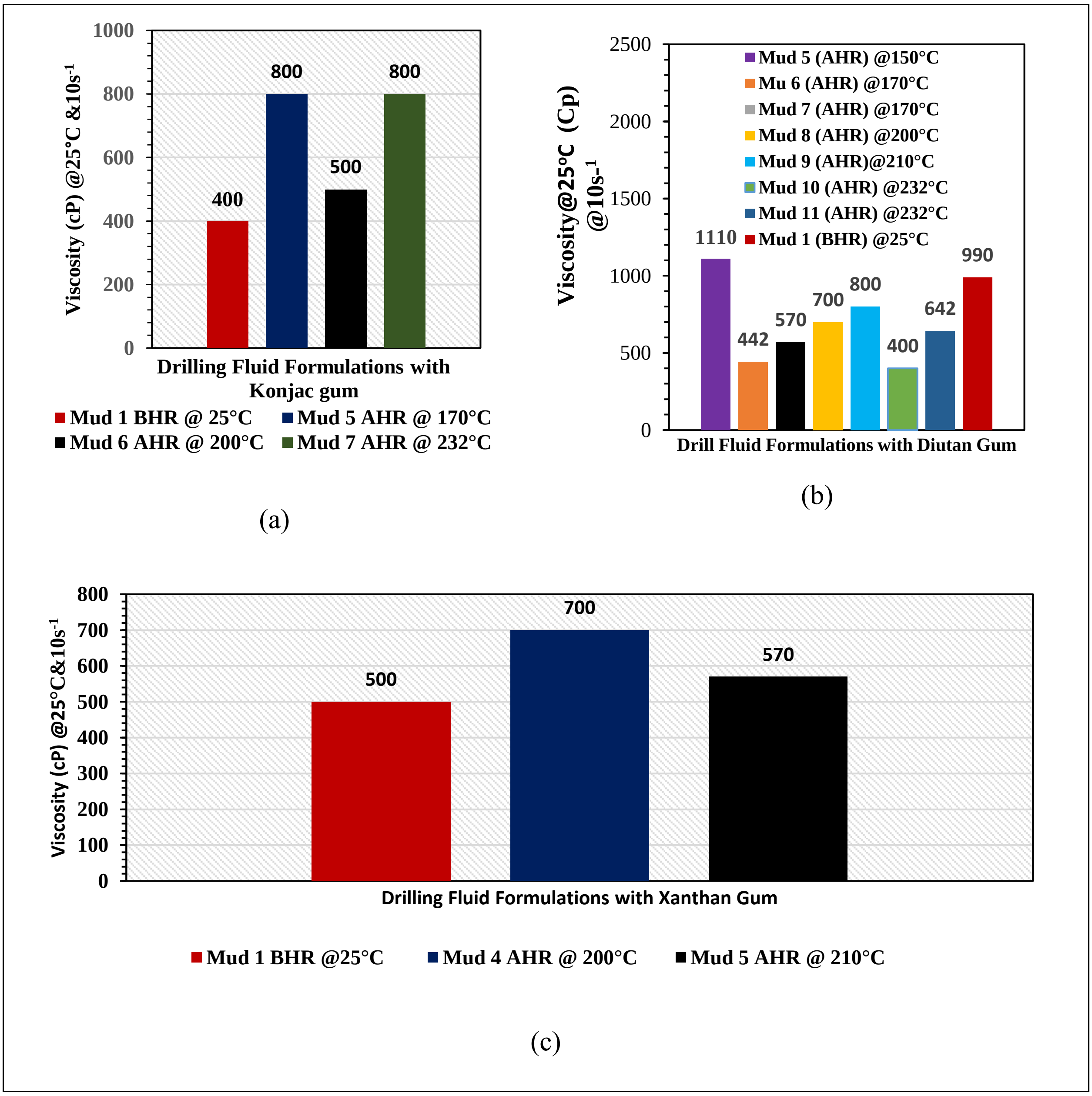
(a)

(b)

(c)

Figure 5.11: Comparison of the viscosities of the drilling fluid formulations with the viscosity of the control mud formulation, Mud 1: (a) Muds formulated with diutan gum; (b) Muds formulated with konjac gum; (c) Mud formulated with xanthan gum.

From Figure 5.11 (a), Mud 5 formulated with potassium formate without the antioxidant and polyethylene glycol remained stable up to 150°C when compared with Mud 1. When aged at 170°C for 16 hours as Mud 6, Mud 5 lost more than 50 % of its viscosity. It can, therefore, be seen that the potassium formate could only protect the biopolymer up to 150°C. This finding confirmed the suggestion that formate salt could stabilise biopolymer up to 150°C (Galindo et al. 2015; Howard et al.,2015). In addition, Mud 9 formulated with a low concentration of polyethylene glycol and a high concentration of the antioxidant (sodium erythorbate) remain stable up to 210°C, when compared with Mud 1. Mud 10 formulated with the same composition and concentration as Mud 9 degrade when aged for 16 hours at 232°C. Therefore, the combination of potassium formate and the antioxidant could only protect the biopolymer in the mud formulations up to 210°C.



(a)

(b)

(c)

Figure 5.12: Low shear rate viscosities of the drilling muds aged at different temperatures: (a) Muds formulated with konjac gum; (b) Mud formulated with diutan gum; (c) Muds formulated with xanthan gum.

Potassium formate raises the transition temperature(T_m) of biopolymers and provides free-radical properties that retarded oxidative processes, thereby stabilising them at high temperatures (Howard et al.,2015); sodium erythorbate, the antioxidant, prevented oxidative processes and reacted with hydroxyl free radicals, thereby stabilising biopolymers at high temperatures.

As shown in Figure 5.11 (a), Mud 11 formulated with a higher concentration of polyethylene glycol remain stable up to 232°C when compared with Mud 1. The combination of polyglycol, a formate salt, and sodium erythorbate, therefore, protected the biopolymer in the mud formulations from thermal degradation at higher temperatures. Polyglycol acted as a sacrificial agent, thereby protecting the biopolymer from thermal degradation (Howard et al.,2015). As shown in Figurs 5.12, the low shear rate viscosities of the muds formulated with the additives were very high, indicating cuttings carrying potentials (A drilling mud with high viscosity at low shear rate is required for a successful drilling operation (Seeberger et al., 1989)). As the maximum operating temperature of the roller oven was 232°C, the experiments were not carried out beyond 232°C. The best additive package that stabilised the mud formulations at high temperatures was the combination of potassium formate, sodium erythorbate, and polyethylene glycol.

5.2.2.2 The plastic viscosities of the mud formulations

Figures 5.13, 5.14 and 5.15 show the effects of temperature on the plastic viscosities of mud samples formulated using diutan gum, konjac gum or xanthan gum with the mud additives before and after aging for 16 hours at different temperatures. Plastic viscosity is a combination of the viscosities of the liquid and solids in a drilling fluid. The experimental data showed a decrease in the plastic viscosities of the mud formulations after aging at high temperatures when compared with that of the control mud sample, Mud 1. This decrease in plastic viscosities could be due to the deflocculation and dispersion of the mud particles after aging at high temperatures. High plastic viscosity is not desirable in drilling fluid as it causes the following: (1) increase in torque and drag, (2) low bit penetration rate, (3) increase surge and swab pressures, and (4) the possibility of pipe sticking. As high plastic viscosity is associated with wellbore problems, the low plastic viscosities at high temperatures indicate that the mud formulations are lubricious and are capable of a fast rate of penetration (ROP). The mud formulations - those that retain their rheological properties and have low plastic viscosities at high temperatures- may be used as drilling fluids.

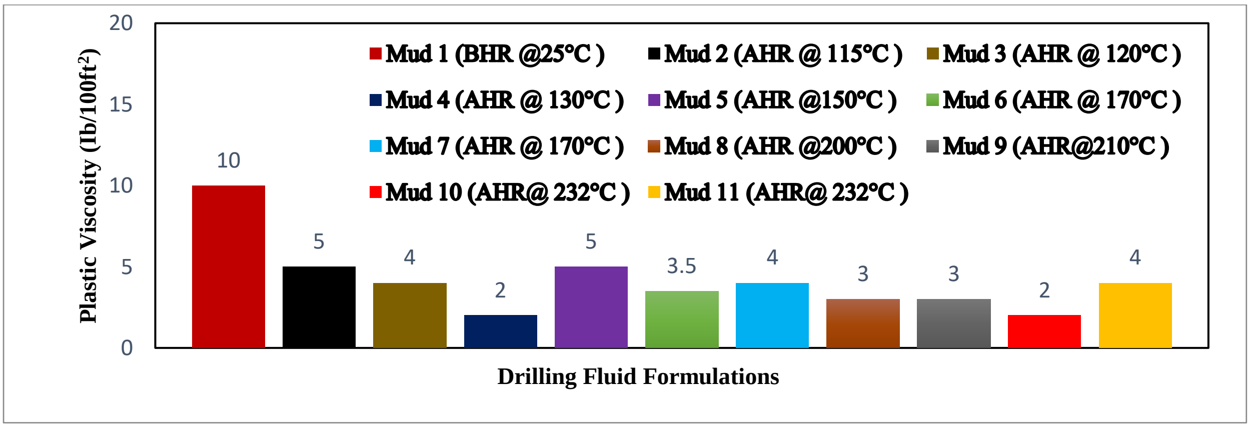


Figure 5.13: Plastic viscosities of mud formulations containing diutan gum after aging at different temperatures.

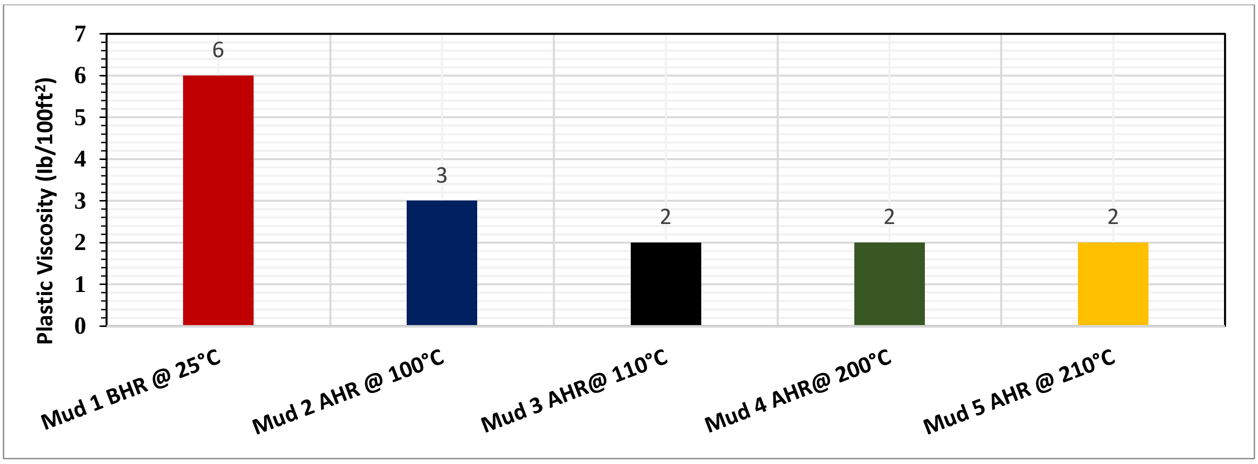


Figure 5.14: Plastic viscosities of mud formulations containing xanthan gum after aging at different temperatures.

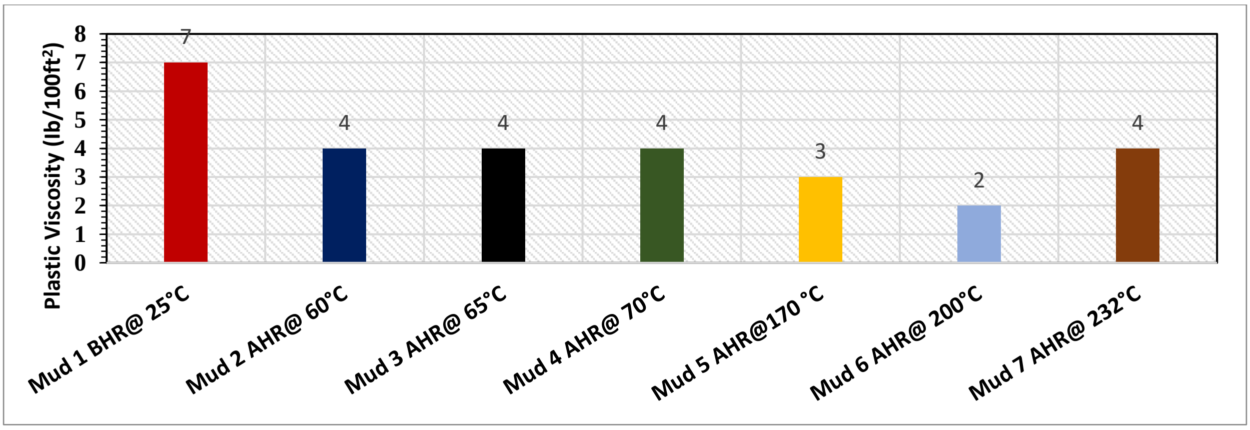


Figure 5.15: Plastic viscosities of mud formulations containing konjac gum after aging at different temperatures.

5.2.2.3 Gel strength of the mud formulations

Figures 5.16, 5.17,5.18 compare the gel strengths (10 seconds and 10 minutes) of drilling muds containing diutan gum, konjac gum or xanthan gum and the additives with those of Mud 1 (formulated with each of the biopolymer). The measure of the attractive forces presents in a drilling fluid when it is static is gel strength. It is the capacity of drilling mud to suspend cuttings and weighting materials when fluid circulation is stopped (Mitchel and Miska, 2011). Very high gel strength is not desirable as it can cause swabbing, surging, difficulty in running logging tools, entrapping of gas in mud, and difficulty in removal of cuttings at the surface (Darley and Gray, 1988). If a drilling mud has no gel strength, solids will settle to the bottom of a wellbore even though it has a high viscosity. When the difference between the10-seconds and the 10-minutes gel is small, the gel strength is said to be flat. Flat gel strength is desirable. Gel strength is progressive when the difference between the10-seconds and 10-minute gel readings is wide. Progressive gel is not desirable. As shown in Figure 4.16, Mud 5 formulated with potassium formate and sodium carbonate without the antioxidant and polyethylene glycol has a higher gel strength than the control mud, Mud 1 even after aging for 16 hours at 150°C. The same mud composition and concentration were used to formulate Mud 6. Aged at 170°C for 16 hours, Mud 6 gel strength was high when compared with Mud 1. The gel strength of Mud 5 was progressive. The potassium formate promoted the linking of solid particles to form gel strength, but the presence of carbonate and bicarbonate caused flocculation in the drilling fluid formulations (Annis and Smith, 1996). Flocculation in water-based fluids increased gel strength while deflocculation decreases the gel strength. The carbonate and bicarbonate in Muds 5 and 6 caused flocculation, which led to the progressive gel strength. As shown in Figure 4.16, Mud 7 aged at 232°C and formulated with a higher concentration of polyglycol, had high gel strength when compared with Mud 1. However, the gel strength of Mud 7 is flat. As shown in Figures 5.16**,** 5.17, 5.18, muds formulated with the additives (sodium erythorbate, potassium formate and polyglycol) have flat gel strengths. The additives used in this work, therefore, create positive conditions for the deflocculation and linking of solid particles in the fluid formulations at high temperatures, hence the flat gel strengths. This result shows that the mud formulations containing the additives have favourable gelling characteristics to suspend solids when circulation is stopped.

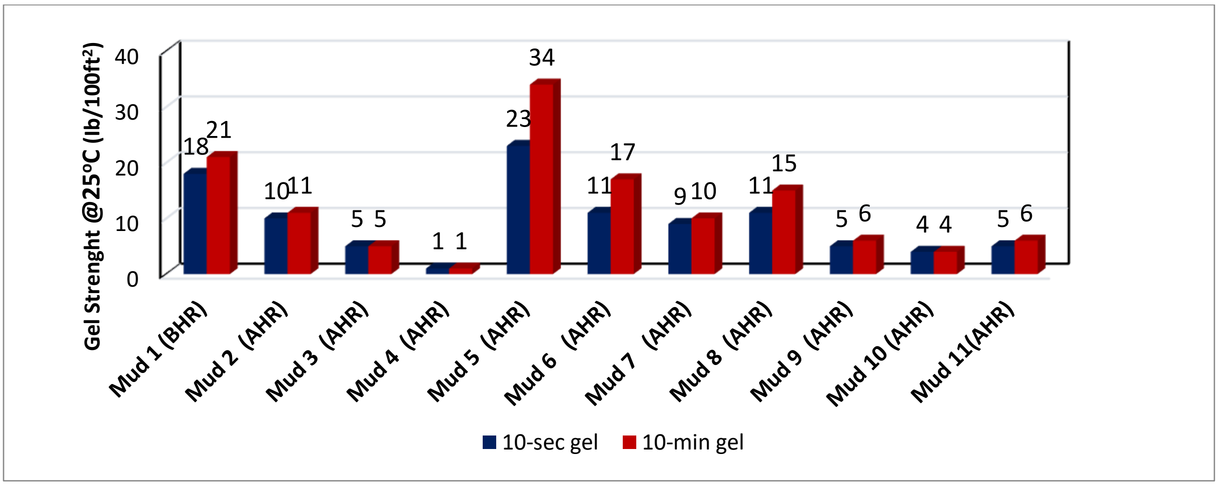


Figure 5.16: Gel strengths of mud formulations containing diutan gum after aging at different temperatures.

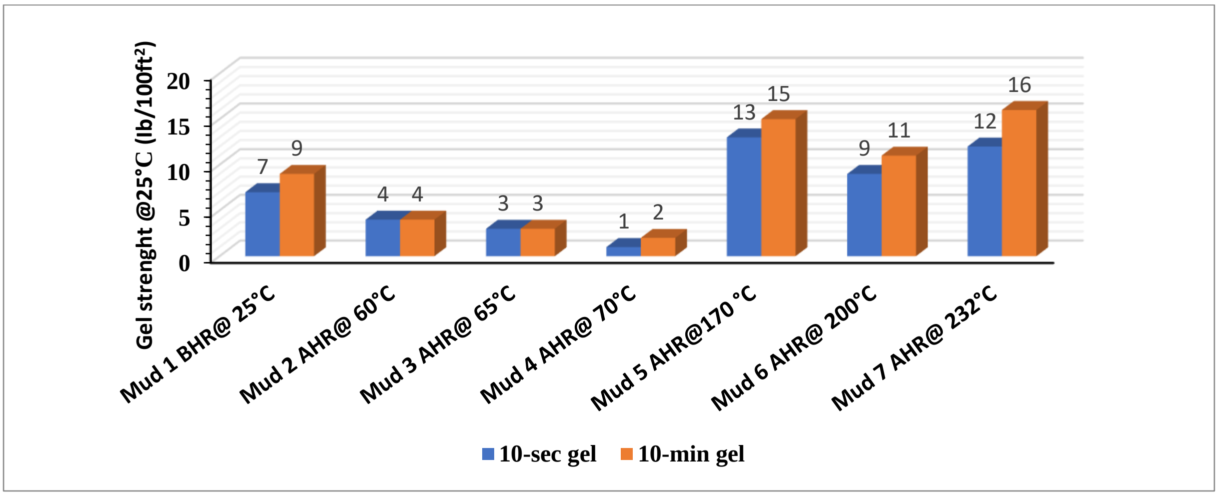
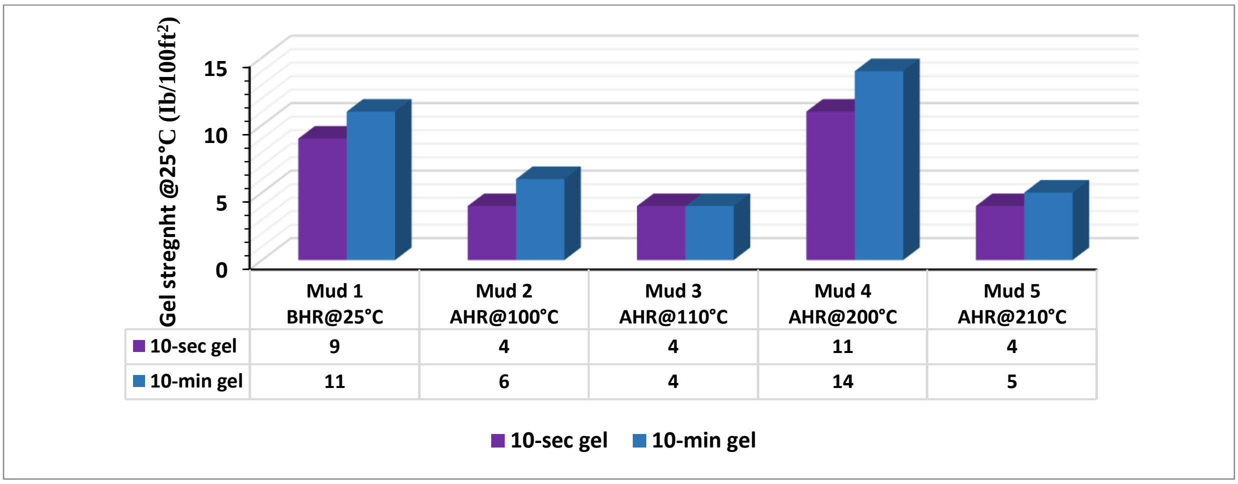


Figure 5.17: Gel strengths of mud formulations containing konjac gum after aging at different temperatures.



	Mud 1 BHR@25°C	Mud 2 AHR@100°C	Mud 3 AHR@110°C	Mud 4 AHR@200°C	Mud 5 AHR@210°C
10-sec gel	9	4	4	11	4
10-min gel	11	6	4	14	5

Figure 5.18: Gel strengths of mud formulations containing xanthan gum after aging at different temperatures.

5.2.2.4 Yield points of the mud formulations

Figures 5.19, 5.20, and 5.12 show the yield points of the drilling fluid formulations with the additives. A high yield point enhances the solids carrying characteristics of a drilling fluid and increases the well-bore drop in the wellbore (Annis and Smith, 1996); and it must be high enough to enable the carrying of drilled cuttings and weighting materials out of a wellbore, but not too high to create excessive pump pressure when the pump starts to pump mud. Furthermore, a high yield point implies that a drilling mud is non-Newtonian and can carry cutting better than any mud with a lower yield point. As shown in Figures 5.19, 5.20, and 5.12, the mud formulations have favourable YP values after aging dynamically at high temperatures. The retained YP values indicate that the mud formulations can carry drilled cuttings and weighting materials from a wellbore to the surface successfully.

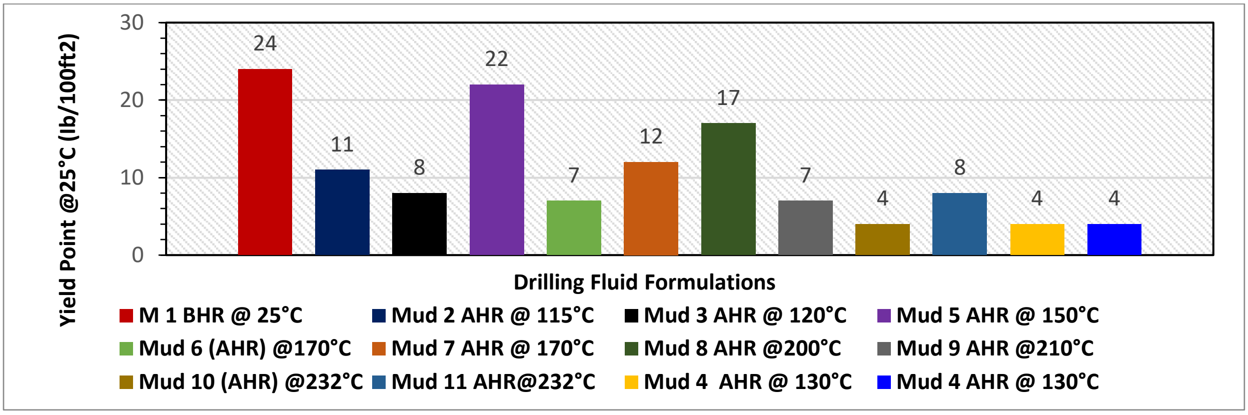


Figure 5.19: Yield points of mud formulations containing diutan gum after aging at different temperatures.

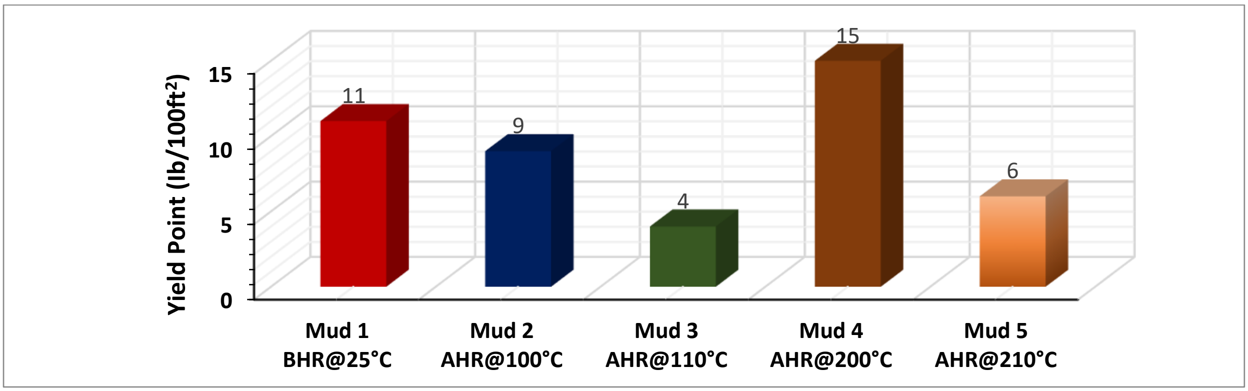


Figure 5.20: Yield points of mud formulations containing xanthan gum after aging at different temperatures.

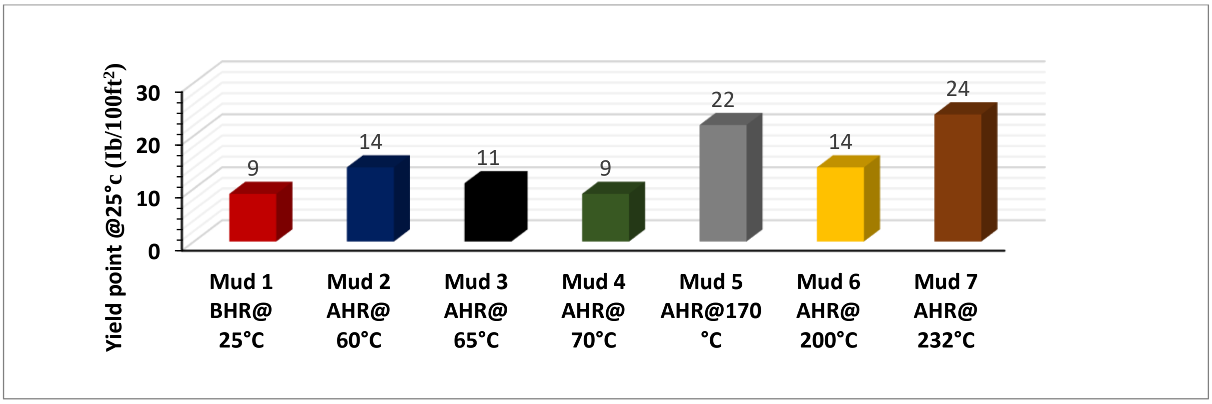


Figure 5.21: Yield points of mud formulations containing konjac gum after aging at different temperatures.

5.3 Phase 2 of research: Shale dispersion investigation

5.3.1 Shale characterisation

The shale samples were characterised using energy-dispersive X-ray spectroscopy (EDX) and SEM photos. The SEM photos showed the presence of illite (Figure 5.22). The presence of illite and smectite in the shale sample was confirmed as the elements, Si, K, Mg, Fe, Ca, Na and Al were found in the shale samples, and other components were calcite, pyrite, and quartz (Figure 5.23). The dry SEM - before aging in freshwater and drilling fluid formulation - showed the clay distribution and pore structure (Figures 5.24 (a) and (c)). Illite has low exchange capacities (CEC), indicating that it is not swelling clay as swelling clays have high CEC values (Behnamanhar et al., 2014), and it is suitable for hardness testing as it is less swelling and dispersible. The most common instability in shale formation is shale swelling and dispersion.

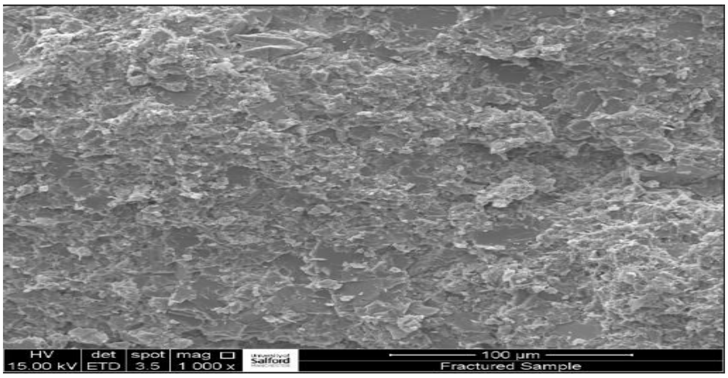


Figure 5.22: SEM Image of shale cuttings

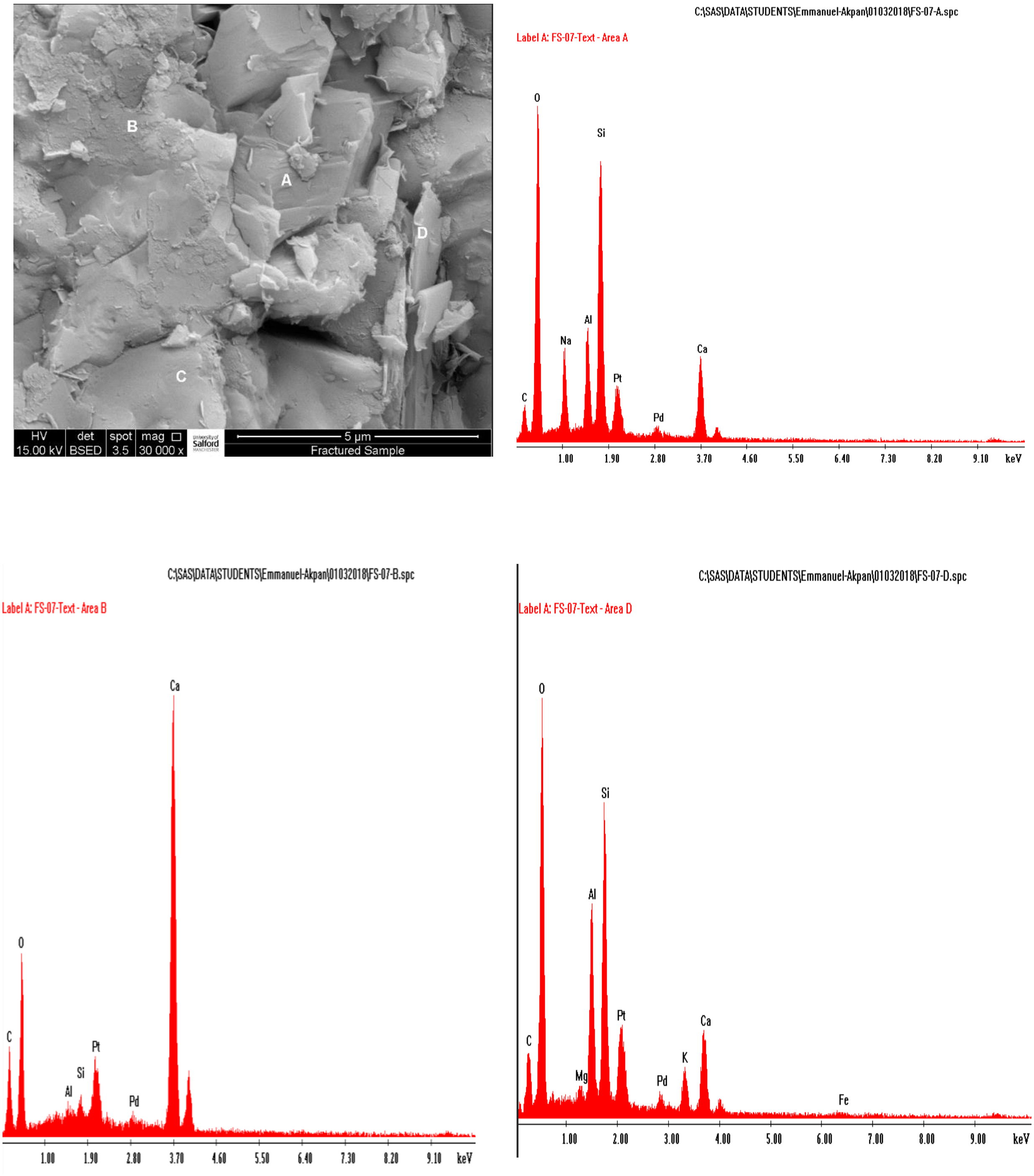
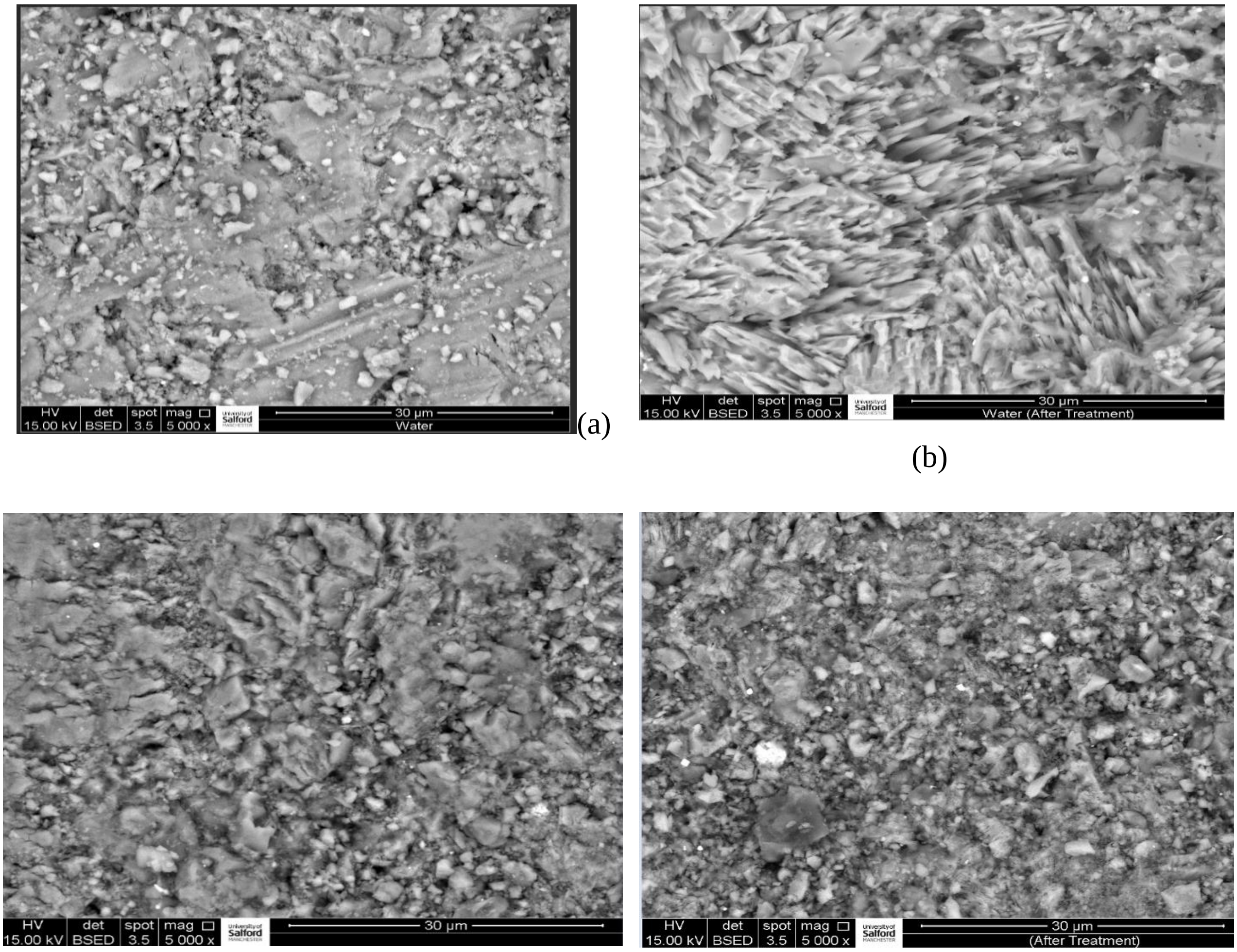


Figure 5.23: EDX of shale sample showing the presence of illite, smectite, calcite, and quartz.

5.3.2 Dispersion test

The problems associated with shale drilling are swelling and dispersion. Swelling involves the expansion of shale when it comes in contact with water. Dispersion involves the disintegration of shale rock when it is exposed to water; the dispersion of shale is caused by stresses in the wellbore, the extent to which the shale is hydrated, the drilling fluids velocity in the wellbore annulus, and the degree of shale brittleness (Al-Arfaj et al., 2018). Reactive shale formations are associated with hole instability problems, which cause wellbore failure. Before testing, the shale samples show well-formed structures (Figures 5.24 (a) and (c)). The post-SEM test analyses showed that freshwater and the drilling fluid formulation interacted with the shale samples**.** Figures 5.24 (a) and (b) show the shale samples before and after aging in freshwater dynamically for 16 hours at 120°C. The Illite/smectite in the shale sample responded negatively to the freshwater (Figure 5.24 (b)). Figures 5.24 (c) and (d) show a shale sample before and after aging dynamically for 16 hours at 120°C in the inhibitive fluid formulation. After testing, the illite had dispersed as it interacted with the freshwater (Figure 5.24 (b)) while the additives in the mud formulation filled the pore spaces in the shale, thereby preventing mud filtrate penetration (Figure 5.24 (d)). The shale sample aged in freshwater showed that the clay mineral had dispersed, thereby leaving a spike-like structure on the surface of the shale sample (Figure 5.24 (b)). Conversely, there was no significant change in the surface structure of the shale sample aged in the inhibitive mud formulation (Figure 5.24 (d)). The additives, therefore, sealed the pores spaces and were absorbed on the shale samples surface, thereby preventing the interaction between water in the drilling fluid and the shale rock. In addition, the potassium formate and sodium erythorbate reduced the water activity of the inhibitive mud formulation, thereby preventing the movement of water into the shale rock. The stabilisation of the shale sample was also achieved through the cation exchange process as the smaller K^+ ions replaced the Na+ ions in the shale sample, thereby reducing the spaces between the shale layers (Darley and Gray, 1988). The interaction among potassium ions, sodium ions, and polyethylene glycol on the clay surface was, therefore, essential in reducing the shale dispersion. The cations, K^+ and Na^+, were provided by non-chloride salts, potassium formate and sodium erythorbate. High concentrations of chloride salts in water-based fluids are environmental concerns (Bloys et al.,1994). The mud formulation was strongly shale-inhibitive as shale-fluid interaction was prevented. When a shale plug (14.99g) was exposed to freshwater, it was found that 79% of the shale plug was recovered. When another shale plug (13.77g) interacted with the inhibitive mud formulation, it was found that 100% of the shale rock was recovered. It is possible that the additives in the inhibitive mud formulation encapsulate the shale rock, thereby preventing water invasion.



(a)

(b)

(c)

(d)

Figure 5.24: Shale samples aged in fluids: (a) Shale sample before being aged in freshwater; (b) Shale sample after being aged in freshwater at 120°C for 16 hours; (c) Shale sample before aging in an inhibitive mud formulation; (d) shale sample after aging in an inhibitive mud formulation.

The shale sample investigated in this work has high clay contents. The weights of shale cuttings recovered from freshwater and inhibitive mud formulation are shown in Table 6; the effects of freshwater and the mud additives on the shale dispersion is shown in Figure 5.25. The %RW value for shale cuttings recovered from freshwater was 78%. The %RM value of cuttings recovered from mud formulated with the additives was 100%. The additives show a positive effect in retarding the dispersion and disintegration of the shale samples. The interaction among potassium ions, sodium ions and polyethylene glycol at the clay surface was vital in preventing the disintegration and dispersion of the shale sample. The shale sample was, therefore, not susceptible to dispersion as the additives restricted the movement of water into the shale. The initial and recovered shale cuttings form freshwater and drilling fluid formulation is presented in Table 5.8. Figure 5.25 shows the effects of freshwater and inhibitive water-based mud on shale recovery performance.

Table 5.8: The initial and recovered shale cuttings

Fluid	Initial Dried Weight (Shale cuttings)	Dried Weight after Dispersion test (Shale cuttings)
Freshwater	6.0	4.69
Mud 11	6.0	6.00

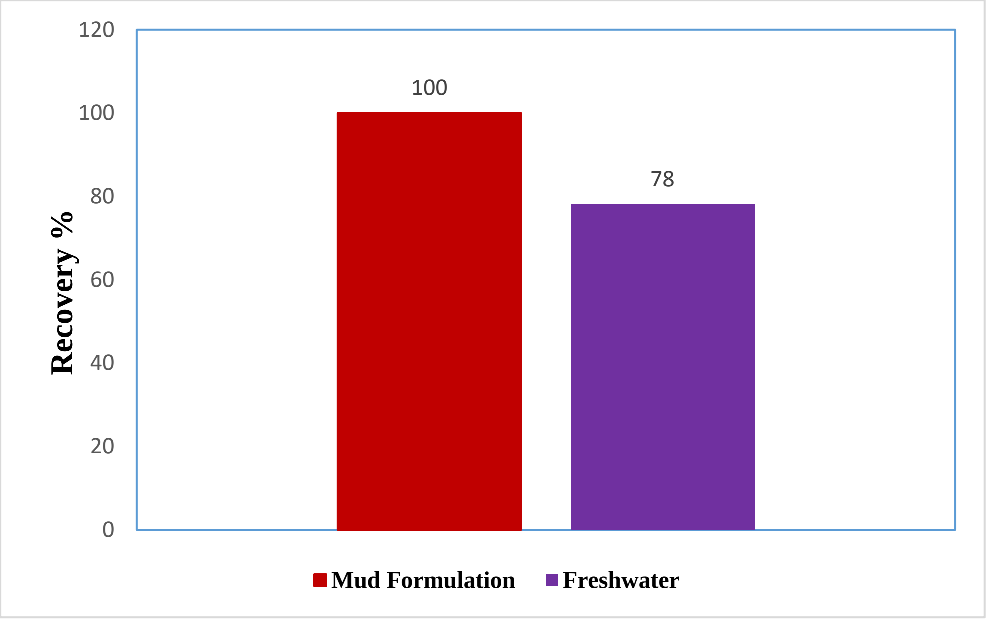


Figure 5.25: Effects of freshwater and inhibitive water-based mud on shale recovery performance.

5.4 Chapter summary

The viscosity of biopolymer in water-based muds collapses with increasing temperature. This sharp collapse in viscosity can be a problem where viscosity maintenance is required. The mechanisms which cause the collapse of biopolymers' viscosities with increasing temperature include acid-catalysed hydrolysis and oxidation-reduction (redox) reactions (Seright and Henrici, 1990). These mechanisms were exploited in this study to stabilise biopolymers in water-based muds at high temperatures. PH preserving agents were added to the drilling fluid samples to counteract acid-catalysed hydrolysis. Potassium formate was deployed as an antioxidant and temperature stabiliser. Sodium erythorbate served as an antioxidant and oxygen scavenger. From previous works the best additives to stabilise biopolymers in water-based drilling fluids at high temperatures include salt brine, polyglycol, and an antioxidant (Seright and Henrici, 1990; Howard et al.,2015; Messler et al., 2004). In this study, the effects of antioxidant, formate salts, and polyglycol on the viscosities of biopolymers in water-based muds at high temperatures and on reactive shale formations were, therefore, investigated. Drilling mud formulations that retained at least 50% of its viscosity after aging at high temperature for 16 hours was classified as stable (Howard et al.,2015). The stability temperatures of konjac gum, xanthan gum, and diutan gum in water-based bentonite muds without the antioxidant, formate salts, and polyglycol added were determined to be 65°C, 100°C, and 115°C respectively. The stability temperature of biopolymers in water-based muds formulated with potassium formate without antioxidant and polyethylene glycol was found to be 150°C. This results confirmed the findings from previous works, which observed that formate salt could only extend the stability temperature of biopolymers up to around 175°C at best (Galindo et al. 2015; Howard et al.,2015). The drilling mud formulated with a low concentration of polyethene glycol, formate salt, and a high concentration of the antioxidant (sodium erythorbate) remain stable up to 210°C. The drilling mud formulated with a higher concentration(0.7%) of polyethylene glycol remain stable up to 232°C. The best additive package combination was potassium formate, sodium erythorbate, and 0.7% polyethene glycol. These additives were able to protect the biopolymers from oxidative and hydrolytic degradation as the stabilisation of biopolymers in water-based muds at high temperatures was achieved.

After the hot rolling tests, a stable, inhibitive mud formulation was selected for shale dispersion test. Shale instability problems occur if a reactive shale formation is drilled with non-inhibitive water-based muds. The effects of freshwater and inhibitive mud formulation on shale rock were investigated. Before testing, the shale samples show well-formed structures. After testing, the shale sample aged in freshwater dispersed, leaving a spike-like structure on the surface of the shale sample. Conversely, there was no significant change in the appearance of the surface structure of the shale sample aged in the inhibitive mud formulations. From the dispersion test, the shale cuttings recovered from freshwater was 78%; the shale cuttings recovered from the inhibitive mud formulated with the additives was 100%. The additives, therefore, show a positive effect in retarding the dispersion and disintegration of the shale samples.

Chapter 6: Conclusion, Recommendations, and Future Work

6.1 Introduction

In this study, the effects of antioxidant, formate salts, and polyglycol on the stability temperature of biopolymers in water-based muds at high temperatures and on reactive shale formations were investigated. Biopolymers are used almost in all water-based drilling fluids. They are non-toxic, less expensive, biodegradable, and environmentally friendly. However, when exposed to high temperatures for a long time, biopolymers in water-based drilling fluids degrade. This degradation of the biopolymer can lead to total failure of a water-based drilling fluid under high temperature conditions. Environmental concerns, cost, and difficulty in handling pose a challenge to the use of oil-based mud systems; and synthetic polymers are expensive, generate high plastic viscosity, and cause formation damage, hence the need to stabilize biopolymers in water-based drilling fluids. To stabilize biopolymers in drilling fluids, the mechanisms through which they degrade at elevated temperatures must be understood. In Chapter 3, it is shown that biopolymer-drilling fluids are unstable and degrade under the following mechanisms at high temperatures:

- Oxidation-reduction reaction
- Acid-catalysed hydrolysis (dependent on the pH)
- Base-catalysed hydrolysis
- Early onset of the helix-coil conformation transition

In addition, in Chapter 3, it is shown that the combination of an antioxidant package, formate salts, buffering agents, and polymer stabilizers could stabilize biopolymers in water-based muds. Based on the above mechanisms of biopolymer degradation, some additives were screened to identify the thermal stabilisers that could extend the 16-hour temperature stability of biopolymers in water-based bentonite muds. The biopolymers evaluated in this study were konjac gum, diutan gum, and xanthan gum, and the additives screened are shown in Table 4.4. The additives with antioxidant qualities were sodium erythorbate and potassium formate; the additives with buffering qualities were sodium carbonate and sodium bicarbonate; and the additive with shale stabilisation qualities was polyethylene glycol. All the efforts of researchers as highlighted in Chapter 3 have brought to the fore the attempt made in stabilising water-based fluids at high temperatures and in inhibiting shale hydration and dispersion. None has, however, considered the combination of additives used in this work.

The temperature stability was defined as the temperature at which a mud sample viscosity is greater than or equal to half of the viscosity of the control mud sample containing a biopolymer and bentonite in water. Shale dispersion test was also carried out to determine the effects of freshwater and inhibitive mud formulation on a shale rock. A Marcellus shale sample was characterised using a scanning electron microscope (SEM) photos and X-ray diffraction to determine its mineral and elemental contents.

6.2 Conclusion

The objective of conducting this study was to investigate the effects of anti-oxidant, formate brine, pH control agents, and polyglycol on the stability temperatures of biopolymers in water-based drilling fluids and on reactive shale formation. The investigation involved laboratory tests to identify the additives package that could extend the 16-hour thermal stability of biopolymer in water-based drilling fluids and inhibit shale hydration and dispersion. The instruments described in Chapter 4 were used to prepare the drilling fluids and to measure the the drilling fluids' properties. Based on the analyses of the results obtained, the following can be concluded from this study:

1. The drilling muds formulated with the additives exhibited shear thinning and thixotropic characteristics. The shear thinning, and thixotropic characteristics are an indicator of good cuttings and weighting materials transport and hole cleaning capacity.
2. The anti-oxidant, potassium formate, pH control agent, and polyglycol stabilised biopolymers in water-based muds up to 232˚C after dynamic aging for 16 hours. The best additive package combination was potassium formate, sodium erythorbate, and 0.7% polyethene glycol. The additives were, therefore, able to counteract oxidative and hydrolytic degradation processes in the mud formulations at high temperatures.
3. The stability temperatures of diutan gum, konjac gum, and xanthan gum in bentonite water-suspension after dynamic aging for 16 hours were found to be 115˚C, 65˚C, and 100˚C respectively.
4. The plastic viscosities of the mud formulations containing antioxidant, formate salts, and polyglycol decrease with increasing aging temperatures, thus indicating reliable lubricity and a fast rate of penetration (ROP).
5. The stability temperature of biopolymers in water-based muds formulated with potassium formate without an antioxidant and polyethylene glycol was found to be 150°C.
6. From this study, it is possible to formulate water-based drilling fluids containing clay and biopolymers for high-temperature drilling operations in the 150-232°C range without using

expensive and formation damaging synthetic polymers.

7. The sodium carbonate and sodium bicarbonate pH buffer had positive effects on the fluid formulations containing antioxidant, formate salts, and polyglycol as the drilling muds had flat rheological profiles and flat gel strengths.
8. The stability temperature of biopolymer in water-based bentonite muds containing a low concentration of polyethene glycol, formate salt, and a high concentration of the antioxidant (sodium erythorbate) was found to be 210°C.
9. The stability temperature of biopolymer in water-based bentonite muds containing a higher concentration(0.7%) of polyethylene glycol, formate salt, and the antioxidant (sodium erythorbate) was found to be to 232°C.
10. The finding of this study confirms the suggestions by other researchers that the best additives to stabilize biopolymers in water-based drilling fluids at high temperatures include salt brine, polyglycol, and an antioxidant.
11. The shale rock aged in freshwater disintegrated and dispersed. In contrast, the shale rock aged in the drilling fluid formulated with the additive package remained virtually the same, thus showing that the additives used in this work prevented shale-fluid interaction.
12. In the shale dispersion test, the recovery rate of shale cuttings from the inhibitive fluid formulation was 100%, meaning that the additives used in this work can inhibit shale dispersion very effectively.

6.3 Recommendations and future work

The aims and objectives of the present study have been met within its scope, following the analyses of laboratory investigation results. However, there is a need to carry out further investigation on the effects of the mud additives on properties of drilling fluids, which are outside the scope of the present study. Further studies will contribute greatly to knowledge and decrease the gap in knowledge with respect to the mud additives used in the present study. For these reasons, and for future research work, the following recommendations are made:

1. As the maximum operating temperature of the roller oven used in this study was 232°C, the experiments were not carried out beyond 232°C. In that regard, further research could be undertaken to ascertain the effects of temperatures above 232°C on biopolymers in water-based bentonite muds containing the additives used in the present study.
2. Water-based muds containing biopolymers are not tolerant to contamination with cations (Na^+, Mg^{++}, Ca^{++}), carbonates (CO_3--, HCO_3--), oil, gases, water, and drilled solids. Further

tests could be carried out to determine the effects of mud contaminants at different concentrations on the mud formulations.

3. As the effects of mud formulations on formation damage were outside the scope of present study, further study areas may include formation damage studies on reservoir rocks.
4. The effects of the additives on the API fluid loss characteristics of water-based bentonite muds could be considered.
5. Further work could focus on the effects of the additives on drilling fluid lubricity.
6. Further investigation could concentrate on the chemistry of the mud formulations and its effects on reactive shale rocks.

References

Abdon C. J., Jackson L. B., and McClelland S. G. (1989). The *development of a deflocculated polymer mud for HTHP drilling*. Paper SPE 17924 presented at the SPE Middle East Oil Show, Bahrain. doi: 10.2118/17924-MS

Aftab A., Ismail A. R. and Ibupoto H. Z. (2017). Enhancing the rheological properties and shale inhibition behaviour of water-based mud using nano silica multi-walled carbon nanotube, and graphene nanoplatelet. *Journal of Petroleum Science and Engineering,* 26 (2), 291–299. doi: 10.1016/j.ejpe.2016.05.004

Al-Ansari A., Yadav K., Anderson D., Leaper R., Dye W., and Hansen N. (2005). D*iverse application of unique high-performance water-based mud technology in the Middle East*. Paper SPE 97314 presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition, Dubai, United Arab Emirates. doi: 10.2118/97314-MS

Al-Arfaj M. K., Amanullah M., and A. Mohammed A. (2018). *An enhanced experimental method to assess the shale inhibition durability of inhibitive water-based drilling fluids*. Paper SPE189380 presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition, Abu Dhabi, UAE. doi: 10.2118/189380-MS

Al-Harbi A.A., Ersoz H., and Abdrabalreda S. (2005). *Influence of sodium/potassium formate-based drilling fluids on nuclear logs.* Paper SPE 94693 presented at the SPE Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil. doi: 10.2118/94693-MS

Ali, M.S., and Al-Marhoun, M. A. (1990). The effect of high temperature, high pressure and aging on water-base drilling fluid. *Society of Petroleum Engineers*. Retrieved from https://www.onepetro.org/download/general/SPE-21613-MS?id=general%2FSPE-21613-MS

Amanullah M. (2007). *Screening and evaluation of some environmentally-friendly mud additives to use in water-based drilling muds,".* Paper SPE 98054 presented at the 2007 SPE E&P Environmental and Safety Conference, Galveston, Texas, USA. doi: 10.2118/98054-MS

Amanullah M.L. (2005). Environment-friendly fluid loss additives to protect the marine environment from the detrimental effect of mud additives. *Journal of Petroleum Science and Engineering,* 48(3-4), 199–208. doi: 10.1016/j.petrol.2005.06.013

Amoco Production Company. (1994). Drilling fluids manual. Retrieved from https://www.slideshare.net/VyanPersad/amoco-drilling-fluid-manual

Annis R. M. and Smith V. M. (1996). Drilling fluids technology. Houston: EXXON Company.

Apaleke S. A, Al-Majed A., and Hossain E. M. (2012). *Drilling fluid: state of the art and future trend.* Paper SPE 149555 presented at the SPE North Africa Technical Conference and Exhibition, Cairo, Egypt. doi: 10.2118/149555-MS

API (American petroleum institute). (1978). *API Recommended Practice Standard Procedure for Testing Drilling Mud*. Washington D.C: API.

Aserud Overas, J. A. (2001). The influence of surge and swab pressures in the Snorre P-35 Well. (Diploma thesis), Norwegian University of Science and Technology, Trondheim.

ASME Shale Shaker Committee. (2005). *Drilling fluid processing handbook.* Burlington, MA 01803, USA: Gulf Professional Publishing.

Behnamanhar H., Noorbakhsh S.S., and Maghsoudloojafari H. (2014). Environmentally friendly water-based drilling fluid for drilling of water-sensitive formations. *Journal of Petroleum and Gas Exploration Research*, 4(4), 60-71. Retrieved from https://www.interesjournals.org/articles/environmentally-friendly-waterbased-drilling-fluid-for-drilling-of-watersensitive-formations.pdf

Bland R. et al. (2006). *"HP/HT drilling fluids challenges,".* Paper SPE 103731 presented at the IADC/SPE Asia Specific Drilling Conference and Exhibition, Bangkok, Thailand. doi: 10.2118/1107-0078-JPT

Bloys et al. (1994). Designing and managing drilling fluid. *Schlumberger Oil Field Review,* 6(2), 33-43.

Bourgogne, A. T., Millheim, K.K., Chenevert, M.E., and Young, F.S. (1986). *Applied Drilling Engineering* (Vol.2). Richardson, Texas: Society of Petroleum Engineers

Bradshaw J.R., Hodge M. R., Wolf O. N., Knox A.D.,Hudson E. C., and Evans E.(2006). *Formate-based reservoir drilling fluid resolves high-temperature challenges in the Natuna Sea*. Paper SPE 98347 presented at the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, USA. doi: 10.2118/98347-MS

Brady E. M., Craster B., Getliff M. J., and Reid I.P. (1998). *Highly inhibitive, low salinity glycol water-base drilling fluid for shale drilling in environmentally sensitive locations.* Paper SPE

46618 presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Caracas, Venezuela. doi: 10.2118/46618-MS

Bungert D, Maikranz S., Sundermann R., Downs J., Benton W., and Dick A. M (2000). *The evolution and application of formate brines in high-temperature/high-pressure operations.* Paper SPE 59191 presented at the IADC/SPE Drilling Conference, New Orleans, Louisiana. doi: 10.2118/59191-MS

Burke C. J. and Veil J. A. (1995). *Potential Environmental Benefits from Regulatory Consideration of Synthetic Drilling Muds.* Illinois: U.S. Department of Energy Office of Policy

Chilingarian, G.V. & Vorabutr, P. (1981). *Drilling and drilling fluids*. Amsterdam: Elsevier Scientific Publishing Company

Clark K.R., Scheuerman, R.F., Rath H., and Van Laar G.H. (1976). Polyacrylamide/potassium-chloride mud for drilling water-sensitive shales. *Journal of Petroleum Technology*, 28(6), 719 – 727. doi: 10.2118/5514-PA

Clarke-Sturman J. A. and Sturla L. P. (1988). *Aqueous polysaccharide compositions.* European patent No 259 939.

Clarke-Sturman J. A. et al. (1986). Influence of anions on the properties of microbial polysaccharides in solution. *International Journal of Bio. Marcromol*, 8(6).355-360. doi: 10.1016/0141-8130(86)90055-3

Darley, H.C. H. and Gray, G.R. (1988). *Composition and Properties of Drilling fluids*. Houston: Gulf Publishing (1988)

Dayawant S. (1999). *An innovative, environmentally friendly and cost-effective approach for polymer-based mud system in Upper Assam oil fields of India*. Paper SPE 57584 presented at theThe *SPE/IADC Middle East Drilling Technology Conference***,** Abu Dhabi, UAE. doi: 10.2118/57584-MS

Downs D. J. (1993). *Formate brines: novel drilling and completion fluids for demanding environments.* Paper SPE 25177 presented at the SPE International Symposium on Oilfield Chemistry, New Orleans, Louisiana. doi: 10.2118/25177-MS

Downs D. J., Killie S., and Whale F.G. (1994). *Development of environmentally benign formate-based drilling and completion fluids.* Paper SPE 27143 presented at the SPE Health, Safety and Environment in Oil and Gas Exploration and Production Conference, Jakarta, Indonesia. doi: 10.2118/27143-MS

Downs D.J. (1992). High-temperature stabilisation of xanthan in drilling fluids by the use of formate salts. *In Proceeding of the 6th IFP Exploration and Production Research Conference: 4-6 September,1991, Physical Chemistry of Colloids and Interfaces in Oil Production* (pp. 197-202). Paris: Editions Technip.

Downs D.J., Howard K.S., and Carnegie W. A. (2005). *Improving hydrocarbon production rates through the use of formate fluids - A Review.* Paper SPE 97694 presented at the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur. doi: 10.2118/97694-MS

Eutech Instruments Pte Ltd **(2005).** PH testr 10. Retrieved from http://www.eutechinst.com/pdt-type-pocket-testers-phtestr10.html

Ezell R., and Ezzat D., Turnerm K. J., and Wu J.J. (2010). *New filtration-control polymer for improved brine-based reservoir drilling-fluids performance at temperatures in excess of 400of and high pressure.* Paper SPE 128119 presented at the SPE International Symposium and Exhibiton on Formation Damage Control, Lafayette, Louisiana, USA. doi: 10.2118/128119-MS

Ezell R., Moshsen A.M.M, Elbialy E. M., Abdulaziz E. M., and Ekpe J. (2011). *Utilization of non-damaging drilling fluid composed of potassium formate brine and manganese tetra oxide to drill sandstone formation in tight gas reservoir.* Paper SPE 147983 presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition, Muscat. doi: 10.2118/147983-MS

Ferrari G., Ceccini F., and Xiao L. (2000). Drilling wastes treatment and management practices for reducing impact on HSE: ENI/AGIP experiences. Paper SPE64635 presented at International Oil and Gas Conference and Exhibition, Beijing, China. doi: 10.2118/64635-MS

Galindo A. K., Zha W., Zhou H., and Deville P. J. (2015). *High temperature, high performance water-based drilling fluid for extreme high temperature wells.* Paper SPE173773 presented at the SPE International Symposium on Oilfield Chemistry, the Woodlands, Texas, USA. doi: 10.2118/173773-MS

Gallino G., Guarneri A., Maglione R., Nunzi P. and P L. Xiao L. P.(1997). *New formulations of potassium acetate and potassium formate polymer muds greatly improved drilling and waste disposal operations in South Italy*. Paper SPE 37471 presented at the SPE Production Operations Symposium, Oklahoma City, Oklahoma. doi: 10.2118/37471-MS

Gallino G., Poli G., and Xiao L. (1996). *Scleroglucan biopolymer enhances WBM performances*. Paper SPE 36426 presented at the SPE Annual Technical Conference and Exhibition Denver, Colorado. doi: 10.2118/36426-MS

Gilbert et al. (2007). *Formate fluids and environmental regulations: a global view of benefits and challenges*. Paper SPE 110891 presented at the Annual Technical Conference and Exhibition, Anaheim, California, U.S.A. doi: 10.2118/110891-MS

Glass E. J., Soules A. D., Ahmed H., Egland-Jongewaard K. S., and Fernando H. R. (1983). *Viscosity stability of aqueous polysaccharide solutions.* Paper SPE 11691 presented at the SPE California Regional Meeting, Ventura, California. doi: 10.2118/11691-MS

Hall, P. L. (1987). Clays: their significance, properties, origins and uses. In M. J. Wilson (Ed.), *A Handbook of Determinative Methods in Clay Mineralogy* (pp.1-25). New York: Chapman and Hall Publishers.

Hastings L., Cooper G.P. and Burg W. (1984). Human sensory response to selected petroleum hydrocarbons. In MacFarland H.N., Holdsworth C.E., MacGregor J.A. et al. (eds.), *Advances in modern environmental toxicology, Applied toxicology of petroleum hydrocarbons* (Vol. VI, pp. pp: 255-270). Princeton, NJ: Princeton Sci. Publ. Inc.

Hemphill T., Campos W. and Pilehvari A. (1993). Yield-Power Law Model more accurately predicts mud rheology. *Oil & Gas Journal*, 91(34), 45-50.

Hosterman W. J. and Whitlow I.S. (1983). *Clay mineral of Devonian shales in the Appalachian Basin, Geological Survey Professional Paper 1298*. Washington: United States Government Printing Office, 1983. Retrieved from https://pubs.usgs.gov/pp/1298/report.pdf

Howard K. S. (1995). Formate brines for drilling and completion: State of the art. Paper SPE 30498 presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas. doi: 10.2118/30498-MS

Howard S., Kaminski L. and Downs J. (2015). *Xanthan stability in formate brines - formulating non-damaging fluids for high-temperature applications.* Paper SPE 174228 presented at the SPE European Formation Damage Conference and Exhibition, Budapest, Hungary. doi: 10.2118/174228-MS

IMCO Services. (1981). Applied Mud Technology. Houston: IMCO Services Division of Halliburton Company.

Ji L. , Quan G., Friedheim E. J., Zhang R., Chenevert E.M., and 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*. Paper SPE 158895 presented at the *SPE Asia Pacific Oil and Gas Conference and Exhibition,* Perth, Australia.doi: 10.2118/158895-MS

Kjøsnes I., Løklingholm G., Saasen A., Syrstad O. S., Agle A., and Solvang K. A. (2003). *Successful water-based drilling fluid design for optimizing hole cleaning and hole stability*. Paper SPE 85330 presented at the SPE/IADC Middle East Drilling Technology Conference and Exhibition, Abu Dhabi, United Arab Emirates. doi: 10.2118/85330-MS

Lal M. (1999). Shale stability: drilling fluid interaction and shale strength. *Society of Petroleum Engineers*, 51 (11), 30-30. doi: 10.2118/1199-0030-JPT

Mahto, V et al. (2004). Rheological study of water-based oil well drilling fluid, *JPSE*, 45 (1-2), 123-128. doi: 10.1016/j.petrol.2004.03.008

Mahto, V et.al. (2005). Tragacanth gum: an effective oil well drilling fluid additive, Energy *Sources*, 27(3), 299-308. doi: 10.1080/00908310390424142

Mehtar A.M., Mielke K.S., Alfonzo E. N., Young S., Brangetto M.,and Soliman A.A. (2010). Effective implementation of high-performance water-based fluid provides superior shale stability offshore Abu Dhabi. *Paper SPE138564 presented at the SPE Abu Dhabi International Petroleum Exhibition and Conference*, Abu Dhabi, UAE. doi: 10.2118/138564-MS

Mellot, J. (2008). *Technical improvements in wells drilled with a pneumatic fluid*. Paper SPE 99162 presented at the SPE/IDAC Drilling Conference, Miami, Florida, USA. doi: 10.2118/99162-MS

Melo, A., Maglione, R., and Paiatti, C. (1995). *An Innovative Model for Drilling Fluid Hydraulic*. Paper SPE 29259 presented at the SPE Asia Pacific Oil and Gas Conference, Kuala Lumpur. doi: 10.2118/29259-MS

Messler D., Kippie D., Broach M. and Benson D. (2004). *A potassium formate milling fluid breaks the 400F barrier in a deep Tuscaloosa coiled tubing clean-out*. Paper SPE 86503 presented at the SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, U.S.A. doi: 10.2118/86503-MS

Mitchel R. F. and Miska S. Z. (2011). Fundamentals of drilling Engineering. Texas: Society of Petroleum Engineers.

Moore, D. M. & Reynolds, R. C., Jr. (1997). X-Ray diffraction and the identification and analysis of clay minerals (2nd ed.). New York: Oxford University Press.

Neff, J. M. (2005). *Composition, environment fates, and biological effects of water-based drilling muds, and cuttings discharged to the marine environment: a synthesis and annotated biography*. Washington, DC: American Petroleum institute.

Neff, J.M., Rabalais N. N., and Boesch F.D. (1987). *Offshore oil and gas development activities potentially causing long-term environmental effects.* London: Elsevier Applied Science Publishers.

Ochoa V. M., (2006). Analysis of drilling fluid rheology and tool joint effect to reduce errors in hydraulics calculations. (A Dissertation), Texas A&M University. Retrieved from https://core.ac.uk/download/pdf/4271305.pdf

Odiete W.O. (1999). *Environmental Physiology of Animals and Pollution*. Lagos: Diversified Resources Ltd.

Odom, I. E. (1984). Smectite clay Minerals: properties and uses. *Philosophical Transactions A*, 311(1517), 391-409. doi: 10.1098/rsta.1984.0036

OFI Testing Equipment Inc. (2019). Model 800 viscometer (instruction manual). Retrieved from http://www.ofite.com/publications/instructions/119-130-10-instructions/file

OFI Testing Equipment, Inc. (2015). Modell 1100 pressurized viscometer (instruction manual). Retrieved from http://www.ofite.com/publications/instructions/128-130-81-instructions/file

OFI Testing Equipment, Inc. (2015). Roller oven with programmable timer, circulating fan, and redundant heat control 5 Roller:173-00-RC (115 Volt) 173-00-1-RC (230 Volt) Instruction Manual. Retrieved from http://www.ofite.com/publications/instructions/739-173-00-rc-instructions/file

OFI Testing Equipment, Inc. (2017). Aging cell instruction manual [online]. Available from: http://www.ofite.com/doc/175-25_instructions.pdf

Okrajni, S., and Azar, J. J. (1986), The effects of mud rheology on annular hole cleaning in directional wells, *SPE Drilling Engineering*, 1(04), 297–308. doi: 10.2118/14178-PA

Oort E. D., Ward I., Chapman W.J., Williamson R., and Aston M. (1996). *Silicate-based drilling fluids: competent, cost-effective and benign solutions to wellbore stability problems*. Paper SPE 35059 presented at the SPE/IADC Drilling Conference, New Orleans, Louisiana. doi: 10.2118/35059-MS

Oort V. E., Bland G. R., Howard K. S.,Wiersma J. R., and Roberson L. (1997). *Improving HPHT stability of water-based drilling fluids.* Paper SPE 37605 presented at the SPE/IADC Drilling Conference, Amsterdam, Netherlands. doi: 10.2118/37605-MS

Oswald J. R., Knox A. D., Monem R. M. (2006). *Taking non-damaging fluids to new extremes: formate-based drilling fluids for high-temperature reservoirs in Pakistan.* Paper SPE 98391 presented at the SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, USA. doi: 10.2118/98391-MS

Overas, J. A. (2011). *The Influence of Surge and Swab Pressures in the Snorre P-35 Well*. Diploma Thesis, Norwegian University of Science and Technology.

PetroWiki (2015). *Drilling Fluid Types*. Retrieved from https://petrowiki.org/Drilling_fluid_types

Pinya L., Jian L., Yabin N., Daming Z., and Tongtai X. (1995). *Improved inhibition and rheological properties are observed in amphoteric polymer mud system*. Paper SPE 29943 presented at the International Meeting on Petroleum Engineering, Beijing, China.doi: 10.2118/29943-MS

Plank, J. P. (1992). Water based muds using synthetic polymers developed for high temperature drilling. *Oil Gas J.*, 90(5), 40-45. Retrieved from https://www.ogj.com/articles/print/volume-90/issue-9/in-this-issue/drilling/water-based-muds-using-synthetic-polymers-developed-for-high-temperature-drilling.html

Powell W. J., Jefferson T. D., and Zamora M. (1993). *Hole-Cleaning Study of Polymer-Based Drilling Fluids.* Paper SPE SPE-26329-MS presented at the Annual Technical Conference and Exhibition, Houston, Texas. doi: 10.2118/26329-MS

Ramirez M. A., Clapper D. K., Sanchez G., Luna E., Preciado O., and Santamaria J. (2005). *Aluminium-based HPWBM successfully replaces oil-based mud to drill exploratory wells in an environmentally sensitive area*. Paper SPE 94437 presented at the SPE Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil. doi: 10.2118/94437-MS

Reid P. I., Minton C. R., and Allan T. (1992). *Field evaluation of a novel inhibitive water-based drilling fluid for tertiary shales*. Paper SPE 24979 presented at the SPE European Petroleum Conference, Cannes, France. doi: 10.2118/24979-MS

Reis J.C. (1988). *Environmental control in petroleum engineering*. Houston: Gulf publishing company.

Saki Y., Dinarvand N., Habibnia B., and Shabazi K. (2010). *Experimental investigation of possibility of replacing oil-based muds with environmentally friendly water-based glycol muds in maroon oil field*. Paper SPE 132769 presented at the Trinidad and Tobago Energy Resources Conference, Port of Spain, Trinidad. doi: 10.2118/132769-MS

Samaei M. S. and Tahmasbi K. (2007). *The possibility of replacing oil-based mud with the environmentally acceptable water-based glycol drilling mud for the Iranian fields*. Paper SPE 106419 presented at the SPE &P Environmental and Safety Conference, Galveston, Texas, U.S.A. doi: 10.2118/106419-MS

Sandra G. and Arvid P. (2013). *Shale inhibition: What works?* Paper SPE 164108 presented at the SPE International Symposium on Oil Field Chemistry held in The Woodlands, Texas, USA, 8-10 April 2013. doi: 10.2118/164108-MS

Sarber G. J., Reynolds C., Michel M. C., Haag K., and Morris A. R. (2010). *The use of diutan biopolymer in coiled tubing drilling mud systems on the north slope of Alaska.* Paper SPE130584 presented at the SPE/ICOTA Coiled Tubing and Well Intervention Conference and Exhibition, The Woodlands, Texas. doi: 10.2118/130584-MS

Sawdon, C.A., Brady, M.E., Steve C., and James, S.G. (1995). *An integrated approach to the development of a water-based mud with oil-based mud performance.* Paper SPE 106419 presented at the SPE SPE/IADC Drilling Conference, Amsterdam, Netherlands. doi: 10.2118/29375-MS

Schaaning M. T., Trannum H. C., Oxnevad J. C., Carroll J., and Bakke J. (2008). Effects of drill cuttings on biogeochemical fluxes and macrobenthos of marine sediment. *Journal of Experimental Marine Biology and Ecology*, 361(1), 49-57. doi: 10.1016/j.jembe.2008.04.014

Seeberger, M.H., Matlock, R.W., and Hanson, P.M. (1989). *Oil muds in large-diameter, highly deviated wells: Solving the cuttings removal problem*. PaperSPE18635 presented at the SPE/IADC Drilling Conference, New Orleans, Louisiana. doi: 10.2118/18635-MS

Seright S.R. and Henrici J. B. (1990). Xanthan stability at elevated temperatures. *SPE Reservoir Engineering*, 5(01), 52-60. doi: 10.2118/14946-PA

Sharma et al. (2003) Behaviour of organic polymers on the rheological properties of Indian bentonite-water based drilling fluid system and its effect on formation damage, *Indian Jounal of chemical Technology*, Vol.10, 525-530. Retrieved from http://nopr.niscair.res.in/bitstream/123456789/22787/1/IJCT%2010%285%29%20525-530.pdf

Sharma P.V. and Mahto V. (2006). *Studies on less expensive environmentally safe polymers for development of water-based drilling fluids*. Paper SPE 100903 presented at the SPE Asia Pacific Oil & Gas Conference and Exhibition, Adelaide, Australia. doi: 10.2118/100903-MS

Simpson A. M., Al-Reda S., Foreman D., Guzman J., Al-Fawzy M. and Vice P. (2009). *Application and recycling of sodium and potassium formate brine drilling fluids for Ghawar field HTHP gas wells.* Paper OTC 19801 presented at the Offshore Technology Conference, Houston, Texas, USA. doi: 10.4043/19801-MS

Simpson A. M., Al-Reda S., Zhou S. S., Ansari A. (2005). *Overbalanced Drilling of extended horizontal sections with potassium formate brines.* Paper SPE 92407 presented at the SPE Middle East Oil and Gas Show and Conference, Kingdom of Bahrain. doi: 10.2118/92407-MS

Soric T., Marinescu P., and Huelke R. (2004). *Silicate-based drilling fluids deliver optimum shale inhibition and wellbore stability.* Paper SPE 87133 presented at the IADC/SPE Drilling Conference, Dallas, Texas. doi: 10.2118/87133-MS

Strickland D. S. (1994). Polymer drilling fluids in the 1990's: Will they replace oil-based muds? *Journal of Petroleum Technology*, 46(08), 619-714.doi: 10.2118/29211-PA

Tehrani M. A. et al. (2007). *A water-based drilling fluid for HT/HP applications*. Paper SPE105485 presented at the 2007 SPE International Symposium on Oil Field Chemistry Houston, Texas, USA. doi: 10.2118/105485-MS

Ujma K.H.W., Preussag G. A., Plank P. J. (1989). *A new calcium-tolerant polymer helps to improve drilling-mud performance and to reduce costs*. Paper SPE16685 presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas. doi: 10.2118/16685-MS

Vikas M. and Rajat J. (2015). Evaluation of polyacrylamide/clay composite as a potential drilling fluid in inhibitive water-based fluid system. *Journal of Petroleum Science and Engineering,* vol.133, 612 – 621. doi: 10.1016/j.petrol.2015.07.009

Weaver, J. et al. (2003). *Guar gum degradation: a kinetic study*. Paper SPE 80226 presnted at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA. doi: 10.2118/80226-MS

Wellington L. S. (1983). Biopolymer solution viscosity stabilisation - polymer degradation and antioxidant use. *Society of Petroleum Engineers Journal*, 23(6),901-912. doi: 10.2118/9296-PA

Wenjun S. et al. (2014). Research on the drilling fluid technology for high temperature over 240°C. *Procedia Engineering*, Vol.73, 218-229. doi: 10.1016/j.proeng.2014.06.191

Wilcox D.R, Fisk Jr. V.J, and Corbett E. G. (1987). Filtration Method Characterizes dispersive properties of shale. *Society of Petroleum Engineers*, 2(2),149-158. doi: 10.2118/13162-PA

Young B. D. (1993). Drilling fluid. In D. Morton-Thompson and A.M. Woods (Eds.), *Development Geology Reference Manual* (pp.76-82). Tulsa, Oklahoma: The American Association of Petroleum Geologists.

Young S. and Ramses G. (2006). D*rilling performance and environmental compliance - resolution of both with a unique water-based fluid.* Paper SPE 103967 presented at the SPE/IADC Indian Drilling Technology Conference and Exhibition, Mumbai, India. doi: 10.2118/103967-MS

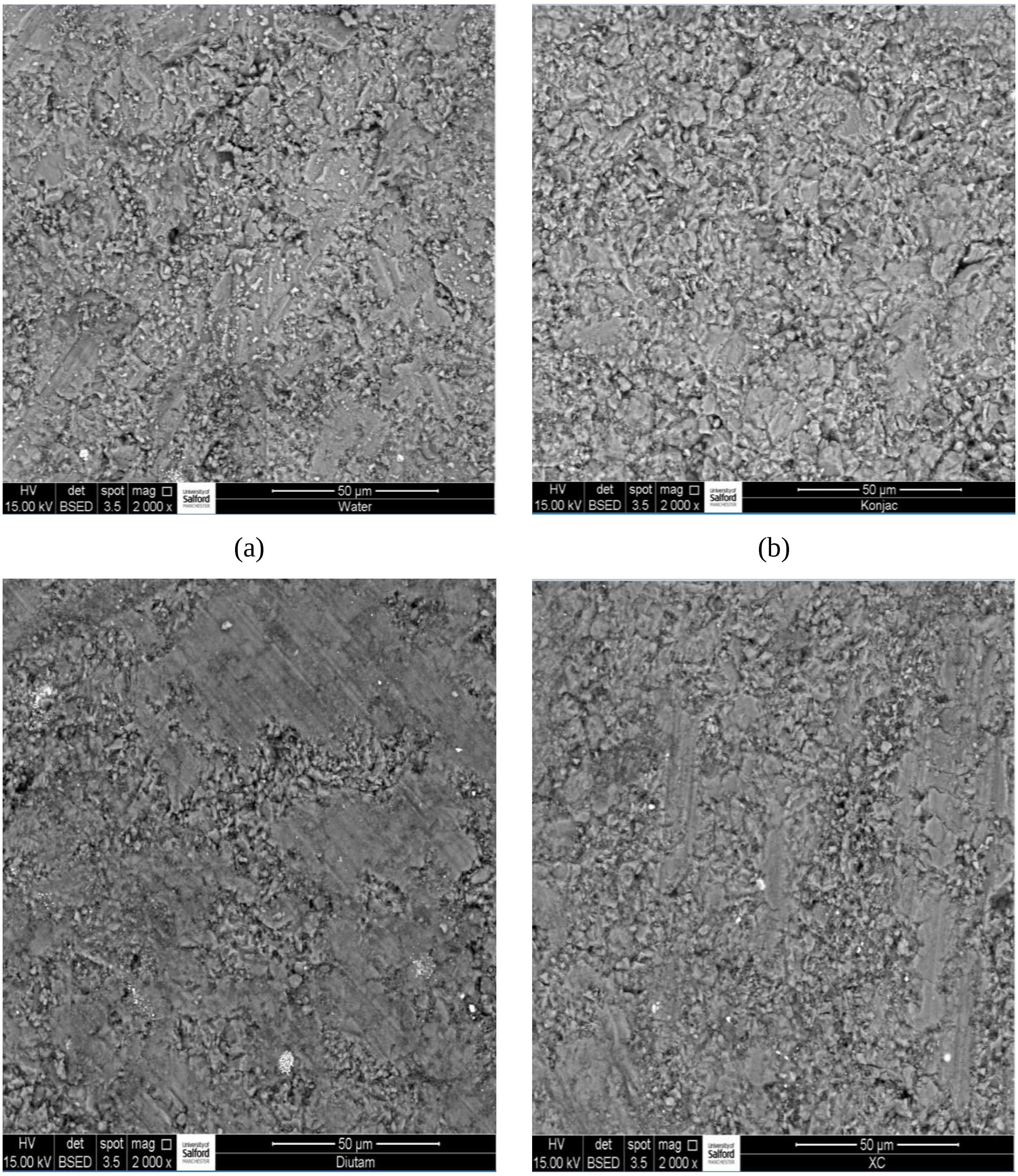
Zhang M. X., Jiang C.G., Xuan Y., Wang L., and Huang B.X. (2016). *The development of a viscosifier for clay-free and water-based drilling fluid with high density and high temperature resistant.* Paper IADC/SPE 180662 presented at the IADC/SPE Asia Pacific Drilling Technology Conference, Singapore. doi: 10.2118/180662-MS

Zuvo M., Bjornbom E., Ellingsen B, Downs C. J., Kelley A., and Trannum C.H. (2005). *High-resolution environmental survey around an exploration well drilled with formate brine in the Barents Sea, Norway.* Paper SPE 94477 presented at the SPE/EPA/DOE Exploration and Production Environmental Conference, Galveston, Texas, USA. doi: 10.2118/94477-MS

Appendices

List of Appendices

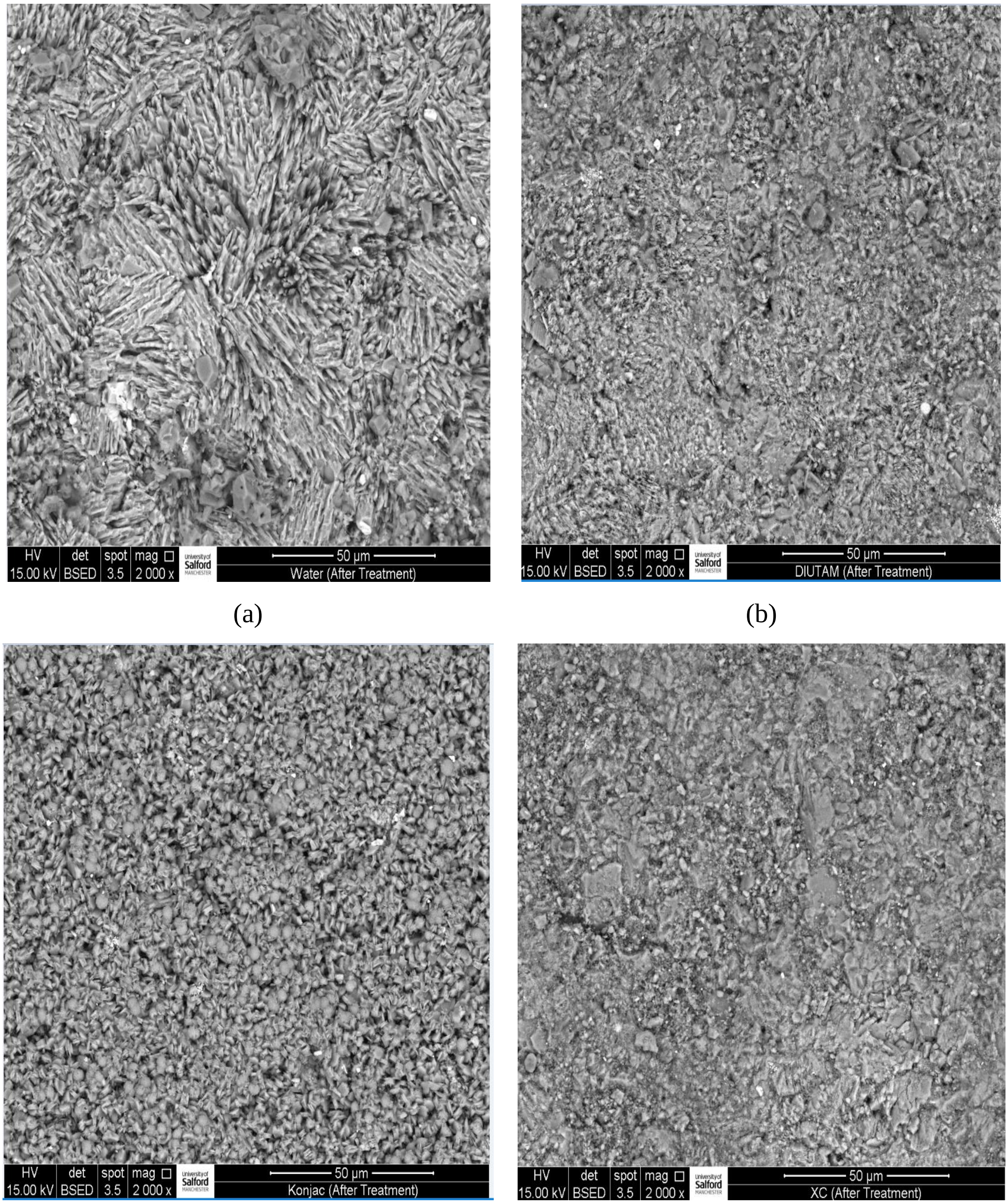
1. Appendix A: Scanning electron microscope (SEM) photos and energy-dispersive X-ray spectroscopy (EDX)
2. Appendix B: Journal publications



(a) (b)

(c) (d)

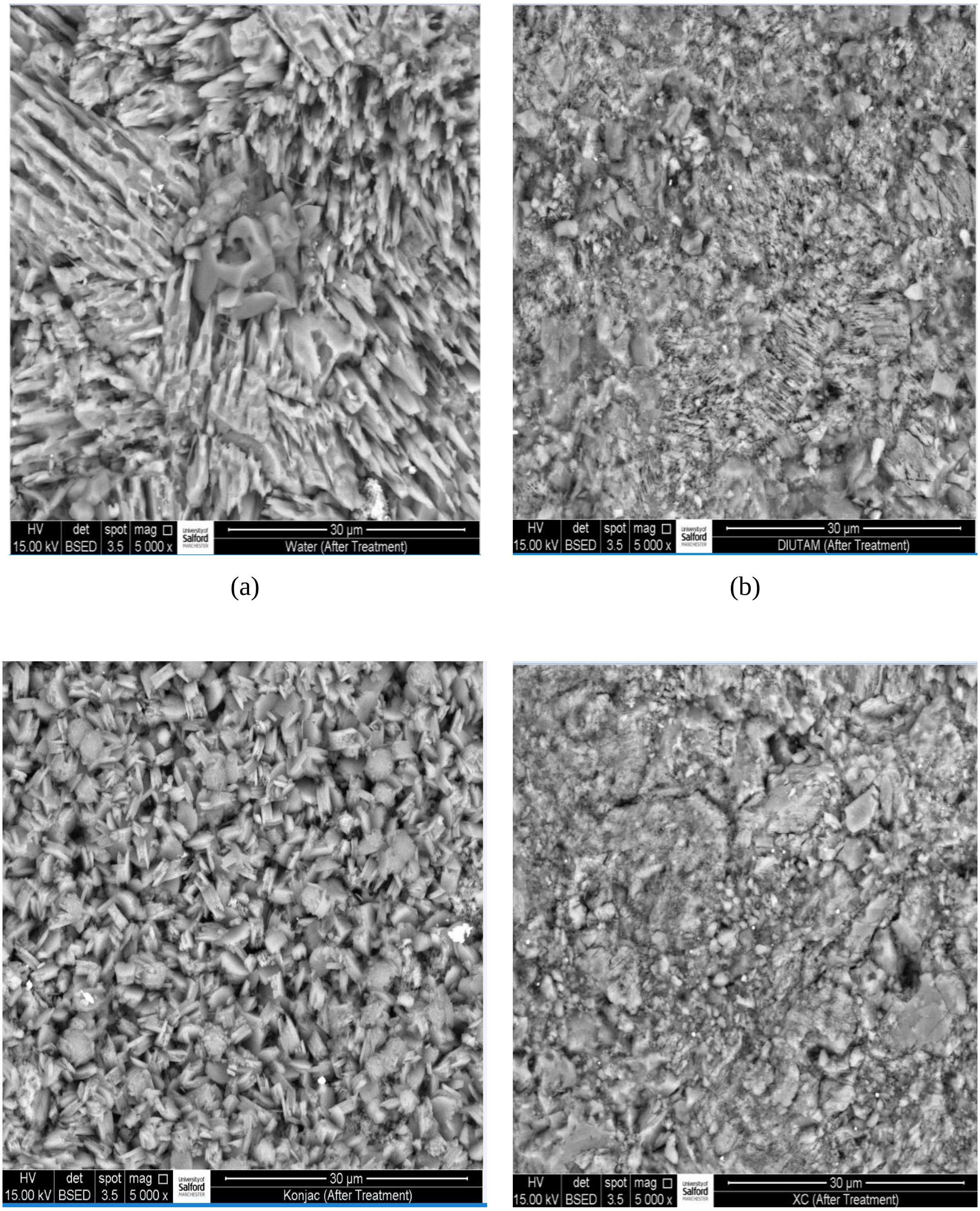
Figure A-1: Sufaces of shale samples before aging in fluids: (a) Shale sample before aging in freshwater; (b) Shale sample before aging in an inhibitive fluid formulated with konjac gum; (c) Shale sample before aging in an inhibitive fluid formulated with diuatn gum; (d) Shale sample before aging in an inhibitive fluid formulated with xanthan gum



(a) (b)

(c) (d)

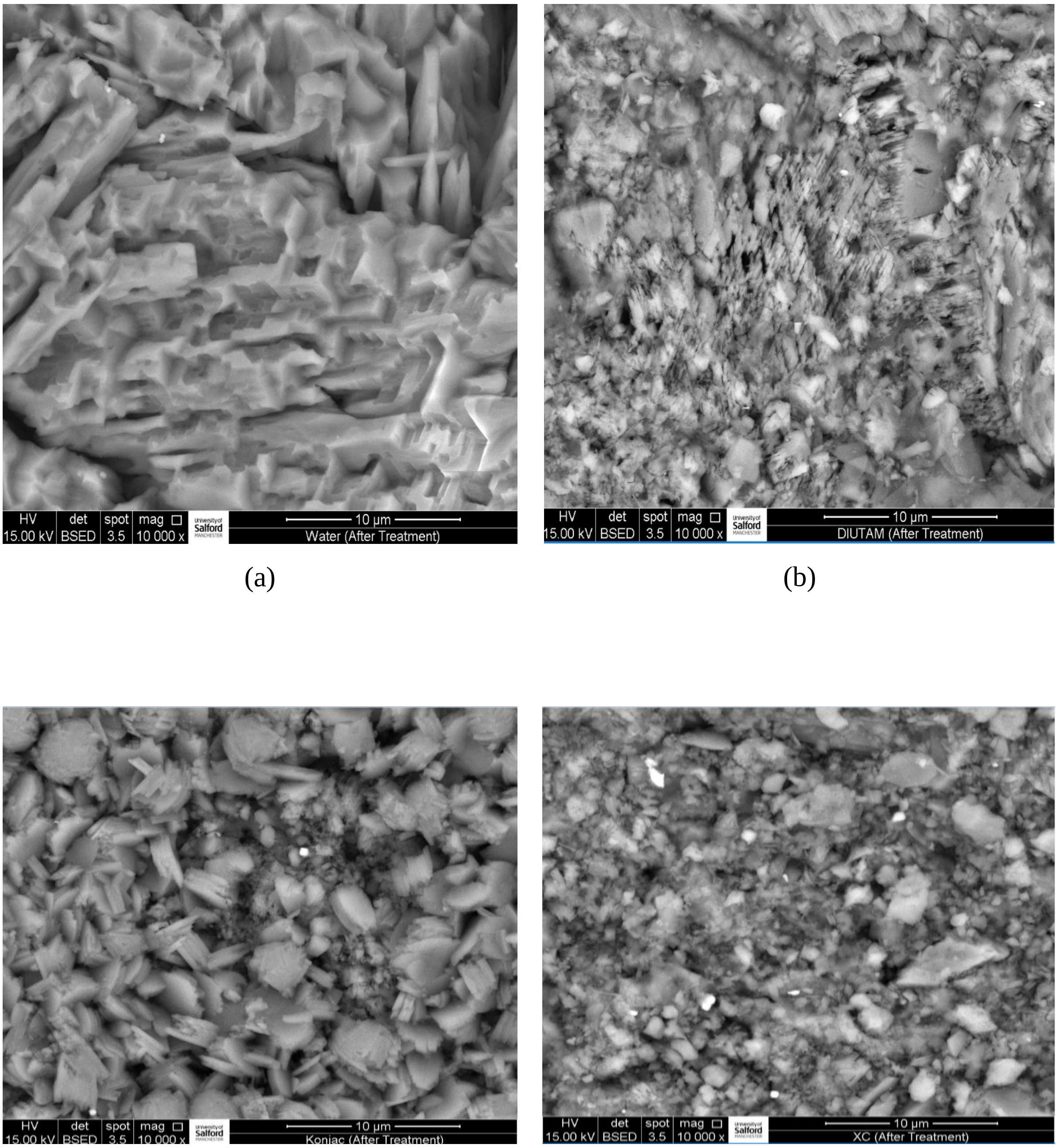
Figure A-2: Shale samples aged in fluids (SEM photos - Mag. 2000x): (a) Shale sample after aging in freshwater at 120°C; (b) Shale sample after aging in an inhibitive mud formulated with diutam gum at 120°C for 16 hours; (c) Shale sample after aging in an inhibitive mud formulated with konjac gum at 120°C for 16 hours; (d) Shale sample after aging in an inhibitive mud formulated with xanthan gum at 120°C for 16 hours



(a) (b)

(c) (d)

Figure A-3: Shale samples aged in fluids(SEM photos - Mag. 5000x): (a) Shale sample after aging in freshwater at 120°C; (b) Shale sample after aging in an inhibitive mud formulated with diutan gum at 120°C for 16 hours; (c) Shale sample after aging in an inhibitive mud formulated with konjac gum at 120°C for 16 hours; (d) Shale sample after aging in an inhibitive mud formulated with xanthan gum at 120°C for 16 hours



(a) (b)

(c) (d)

Figure A-4: Shale samples aged in fluids(SEM photos - Mag. 10,000x): (a) Shale sample after aging in freshwater at 120°C; (b) Shale sample after aging in an inhibitive mud formulated with diutan gum at 120°C for 16 hours; (c) Shale sample after aging in an inhibitive mud formulated with konjac gum at 120°C for 16 hours; (d) Shale sample after aging in an inhibitive mud formulated with xanthan gum at 120°C for 16 hours

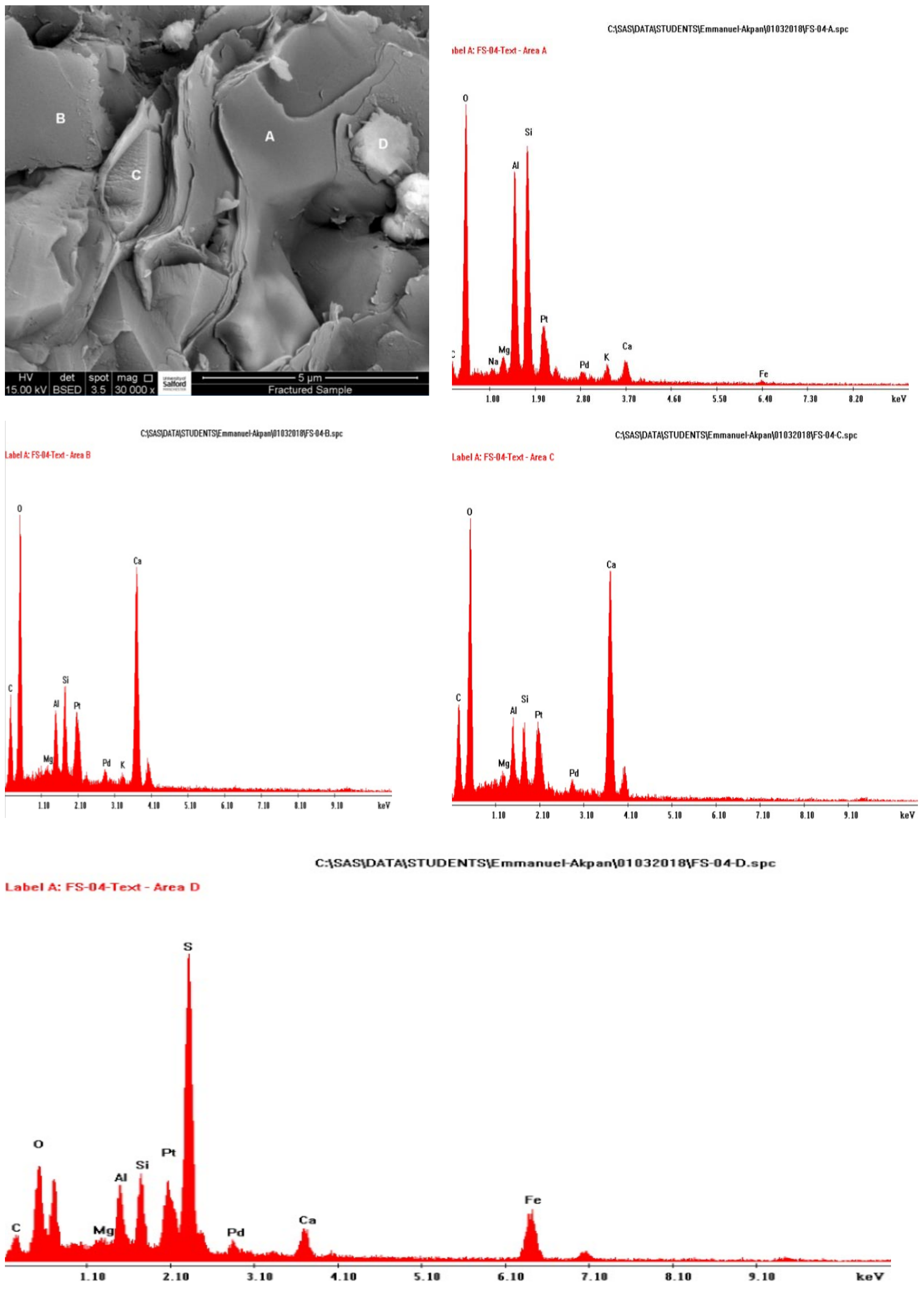


Figure A-5: EDX of shale sample showing the presence of illite, smectite, calcite, and quartz.

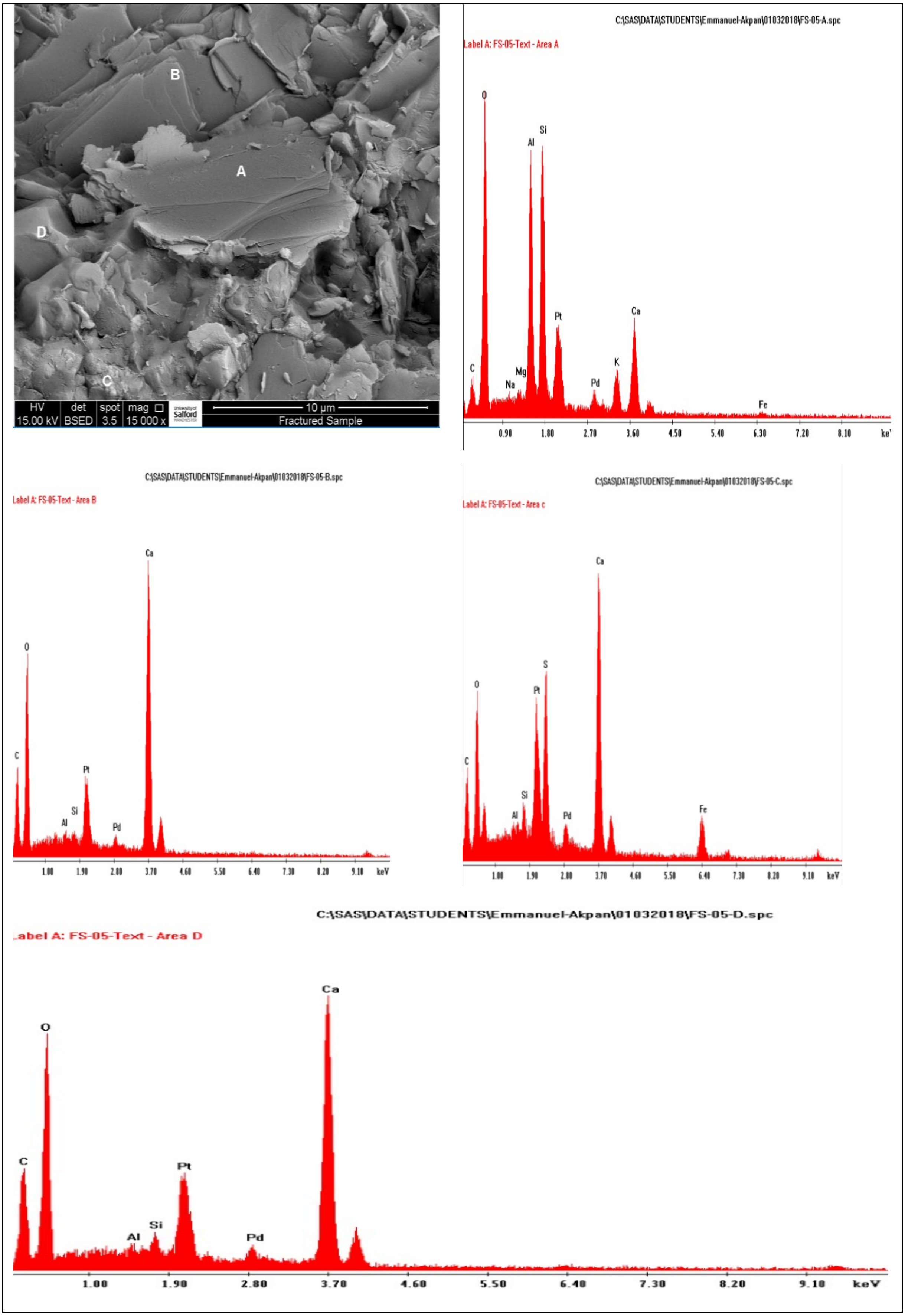


Figure A-6: EDX of shale sample showing the presence of illite, smectite, calcite, and quartz.