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Developing novel high performance to drilling muds for applications in high pressure and high temperature oil wells.

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Abstract

In the present research, a novel organo-layered mixed metal layered double hydroxide material (based on an Mg/Al layered double hydroxide (LDH) modified with adamantane acid and described in US Patents: 2017 / 267910 A1[1], 2017, US 2018 /10,087,355 B[2], US2019/0055451A1[3]) has been studied for use in an invert emulsion drilling fluid for applications in high pressure high temperature (HPHT) wells. In particular, the ability of the new material to maintain the rheological properties and emulsion stability of the formulated fluid under high pressure and high temperature conditions has been investigated. The experimental phase has assessed and compared two rheology modifiers, firstly the novel organo-LDH rheology modifier developed by the Greenwell group, Durham University, and jointly patented with Saudi Aramco, and secondly a commercial rheology modifier (Bentone 42).

The drilling fluid formulations used to compare and evaluate the performance of the new material [1,2,3] were based on commercial formulations, which usually utilised Bentone 42 as the rheology modifier. Bentone 42 was compared to the new material in a range of formulations in order to observe the compatibility of the new rheology modifier with all the formulation constituents. Also, performance of the new organophilic layered mineral rheology modifier based on the Mg/Al LDH was assessed over a concentration range to determine the rheological profile at low shear rate, in order to define the further work needed to investigate the performance of this new rheological modifier.

This research project assessed the resistance to degradation and the rheological behaviour of the formulation with the new rheological modifier[1,2,3]. Experiments were undertaken drawing attention to rheological behaviour, such as rheological measurements in low temperature low pressure and high pressure high temperature conditions, focussing on yield point, plastic viscosity and thixotropy properties. Also, some experiments were conducted to evaluate the contamination tolerance for both the new and commercial rheological modifiers. Emulsion stability with the new rheological modifier was measured in oil, a colloidal suspension and with all the formulation compounds from the drilling fluid evaluated. The suspension weighting capacity was measured with a sag test correlating with the yield point property. Finally, a fluid loss test was undertaken to assess if the new rheological modifier can minimize fluid loss.

This thesis demonstrates the rheological behaviour and the stability of the new rheological modifier at different temperatures and pressure, and the concentration dependent interaction of a rheological modifier in a drilling fluid formulation. Although, the new rheological modifier shows instability in the formulation[1,2,3], the work undertaken here-in aids define future work required to develop this new rheological modifier. This will lead to more knowledge about the material, such as particle size

dispersion and ion exchange of the alkaline-earth diamondoid compound for the new rheological modifier, and optimization of the drilling fluid formulation cited in the patents mentioned above, which might influence the material behaviour to develop viscosity and suspension capacity.

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Declaration

The work in this thesis was sponsored by CONACYT (The Mexican National Council for Science and Technology) and SENER (Energy Secretariat from Mexican Government).This research is based on research carried out at in Prof. Chris Greenwell Research Group, with a material developed from Durham University and patented by Saudi Aramco, in the Earth Sciences and Chemistry Department Durham, England. No part of this thesis has been submitted elsewhere for any other degree or qualification and it is all my own work and part of my professional background in the industry in drilling fluids, unless referenced to the contrary in the text.

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Chapter 1

Introduction

1.1 Background

Oil and gas continues to be used in a wide variety of essential services such as power generation, transportation fuels, and consumer products[4]. Driven by an increasing population and purchasing power of individuals in developing economies, total global energy in oil and gas consumption is expected to increase[5] by 34% from present day to 2030. According to the Organization for Economic Cooperation and Development (OECD), demand has rapidly grown since 1990 and a higher oil and gas price has resulted over the last years. This is due to a progressively declining trend in locating new oil and gas reservoirs, and the industry is shifting to high risk and challenging, and more extreme conditions to meet global energy demands[4]. Mainly, this demand has led to the development of complex subsea/deepwater and ultra-deepwater oil and gas fields.[5]

The extreme conditions encountered can be classified into (i) deep-water wells and (ii) high pressure and high temperature wells due to the fact that these kind of wells require different well plan considerations and special tool requirements for their exploration[6]. Some governments have provided the oil and gas contractors with an incentive scheme, such as in the case of the UK and Norway governments[5]. The areas with a major number of these types of fields are the deep-water Gulf of Mexico continental shelf[7,8], northern India[9], Saudi Arabia[10] and Brunei[11]. Also, Indonesia, Thailand and Northern Malaysia[12] have increased the number of fields under development with high pressure and high temperature conditions[11, 9].

Currently, one of the challenges for oil and gas exploration is working under HPHT conditions, which may be defined as wells with temperatures greater than 150 °C (300 °F) and a bottom hole pressure more than 69 MPa (10,000 psi) [13].Such extreme conditions, when encountered during drilling operations, cause severe complications to the fluid system and limitations to annular pressure while drilling (PWD), and measure while drilling/logging while drilling (MWD/LWD) tools[4].

Drilling fluid selection and performance is related either directly, or indirectly, to almost every drilling problem[14]. The successful completion of an oil well and its costs will be dependent directly on the drilling fluids performance. The cost of drilling fluid depends on the drilling fluid system, it might be relatively low cost for a water base drilling fluid system, or relatively expensive if it is a synthetic base drilling fluid system. The correct fluid choice and the appropriate maintaining of its properties will have a big impact on the total well costs. For example, the number of rig days required to drill the well will depend on the rate of penetration of the bit[15] (ROP), and the delays caused by operational problems such as cavings in shales[16], stuck drill pipe[14,15,17], loss of circulation[14,15,17] etc. These kinds of problems are directly influenced by the physical-chemical properties of the drilling fluids[17].

The design of the drilling fluids programme is specific for every lithology to be drilled, which may encompass carbonates, sand, and shale sections. The wrong selection and formulation of a drilling fluid for the wellbore could provoke formation damage in the reservoir. For this reason, drilling fluids plays an important role for the success of drilling operations, which must be accomplished with appropriate characteristics for exploring and evaluation of hydrocarbon reservoirs with regard to the seismic interpretation model.

HPHT wells constitute a challenge for drilling fluid (called "muds" in the industry) performance owing to the kind of issues which will be present during the drilling operations[4]. Contractors prefer to drill with oil-based muds (OBM), rather than water based mud (WBM), in HPHT conditions, since the OBM develop a better viscosity profile and have superior thermal stability and high shale inhibition properties[18].

However, OBM is not exempt from suffering degradation[19]. For this reason, the operators are increasingly focusing on developing additives to enhance the rheological performance of drilling fluids under HPHT conditions[20]. Sometimes, oilfield service companies find difficulty in avoiding degradation or disintegration of materials into the fluid system[20,21]. This is because a lot of phenomena occur under the extreme environments encountered in the bottom hole area, which tend to cause emulsion instability[22]. For this reason, every compound which may be added to the drilling fluid system needs to be characterized and analysed under different wellbore conditions in order to avoid any reactivity among the diverse compounds within the formulation. Emulsion instability might cause alteration in thousands of cubic meters of drilling fluid in the mud pits and, as a consequence, oilfield service providers would lose significant revenue trying to remediate an emulsion breakdown.

Materials for drilling fluids which can resist temperature variation and reach high temperature while maintaining their properties are continually researched by the industry. The development of novel additives which can resist temperatures up 150 °C (300 °F) for high pressure and high temperature operations are required to ensure high performance during drilling [23–25].

Many recent developments are based on nanoparticles[26–31], owing to the fact that nanoparticles co-deliver technical and economic benefits including increased rheological performance, reduced formation damage and increased thermal stability during the drilling operation[24], which will be discussed more throughout this thesis.

1.2 Outline of introduction

The remainder of this introduction seeks to give an overview of high pressure and high temperature drilling challenges, the classification of high pressure and high temperature that oilfield service companies use, with their restrictions on design in equipment and tools, effects of HPHT on drilling fluids properties and the arising drilling fluids challenges for the Gulf of Mexico. Finally, the aims and objectives of this thesis are stated.

1.3 Drilling Operations in High Pressure and High Temperature conditions

1.3.1 High Pressure High Temperature Drilling Challenges

Shadravan et al.[9] mentions that some studies have shown that the U.S extended continental shelf (ECS) contains more than 75% of undiscovered reservoirs. Mainly it was noted that these kind of reservoirs, with their high pressure-high temperature conditions would be present in the U.S. extended continental shelf and deep-water fields in the Gulf of Mexico.

HPHT conditions represent a significant challenge for the drilling contractor, owing to the need to undertake development of innovative technologies and materials for HPHT drilling. The exploration of high pressure and high temperature fields needs specific rig requirements in order to manage the high pressure that could be present during drilling operations. These rigs can be more expensive than the conventional drilling rigs due to the fact some of the requirements are from hook load, mud pumps, drill pipe and surface mud capacity[11]. These type of wells require higher density drilling fluids[21], which depend on the operational window boundaries of the lithology being drilled.

The temperature and pressure encountered in these kinds of wells may also affect some components from the tools used during drilling operations. If the wellbore exceeds the operational work limits for the tool, components of the tool will be affected and, as a consequence, an operational stop may be required to change the bottom hole assembly (BHA). These conditions become a challenge for MWD/LWD/PWD tools,[32] which play an important role during the drilling operations because they are responsible to control the trajectory of the wells and to record pressures, temperature, depth during the drilling operations. Therefore, it is necessary to develop fluids which can allow control of the thermal effects in the system to maintain cooler LWD/MWD[9], and to avoid non-productive time (NPT) for replacement of a LWD/MWD tool during drilling operations.

Under some circumstances during drilling operations the tool may fail and it becomes impossible to accurately follow whether equivalent circulation density (ECD) has developed along the whole depth interval. The probability to get a gas influx or water influx from the drilled formation becomes higher, because the drill pipe is drilling the formation without any real-time record to react immediately to when the ECD exceeds the formation pressure, or if the well needs more density above pore pressure (under down-hole conditions).

HPHT wells are invariably considered as having high operational costs, mainly because HPHT conditions are encountered in deep-water[8]. Hence, deep-water projects represent high costs for the cost of the rig rental per day alone and adding the need to drill into extreme environments would affect the profitability of projects.

Drilling wells in HPHT conditions gives rise to a variety of problems during the operations, and for that reason these kind of wells are known as complex fields. Shadravan et al.[9] stated that the average drilling time of HPHT wells could be 30% longer than found in other kinds of drilling conditions, because of compacted formations[9]. Therefore, the main type of problems arising from HPHT or deep-water can be operational and mechanical ones.

The most common operational problems presented along the wellbore drilled are those such as: low rate of penetration (ROP) in the producing zone; a too narrow operational window inducing fracture of the formation; drilling fluid loss to the formation in the overpressure zone; mud storage due to hole ballooning; the solubility of methane and H_2S in oil based drilling mud[9].

In addition, an accurate well design is crucial for the development of fields in high pressure and high temperature environments because mechanical failure, or well design failure, can cause several issues for these complex fields and the complexity of these wells make this more prevalent[33].For these reasons, it is important to consider some aspects for the well design such as formation pressure prediction, casing setting depth, rheological properties for drilling fluids, hydraulics, bit selection and a correct selection of slurries and a good cementing design programme.

1.3.2 Classification of High Pressure High Temperature Operations

The definition on the classification of the field will depend on the region, the operator and the service company[32]. Most of the service companies and operators describe the range of pressure and temperature according to the operational working limits for their tools, equipment, fluids and cement[9].

For example, Payne et al.[32] reported that Offshore Magazine effected a review of 239 MWD/LWD tools from 12 different contractors with the objective to get a ranking for the MWD/LWD technology appropriate to operate under high temperature conditions.

The maximum operating temperature for the majority of MWD tools is 150 °C (302 °F), with just 23 tools rated for operations of 175 °C (347 °F). For that reason, companies have different operational work limits, where the classification for HPHT can be different for all of them.

According to Greenaway et al.[34] from Schlumberger company, as Figure 1.1 shows, HPHT conditions can be classified as those fields which have the bottom hole temperature of greater than 300 °F (149 °C) and a borehole pressure up to 10,000 psi (69 Mpa)[34]. To be considered ultra HPHT conditions, wells would need to develop temperatures in the range of 204.44 °C – 260 °C (400 °F - 500 °F) and a pressure range between 20,000 psi - 35,000 psi [35,21].Finally, for extreme HPHT, these include fields with borehole temperature in the range 260 °C - 315.55 °C (500 °F - 600 °F), and borehole pressure above 35,000 psi.

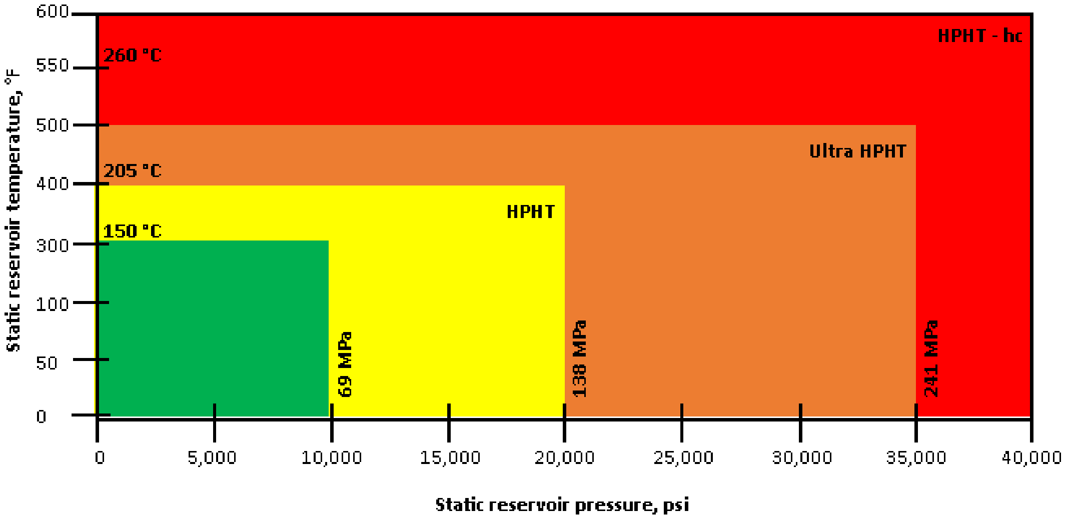

Figure 1.1HPHT Tiers. Modified from, Greenaway et al.[34]

Table 1.1 and Table 1.2 illustrate the different operational range of pressure and temperature classification considered by different oilfield service companies. As can be seen in the tables, there exists similarities between the different companies.

Table 1.1 Temperature Borehole (HPHT). Modified from Shadravan et al.[9]

Borehole Temperature

			Temperature			
HPHT Operation	Halliburton		Baker		Schlumberger	
	°F	°C	°F	°C	°F	°C
HP/HT	300-350	150-175	300-350	150-175	300-401	150-205
Extreme HP/HT	350-400	175-200	350-400	175-200	401-500	205-260
Ultra HP/HT	> 400	> 200	> 400	> 200	> 500	> 260

Table 1.2 Borehole Pressure (HPHT). Modified from Shadravan et al.[9]

Borehole Pressure

			Pressure			
HPHT Operation	Halliburton		Baker		Schlumberger	
	Psi	Mpa	Psi	Mpa	Psi	Mpa
HP/HT	10,000-15,000	69-103	10,000-15,000	69-103	10,000-20,000	69-138
Extreme HP/HT	15,000-20,000	103-138	15,000-20,000	103-138	20,000-35,000	138-241
Ultra HP/HT	>20,000	>138	>30,000	>207	>35,000	>241

1.3.3 The effect of Temperature and High Pressure on drilling fluids properties.

Gelation, syneresis, high fluctuating rheologies, loss of rheological properties such as the yield point, which can cause high sag levels for the weight material[35],are some of the typical problems faced by the invert drilling fluid present under high pressure and high temperature and ultra-high pressure and high temperature conditions[21,35]. These kind of issues can cause several well control problems. Mostly, the challenges to the invert emulsion drilling fluids are the thermal degradation of the emulsifier, wetting agents and fluid loss control additives. This cause gelation and syneresis in the system. These effects can occur because the invert emulsion suffers changes and becomes an unstable system, causing several problems during the drilling operations[35].The filter cake quality and thermal stability of the drilling fluid play an important role in the drilling fluid design, to avoid these kinds of problems occurring during the drilling operations. Due to the fact several problems may occur for drilling fluids under HPHT conditions, Table 1.3 mentions some of properties which might be helpful for drilling a HPHT campaign.

Table 1.3 The desired properties of the drilling fluid for optimum performance at HPHT condition. Modified from Shadravan et al.[9]

Drilling Fluid Properties	Required performance in HPHT wells
Plastic Viscosity	As low as reasonably possible to minimize ECD.
Yield Stress and Gel	Sufficient to prevent sag, but not so high as cause gelation, or high surge and swab pressures.
HPHT Fluid Loss	As low as reasonably possible to prevent formation damage and risk of differential sticking.
HPHT Rheology	Stable and predictable to control sag, gelation and ECD.
Compressibility	Must be known to estimate downhole pressures and ECD.
Stability to contaminants	Stable in presence of gas, brine and cement.
Gas Solubility	Needed for accurate kick detection and modelling.
Stability to Aging	Properties do not change over time under either static or dynamic conditions but in reality properties slightly, drop after dynamic aging and increase after static aging.
Solid Tolerance	Properties insensitive to drilling solids.
Weighting	Must be able to avoid sag of weighting material.

1.3.4 Drilling Fluid Challenges for High Pressure and High Temperature conditions in the Gulf of Mexico

One of the greatest challenges for oil and gas exploration in the Gulf of Mexico is the high temperature and high pressure found in deep water wells. The maximum temperature which has been recorded to categorize the HPHT wells offshore was between 150 ˚C and 190 ˚C. Shadravan et al.[9] examined conditions of US onshore and the Gulf of Mexico continental shelf operations, suggesting these are in the HPHT and Ultra HPHT deepwater gas/oil wells category, with pressures encountered up of 30,000 psi and temperature up to 260 ˚C (500 ˚F). However, in Mexico, there have not been reports of HPHT or Ultra HPHT conditions in deepwater fields. Arrieta et al. [7], reported of an ultra-deepwater area in Mexico with maximum temperatures only in the order of (55 ˚C - 70 ˚C) in the bottom-hole. More recent evidence from Ruiz[8] reveals records of ultra HPHT conditions in exploratory deepwater wells, recording pressures around 19,200 psi and temperatures around 205 ˚C (400 ˚F). If conditions approach even further extreme HPHT conditions, it could compromise the drilling operation. For this reason, it is important to explore alternatives to enhance drilling fluids in order to avoid degradation of additives under these HPHT conditions.

1.4 Aims

The overall aim of this study is to investigate the interaction of the MgAl LDH nanoparticles as rheological modifier in a synthetic oil base mud under conditions relevant to drilling operations, including high pressure and high temperature and to observe its rheological behaviour and stability with all the compounds encountered.

1.5 Objectives

The research described in this thesis examines the rheological behaviour of a new organophilic layered mineral rheology modifiers based on an Mg/Al layered double hydroxide (LDH) that has been modified with adamantane-1-carboxylic acid (MgAl-Ada LDH).[36] This material has previously been tested at small scale in an oil based mud, in a formulation cited in the patent US 2018 /10,087,355 B "Oil-Based drilling fluids containing an Alkaline-Earth Diamondoid compound as rheology modifier".[1], and US2019/0055451A1[3] "Layered Double Hydroxides for Oil-based drilling Fluids". The main aim of the research is to understand if the MgAl-Ada LDH performs well as a rheological modifier once it is formulated as a technical drilling fluid with the rest of the fluid additives in the formulation. Drilling fluids are considered as complex fluids, containing many different chemical compounds to provide the necessary properties to maintain drilling efficiency and without compromising the stability of the walls of the wellbore. Therefore, it is crucial for every new additive developed, which is added in a drilling fluid formulation, that it is possible to predict its behaviour under different formulations, shear rate, mixing time, pressure and temperature. This thesis examines the effect of stability and rheology of this formulation with the MgAl-Ada LDH material at low temperature and standard pressure, and at high pressure and high temperature.

Specific objectives are:

- To observe the rheological behaviour of MgAl Ada LDH at low shear rate in base oil and emulsions, comparing the performance to a commercial rheological modifier.
- To observe the dispersion of MgAl Ada LDH in non-aqueous solutions, comparing with a commercial rheological modifier.
- To determine an industry comparable rheological data set[*] from the oil based mud with both rheological modifiers, from different aging temperatures.
- To understand the capacity of the fluid formulated to hold solids and to shear thin, through assessing the gel strength[†] of the oil base mud with both rheological modifiers.

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[*] This experimental phase has been named as low temperature and low pressure conditions because the maximum pressure reached is 180 ˚F with a standard pressure conditions 100 kpa.

[†] This experimental phased was evaluated in standard pressure conditions 100 kpa.

- To assess the capacity of the fluid to form a filtercake to line the well bore will be assessed. The mudcake thickness will be tested through static filtration (HPHT) of the oil based mud with both rheological modifiers.
- To evaluate the HPHT performance of the fluid systems will be established. Rheological data set from the oil base mud with both rheological modifiers will be collected at different temperatures in a HPHT rheometer with a maximum pressure at 20,000 psi, before hot rolling and after hot rolling.
- To assess the impact of contamination on the rheological data set from the oil base mud with both rheological modifiers, a contaminant (fine particles representing cuttings) will be tested at different temperatures in a HPHT rheometer to assess the contamination tolerance[‡]. This will be tested at a maximum pressure at 20,000 psi.

1.6 Thesis Outline

The remainder of this thesis contains:

Chapter 2. A review of the function, types, physical-chemical properties and composition of drilling fluids, highlighting the importance for the rheological properties and the formulation to be calculated using them for their application in oil based-drilling fluids. Finally, a detailed description and discussion of the nanomaterials used, the layered double hydroxides (MgAl-Ada LDHs) properties and its potential to be a novel rheological modifier, is given throughout the chapters.

Chapter 3. A detailed description of the various materials used for the formulations tested in this thesis is given. A review of the operational temperature limits from the additives is given as well as the technical equipment for different tests, any special consideration for the measurements and methods used for the experiments is discussed.

Chapter 4. Initial results from the evaluation of the new rheological modifier interacting with oil and emulsion at low temperature and low pressure are presented.

Chapter 5. This is followed by the evaluation of the new rheological modifier interacting with the drilling fluid at low temperature and low pressure, selecting some tests from API 13B-2[89] standards for assessing of the nanoparticle behaviour such as rheological measurements, thixotropy, filtration loss and sag testing.

[‡] The tolerance contamination test is common to observe the drilling fluid stability under different contaminants. This test just was considered contamination by drilled solids. The most common contaminants present in drilling operations are cement, magnesium, carbon dioxide, hydrogen sulphide and oxygen.

Chapter 6. A rheological characterization of the new rheological modifier and the contaminant tolerance under HPHT conditions are presented.

Chapter 7. A final discussion of the potential for use of the new rheological modifier in oil-based drilling fluids, with conclusions and further work, is given.

Chapter 2

Drilling Fluids and Nanomaterials

2.1 Introduction

Drilling fluid technology has become increasingly sophisticated and requires strong physical chemistry knowledge to further understand the molecular behaviour of the materials when they are interacting with geological formations within the well, and the reactions that take place during the drilling of wells. The drilling operation can become complex, because there are different phenomena that occur in the bottom hole region[37].For this reason, it is important to understand the main roles that a drilling fluid plays in the wellbore and the technological gap that has developed according to the characteristics of the reservoir. In this Chapter 2, understanding of why the performance of a drilling fluid is crucial for the drilling operations, the types of drilling fluid system for different well requirements and the rheological model most commonly applied to fit the behaviour of drilling fluids are discussed.

2.2 Function of drilling fluids

The drilling fluids principal functions are:

1. To suspend drilling cuttings/ weight material when the circulation decreases, remove them from the bottom of the hole and transport them to the surface[38,39,16].
2. Corrosion control of drill string, casing and tubular mechanism[40,14].
3. To cool and clean the drill bit[41,39].
4. Prevent the inflow of fluids oil, gas or water from permeable rocks penetrated[41].
5. To control formation pressure and maintain well-bore stability[39,40].
6. To build a thin, low permeability filter cake to seal the formation penetrated by the bit throughout the wellbore[41].
7. To assist in the collection and interpretation of information available from drilling cutting, cores and electrical logs[41].
8. Minimize the formation damage in the reservoir.

2.3 Types of drilling fluids

Drilling fluids are classified according to their base fluid, such as water based muds, oil based muds and gas[41]. Figure A.1 and Figure A.2 in Appendix A show a classification of water-based drilling fluids and oil-based drilling fluids, respectively. Both figures show different variations of both systems. Each fluid system is designed for a particular well requirement. Every geological formation requires different specific drilling fluid properties. Figure A.1 and Figure A.2 attempt to express the variability of parameters on the drilling fluid system. This thesis will tackle just one invert emulsion system, which is a synthetic oil based drilling fluid.

2.3.1 Water-based muds

These kinds of fluids are the most commonly used in drilling operations due to their low cost in comparison with other systems, such as the oil based muds[42,43]. This system is integrated with solid particles which are suspended in water or brine[15]. Oil may be emulsified in the water, and the water is called the continuous phase[41].

2.3.2 Inhibitive Fluids

All those fluid systems which appreciably retard shale swelling and achieve inhibition through the presence of cations[17]; typically, sodium (Na^+), calcium (Ca^{2+}) and potassium (K^+) are termed inhibitive . Generally, K^+ or Ca^{2+}, or a combination of the two, provide the greatest inhibition to clay dispersion. These systems are generally used for drilling reactive, hydratable clays and sands containing hydratable clays[16]. The source of the cation is generally a salt. Disposal can become a major portion of the cost of using an inhibitive fluid[40].

2.3.3 Non-Inhibitive Fluids

All those fluids which do not significantly suppress clay swelling, are generally comprised of native clays or commercial bentonites with some caustic soda or lime[15]. They may also contain deflocculant or dispersants such as: lignite, lignosulfonates, or phosphates[44]. Native solids are allowed to disperse into the system until rheological properties can no longer be controlled by water dilution[17].

2.3.4 Polymer Fluids

All those fluids which rely on macromolecules, either with, or without, clay mineral interactions to provide mud properties, and are very diversified in their application[41]. These fluids can be inhibitive or non-inhibitive depending upon whether an inhibitive cation is used[45]. Polymers can be used to increase viscosity of fluids, control filtration properties, deflocculated solids, or encapsulate solids[15]. The thermal stability of polymer systems can range upwards to 400°F[16].

2.3.5 Oil base muds

The formulation of these fluids are composed of solid particles, which are suspended in oil. Water or brine is emulsified in the oil, the oil is the continuous phase and the water or brine is the dispersed phase[41,15].These systems are generally more expensive and require more environmental assessment in their use[43]. However, the most common uses for oil based muds (OBM) by the operator is to drill reactive shale formations, which OBM improve the wellbore stability for [17]. These kinds of OBM fluids have different special applications, such as high temperature and high pressure wells. They also minimize formation damage, and native-state coring[14]. This is because of their lubricity properties and their ability to prevent hydration of clays minerals[17,46]. Another reason for choosing oil-based fluids is that they are resistant to contaminants such as anhydrite, salt, and CO_2 and H_2S acid gases[45]. These kind of muds also have the advantage that they can be reconditioned and reused. The costs on a multi-well programme may then become comparable to using a water-based mud system[17].

2.3.6 Gas/liquids

This system is used when the geological formation is capable of producing water at significant flow rate[39]. Cuttings can be removed by a high velocity stream of air or natural gas and foaming agents are added to remove minor inflows of water[43].

2.4 Drilling Fluids Selection Criteria

The criteria for selecting the drilling fluid will be dependent on different factors from the drilling programme, such as location, mud making shales, geo-pressured formation, high temperature, hole instability, fast drilling fluids, rock salt, high angle holes, formation evaluation and productivity impairment[14,15,17,40]. The costs of drilling fluids can represent around 30%-70% from the total costs of a well from previous well planning experience. The costs considered for drilling fluids can vary due to the fact that during the operation various operational issues may arise, which can considerably increase the total cost for the well[16,39]. For example, application and performance, production concerns, logistics exploration concerns, environmental impact and safety. A detailed description for the recommendation of a drilling fluid system according to the well requirements can be found in Table A.1 and Table A.2, in Appendix A.

2.4.1 International guidelines for drilling fluid evaluation

The official guidelines used by all the oilfield service companies, detailing drilling fluid requirements and assessment are indicated in the American Petroleum Institute[47] (API) procedures. These are the recommended practices standardized for the procedures associated with the petroleum industry.

The recommended practices (RP) related to drilling fluids[§] are shown below:

ANSI ISO10416:2008/API 13 I[**], recommended practice for laboratory testing of drilling fluids.

API 13B-2[††] recommended practice for field testing of oil-based drilling fluids.

RP 13B-1, RP for field testing water-based drilling fluids.

RP 13D, RP on the rheology and hydraulics of oil-well drilling fluids.

RP 13J, Testing of heavy brines.

RP 13 L, RP for training and qualification of drilling fluid technologies.

RP 13M, RP for the measurement of viscous properties of completion fluids.

RP 13 C, RP on drilling fluids processing systems evaluation.

SPEC 13A, Spec for drilling fluid materials.

API RP 13K, Recommended practice for chemical analysis of Barite.

ASTM D422, Standard test method for particle size analysis of soil.

Physical and Chemical Properties of Fluids

2.5 Physical and chemical properties of fluids

During the drilling operations, the monitoring of physical and chemical properties of a drilling fluid is crucial for optimal operation, due to the fact that any parameter change in the well can cause instability of the drilling fluid emulsion and potentially affect the wellbore integrity. For this reason,

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[§] These industry standard practices are available online under purchase for single user copy: https://www.api.org/products-and-services/standards/purchase

[**] API 13 I is used to follow the correct protocol in the laboratory to undertake the experiments.

[††] API 13B-2 is used through the experiments to meet the criteria for this international standard for oil-based drilling fluids.

these properties usually receive the greatest attention by the operator to avoid the potential total loss of the wellbore during the drilling process.

2.5.1 Density

It is one of the most important properties to manage when drilling a well. The weight of a mud provides a hydrostatic pressure between the wellbore walls and the mud column. The mud density balances the formation pressure and maintains the wellbore stability. The ROP is affected by this property during drilling operations. ROP decreases as the pressure differential across the rock face increases[14]. The density programme in the well will depend on the operational window designed for the well[‡‡]. This is designed considering the pore pressure and fracture pressure of the formation, where the mud density needs to stay within the pressure limits for well control and wellbore integrity[48]. The success of drilling a wellbore will depend on a density high enough to control formation fluids, but not so high as to induce a fracture[46,49, 48].

2.5.2 Filtration

Filtration occurs when a permeable formation is exposed to a drilling fluid at a pressure higher than the formation pressure[14]. This pressure generates filtrate flow into the rock and deposits mud solids on the wall of the borehole[41]. The filtrate invasion from drilling fluid through the rock and the filter cake deposition are issues of most concern to the operators during the drilling operations, as these cause problems in cementing jobs and formation damage[40]. There are two types of filtration test: static[§§] and dynamic,[16] which measure the quantity of oil and the amount of solids left. The relationship between the methods is that static filtration occurs when the drilling fluid in the wellbore is static and the dynamic filtration when it is circulating[50]. The fluid velocity developed during the drilling fluid circulation through the annular space tends to erode the mud cake, even as it is being deposited, on permeable formations[14].

2.5.3 Alkalinity

An excess of alkalinity is a desirable property to maintain the emulsion stability[41,40]. This can neutralize the acid gases such as hydrogen sulphide and carbon dioxide[15], which might be present in some geological formations during the drilling operations.

[‡‡] High density of drilling fluids used to be common for the High Pressure and High Temperature operations.

[§§] The filtration tests will be analysed in static conditions.

2.5.4 Solids

The level of solids in the drilling fluid is a great concern during operations for the operators. The rheological and filtration properties[16] depend directly on the quantity, type and size of suspended solids. During the drilling operations the low-specific solids level must to be held below (4- 6%) in total volume to avoid effect of those properties and decline in ROP[45,39,41]. Generally, a drilling fluid is a mix of water or oil with a clay. Other products are added to get a good performance in the system of interest. Drilling fluids are comprised of two phases, solid and liquid. The liquid phase can be; water, oil, liquid surfactants and the solid phase can be divided in two forms such as, desirable solids (high specific gravity) and undesirable solids (low specific gravity)[45]. The high-specific gravity solids are all the materials which are incorporated into the drilling fluid such as weighting materials; barite, bentonite and calcium carbonate and some cases loss of circulation additives[45]. The low-specific gravity solids[***] are contaminants, such as drilled solids[16].

2.6 Rheological properties for drilling fluids

2.6.1 Rheology

Rheology describes the deformation of matter under the influence of stresses[16,51],where matter can be either solids, liquids or gases. Ideal solids are deformed elastically[44] and the energy required for the deformation is fully recovered when the stresses are removed[15]. Ideal fluid such as liquids and gases deform irreversibly when they flow[52]. The energy required for the deformation is dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses[53]. Real solids can also deform irreversibly under the influence of forces of sufficient magnitude as creep and flow[51]. The properties of flow can be analysed by different techniques. For example, the time measurement flow through a capillary, measuring the force necessary to rotate a cylinder at given angular velocity through a fluid, or measuring the time for a falling sphere to move through a fluid[51]. Absolute viscosity[†††] is usually measured by the rotating cylinder technique[52].

2.6.2 Viscosity

The viscosity of a drilling fluid plays an important role in providing suspension of solids in the wellbore, including the hole cuttings from the wellbore[15]. The viscosity is a function of all of the rheological properties of the drilling fluid[45]. The viscosity values will be related to the cleaning of the well. The optimization of hydraulic properties in drilling fluids is directly influenced by the viscous

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[***] The Hymod Prima Clay will be used to simulate the incorporation of drilled-solids in the drilling fluid formulation for developing the laboratory tests.

[†††] The absolute viscosity at high shear rate and low shear rate will be measured through the experiments.

value, which guarantees a good cleaning in the wellbore. The traditional units of viscosity are dyne-second/centimeter^2, which is termed poise. Since one poise represents a relatively high viscosity for most fluids, the term centipoise (cP) is normally used. A centipoise[‡‡‡] is equal to one-hundredth of a poise or one millipascal-second, shear stress with τ (lb/100ft^2), and shear rate (s^{-1}).

$$\mu = \frac{\tau}{\dot{\gamma}} \tag{1.1}$$

For non-Newtonian fluids, the relationship between shear stress and shear rate is defined as the effective viscosity[17]. However, the effective viscosity of a non-Newtonian fluid is not constant. The most common viscosity measurements evaluated in the oil field in order to provide a good rheological condition to the wellbore are shown below[15].

2.6.3 Shear stress

Shear stress[§§§] is an applied force (F), acting over an area (A), causes the layers to slide past one another as is shown in Figure 2.1. However, there is a resistance, or frictional drag, force that opposes the movement of these plates[17] .This resistance or drag force is called shear stress (τ). Additionally, the fluid layers move past each other easier than between a pipe wall and fluid layer[52]. Therefore, we can consider a very thin layer of fluid next to the pipe wall as stationary[50, 14].

$$\tau = \frac{Force(F)}{Area(A)} \tag{1.2}$$

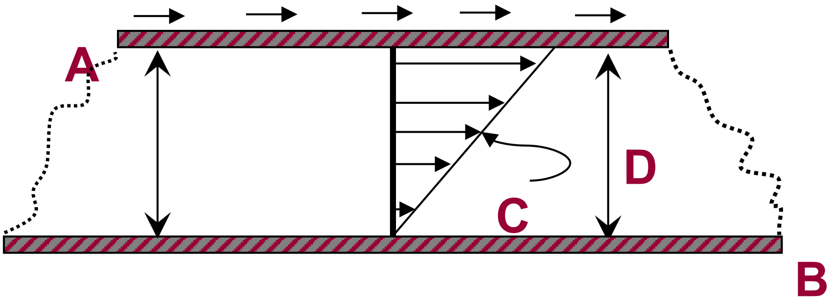

Figure 2.1 Parallel plates showing shear rate in fluid-filled gap as one plate slides past another. Adapted from American Petroleum Institute API 13 D[48].

A is the moving plate with a velocity e.g. 1.0 cm/s

B is the stationary plate.

C is the velocity profile.

D is the velocity gradient, velocity divided by height, ΔV/h, and 1.0 cm/s/ 1cm= 1 s^1.

[‡‡‡] The viscosity for drilling fluids in the Oil and Gas industry is reported in centipoise units (cP).

2.6.4 Shear rate

Shear rate is a velocity gradient measured across the diameter of a pipe or annulus[50]. It is the rate at which one layer of fluid is moving past another layer[17,16].Where (*dv*) is the velocity change between fluid layers and (*dr*) is the distance between fluid layers.

Shear rate ($\dot{\gamma}$) is defined as:

$$\dot{\gamma} = \frac{dv}{dr} \quad \frac{ft/sec}{ft} = \frac{1}{sec} = sec^{-1} \tag{1.3}$$

2.6.5 Plastic viscosity

This a function of the viscosity of the liquid phase and the volume of solids contained in a mud[40]. Plastic viscosity increased if the volume percent of solids increases, or if the volume percent remains constant, and the size of the particle decreases[17]. Decreasing particle size increases surface area, which increases frictional drag[45]. Plastic viscosity can be decreased by decreasing solids concentration or by decreasing surface area[17]. Also, plastic viscosity values can be increased by presence of water-soluble polymers used for fluid-loss control, saturated salt water and oil muds[40].

The plastic viscosity in the drilling operations is related directly with the ROP. If plastic viscosity is decreased, it will improve the rate of penetration (ROP). If there is an increase of plastic viscosity during the operation, this is an indicator that the hole cleaning will not be good enough[40]. Figure 2.2 shows the minimum and maximum range of plastic viscosity according to the mud weight for a water based mud. The plastic viscosity is commonly known in the oil and gas industry with the abbreviation of PV. However, it will be used as (μ_p), which is calculated by measuring the shear rate and stress of the fluid. These values are derived by using a Fann 35 viscometer, which is a rotating-sleeve viscometer[14]. The speed of rotation (rpm) is analogous to the shear rate[16]. It can be obtained by the subtraction of the dial reading from the Fann 35 viscometer at 600 rpm (θ600) and 300 rpm (θ300). More details about this viscometer and its use will be given in Chapter 3.

$$\mu_p = \theta 600 - \theta 300 \tag{1.4}$$

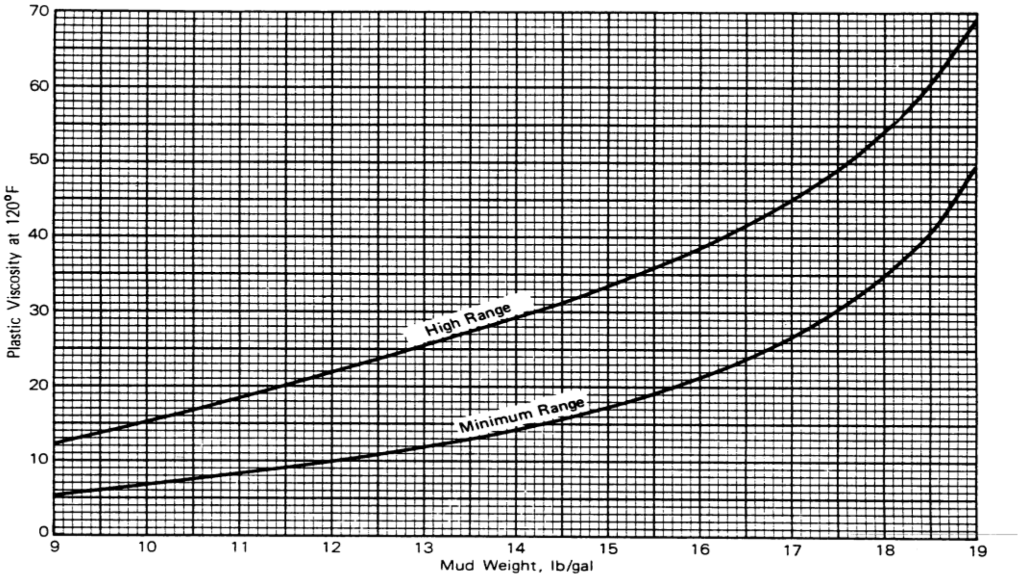

Figure 2.2 Plastic viscosity (cP) of water base mud vs mud weight. Adapted from Annis Max et al.[40]

2.6.6 Apparent Viscosity

This viscosity can be measure by the Fann 35 viscometer at 300 rpm (θ300). It can be obtained by dividing the dial reading[16] at 600 rpm (θ600). Generally, it is known with the abbreviation VA. It will be used as (μ_a) where:

$$\mu_a = \frac{\theta\ 600}{2} \tag{1.5}$$

2.6.7 Yield Point

Yield point well known in the industry as YP, it will be used as (τ_y).This is a rheological parameter also obtained from the viscometer[15] and is the force required to start the flow from a fluid which is stationary or gelled, and is independent of the time. Therefore, it can be related with the Bingham plastic model[14,16]. Figure 2.3 shows the yield point range considered as optimum range values for a specific mud weight. It can be obtained by the subtraction of the dial reading from the Fann 35 viscometer at 300 rpm (θ300) and (μ_P).

$$\tau_y = \theta 300 - \mu_P \tag{1.6}$$

$$\tau_y = (2 \text{ x } \theta 300) - \theta 600 \tag{1.7}$$

For yield point measurements at low shear rate (LSRYP), Equation 1.7 may be modified by replacing the high shear rate to low shear rate as:

$$\text{LSRYP} = (2 \text{ x } \theta 3) - \theta 6 \tag{1.8}$$

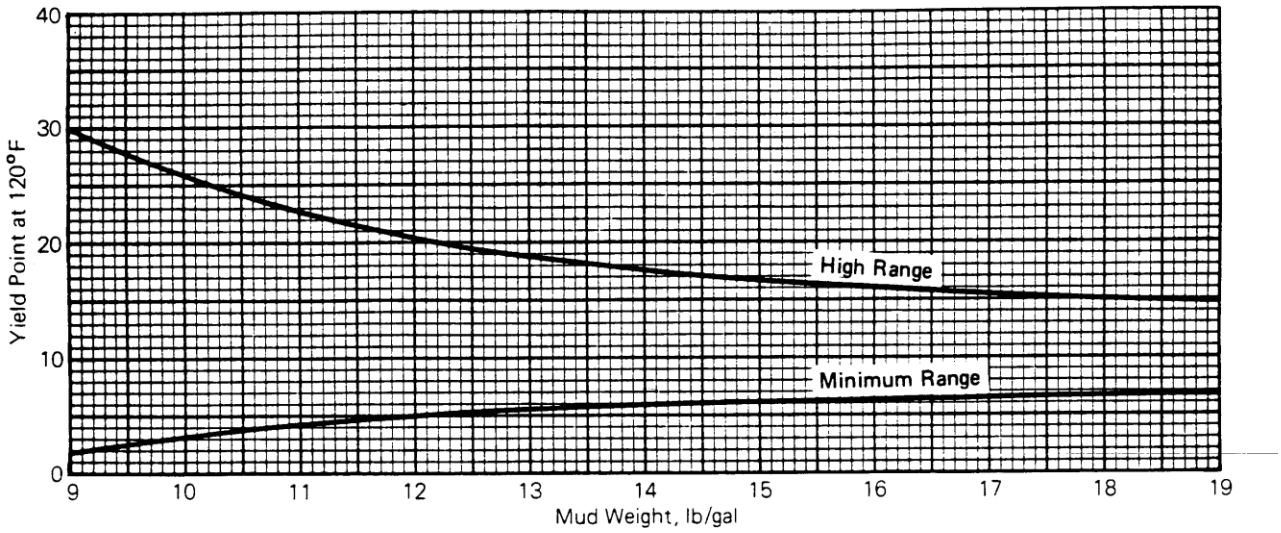

Figure 2.3 Yield point (lbf/100 ft^2) of water base muds vs mud weight. Adapted from Annis Max et al.[40]

2.6.8 The effect of thixotropy on drilling muds

If the gel strength of a mud is measured immediately after being sheared, and repeatedly after increasingly longer periods of rest, the values obtained will be generally found to increase at a decreasing rate until a maximum value is reached[41,14]. This behaviour is a manifestation of the phenomenon of thixotropic, originally defined by Freundlich as a reversible isothermal transformation of a colloid to a gel[17]. Thixotropic fluids are fluids with a memory[38]. As this and yield point are both measures of flocculation, they will tend to increase and decrease together[14]. The Fann 35 viscometer can be used to measure the gel strengths[****], at 10 seconds and 10 minutes in order to evaluate strength of attractive forces (gelation) in a drilling fluid under static conditions. Excessive gelation is typically caused by a high solids concentration leading to flocculation[15,17]. Signs of rheological problems in a mud system often are reflected by a mud's gel strength development with time[16]. As can be seen, Figure 2.4 reveals the desirable and undesirable gel strength for a drilling fluid. This illustrates that when there is a wide range between the initial and 10 minutes gel readings they are called progressive gels[15]. This is not a desirable situation. If initial and 10 minutes gels are both high, with no appreciable difference in the two, these are high flat-gels, which are also undesirable. The magnitude of gelation with time is a key factor in the performance of the drilling fluid[16]. Gelation should not be allowed to become much higher than is necessary to perform the function of suspension of cuttings and weight material[17,14].

[****] The gel strength will be evaluated in Fann 35 Viscometer at 10s and 10 min. An analysis detailed with different time schedule will be evaluated in a Brookfield viscometer.

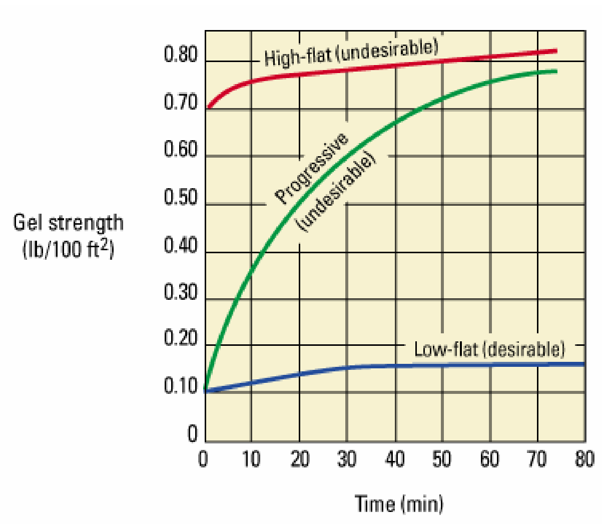

Figure 2.4 Gel strength characteristics vs time.Adapted from Baker Hughes[16]

2.6.9 Low shear rate viscosity (LSRV)

This rheological property is a parameter required to obtain an optimum hole cleaning for deviated (non-vertical) wells[45]. MI SWACO observed, in one of its fluid systems, that the low shear rate viscosity was a critical parameter to assure hole-cleaning and solid suspension in deviated and high angle wells[15]. The LSRV can be measured in a Brookfield viscometer with a shear rate of 0.3 rpm or, 0.037 rpm for a Fann 35 viscometer[15]. An elevated viscosity at low shear rates reduces the efficiency of low shear devices such as centrifuges, in as much as particle settling velocity and separation efficiency are inversely proportional to viscosity[39].

2.7 Flow Regimes

2.7.1 Newtonian

If the shear stress versus shear rate plot is a straight line through the origin (or a straight line with a slope of unity on a log-log plot), the fluid is Newtonian[50, 54].Where (τ) is shear stress,(μ) viscosity and ($\dot{\gamma}$) shear rate.

$$\tau = \mu\dot{\gamma} \tag{1.9}$$

2.7.2 Non-Newtonian

Non-Newtonian fluids (most drilling fluids fit this general classification) do not show a direct proportionality between shear stress and shear rate. The ratio of shear stress to shear rate (viscosity) varies with shear rate and the ratio is called “effective viscosity”, but this shear rate must be identified for each effective viscosity value[17]. For most drilling fluids, the effective viscosity will be relatively high at low-shear rates, and relatively low at high-shear rates[16]. In other words, the effective viscosity decreases as the shear rate increases. When a fluid behaves in this manner, it is said to be shear thinning[17]. Shear thinning is a very desirable characteristic for drilling fluids[45]. The effective viscosity of the fluid will be relatively lower at the higher shear rates in areas such as the drill pipe and bit nozzles[14]. Likewise, the effective viscosity of the fluid will be relatively higher at the lower shear rates in the annulus where the higher effective viscosity of the fluid aids in hole cleaning[17]. Figure 2.5 is shown the effective viscosity relating with the (rpm) from Fann 35 at low shear rate and high shear rate.

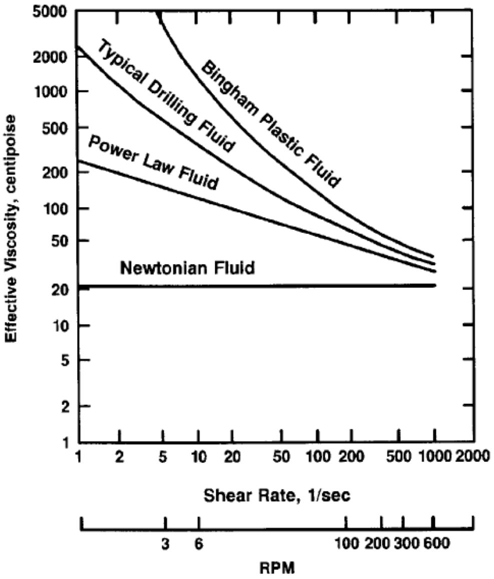

Figure 2.5 Viscosity vs shear rate profile. Adapted from AMOCO[17].

2.7.3 Bingham Plastic model

A Bingham plastic fluid is one in which flow occurs only after a finite stress, known as yield stress or yield point, is applied[54]. The stress required to initiate flow can vary from a small to a large value. After the yield stress has been exceeded, the shear stress is proportional to the shear rate [50,48]. The Bingham plastic exhibits a shear thinning viscosity; the larger the shear stress or shear rate, the lower the viscosity[54]. Where (τ_y) is the yield point and (μ_p) plastic viscosity.

$$\tau - \tau_y = \eta\dot{\gamma} \tag{1.10}$$

$$\tau = \tau_y + \mu_p(\dot{\gamma}\ ) \tag{1.11}$$

2.7.4 Law Potential

If the data, such as shear stress or viscosity exhibit a straight line on a log-log plot, the fluid is said to follow the power law model[54], which can be represented as;

$$\tau = K(\dot{\gamma})^{n-1}\dot{\gamma} \tag{1.12}$$

$\tau = K\dot{\gamma}^{n}$ If τ and $\dot{\gamma}$ are (+)

$\tau = -K(-\dot{\gamma})^{n}$ If τ and $\dot{\gamma}$ are (-)

The two viscous rheological properties are K or (m cited in others literature reviews), the consistency coefficient, and n, the flow index. The apparent viscosity function for the power law model in term of shear rate is[48,50,54]

$$\mu(\dot{\gamma}) = K\dot{\gamma}^{n-1} \tag{1.13}$$

Or, in terms of shear stress,

$$\mu(\tau) = K^{1/n}\lfloor\tau\rfloor^{(n-1)/n} \tag{1.14}$$

The variable n is dimensionless but m has dimensions of (Ft^{n}/L^{2}). However, m is also equal to the viscosity of the fluid at a shear rate of 1 s^{-1}, so it is a “viscosity” parameter with equivalent units[54].

It is evident that if $n=1$ the power law model reduces to a Newtonian fluid with $K=\mu$.

If $n<1$, the fluid is shear thinning (or pseudoplastic); and

If ($n>1$), the model represents shear thickening (or dilatant) behaviour.

Most non-newtonian fluid are shear thinning, whereas shear thickening behaviour is relatively rare, being observed primarily for some concentrated suspensions of very small particles and some unusual polymeric fluids[16]. The power law model is very popular for curve fitting viscosity data for many fluids. However, it is dangerous to extrapolate beyond the range of measurements using this model, because for ($n<1$) it predicts a viscosity that increases without bound as the shear rate decreases and a viscosity that decreases without bound as the shear rate increases, both of which are physically unrealistic[16,48,50,54,55].

2.7.5 Herschel-Bulkley

The Herschel-Bulkley model[††††] is more widely used than previously discussed models as it is seen to more accurately describe most fluids than the simpler Power Law and Bingham models[14]. This model is a Power Law Model that includes a yield stress parameter[56]. The H-B model can be

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[††††] Hershel Bulkley model is used in the hydraulic software in the majority of companies to measure the drilling fluid performance under downhole conditions.

considered the unifying model that fits Bingham plastic fluids, power law fluids, and everything else in between[48]. The Herschel-Bulkley model gives mathematical expressions which are solvable with the use of computers[48].

For that reason, the oil and gas industry has used the Herschel-Bulkley model for the calculation of drilling fluid hydraulic properties because this model fits approximately with the majority of drilling fluid behaviour. However, this model has presented some inaccuracies in the correlations between drilling fluid parameters measured in the field and hydraulic calculation[16]. Where τ_y is the yield point or yield stress (lb/100ft^2), $\dot{\gamma}$ is the shear rate (s^{-1}), n is the flow index and K the consistency index, both of them are dimensionless.

$$\tau = \tau y + K \dot{\gamma}^n \tag{1.15}$$

2.8 Performance and rheology modifiers

2.8.1 Rheology modifier characteristics

A rheology modifier is an additive able to provide high viscosity at low shear rates and thinning behaviour as shear rate is increased. This is useful during drilling operations to allow the fluid to carry rock cuttings from the drilling face to the surface and to prevent sag and settling of weighting material[‡‡‡‡]. When drilling is suspended to extend reach, or circulation is otherwise stopped, the drilling fluid needs to gel and prevent the suspended material settling. Also, this additive is used to adjust the flow behaviour of muds under extreme conditions. Caenn et al. [57] observed that the organophilic clay used as rheology modifiers in OBM, after being subjected to temperatures above 350 °F (177 °C), show degradation and the viscosity decreased substantially, affecting the carrying capacity and hence cutting removal.

Portnoy et al. [58] introduced sulfonated polystyrene to attempt to solve this issue due to the fact that experimental work in the laboratory indicated that sulfonated polystyrene provided good rheological properties at temperatures up to 400 °F (204 °C) and it has developed high performance in the field with temperatures up to 432 °F (222 °C). However, sulfonated polystyrene does not develop good rheology until it reaches temperatures in the region of 300 °F (149 °C), and it is better to combine it with organophilic clay to provide good rheological properties at low temperatures. For this reason much research has been focused to find alternative additives to control the rheological parameters and maintain performance at HTHP conditions, which is the aim of this thesis.

[‡‡‡‡] Sag testing will be evaluated in the experimental phase to observe the capacity of weighting material for the Mg Al Ada LDH as rheological modifier.

2.8.2 Nanotechnology

Nanotechnology is a relatively new technology which has been gaining advancements in different areas such as civil and material engineering and within the oil and gas industry in recent years[59]. This has shown substantial potential for applications in the oil and gas sector, in areas as diverse as drilling, production technology, completions, enhanced oil recovery, and refinery operations[60]. Nanoparticles (NPs) are defined as particles with the size between 1 and 100 nm and characteristically have a large surface area to volume ratio compared to micro sized particles. Nanotechnology promises a range of solutions to minimise some of the problems encountered in the oil and gas sector due to the fact that these nano-sized particles possesses features for enhancement of physical and chemical properties[61].

Nanomaterials, when compared to conventional materials, offer different capabilities in drilling fluids to tackle wellbore problems such as pipe sticking[62,63], formation damage[64,65] and high torque and drag[31,66]. Such materials could be a solution for drilling complex wells, as well as extended reach hydrocarbon wells or high angle HPHT wells that limit the performance of drilling operations.

2.8.3 Nanomaterials in drilling fluids for high pressure high temperature applications.

The use of nanoparticles (NPs) to enhance the properties of drilling fluids have been studied in recent years[67,24].Different types of NPs have been tested for enhancing and controlling the rheology of drilling fluids[68,27,69,66,29], for fluid loss mitigation[65,62,70] and wellbore stability[30,63]. A significant driver has been because several investigations have reported a higher fluid stability at elevated temperature[66,65,71,72,69]. This class of materials have demonstrated many applications for drilling fluids due to their performance enhancement in areas such as: better dispersion, minimum particle size and adjusting physical properties such as heat transfer, wettability and surface tension[24,27]. For example, nanomaterials based on metal oxides have attracted great attention for drilling operations since they support heat transfer by increasing thermal conductivity[73]. Also due to this fact, these material can be potentially used in HPHT drilling fluids[24].

2.8.4 Layered double hydroxides materials

In the mid-19th Century the materials layered double hydroxide (LDH) minerals were discovered by Manasse, with the first mineral discovered named hydrotalcite[74]. For many years LDHs have been researched as a host for anion exchange intercalation reactions. In this role they have been used extensively as ion-exchange materials, catalysts, sorbents and halogen absorbers[74]. These materials have also been applied for removing toxic anionic species from aqueous systems[75]. Among functional materials, they have shown beneficial properties including photo-chemical activity, redox chemistry, anion exchange, surface basicity and reversible thermal behaviour[36].

Structurally the main class of LDHs consist of stacked brucite-like ($M^{2+}(OH^-)_2$) layers in which M^{2+} ions are partially substituted by M^{3+} ions[76,3].The substitution in the layers necessitates the incorporation of anions, such as CO_3^{2-},Cl^-, and OH^-, between the interlayer to balance the resulting positive charge[77]. Various LDH compounds can be synthesized with several preparation methods. It has a particle size of less than 1 μm and a layer aspect ratio in the range of 10–100 within polymer nanocomposites[36]. In general, the most commonly used method of synthesis is co-precipitation at various or constant pH, followed by aging at a certain temperature[77].

2.8.5 High pressure and high temperature stability of layered mineral rheology modifiers.

Iyi et al. [76] reported that LDHs hybrids containing isothionate showed water-swelling properties and formed viscous gels on contact with water. This indicates that the incorporation of isethionate in the LDHs interlayer makes the resulting LDHs hybrid water-swellable. Manohara et al. [36] reported that a Mg/Al LDH intercalated with adamantane carboxylate anions (termed MgAl-Ada LDH) showed high thermal stability up to around 1022 °F (550 °C) and these materials might be ideal for rheology modifier applications in oil base fluids owing to their organophilic nature that would allow dispersion in OBM. The typical thermal decomposition for LDHs materials are in the region[75] of 420 ˚C. For this reason, MgAl-Ada LDH has been identified as a candidate material to be evaluated in a HPHT drilling fluid.

2.8.6 Advantages of nanoparticles in high pressure high temperature drilling operations.

Operators are presently looking for materials which are chemically and thermally stable, biologically degradable, made from environmentally benign chemicals, polymers or natural characteristics[78] in order to obtain alternatives to work under harsh environments and comply with the environmental policies in every specific site, and nanomaterials represent one of the best candidates to deliver those requirements. Drilling operations under high pressure and high temperature[28] represent challenges for drilling fluids due to degradation of materials[11], this is reflected as flocculation and instability in the system[66]. Hence, additives based on nanoparticles might become attractive for their possible use in drilling fluids technology,[§§§§] as these may be engineered to resist high temperatures and hostile environments. However, the majority of studies which have reported the use of nanoparticles to enhance performance in drilling fluids have been aimed at water base muds (WBM). The

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[§§§§] The evidence of good performance from drilling fluid systems data from water base muds, it is a profitable system for the industry for the low cost instead of oil base muds. Therefore, oilfield services have studied the incorporation of NPs in WBM to improve the performance for the costs and environmental concerns.

incorporation of nanoparticles in the formulation of WBM has developed good rheological properties[79–82], filtration properties[59,83] and reduction of formation damage[30].

Abdo et al.[66] investigated the application of ZnO-Clay nanocomposites as a rheology modifier in a water-based mud for HPHT conditions, where this presented good rheology stability, developing a high performance in rheological parameters such as plastic viscosity and yield point. Sadeghalvaad et al. [84] presented an experimental study of synthesis of TiO_2 polyacrylamide nanocomposite and their use in drilling muds. It was observed that the additive improved the viscosity, filtration loss volume at ambient pressure and temperature, and deposited a thin, impermeable mud cake. Aftab et al. [24] concluded that macro size organic particles and inorganic particles can enhance rheological performance, reduce filtrate loss volume and improve shale inhibition characteristics of environmental friendly water-based muds. Many studies are reported about the applicability of nanoparticles in water base mud and the resulting enhanced performance in its properties[59,26,61,70,29] however, no appropriate studies found to be drilling with synthetic oil based fluids.

Chapter 3

Experimental Methods

3.1 Introduction

As was mentioned above, the experimental phase assesses two rheology modifiers: one of them is a new rheology modifier developed by the Greenwell group in the Department of Chemistry, Durham University and patented with Saudi Aramco[1,2,3]. The other was a commercial organo-clay rheology modifier, developed by Elementis Specialties[85] and used by the Schlumberger oilfield services company[86] and the target is to observe the behaviour of the new rheological modifier with the interaction with others compounds in the drilling fluid formulation. The new rheology modifier, MgAl Ada LDH, is an LDH material intercalated with adamantane-1-carboxylic acid. Following small-scale evaluation in a previous project, this material was provided at kg quantity by High Force Research Ltd[87](OS number13982), a contract manufacturing company which makes materials to commercial quantities.

The structural formula of the material is $[Mg_2Al(OH)_6]^+.C_{11}H_{15}O_2^-$. Henceforth, it will use the nomenclature MgAl-Ada LDH through this thesis. The commercial rheology modifier Bentone 42, an organo-modified aluminosilicate clay, will be a reference point to compare the performance for the new MgAl-Ada LDH material. Chapter 3 presents a description of each of the materials used for preparing the drilling fluid formulations used to evaluate both rheological modifiers. This will then lead to a description of the material order for mixing, and mixing time to add each material according to the patent mentioned. Finally, it will describe the different equipment and the methodology used for the evaluation of each experiment.

3.2 Formulation

Drilling fluids are complex fluids which contain in their formulation many chemical compounds to provide the necessary properties to maintain wellbore stability in troublesome zones during drilling operations. The chemical compounds used to provide the physical-chemical properties of the formulated fluids used were provided by Schlumberger Oilfield Services, Client Support Laboratory for Europe[86], CIS and Africa at Enterprise Drive, Westhill Industrial, Estate Aberdeenshire, AB32 6TQ UK. Table 3.1 shows a chemical description and the function of each compound used. The drilling fluid formulations with different rheological modifiers were prepared at one laboratory barrel

(350 mL) small-scale in a Hamilton Beach mixer at low shear and 4 lab barrel volume (1404 ml) in a Silverson L-4 mixer for large-scale tests at 6000 rpm. Figure 3.1 illustrates the different mixers used. The Hamilton Beach mixer high shear rate was used to mix all the chemical materials to prepare all the samples as is specified in the recommended practice API 13I[88] and API 13-B2[89]. In addition, one batch of samples were prepared with the Silverson mixer to observe if the drilling fluid formulation properties were influenced under higher shear rates during mixing. Table 3.2 shows the mixers features used for the formulation.

Table 3.1 Description of chemical compounds and function to drilling fluid formulation.

Fuction	Description
Oil-based	Mineral oil
Emulsifier	Amido amine emulsifier
Wetting Agent	Oleic acid (60-100%), fatty acid blend (10-30%), linoleic acid (10-30%)
Emulsifier	Nitrogen-free
Viscosifier	Hectorite-based organoclay
Rheology modifier 1 (Bentone 42)	Organoclay modified hectorite and attapulgite.
Rheology modifier 2 (MgAl-Ada LDH)	Magnesium aluminium layered double hydroxide (LDH) intercalated with adamantane-1-carboxylic acid.
Alkalinity Control	Calcium Hydroxide
Fluid-loss agent	Amine-treated tannin
Fluid-loss agent	Co-polymer
Shale inhibition	$CaCl_2$
Weighting material	Barium Sulphate

Table 3.2 Description of mixers for used for preparing formulations.

Equipment	Model	Serial number
Mixer Durham University	Hamilton Beach	2MIXERL637
	Hamilton Beach	2MIXERL638
Mixer Schlumberger Facilities	Silverson L4-R mixer	39250
	Hamilton Beach	39140

Figure 3.1 Mixer used for the formulation, with left hand image showing Hamilton Beach and right hand image showing the Silverson mixer.

3.3 Chemical properties of materials for the formulation

3.3.1 MgAl-Ada LDH new rheology modifier

The patents [1,2,3] denoted that MgAl adamantane carboxylate (LDH) is an alkaline-earth diamondoid material.[1,2] This LDH material, obtained by hydrothermal treatment of Mg and Al hydroxides, is organophilic and designed for applications as a rheology modifier in an oil-based mud. It has the chemical formula $[Mg_2Al(OH)_6]^+.C_{11}H_{15}O_2^-.nH_2O$,[2] and has high aspect ratio. Manohara et al. [36] reported this material as prepared at 150 °C for 24 h in a Parr stirred autoclave, with a similar material prepared with different crystal morphology via anion exchange. Within the set of experiments through this thesis, the material used was a batch from High Force, though it should be noted there were some methodology variations the company used to process this material during scale-up.

3.3.2 Bentone 42

Bentone 42 is an organoclay chemically modified to enhance the performance of drilling fluids to temperatures as high as 450 °F for as long as 600 hours[85]. This maintains the gel strength and viscosity in synthetic based or invert emulsions for drilling fluids[85]. This organoclay improves the rheological properties while maintaining the flat rheology over temperature and minimizing the barite sag[85]. In the patent (US 8,389,447B2), it was shown that this organophilic additive comprises a combination of a hectorite organoclay composition and an attapulgite organoclay composition [90]. This additive can be used in oil based invert emulsion drilling fluids employed in high temperature drilling applications[85].

3.3.3 Saraline 185 V

Shell Saraline 185V is a hydrocarbon product derived from natural gas feedstock converted into a hydrocarbon fluid using proprietary catalysis technology[91]. This process delivers a synthetic base fluid of C8-C26 branched and linear paraffins[92,91]. Figure 3.2 shows the diagram process for the production of this Synthetic Base Fluid (SBF). This is in the classification of synthetic Oil-Based Group III which is a group of low to negligible aromatic content[93]. The most common application is for Non-Aqueous Drilling Fluid (NADF), under the drilling fluid definition by International Association of Oil and Gas Producers (OGP)[93].

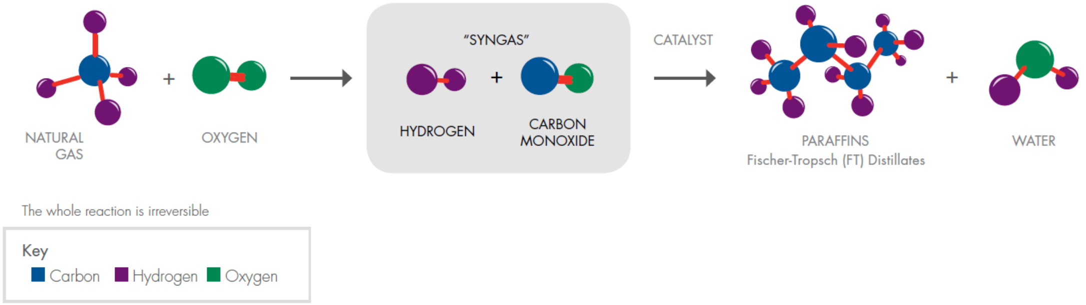


Figure 3.2 Process Diagram for the production of Synthetic Base Fluid (paraffins) from the natural gas. Adapted from Shell Chemicals[92]

3.3.4 Emulsifiers

Fatty acids work as primary emulsifiers for this kind of systems which react with calcium hydroxide or (lime) to obtain a more stable emulsion[94,35]. An alkanomide, which is a partially water soluble emulsifier is used as the secondary emulsifier[94] . Stamatakis et al.[35] reported results for some emulsifiers based on amido-amine structures, where the fluids were prepared to different concentrations with this kind of emulsifier and all the formulations failed[35]. The tests were performed at 500 °F (260 °C) and 300 psi over 16 hours to test the limits of each formulation. The results from the tests were negative indicating the degradation of the emulsifier showing solids settling after ageing when the test were conducted up to 475 °F (246.11 °C).

In addition, Stamatakis et al.[35] optimised the formulation and this worked under 500 °F (260 °C) ageing conditions. The best formulation to work under these conditions was a formulation with an emulsifier package integrated (non-amide based), which was designed for thermal stability above 500 °F (260 °C). Other components included a fluid loss additive based on a thermally stable synthetic ter-polymer and organo-tannin combination, a thermally stable organo-clay at low concentration and the barite treated with a wetting agent. This formulation was reported as having good rheological stability, emulsion stability and fluid loss stability under the 500 °F (260 °C) ageing conditions. The thermal ageing was performed at 525 °F (273.88 °C) and 300 psi over 24 hours. The gel and yield point of this formulation increased in performance after ageing. The nitrogen free surfactant chemistry developed by MI SWACO represents a powerful thinning, or higher levels of oil wetting effects, on the invert emulsion system, which maintained a low stable rheological profile with a low fluid loss[15].

3.3.4.1 SUREMUL

This is a primary emulsifier in the synthetic drilling fluid system which provides emulsion stability, preferential wetting of solids by the continuous phase, filtration control and temperature stability[96]. The specific gravity of this compound is in the order of 0.89-0.92 g/cm^3.

3.3.4.2 MUL XT

This is an emulsifier which is used as the primary emulsification [97] .The use of this emulsifier is recommended for a temperature > 572 ˚F (300 ˚C). The specific gravity is around 0.93-0.96 g/cm^3.

3.3.5 Viscosifiers

A good rheology profile is critical for the well integrity as this allows good solids suspension while the bit is cutting the formation, minimising the circulation pressures. Organophilic-treated clay minerals (organo-clays) play an important role as rheological control additives[35]. The properties of each rheological control additive will depend on the chemical treatment, with surfactant used to organo-modify the clay mineral, and the clay mineral substrate, both of which are responsible to provide the rheology profile, impacting gelation effects with solids and thermal stability. The organo-clays can typically resist temperatures exceeding 500 °F (260 °C) [21].

3.3.5.1 VERSAGEL HT

This is a primary viscosifier in invert emulsion drilling fluid system[98]. This material is a hectorite clay with an amine-treatment[86]. The specific gravity is 1.7 g/cm^3.

3.3.6 Wetting Agent

SUREWET, this is a surfactant with the main function of a secondary wetting agent and emulsifier. The work of this wetting agent is wet barite and cuttings to prevent water-wetting of solids[99]. Specific gravity is 0.891 g/cm^3 at 68 ˚F (20 ˚C).

3.3.7 Fluid loss control

There are two groups of fluid loss control additives. The first includes materials such as gilsonites, asphalites and treated lignite, which provide physical-chemical properties to the filter cake[94]. These kinds of properties are able to plug any permeability between the formation and the filter cake and, at the same time result in a thin and strong filter cake. The second group consist of oil soluble or swellable polymeric materials, although these kind of materials have working temperature limits, which are not found in the literature[94]. These are used to help plugging and bridging solids in the filter cake to provide a thin, flexible filter cake[100,60].

3.3.7.1 ONE-TROL HT

This is a filtration-control base in amine-treated tannin for synthetic based drilling fluid systems[86]. This fluid-loss control agent is used to a temperature of 500 °F (260 °C) [101].

3.3.7.2 ECOTROL RD

This is a polymeric fluid loss reducer[86]. This filtration-control additive is a primary additive used in all oil and synthetic-base drilling fluid system[86]. This is an emulsifier complement to provide HPHT Fluid-loss control at low concentrations[86]. It also is very effective in 100% oil-based systems and at very high temperatures up to 500 ˚F (260 ˚C) [86].The specific gravity is sg 1.03 g/cm^3.

3.3.8 Calcium Hydroxide, $Ca(OH)_2$(lime)

Lime or $Ca(OH)_2$ has the function to activate the fatty acid emulsifier due to the fact that it undergoes saponification in alkali solution and produces a calcium soap[35]. This is hydrophilic on one end and lipophilic on the other[97]. The alkali helps in the process to create a water-in-oil emulsion[17]. The excess of lime $Ca(OH)_2$ is added to have the property to maintain a stable emulsion in an oil-based drilling fluid[35]. The excess of lime is added into an oil-based drilling fluid formulation due to the fact if an influx of CO_2 or H_2S is encountered[94], this will introduce acidity and tend to decrease the alkalinity for the system causing destabilization of the system[21]. The excess of $Ca(OH)_2$ helps to balance this effect. The specific gravity is 2.2 g/cm^3.

3.3.9 Internal phase ($CaCl_2$ Brine)

The calcium chloride brine is used for the internal phase, this provides the salinity to the system, removing water from the shale via an osmotic effect[94].The interfacial film surrounding each water droplets acts like a semipermeable membrane[102].The water or brine droplets, when they are emulsified, act as solid particles and can help reduce the fluid loss even though they are distorted with pressure[94]. These emulsified droplets can plug the filter cake pores and reduce the fluid loss and permeability into the surrounding geological formation[35].

3.3.10 Weighting material

One of the biggest challenges in using drilling fluids under high temperature and high pressure is the barite sag. Superior suspension properties for the drilling fluids are demanded for high temperature and pressure conditions. As these kind of conditions require high density drilling fluids[21], the weighting additive, barite, represents around 33-35% in volume in the system, if API grade barite is used, which has a specific gravity of 4.2 g/cm^3. Severe sagging problems in the wellbore can occur if the drilling fluid design is not optimised with respect to the high density. There are some solutions that the oilfield services are innovating to avoid these sagging problems. One of the alternatives can be replacement of barite for the use of a new weighting material[35,103]. M-I SWACO have developed a high-grade barite with a physical-chemical treatment with a thermally stable oil wetting agent and are then milled to obtain an average particle size of 2 microns[35].

3.3.10.1 MI Bar

MI Bar is a weighting material also it is known as barium sulphate used to increase the density of drilling fluids[86]. The specific gravity is 4.2 g/cm^3.

3.3.11 Other Materials

3.3.11.1 Hymod Prima (HMP)

The drilling fluids stability is affected by different interface interactions with solid materials such as weighting agents, fluid loss control additives and drill solids[35]. Therefore, in some tests the incorporation of Hymod Prima Clay was undertaken as a simulation of formation solids. This was undertaken to observe if the drilling fluid underwent alteration with the incorporation of solids into the system. The HYMOD PRIMA or HMP used during the experiments was from POTTERY CRAFTS marketed as Hymod AT Ball Clay[104]. The specific gravity is (2.6-2.7 g/cm^3).

3.4 Fluid Formulation and thermal treatment

3.4.1 Formulation of oil-based nanoparticle interaction

The rheology modifier Bentone 42 (supplied by M-I SWACO, Schlumberger[86]) and MgAl-Ada LDH were analysed mixed with the base oil Saraline 185V[92]. This base oil has presented advantages for deepwater wells and HPHT wells, in particular to control the temperature effects in the bottom hole of the well[105,106]. For this reason it is used in a considerable number of commercial drilling fluid systems[86,44,107,108]. It is important to evaluate the new rheology modifier compound with the base oil to observe behaviour and compatibility. The preparation steps for the two formulations for assessment are shown below, in Table 3.3;

1. Sample 1, 2 g Bentone 42 and 250 mL of Saraline 185V was mixed by stirring in a Hamilton beach model for 20 minutes.
2. Sample 2, 2 g MgAl-Ada LDH and 250 mL of Saraline 185V was mixed by stirring in a Hamilton beach model for 20 minutes.

The preparation for the two solutions for assessment are shown below;

Table 3.3. Formulation and mixing order used for oil-based nanoparticle interaction testing.

Solution with rheology modifier			
Quantity		**Chemical compounds**	**Oil**
Grams	**mL**		
2	250	MgAl-Ada LDH	Saraline 185 V
2	250	Bentone 42	Saraline 185 V

3.4.2 Formulation of the emulsion nanoparticle interaction

All the interactions with the new nanoparticle rheology modifier have been studied separately due to the fact that oil-based mud (OBM) is a complex fluid and its behaviour can be unpredictable with the addition of any different material into the system. Also, the nanoparticle interaction with the emulsion has been analysed to understand the behaviour between the continuous and discontinuous phases within the emulsion. The preparation of the emulsion with the nanoparticle as was formulated is shown in Table 3.4.

1. 157 mL of mineral oil was added to a Hamilton Beach mixer cup.
2. The emulsifier package was added and mixed for 5 minutes at low speed.
3. The viscosifier, rheology modifier and alkalinity control was added for 10 minutes at low speed.
4. The $CaCl_2$ brine was progressively added and mixed for 15 minutes at high speed.

Table 3.4 Formulation and mixing order used for emulsion nanoparticle interaction.

Formulation of emulsion with the rheology modifier				
Product	**Function**	**Bentone 42 (g / mL)**	**MgAl-Ada LDH g/mL**	**Mixing order and time**
Saraline 185V	Base Oil	122.0 g / 157 mL	122 g / 157 mL	Stage1
SUREMUL	Emulsifier	10 g / 10.42 mL	10 g / 10.42 mL	5 min
MUL XT	Emulsifier	4 g / 4.21 mL	4 g / 4.21 mL	
VERSAGEL HT	Viscosifier	2.75 g / 1.62 mL	2.75 g / 1.62 mL	Stage 2
BENTONE 42	Rheology Modifier	2.75 g / 1.62 mL	0	
MgAl-Ada LDH	Rheology Modifier	0	2.75 g / 1.62 mL	10 min
$CaCl_2$ Brine	Internal phase	28.5 g / 20.96 mL	28.5 g / 20.96 mL	Stage 3
Fresh Water	Internal phase	5.9 g / 5.90 mL	5.9 g / 5.90 mL	5min

3.4.3 *Formulation of the oil-based drilling fluid.*

The samples were analysed in the ranges of temperature from 120 ˚F (49 ˚C) up to 180 ˚F (82 ˚C). All samples used were mixed and prepared in the Department of Chemistry at Durham University, except for the experiments developed for high pressure and high temperature conditions from a range of temperature at 120 ˚F (49˚C) - 350˚F (177˚C) and maximum pressure of 20,000 psi, which were mixed and formulated in Schlumberger Oilfield Services facilities in the Client Support Laboratory for Europe[86], in the UK. The concentration used for the drilling fluids with MgAl-Ada LDH was kept the same concentration as the fluid with Bentone 42 to have a reference pattern of behaviour with this material during this experimental phase. To sum up briefly, Table 3.5 shows the order of mixing and the mixing time of each stage according to a mixing plan provided by Schlumberger for the blending of its products. This is showing quantities needed for 1 lab barrel and 4 lab barrel, for each of the rheology modifiers tested. As can be seen in Table 3.5 the CSIPRO and SIRN is referenced to the batch number, allowing tracking of each compounds performance used in the formulation.

Table 3.5 Additives formulation used for the drilling fluid preparation. Modified from Mohammed et al.[2]

O-S DURHAM	DURHAM	SLB	Formulation	Function	1 bbl Bentone 42	1 bbl MgAl-Ada LDH	4 lb bbl	Mix order	Mix time (min)
SIRN	**CSIPRO**		**Product**		**QTY (g)**	**QTY (g)**	**QTY (g)**		
-	C015361	CO17850	SARALINE 185V	Base Oil	122	122	488	1	5
2015-5200	C014556	CO14557	SUREMUL	Emulsifier	10	10	40		
-	C015324	CO15325	SUREWET	Wetting Agent	4	4	16		
2015-5290	C016429	CO11938	MUL XT	Emulsifier	4	4	16		
2015-5241	C016425	CO16425	VERSAGEL HT	Viscosifier	2.75	2.75	11	2	10
2015-5182	C016427	CO17905	BENTONE 42	Rheology modifier	2.75	-	11		
13982	13982	-	MgAl Ada LDH	Rheology modifier	-	2.75	11		
2014-883	C014489	CO17310	LIME	Alkalinity control	6	6	24		
-	C011646	CO11646	ONE-TROL HT	Fluid loss control	8	8	32	3	10
2013-4237	C015076	CO15076	ECOTROL RD	Fluid loss control	0.8	0.8	3.2		
-	Lab	CO15286	$CaCl_2$	Internal phase	28.5	28.5	114	4	15
N/A	N/A	N/A	WATER	Internal phase	5.9	5.9	23.6		
API SAUDI	FOSS BARITE	SAUDI	MI BARITE	Weight Material	577.2	577.2	2308.8	5	20
			Total/final		771.9	771.9			60

All the drilling fluid samples were prepared at lab barrel (350 mL) scale. Every sample was prepared with the same procedure and time of reaction from the constituent chemical compounds by Schlumberger[86] standards and as cited in the patents[1,2] . The quantities used for rheology modifiers added to the drilling fluid was the same quantity for the original formulation, which is 2.75 g of Bentone 42 and for the other drilling fluid formulations, with 2.75 g of MgAl-Ada LDH. The method followed for the formulation is mentioned below:

1. Base oil, emulsifiers and wetting agents were mixed together first for 5 min during Stage 1.
2. Secondly, the viscosity modifiers and rheology modifiers were added and mixed for another 10 min during Stage 2.
3. Next, in Stage 3, the fluid-loss control additives were added and mixed for 10 min.
4. The brine was added and was mixed for 15 min in Stage 4.
5. Barite was added in the Stage 5 and mixed for 20 min.
6. In the case for the fluids to be contaminated with solids, the HMP was added at the end and mixed for 10 min.

3.4.4 High-Temperature Aging for Drilling Fluids

Thermal aging of the samples is conducted to test thermal stability for different temperatures and pressures in a portable roller oven[109] (produced by OFITE), as is illustrated in Figure 3.3. Initially, the tests were performed at 250 °F (121 °C) and 50 psi for 16 hours. Later tests were conducted at 350 °F (176.6 °C) and 150 psi, 400 °F (204.44 °C) and 250 psi, finally at 450 °F (232.2°C) and 300 psi, following the instructions recommendation by OFITE, to pressurise the cells according with the temperature reached[110]. The roller oven has 3 rollers and can hold four 260 mL or two 500 mL aging cells[109]. The cells used to develop this tests along all the thesis were of 500 mL total cell capacity[110]. The speed for this portable equipment is factory pre-set to 25 rpm and the operational work temperature limit between 100 °F and 450 °F (38 °C – 232 °C) [109].

The cells used for this test are illustrated in Figure 3.3 The OFITE aging cell is a patented pressure vessel that enables samples to be subjected to temperatures higher that the boiling point of water and still be maintained in a liquid state[110]. The cells may be used for static temperature exposure or in a dynamic mode in a roller oven with a pre-set minimum aging time of 16 hours[109].The pressure applied for pressurizing the cell for each temperature condition was followed as detailed by the operational manual of aging cell[110] to set up the appropriate pressure. This was for the purpose of avoiding the evaporation of the samples and to preserve the same oil/water ratio of the emulsion[110].Table 3.6 shows the pressure recommended to pressurize the cell, according to work temperature limits.

Figure 3.3 Portable roller oven with an aging cell of 500 ml (not the same scale). Modified from OFITE.[109,110]

Table 3.6 Temperature and pressure recommended for aging test[*****]. Modified from OFITE[109].

Aging Temp		Water vapor pressure	Coefficient of expansion of water	Suggested applied pressure		Mud volume in 260 mL cell	Volume with teflon liner	Mud volume in 500 mL cell	volume with teflon liner
°F	°C	psi		psi	kPa	mL			
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	1034	200	116	400	289
400	204	247	1.16	250	1724			375	271
450	232	423	1.2	300	2069			375	253
500	260	680	1.27	375	2586			325	235

3.5 *Fluid testing*

The testing of technical drilling fluids to API13B-2[89] involves measuring the rheological parameters, and filtration and stability properties. Table 3.7 shows the equipment used during the evaluation of the new rheological modifier. Details of equipment used is essential for reproducibility of data obtained in this thesis for further work.

Table 3.7 Equipment used for fluid testing

Equipment	Model	Serial number	Slb	Durham
Rheometer	Grace M7500 Ultra HPHT	3	x	
Viscometer	Fann 35	39188	x	
		39066	x	
		40906	x	
Controller temperature	Hilton	39368		x
	Fann	N/A	x	
Electrical Stability meter		E004041	x	
	Without Serial number	N/A		x
Controller temperature	Fann	N/A	x	
Filter loss HPHT	OFITE filter loss HPHT	2FPRES770	x	
	OFITE filter loss HPHT	N/A		x
Brookfield DV2T	DV2T	N/A		x

[*****] The table shows 2 different cells capacities of 260 mL and 500 mL. Temperatures above of 400 °F is recommended the use of a cell of 500 mL for the fluids expansion. The Teflon liner is an adaptable part to the cell which is used for samples susceptible to contamination (it wasn't the case).

3.5.1 Rheological characterization

3.5.1.1 Couette coaxial cylinder rotational viscometer

The equipment used to measure the absolute viscosity for the samples was throughout a Couette coaxial cylinder rotational viscometer. This is generally referred to by the term Fann 35, which has been used for a long time in the petroleum sector, although the name may not be the most appropriate[111]. This arises owing to the fact that this viscometer is technically correctly called a Couette coaxial cylinder rotational viscometer[111], and FANN company produces this as the Model 35[111]. Figure 3.4 illustrates the equipment mentioned.

Figure 3.4 Fann 35 Viscometer.

This type of viscometer was designed to evaluate materials with a non-Newtonian behaviour, adjusting to the rheological Bingham plastics model[16]. Although not all drilling fluids fit to this Bingham plastic model, it is a good predictor for drilling fluid performance and widely applied to diagnose mud problems at the operations site[40]. The Fann 35 is the most commonly used instrument because it covers specifications such as R1 Rotor Sleeve, B1 Bob, F1 Torsion Spring, and a stainless steel sample cup for testing, according with the guidelines of good practice defined by the American Petroleum Institute specification API13B-2[89]. The mud is contained in the annular space between the coaxial cylinders. This is sheared at a constant rate between an inner bob and an outer rotating sleeve[43]. The viscous drag exerted by the fluid creates a torque on the inner cylinder or bob. This torque is transmitted to a precision spring where its deflection is measured and then related to the test conditions and instrument constants[111].

The torque is proportional to shear stress and the rotational speed is proportional to shear rate. The indicated dial reading times 1.067 is equivalent to shear stress[40] in lb /100 ft^2. Therefore, the rotational speed at 600 rpm is equivalent (1022 sec^{-1}) and 300 rpm (511 sec^{-1}). The rotational speeds for the Model 35 are six-speed,[111] at 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. The rheological properties obtained from the tests in this type of viscometer were apparent viscosity, plastic viscosity and yield point. The calculation to obtain these values from the dial reading of Fann 35 was defined in Chapter 2. Finally, gel strength values are obtained noting the maximum dial deflection when the rotational viscometer is turned at a low rotor speed at 3 rpm after the mud has remained static for some period of time[40]. If the mud is allowed to remain static in the viscometer for a period of 10 seconds, the maximum dial deflection obtained when the viscometer is turned on is reported as the initial gel strength. To obtain the 10 min gel strength, the mud has to remain static for 10 minutes, the maximum dial the deflection is considered yield point for 10 minutes. In Chapter 2, the description of the gel strength values desired from the readings was discussed.

The procedure to take the dial readings in the viscometer is shown below. This is based in the recommended practice for field testing of oil-based drilling fluids API 13-B2[89].

1. A sample of the drilling fluid was placed in the viscometer cup. Enough empty volume (approximately 100 cm^3) was left in the cup for displacement of fluid due to the viscometer bob and sleeve.
2. The rotor sleeve was immersed exactly to the scribed line.
3. The sample was heated to the selected temperature with the thermocup, setting the thermometer to check the temperature reached.
4. With the sleeve rotating at 600 rpm the viscometer dial reading was allowed to reach a steady value and the dial reading recorded at 600rpm.
5. The rotor speed was reduced to 300 rpm and the dial reading allowed to reach a steady value and the dial reading recorded at 300 rpm.
6. With the sleeve rotating at 200 rpm, wait for the viscometer dial reading to reach a steady value. Record the dial reading 200 rpm.
7. Reduce the rotor speed to 100 rpm and wait for the dial reading to reach steady value. Record the dial reading 100rpm.
8. With the rotor speed to 6 rpm and wait for the dial reading to reach steady value. Record the dial reading 6 rpm.
9. Reduce the rotor speed to 3 rpm and wait for the dial reading to reach steady value. Record the dial reading 3 rpm.

10 The drilling fluid sample was stirred for 10 s at 600 rpm. The drilling fluid sample was then allowed to stand undisturbed for 10 s. The hand-wheel was slowly turned at 3 rpm to produce a positive dial reading. The maximum reading was recorded as the initial gel strength (10-second gel strength).

11 The drilling fluid sample was re-stirred at 600 rpm for 10 min and then allowed to stand undisturbed for 10 min. The hand-wheel was slowly turned at 3 rpm to produce a positive dial reading and the maximum reading recorded as the gel strength (10-minutes gel) strength.

3.5.1.2 Brookfield DV2T

One of the key rheological properties for drilling fluids is gel strength. This is the ability to form gels as a function of time, or thixotropy[112]. This is with the exception of yield point which is measured under dynamic conditions[15]. For these experiments, the Brookfield[113]model used was a DV2TRV with a small sample adapter[114], located in the Physics Department in Durham University, and the instrument type used is shown in Figure 3.5. Therefore, gel measurements were taken using this viscometer model due to the high accuracy and the temperature control for the variation of temperature during the experiments. The Brookfield DV2T Viscometer by AMETEK[113]company measures fluid viscosity at given shear rates. The industry oil and gas use this viscometer to measure the gel strength due to its data accuracy and the low shear rate to break gels[115]. All the Brookfield viscometers are well known for containing accuracy within: ±1.0% of the range in use and having a reproducibility[116] within ±0.2%. This DV2TRV model used for this experiments is a digital programmable viscometer which allows us to perform flow experiments at different temperatures and shear rate in a programmable sequence using the software from this equipment called RheocalcT[114]. The principal of operation of the DV2T is to drive a spindle (which is immersed in the test fluid) through a calibrated spring[114]. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer[116]. The measurement range of a DV2T (in centipoise or milliPascal seconds) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring[115]. The spring torque of this model DV2TRV used for this experiments was[115] of 7,187 Dyne.cm or (0.7187 miliNewton.m).


Complete system shows the DV2T Viscometer and Small Sample Adapter with Circulating Water Bath for temperature control.

Figure 3.5 Brookfield DV2TRV with the circulating water bath. Modified from Brookfield[116]

Figure 3.6 shows the spindle SC4-27, a coaxial cylinder geometry, which was used in the small sample adapter. During operation this system comprises a water jacket to allow temperature control of the sample, a sample chamber to place the sample, and the spindles to analyse the sample in this coaxial cylinder geometry[114]. The sample chamber fits into a water jacket so that precise temperature control can be achieved when the Brookfield circulating temperature bath is used[114]. Working temperature range for the small sample adapter is from[115] 1 ˚C to 100 ˚C. The experiments here were run with a maximum temperature of 75 ˚C (177 ˚F) with a low shear rate at 0.5 rpm and 100 rpm. The operational work limits regarding the viscosity range and rpm that the model used was of 100 cP to 40mcP and 0.100-200 rpm, respectively[115].

Figure 3.6 Small sample adapter kit. Modified from Brookfield[116]

The method used for the equipment is described below;

1. The sample was preheated to room temperature (26.0 °C) and then stirred for 10 minutes on a Hamilton Beach mixer.
2. The temperature bath was turned on.
3. The DV2T viscometer was switched on, and checked that the screen displayed the Autozero option. This was performed without any spindle on the viscometer before the equipment was turned on. This step was to calibrate the equipment before use.
4. The spindle SC4-27 was attached to the pivot shaft. The lower shaft was secured and slightly lifted with one hand while screwing the spindle on in a clockwise direction.
5. The fluid was poured into the thermocup to a level around ¼” below the edge.
6. The coaxial-cylinder was inserted into the jacket of the small sample adapter.
7. The software programme was run.

The test sequence was performed using the software Rheocalc T.1.1.13 by Brookfield, as shown in Table 3.8.

Table 3.8 Detailed test sequence in Rheocalc T.1.1.13 software in Brookfield viscometer.

Shear rate	**Temperature**		**Data collection**	**End value**	**End value**	**type**
RPM	°F	°F	(s)	(s)	min:s	
100	77	167	30	900	00:15:00	Speed
0	77	167	1	10	00:00:10	Static
0.5	77	167	0	1	00:00:01	First reading
0.5	77	167	10	120	00:02:00	Speed
100	77	167	10	300	00:05:00	Speed
0	77	167	30	600	00:10:00	Static
0.5	77	167	0	1	00:00:01	First reading
0.5	77	167	10	120	00:02:00	Speed
100	77	167	10	300	00:05:00	Speed
0	77	167	30	1800	00:30:00	Static
0.5	77	167	0	1	00:00:01	First reading
0.5	77	167	10	120	00:02:00	Speed

3.5.1.3 Grace M7500 Ultra HPHT Rheometer

The Grace Instrument M7500 Ultra HPHT Rheometer is a coaxial cylinder, rotational, high pressure, and high temperature rheometer[117]. It is engineered to measure various rheological properties of fluids under a range of pressures and temperatures[117], up to 30,000 psi and 600 °F. The unit is also fully compliant with API[89] 13B-2 standards. To obtain a rheological profile under HPHT conditions, the method most commonly used is called a rheology sweep, which is set at a determined temperature at two pressures, and then alternate to set a pressure with two temperatures, and successively, to reach the maximum, successively swapping two pressure and two temperature steps[69]. When the fluid reach the temperature and pressure determined, then the speeds cited at 600 rpm, 300 rpm, 200rpm, 100rpm, 6rpm and 3rpm will be measured from the dial reading.

10 seconds and 10 minutes gel strength analyses were undertaken. As is shown in Table 3.9, each Temperture/Pressure points was evaluated at 8-speeds[118]. Table 3.9 shows an example of a test sequence at 120 °F, without a pressure point, the initial phase for the test. Different sequences at different temperature and pressure were evaluated following the recommended practices in the Grace Instrument Manual[118] by Schlumberger[86]. The procedure used to operate this equipment was defined under Schlumberger standards,[118] from the Client Support Laboratory, Aberdeen. Figure 3.7 illustrates the equipment used. Below is a description of the general procedure used to run a test with this equipment[118].

1. The unit was powered up.
2. The fluid test sequence was programmed within the equipment's software.
3. The cell assembly was calibrated into the equipment.
4. The dial reading zero was set for the equipment calibration.
5. A test sequence was run.
6. After the test, the test data was saved.
7. The results report was displayed.

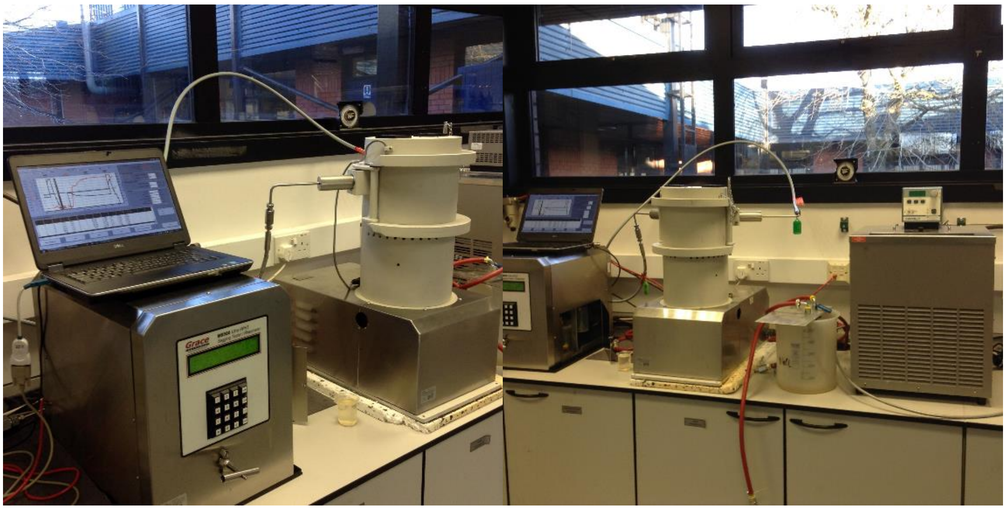


Figure 3.7 Grace 7500 Rheometer instrument used for HPHT testing in this thesis.

Table 3.9 Test sequence for the rheology measurement. Adapted from Schlumberger[118].

Step No	Elapse time (min)	Temp (°F)	Temp error (°F)	Speed (rpm)	Pressure (psi)	Record interval (sec)	Cycle	Ramp	
1	90	120	2	300	0	5	1	0	Check/Stabilisation/Heat up/ Pressure up
2	1	120	2	600	0	1	1	0	600 rpm reading
3	1	120	2	300	0	1	1	0	300 rpm reading
4	1	120	2	200	0	1	1	0	200 rpm reading
5	1	120	2	100	0	1	1	0	100 rpm reading
6	1	120	2	6	0	1	1	0	6 rpm reading
7	1	120	2	3	0	1	1	0	6 rpm reading
8	0.5	120	2	600	0	1	1	0	600 rpm spin before gel measurement
9	0.37	120	2	0	0	1	1	0	10 second gel period
10	0.5	120	2	3	0	0.5	1	0	10 second gel measurement
11	0.5	120	2	600	0	1	1	0	600 rpm spin before gel measurement
12	10.2	120	2	0	0	5	1	0	10 minute gel period (includes 0.2 min deceleration of sleeve)
13	0.5	120	2	3	0	0.5	1	0	10 minute gel measurement
14	0.5	120	2	600	0	1	1	0	600 rpm spin before gel measurement
15	10.2	120	2	0	0	5	1	0	30 minute gel period (include 0.2 min deceleration of sleeve
16	0.5	120	2	3	0	0.5	1	0	30 minute gel measurement

3.5.2 Filtration high temperature/high pressure (HTHP).

Static filtration control plays an important role in controlling the characteristics of the filter cake deposited downhole[40], and the filter cake quality is related to the wellbore stability and potential formation damage. The filtration test evaluates the stability of the oil-water emulsion through the filtration[89]. Figure 3.8 shows the filter press HTHP equipment used for this experiment. Filtration characteristics of an oil-based drilling fluid are affected by the quantity, type and size of solid particles and emulsified water in the drilling fluid, and by properties of the liquid phase. Interactions of these various components can be influenced by temperature and pressure[89]. This experiment was looking at the thickness of the cake, its permeability, slickness, and texture [40] and the filtrate volume. This is related to the instability of the emulsion based drilling fluid. When the correction volume is higher than 4 mL fluid, from prior experience, it is an indicator of potential wellbore problems. The procedure used to do this test is based in the recommended practice in API 13-B2[89].The pressure applied to the cells at 300 ˚F is shown in Table 3.10, and is followed by the methodology used for this experiment.

Figure 3.8 Filter Press HT/HP equipment. Modified from OFITE[119].

Table 3.10 Recommended minimum back-pressure. Adapted from API 13B-2[89]

Test temperatures		Vapour pressure		Minimum back pressure	
°C	°F	kPa	psi	kPa	psi
100	212	101	14.7	690	100
120	250	207	30	690	100
150	300	462	67	690	100
Limit of "normal" field testing					
175	350	932	135	1104	160
200	400	1704	247	1898	275
230	450	2912	422	3105	450

1. The preheated jacket was used until measured temperature reached 300 °F.
2. The room temperature sample was stirred with a Hamilton Beach mixer for 15 minutes to homogenise the sample.
3. The sample mixed was poured into the filter cell, leaving around ¼ inches from the top, allowing for fluid expansion. Filter paper was placed on top before closing the cell.
4. The filter cell was placed into the heating jacket. The high pressure regulator and back pressure regulator were connected to each appropriate valve. The two valve stems were kept closed before putting the safety pin in place.
5. The CO_2 bulbs were connected with the high pressure regulator and backpressure regulator.
6. Both valves were opened a ¼ turn. 100 psi was let in to both regulators to reach the temperature slightly faster.
7. Once a temperature at 300 °F was reached, more pressure was added to 600 psi. In this way the system will have a differential of pressure of 500 psi.
8. After Point 7, 30 minutes elapsed for undertaking the filtration test.

9. After 30 minutes elapsed, both valves were closed.
10. Both regulators, were unscrewed to release the pressure.
11. The receiver valve was opened to collect all the filtrate.
12. The filtrate collected was measured and the volume obtained was multiplied for 2 to do the correction[†††††].

3.5.3 Emulsion stability test

The stability of a water-in-oil emulsion mud is indicated by the breakdown voltage at which the emulsion becomes conductive[17]. The electrical stability (ES) of an oil-based drilling fluid is a property related to its emulsion stability and oil-wetting capability. ES is determined through applying a voltage via the electrodes[‡‡‡‡‡]Figure 3.9, submerged into the drilling fluid until the mud provides an electrical current[89] of around 61 µA. Figure 3.9 shows a typical emulsion tester, as used in this work.

Figure 3.9 Electrical stability meter. Modified from OFITE[120].

The standard practise for developing an emulsion stability test, as used in the project, is listed below[89].

1. The sample was placed in a viscometer cup and hand-stirred with the ES probe for 30 seconds. The sample was maintained at 50 °C ± 2 °C (120 °F ± 5 °F).
2. The ES meter dial was set to zero. The probe was immersed into the mud sample, ensuring that the probe did not touch the sides or bottom of the thermal cup.
3. The power button was held down for the entire test.
4. Starting from a zero reading, the voltage was gradually ramped up.

[†††††] API 13B-2 set up as standard that the filtrate volume obtained from HTHP filter press must to be corrected to filter area of 4580 mm^2 (7.1 in^2). The HTHP filter cells has a filter area (2258 mm^2) (3.5in^2).

[‡‡‡‡‡] ES is determined immersing the flat-plate electrodes in the drilling fluid. A sinusoidal electrical signal is sending through of those parallel electrodes[89].

5. The voltage ramp test was repeated twice, to check that the reading did not differ by more than 5 %.

3.5.4 Sag testing (Static Aging)

Sag is one of the major problems that drilling contractors encounter during drilling operations. This becomes more severe in wells of high angle (> 45°) and horizontal (>85°)trajectory[121]. The sagging of barite has been reported to be more noticeable during the drilling of wells using an invert emulsion drilling fluids and this can happen in different fluid densities[122]. However, the problem has also been highlighted in higher fluid densities and in HPHT conditions[123]. For that reason, it is important that the sag testing be undertaken in order to observe if there is a higher barite setting that can cause problems in the wellbore. This test assessed the barite sagging from a sample placed in static conditions, varying the angle of the cell, temperature and aged time[89]. Equation 3.1 was used to calculate the sag factor for the static conditions.

$$sagfactor = \frac{SG\ bottom}{SG\ bottom + SG\ top} \tag{3.1}$$

where, SG_{bottom} is the density of the sample at the bottom of the aging cells, SG_{top} is the density of the sample at the top of the aging cell[89]. For a fluid be considered to have acceptable suspension characteristics the sag factor should be between[31] 0.50 and 0.53. A sag factor greater than 0.53 implies that the fluid has the potential to sag[122] .

The method used to develop the sag testing is detailed below;

1. Fluids were mixed in a Hamilton Beach mixer at low shear rate and then placed in the HPHT stainless steel cells and pressurized at 50 psi.
2. The fluids were aged in HPHT stainless steel cells of 500 mL in a hot rolling oven at the set up temperature of 250 ˚F (121 ˚C) for 16 hours.
3. The samples were then mixed for 10 minutes and placed in HPHT cells.
4. The HPHT stainless steel cells were placed in the oven up right at a set temperature of 150 °F for 24 hours.
5. The samples were taken out after 24 hours, then the cells were unpressurized to open them.
6. The fluid was inspected *in situ* for oil separation. The base oil separated was taken with a syringe from the top. The density of the samples was calculated for a volume of 5 mL.
7. The remaining solids were sampled from the bottom under a volume of 5mL and weighed.
8. Finally, sag factor was calculated using Equation 3.1.

3.6 Characterization using scanning electron microscopy (SEM)

Analysis of oil and emulsion with the nanoparticles were conducted to qualitatively assess the degree of dispersion and to understand the morphology of the nanoparticles and aggregates formed. This experiment was undertaken in an attempt to investigate the cause of settling of MgAl-Ada LDH compared to Bentone 42. SEM was undertaken by Shansi Tian at the G. J. Russell Microscope Facility, in the Department of Physics at Durham University. The SEM analysis was carried out using an Hitachi SU70 analytical scanning electron microscope, employing an accelerating voltage of 5 kV under a vacuum of 3 mbar.

The method used to prepare the samples is detailed below:

1. A drop of oil /emulsion was placed in a microscope slide carefully.
2. The microscope slide was placed on a petri plate to carry out to dry the sample for 48 hours.

Chapter 4

New Rheology Modifier Interactions In Non-Aqueous Phase

4.1 Introduction

During drilling under high pressure, high temperature (HPHT) conditions, it is known that oil based muds (OBM) offer a stable fluid system relative to water based muds (WBM) owing to the fact that WBM are more susceptible to become contaminated by brine, or other flocculants, and when contaminated it becomes impossible to control the rheological properties[41]. This area represents a significant challenge for the contractor, due to the fact that there is an ongoing need for development of ever newer and better alternative processes and, especially, mud formulations in order to minimise environmental impact and enhance performance for HPHT conditions, both for onshore and offshore operations[124,125]. Although the costs of using WBM may appear lower across the total cost of the drilling operations on an environmental basis, with less clean-up required, the costs owing to fluid failure could increase beyond those associated with using an OBM system[125,126]. Therefore, the development of new environmentally friendly materials used for drilling fluid formulation, such as oil and rheological modifiers, are required for both WBM and OBM systems, and improved rheology modifier alternatives for HPHT conditions[20] are increasingly of interest as one of the challenges for oil and gas exploration, in wells with temperatures greater than 150 °C (300 °F) and bottom hole pressures of more than[127,128] 69 MPa (10,000 psi).

There are also concerns about the environmental impact of fluids, which must be taken into consideration by the operators, and are defined by various environmental regulations, which increasingly restrict the use of toxic and non-biodegradable materials[129,130], especially the base oil used for the formulation of OBM. This is exemplified in the case of the regulatory Oil and Gas Authorities in the UK and Norway[125,131]. This Chapter studies the interaction effects between the new rheological modifier with a base oil. Also, the rheological modifier stability in an emulsion was studied, where a flat rheology profile with the base oil and the invert emulsion is desired. Therefore, in this experimental phase it will be observed whether the new rheological modifier MgAl-Ada LDH meets the criteria to maintain constant rheology at low shear rate yield point and viscosity as the temperature increases. Finally, the morphology of both rheology modifiers, and aggregates formed, were observed using SEM analysis, after interacting with oil and emulsion. The commercial best available technology rheological modifier Bentone 42 was used as a comparison point of performance.

4.2 *Composition, properties and environmentally aspects of base oil for Oil Based Muds.*

4.2.1 *Types of Oil*

Depending on the base oil used, different properties will arise in the mud formulation due to the fact that every specific oil varies regarding the density, viscosity and chemical treatment[94]. Diesel base oils have been used for a long time to formulate oil based muds[132]. However, there have been many concerns about the use of diesel owing to the environmental impact that it can represent[94]. In Mexico, diesel base oil is used in the majority of fields with HPHT conditions, although, thus far deepwater fields have been the exception. Mineral oil base fluid consists of a paraffinic-based oil phase, and were the first mineral oils in the market after the diesel base oils[133]. Presently, in the market there exist different types of mineral oil, however not all of them accomplish the physical-chemical requirements that the base oil needs to have to be incorporated into a drilling fluid formulation[19]. The principle factors which need to be considered are the viscosity and pour-point, which affect the drilling fluid performance directly[46,133].

Synthetic base oils are those produced from gas to liquid processes, including linear alpha olefins (LAO), internal olefins (IO), synthetic paraffins, and esters and these are some of the synthetic base fluids (SBF) used as part of a drilling mud formulation[134] in deepwater HPHT operations. The oilfield service industry has explored new alternatives to find a base oil which can be environmentally friendly, and can still provide good properties to the drilling fluids[124].Cuttings generated while drilling, impregnated with synthetic oil can be discharged into the marine environment safely because of their benign environmental properties[135]. From the environmental point of view, SBM need to have a low aromatic fraction to be accepted as drilling fluids with low toxicity[19].

Bennett[133] analysed the performance of diesel oil and SBF in a drilling formulation, where the SBF had the same rheological properties as a diesel oil-based mud. Also, it was reported that the SBF fluid was temperature stable to 287.7 °C (550 °F). However, the pressure attained was not reported[§§§§§]. This information is not provided by the author. Saraline SBF has a thermal stability in borehole temperatures up to 400 ˚F or 205 ˚C[93]. As can be seen in Figure 4.1 which shows the density and viscosity profile under pressure and temperature.

[§§§§§] This research was focusing in some parts of rheological properties and stability of the material. This is not analysing the effects of pressure-volume-temperature (PVT) of this specific drilling fluid. As has been mentioned before, drilling fluids are complex and there are a lot of phenomena which are interacting and it will be impossible to embrace all of those phenomena in this thesis.

The costs for SBF are typically around 20 to 30% more than these for diesel OBM. For that reason, in Mexico, SBF are just used in deepwater fields, because the profitability of such projects is higher than the shallow water or onshore fields. Another aspect regarding the costs is that while the SBF is a much lighter oil, higher concentrations of additives are required[102]. For example, a dramatic increase of organophilic clay quantity is necessary for this kind of oil, with its thin characteristics, which makes the drilling fluid system more expensive. For that reason this drilling base fluid was considered in the formulation for the drilling fluid OBM for high pressure, high temperature (HPHT) applications as described in the patent[1,2]and used for all the formulations developed during the characterization of all the tests in this thesis.

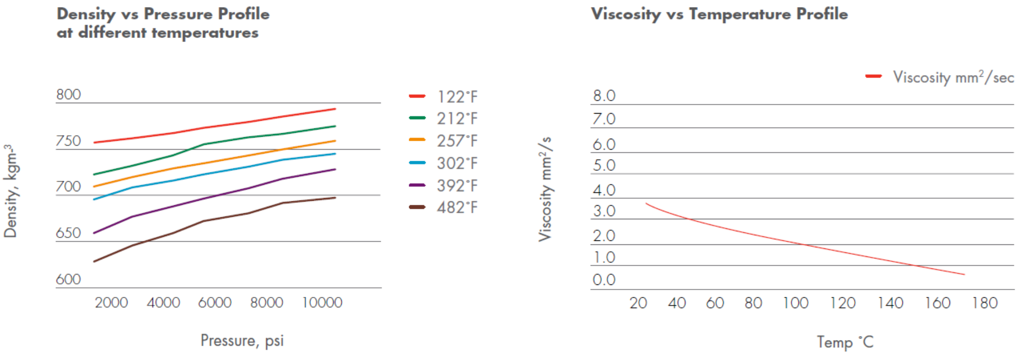
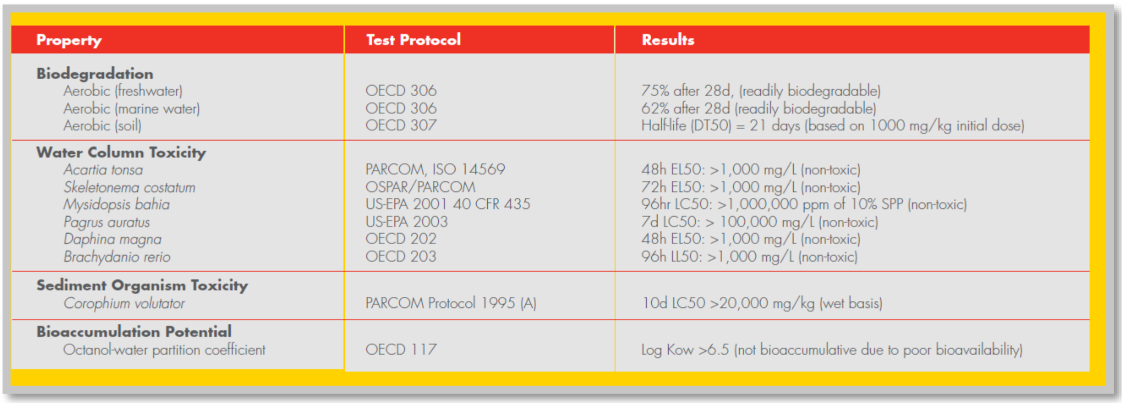


Figure 4.1 Density profile and viscosity profile for different temperatures for the Saraline 185V. Modified from Shell Chemicals[92].

4.2.2 Biodegradability of Saraline 185V

Saraline 185V as a drilling mud base fluid has the characteristics to be a SBF, and is environmentally friendly due to the carbon number range, branching and molecule type[93]. This provides the desired biodegradation properties and low aquatic toxicity[135]. Figure 4.2 illustrates the biodegradation and toxicity properties for Saraline 185V.



Property	Test Protocol	Results
Biodegradation Aerobic (freshwater) Aerobic (marine water) Aerobic (soil)	 OECD 306 OECD 306 OECD 307	 75% after 28d, (readily biodegradable) 62% after 28d (readily biodegradable) Half-life (DT50) = 21 days (based on 1000 mg/kg initial dose)
Water Column Toxicity *Acartia tonsa* *Skeletonema costatum* *Mysidopsis bahia* *Pagrus auratus* *Daphina magna* *Brachydanio rerio*	 PARCOM, ISO 14569 OSPAR/PARCOM US-EPA 2001 40 CFR 435 US-EPA 2003 OECD 202 OECD 203	 48h EL50: >1,000 mg/L (non-toxic) 72h EL50: >1,000 mg/L (non-toxic) 96hr LC50: >1,000,000 ppm of 10% SPP (non-toxic) 7d LC50: > 100,000 mg/L (non-toxic) 48h EL50: >1,000 mg/L (non-toxic) 96h LL50: >1,000 mg/L (non-toxic)
Sediment Organism Toxicity *Corophium volutator*	 PARCOM Protocol 1995 (A)	 10d LC50 >20,000 mg/kg (wet basis)
Bioaccumulation Potential Octanol-water partition coefficient	 OECD 117	 Log Kow >6.5 (not bioaccumulative due to poor bioavailability)

Figure 4.2 Summary of the Biodegradation and toxicity for Saraline 185 V. From Shell Chemicals[92].

4.2.3 *Regulation of base oils in drilling fluids*

Synthetic base fluid is used for offshore activities due to the fact that the drilling cuttings discharge in the sea is approve when impregnated with oils having these characteristics[134,136]. Mostly, the use of SBM are in countries such as: Malaysia, Australia, New Zealand, Thailand, Indonesia, Brunei, India, Nigeria, Dubai and, most recently, in China[93]. The Department for Business, Energy & Industrial Strategy (BEIS) in the UK[129], and the Netherlands State Supervision of Mines[130] have designed a strategy together with CEFAS[137], which is related to environmental offshore regulation[129,130,137]. This scheme is called the Offshore Chemical Notification Scheme[131] (OCNS) and regulates chemicals that are intended for use and discharge in exploration, exploitation and associated offshore processing of petroleum in the UK and Netherlands[131]. The scheme's ratings work with Group A as the most toxic, while Group E is the least toxic[93]. The Saraline 185V oil used in this study is encountered in Group E, which means a low toxicity oil base. Tables 4.1 shows the classification of toxicity for this scheme.

Table 4.1 Summary of toxicity for the Saraline 185V rating vs others according OCNS. Modified from Shell Chemicals[92]

Parameters	Shell GTL Saraline 185V	Diesel	LTMO1	LTMO2
Total BTEX ppm	ND	3840	ND	ND
Total Aromatics %m	~0.02	34	~0.02	~0.03
Sulphur, ppm	~1	10-5000	10 max	~1
OCNS designation	E	A	C	D

4.2.4 *Physical Properties of Saraline 185V*

Shell GTL Saraline 185V has a low viscosity, a low pour point and relatively high flash point for drilling in different environments, as is shown in Table 4.2. Mostly, the use of these fluids is in deep-water environments, with sea bed temperatures as low as 40 ˚F (4.4 ˚C).

Table 4.2 Physical properties for the Saraline 185V. Modified from Shell Chemicals[92].

	Unit	Test Method	Typical Values
Density@15C	kg/m^3	ASTM D4052	779
Flash point	°C	ASTM D93	85
Kinematic viscosity @40C	mm^2/s	ASTM D445	2.8
Pour point	°C	ASTM D97	-21
Aniline point	°C	ASTM D611	94

4.3 Hydraulic behaviour of base oils

Oil-based drilling fluids under HPHT conditions vary considerably as to the pressures and temperatures recorded through the depth of the wellbore, and this becomes more critical in deep water wells[106]. Also, it becomes a challenge to predict an appropriate ESD (equivalent static density) and ECD (equivalent circulation density) during the operations because the rheology and density can be affected rapidly, causing instability in the well[23]. This is due to the fact that in HPHT conditions the oil base mud is under compressibility and thermal expansion phenomena related effects[23]. Therefore, a rheology modifier which can provide a constant rheological profile over a wide temperature and pressure range is essential to prevent problems[138].

4.4 Emulsions in drilling fluids

Oil base muds (OBM) are called invert emulsions as well, which are dispersions usually showing a complex rheology behaviour[57]. The invert emulsion mainly encountered in the oil industry is the water in oil (W/O) emulsion, where this is dispersion of a smaller amount of water dispersed in the immiscible liquid phase, i.e. the oil[139]. Generally speaking, OBM and SBM are comprised mainly of three components, a liquid system such as where the continuous phase is the oil base, the discontinuous phase, which is the brine, and an emulsifying agent[94,140]. The emulsifier makes a stable dispersion between the liquids, lowering the interfacial tension between liquids to obtain a stable emulsion. The oil-based mud has showed a good performance to stabilize sensitive formations due to the oil-phase which provide inhibition of the shale swelling[72]. The brine, dispersed phase plays an important role removing water from the shale and building an osmotic effect on the shale[94].

4.5 Methods

As a baseline for developmental testing, the rheological stability of the new rheology modifier with the non-aqueous base oil was evaluated within an oil and water emulsion to understand its rheological behaviour without other compounds which provide other kind of properties in the drilling fluid formulation. The formulation to prepare the sample of MgAl-Ada LDH in oil is shown in Table 3.3 and the sample of MgAlAda-LDH is shown in Table 3.4. To undertake the rheological measurements of these samples, a Fann 35 was used for first set of samples, the reading was taken at a speed of 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6rpm and 3 rpm and at different temperatures 120 °F (49 °C), 140 °F (60 °C), 160 °F (71.1 °C), 180 °F (82.2 °C). The MgAl-Ada LDH was also placed in the base oil and observed across 5 days to qualitatively investigate the dispersion with respect to time.

A second set of samples were analysed before hot rolling (BHR) and after hot rolling (AHR) using a Discovery hybrid rheometer HR-2 from 25 °C (77 ˚F) to 120 °C (248 ˚F) at 100 1/s low shear rate with a Peltier plate with a geometry plate of 40 mm to reach a higher temperature than Fann 35 to measure the rheological behaviour. The hot rolling was performed at 121 °C (250 °F) for 16 hours in aging cells. Finally, to observe the morphology and aggregate structure of MgAl-Ada LDH and Bentone 42 with oil and the emulsion SEM analysis was undertaken. Chapter 3 gives the methodology used in more detail.

4.6 Results and Discussions

4.6.1 Rheology modifiers with a synthetic oil

The dial deflection obtained using the Fann 35 for high and low shear rate are shown in Table 4.3.The experiment focused on the data at 6 rpm and 3 rpm, obtaining the low shear yield point (LSYP) at 120˚F, 140˚F, 160˚F, 180˚F. This was to observe if the new rheological modifier followed the same behaviour of the present best available rheology modifier, Bentone 42. LSYP can predict the rheological profile, if it is maintained at constant value, or suffers any variation as the temperature increases. This is illustrated in Figure 4.6, which shows the rheological profile at low shear rate yield point, for Bentone 42 and MgAl-Ada LDH in the range of temperature from 120 °F to 180 °F.

Table 4.3 Rheological measurements for oil and rheological modifiers by Fann 35 viscometer.

Temperature/°F	**Bentone 42 + Saraline 185V**				**Mg Al adamantane + Saraline 185V**			
	120°F	140°F	160°F	180°F	120°F	140°F	160°F	180°F
θ600	9	6	6	6	7	7	7	5
θ300	6	5	4	5	5	5	4	4
θ200	4	3	3	2	4	4	3	3
θ100	3	2	1	1	3	3	2	2
θ6	2	1	1	1	2	2	2	2
θ3	1	1	1	1	2	1	1	1
μ_a (cP)	4.5	3	3	3	3.5	3.5	3.5	2.5
μ_p (cP)	3	1	2	1	2	2	3	1
τ_y(lb/100 ft^2)	3	4	2	4	3	3	1	3
LSYP (lb/100 ft^2)	2	0	0	0	0	2	2	2

The MgAl-Ada LDH trend line is a LSYP constant of 2 lb/100ft^2 from 140 °F to 180 °F in comparison with the Bentone 42, which fell down at 140 °F without any value of LSYP as can be seen in Figure 4.2.These measurements may need checking with a recalibration of the viscometer.

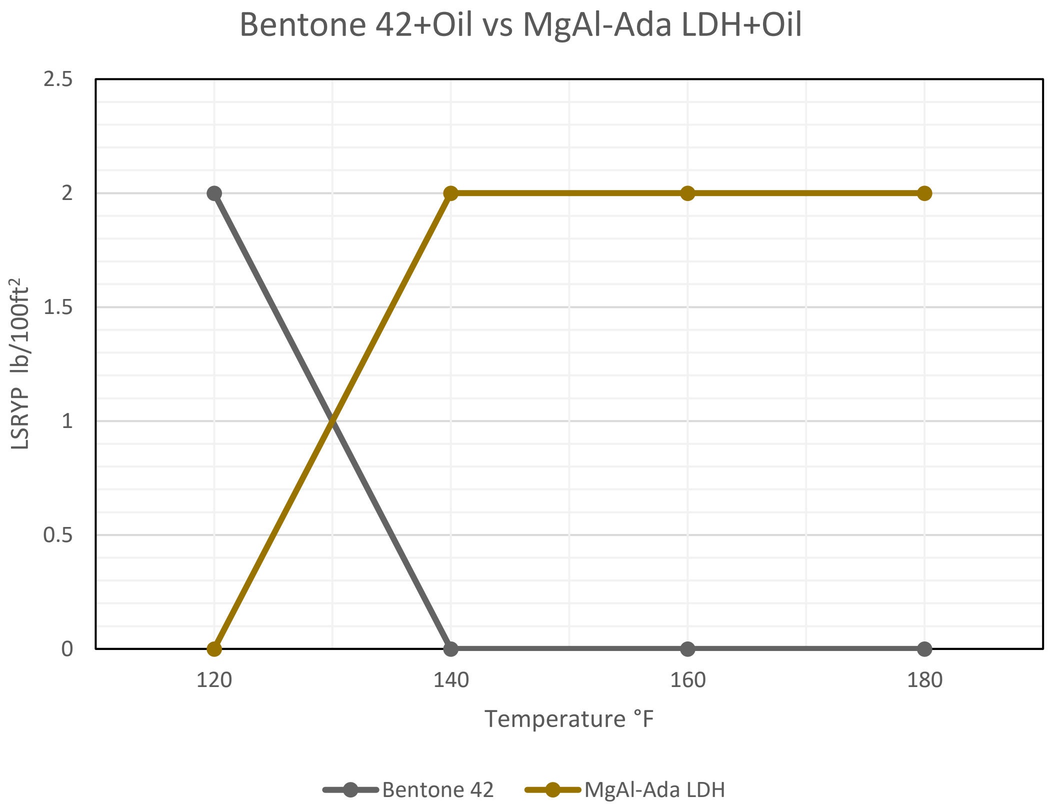
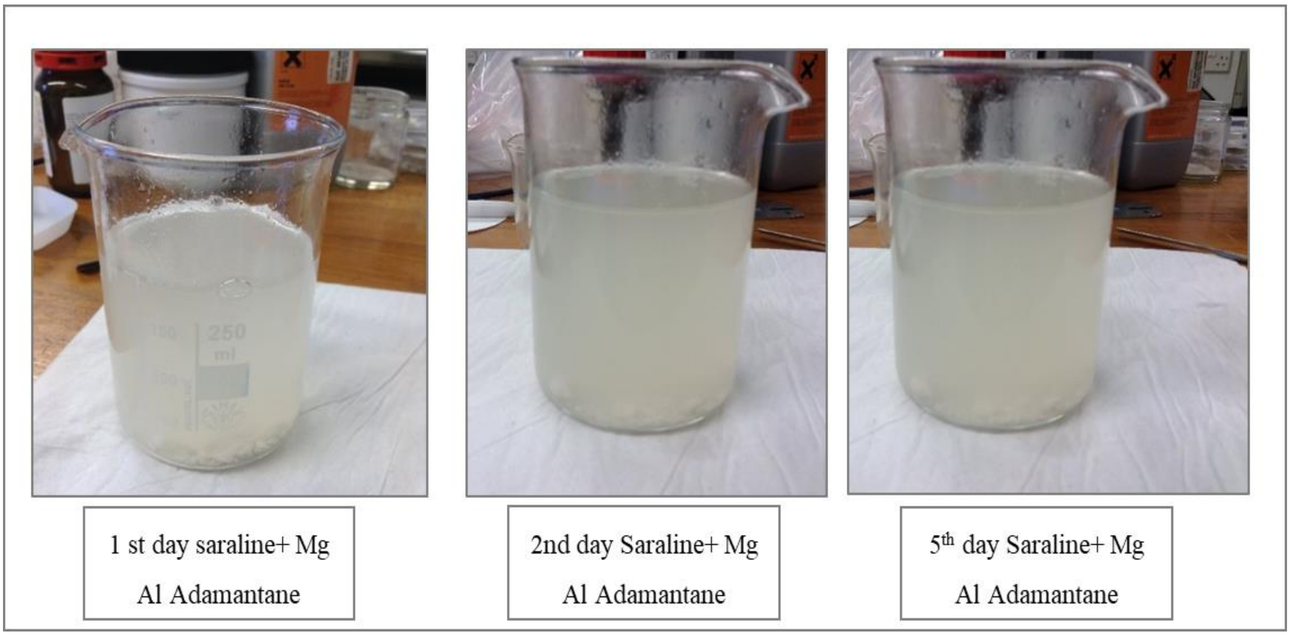


Figure 4.3 Rheological profile at low shear rate yield point vs temperature by Fann 35 for the new rheology modifier compared to Bentone 42.

The mix of Bentone 42 and Saraline 185V was homogenous at first observation. However, on further inspection of the sample with the MgAl-Ada LDH rheology modifier wasn't homogeneous in the longer term, and settling on the bottom of the vessel was observed after a short time period following cessation of stirring. For this reason, the rheological behaviour obtained by the MgAl-Ada LDH would not seem to be linked with the settling.

4.6.2 Stability and structure of the rheology modifiers in oil

Figure 4.4 shows the mixture of MgAl-Ada LDH and Saraline 185V at the 1st day, 2nd day and 5th day, with the same sample. The MgAl-Ada LDH is not fully soluble at the loading used. As can be seen in Figure 4.4 after the 5th day, MgAl-Ada LDH looks slightly more soluble. The MgAl-Ada LDH material evaluated from the toll manufacture, High Force has a granular appearance. This contrasted with the samples made in the small scale in laboratory by Manohara et al.[36], which were very soft. Thus, it was speculated that the texture and size of particle was affecting the solubility of the material in the oil.



1 st day saraline+ Mg Al Adamantane

2nd day Saraline+ Mg Al Adamantane

5th day Saraline+ Mg Al Adamantane

Figure 4.4 Solubility in oil of MgAl-Ada LDH before grinding. Careful observation notes the presence of powder at the base of the beaker.

The material was ground by a mortar and pestle to have a powder appearance and then it could be observed more fully what the effect on solubility with the oil was for the MgAl-Ada LDH. Figure 4.5 illustrates both samples, Bentone 42 and MgAl-Ada LDH. The solubility of MgAl-Ada LDH was better after grinding. However, after time without stirring the precipitation of the nanoparticle was considerable.

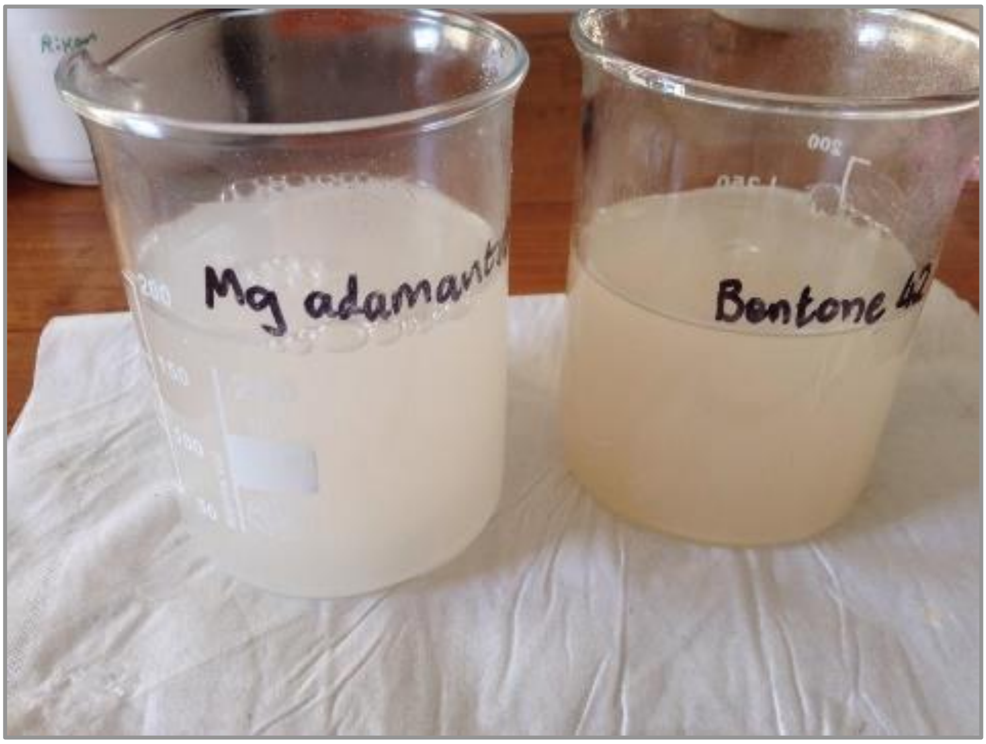
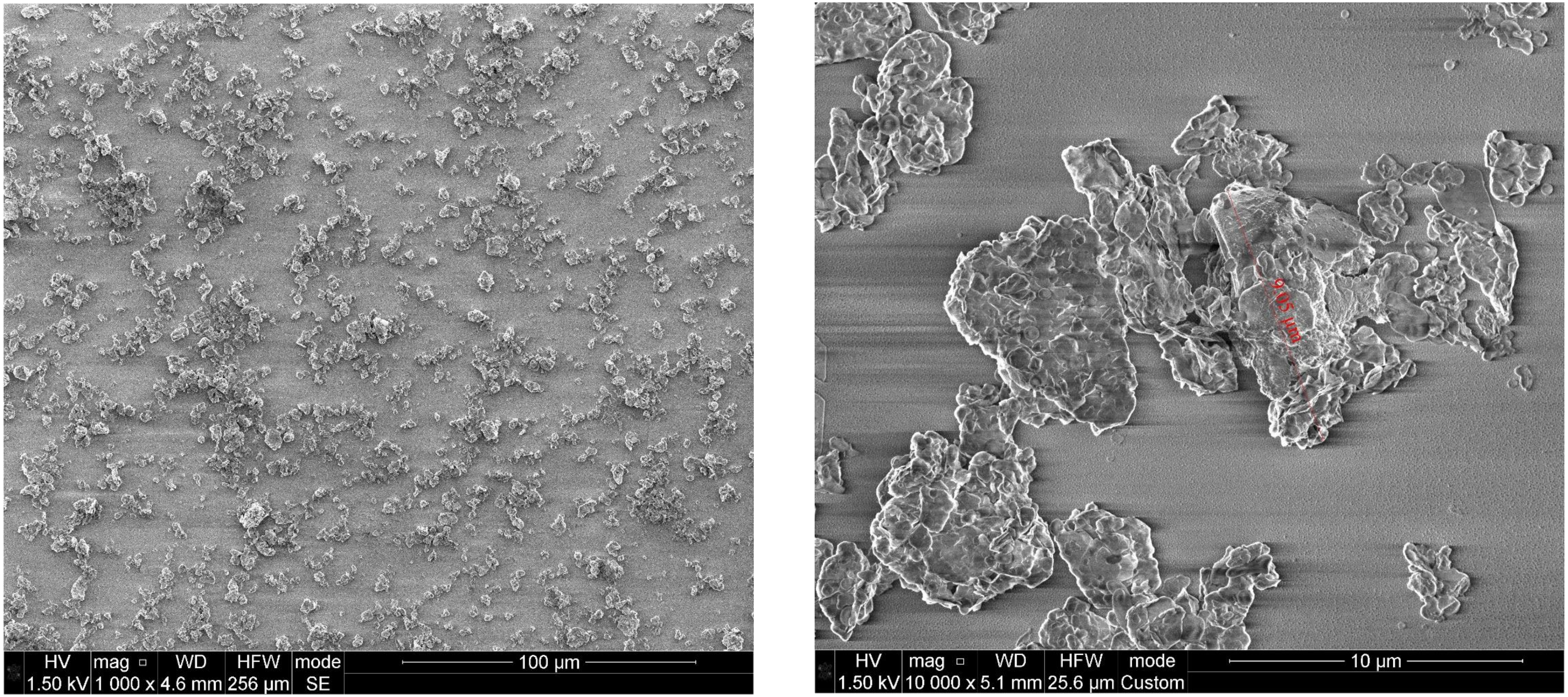


Figure 4.5 Comparison of samples with MgAl-Ada LDH after being ground + oil (left beaker), and Bentone 42 + oil (right beaker).

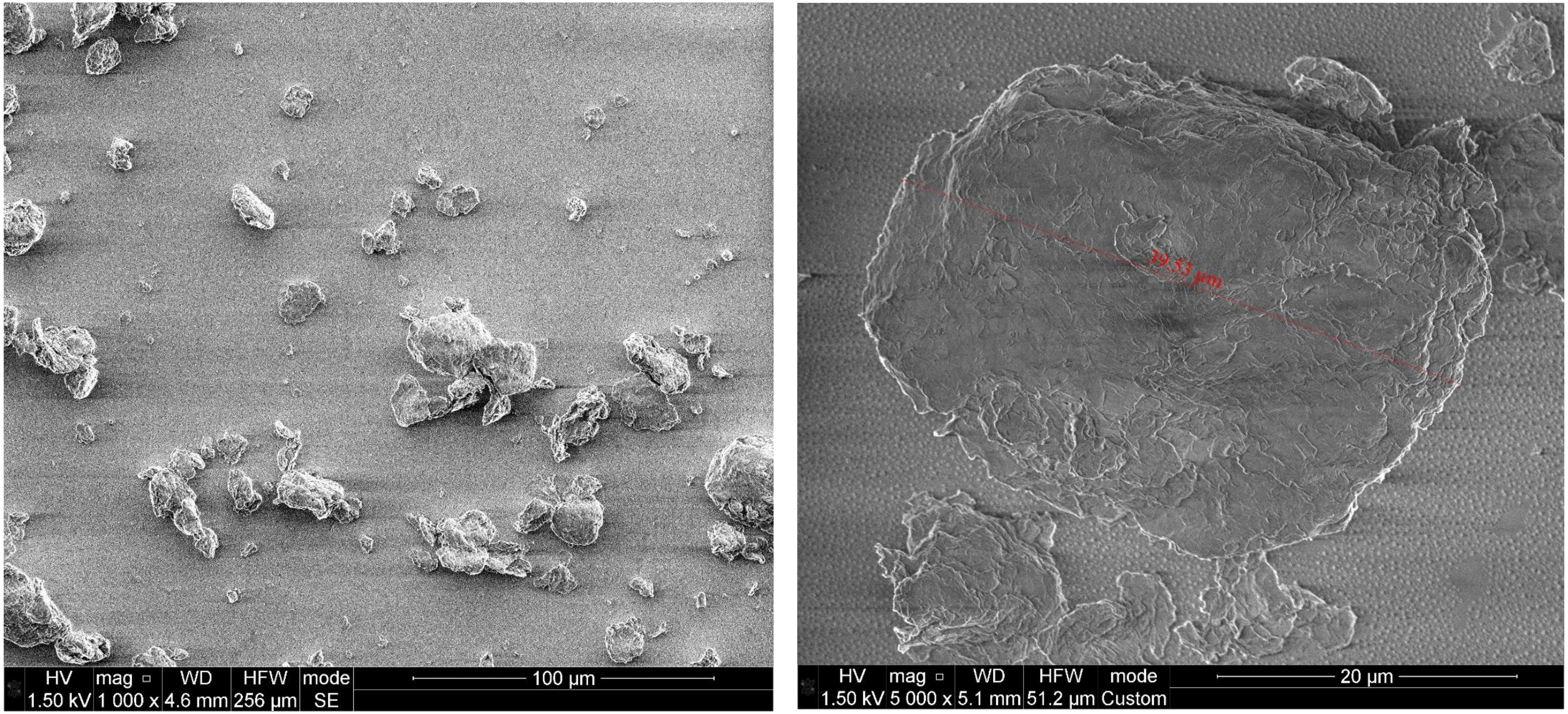


a) Bentone 42 dispersion

b) Bentone 42 particle

Figure 4.6 SEM images of the surface of the Bentone 42 particle impregnated with synthetic base oil.

a) (X 1000-100 µm magnification) dispersion of Bentone 42 in base oil, b) (X 10,000-10 µm magnification) Bentone 42 particle in base oil. The images (a) and (b) were taken to find a morphology in order to figure out the behaviour of Bentone 42 in the oil.



a) MgAl-Ada LDH dispersion

b) MgAl-Ada LDH particle

Figure 4.7 SEM images of the surface of the MgAl-Ada LDH particle impregnated with synthetic base oil.

a) (X 1000-100 μm magnification) dispersion of MgAl-Ada LDH in base oil, b) (X 5,000-20 μm magnification) Bentone 42 particle in base oil. The images (a) and (b) were taken to find a morphology in order to figure out the behaviour of the MgAl LDH in the oil.

Figure 4.6 (b) shows the Bentone 42 particle with the impregnation of synthetic oil, with a structure size around 9.05 µm. As the Figure 4.7 (b) the MgAl Ada LDH shows a structure size around of 39.53 µm, higher than Bentone 42. It seems that the particle tend to aggregate with the oil interaction. It may be linked with the precipitation observed in the sample after stirring.

4.6.3 Rheology modifier with emulsion

In order to observe the rheological behaviour of MgAl-Ada LDH in the emulsion BHR and AHR to temperatures up of 180 ˚F (82 ˚C), which was limited in the Fann 35 viscometer, this experiment was developed in the Rheometer HR-2 to reach a higher range of temperature, from 25 ˚C to 120 ˚C. Figure 4.8 reveals the rheological profiles from the four samples containing the MgAl-Ada LDH and Bentone 42, before hot rolling (BHR) and after hot rolling (AHR). As is shown in Figure 4.8, the viscosity of the Bentone 42 emulsion BHR and AHR is higher than the viscosity of the MgAl-Ada LDH emulsion BHR and AHR. It can be seen from the graph that the viscosity of the Bentone 42 emulsion declined from 25 °C (77 °F) to 100 °C (212 °F) BHR and AHR. In contrast the trend of viscosity for the MgAl-Ada LDH emulsion BHR and AHR shows relatively low values, but appears stable with low values of viscosity in comparison with the Bentone emulsion BHR and AHR, which displayed an abrupt fall with high temperature.

In summary, the Bentone 42 emulsion BHR and AHR was shown to have a higher viscosity through the range of temperature analysed from 25 °C (77 °F) to 120 °C (248 °F) compared to the MgAl-Ada LDH emulsion. The viscosity profile for the MgAl-Ada LDH emulsion before hot rolling was slightly higher than the MgAl-Ada LDH emulsion after hot rolling. Although, the viscosity values for MgAl-Ada LDH emulsion were considerable lower, BHR and AHR, for the temperature at 110 °C to 120 °C the MgAl-Ada LDH profile increased slightly BHR at 118 ^{o} C. This trend was converse relative to the Bentone 42 profile, which was going down accordingly with the temperature increased. However, this observation could indicate that the MgAl-Ada LDH under thermal treatment of 250 ºF caused instability in the emulsion. It could have caused negative effects with the activation of the emulsifier or the viscosifier causing the emulsion degradation. In the case of Bentone 42 the thermal treatment actived the other compounds[******] of the emulsion obtaining a profile slightly higher AHR than BHR.

[******] In the field work, it is common not over treatment the drilling fluid before to circulate through the wellbore and start to drilling in order to the other compounds can be activated with the thermodynamics effects during the operations.

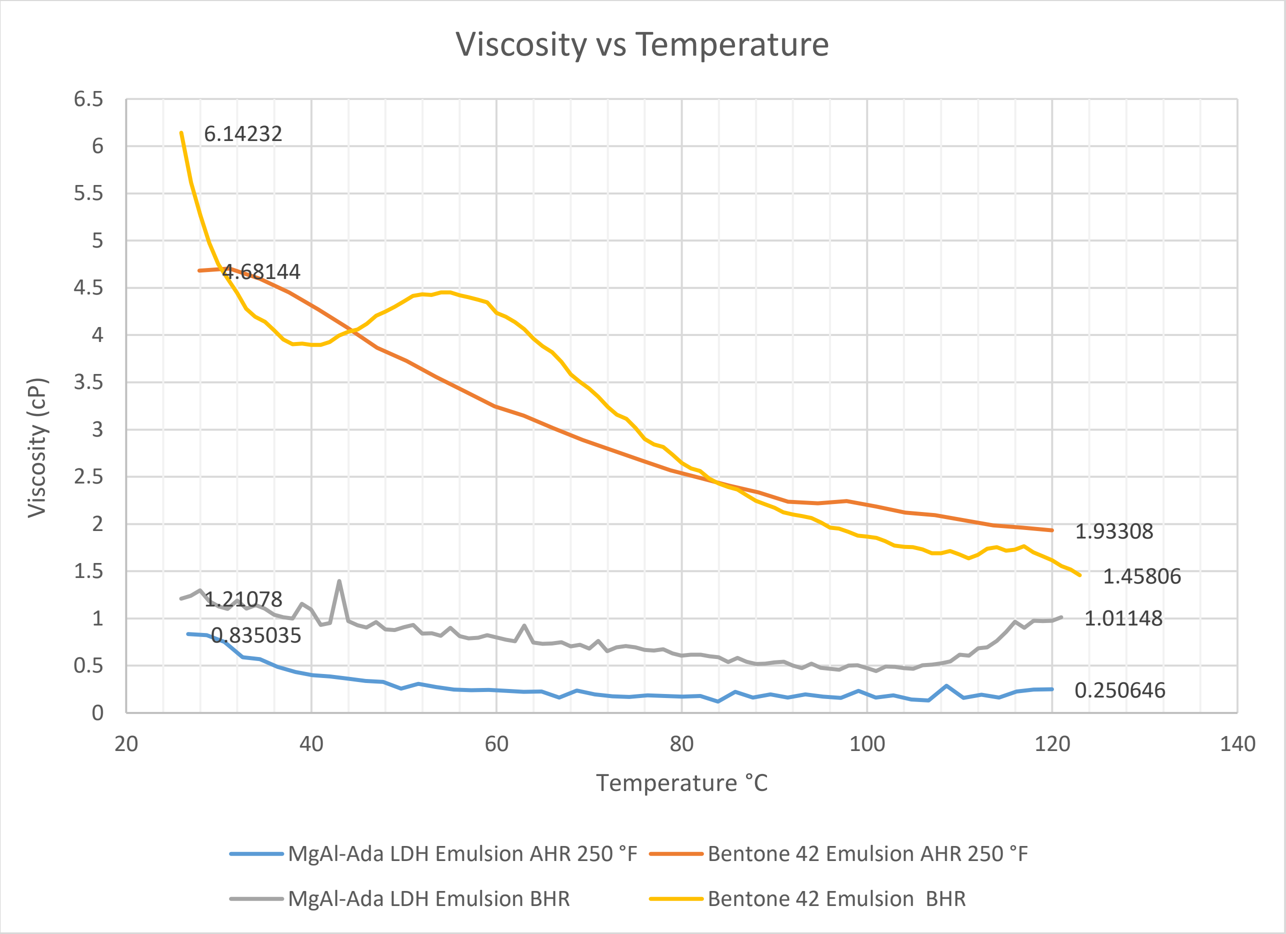


Figure 4.8 Analysis of experimental of viscosity vs temperature of MgAl-Ada LDH emulsion AHR and BHR and Bentone 42 emulsion AHR and BHR from 25 °C to 120 °C.

4.6.4 Stability and structure of the rheology modifiers in emulsion

The emulsion with the rheology modifiers was observed BHR and AHR to check for any phase separation. It was found that the rheology modifier MgAl-Ada LDH, before hot rolling, shows settling on the bottom of the vessel, far more than the emulsion formulated with the rheology modifier Bentone 42. Also, after the hot rolling the behaviour of the emulsion with MgAl-Ada LDH shows a settling of particles on the bottom of the cell as is illustrated in Figure 4.9. This behaviour was not observed on the bottom of the cell with Bentone 42.

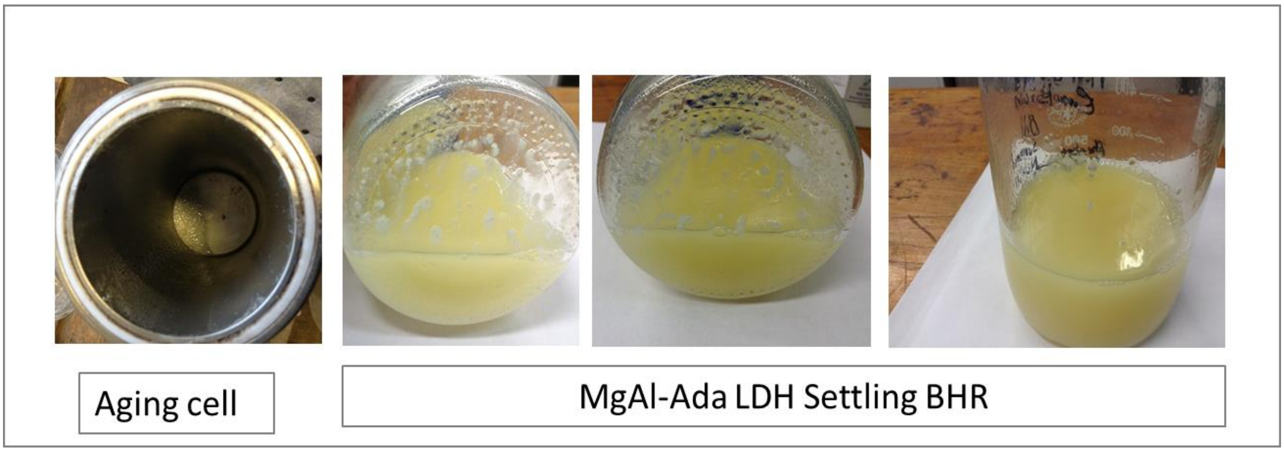


Figure 4.9 Settling of MgAl-Ada LDH on the bottom of the base oil, before hot rolling.

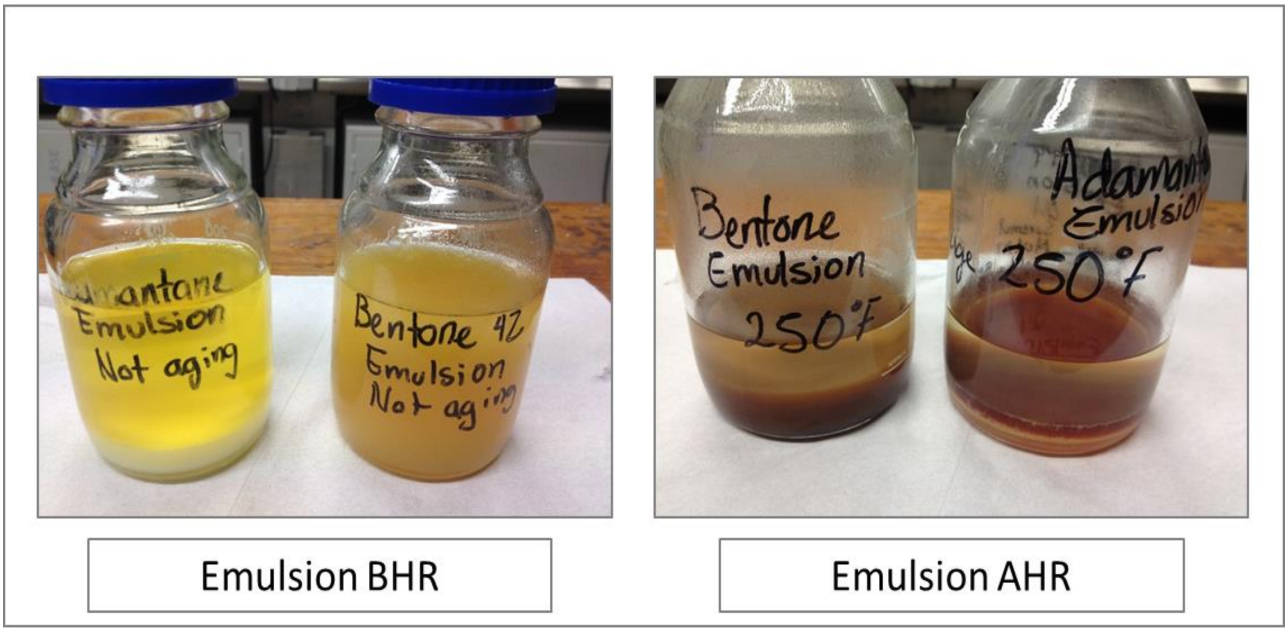
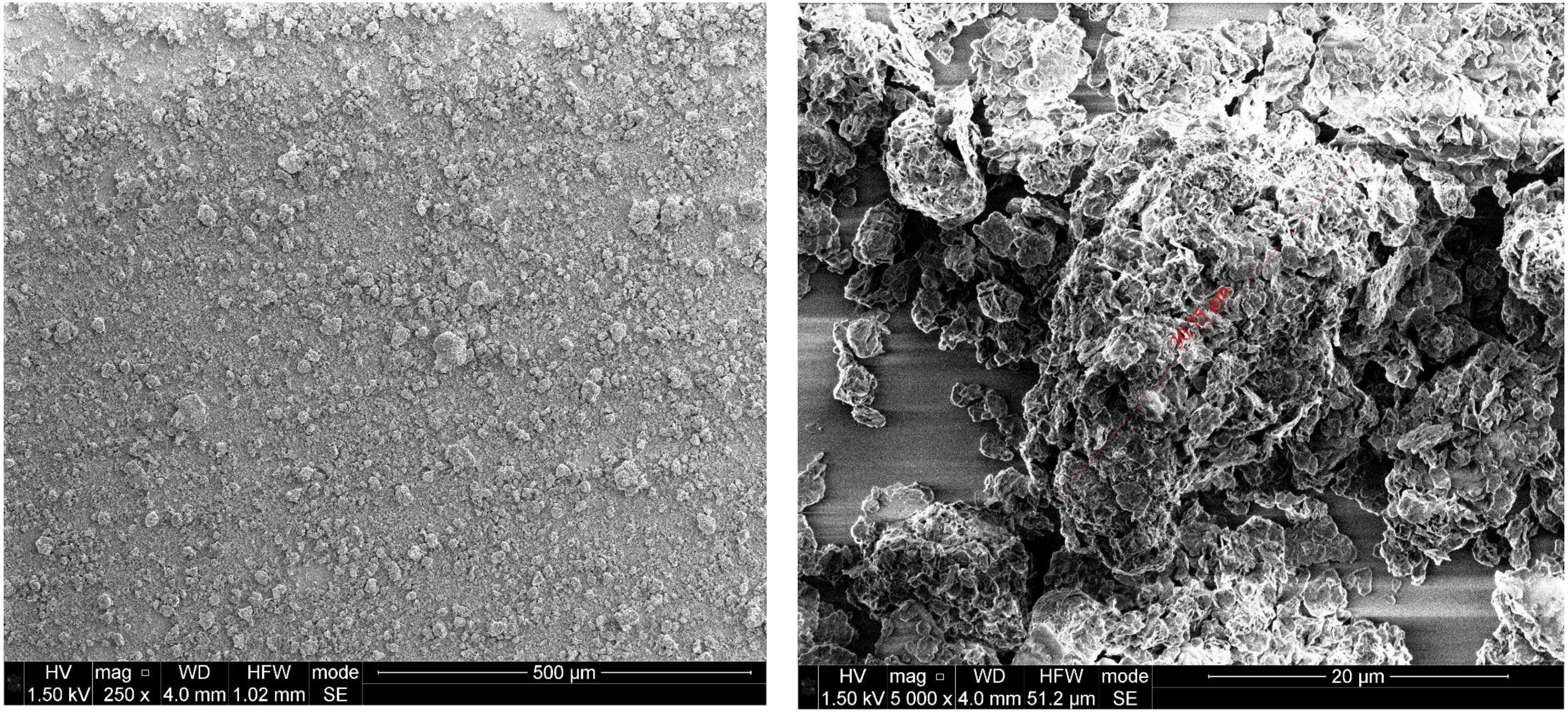


Figure 4.10 MgAl-Ada LDH emulsion and Bentone 42 emulsion before and after hot rolling at 250 °F.

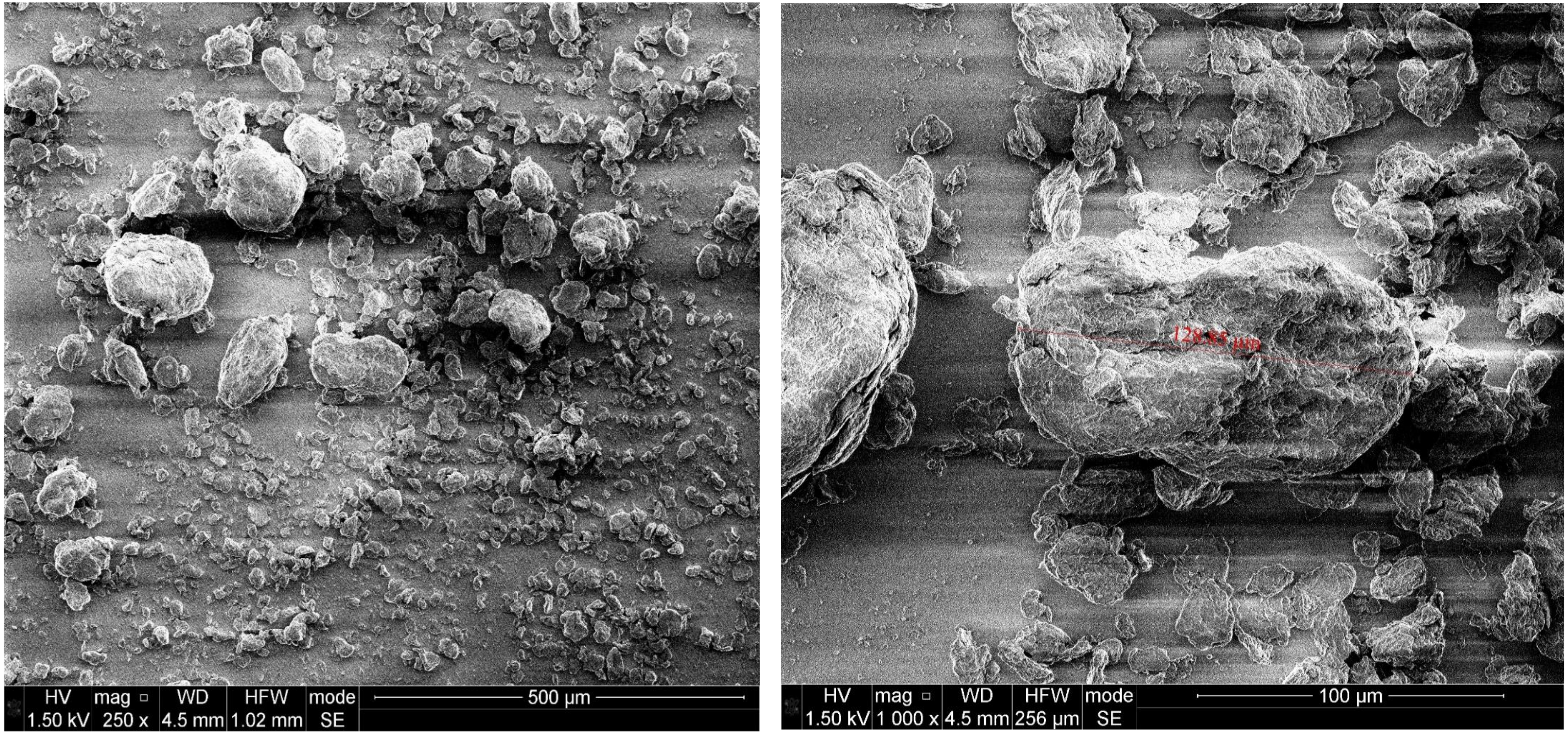
As was mentioned, the emulsion with the rheology modifier MgAl-Ada LDH appears to have good dispersion when mixed with the viscosifiers, emulsifiers and the continuous and discontinuous phase as can be seen in Figure 4.9. However, after 5 minutes without stirring or agitation of this mix, it seems that the MgAl-Ada LDH did not form a stable suspension as it is shown in Figure 4.10. The sample of MgAl-Ada LDH AHR presented a white segregation of solids in the bottom in comparison with the Bentone 42 AHR in Figure 4.10. This behaviour was observed with the rheology modifier Bentone 42 but the concentrations of solids on the bottom are not as much.



a)Bentone 42 dispersion **b) Bentone 42 particle**

Figure 4.11SEM images of the surface of the Bentone 42 particle impregnated with emulsion.

a) (X 250-500 µm magnification) dispersion of Bentone 42 in emulsion, b) (X 5000-20 µm magnification) Bentone 42 particle in emulsion. The images (a) and (b) were taken to find a morphology in order to figure out the behaviour of Bentone 42 in the emulsion. As the image (b) shows the Bentone 42 particle is impregnated of emulsion, which it predicts that there are good dispersion for the material in the emulsion.



MgAl-Ada LDH dispersion

b) MgAl-Ada LDH particle

Figure 4.12 SEM images of the surface of the particle impregnated with emulsion.

a) (X 250-500 μm magnification) dispersion of MgAl-Ada LDH in emulsion, b) (X1000-100 μm magnification) MgAl-Ada LDH particle in emulsion. The images (a) and (b) were taken to find a morphology in order to figure out the behaviour of MgAl-Ada LDH in the emulsion.

Figure 4.11 (b) shows the Bentone 42 particle after contact with the emulsion, with a structure size of around 30.75 µm. As shown in Figure 4.12 (b), the MgAl Ada LDH shows a structure size around 128.85 µm higher than Bentone 42. The MgAl-Ada LDH particle contacted with emulsion seems to conglomerate, developing larger particles than Bentone 42, as is shown in Figure 4.12. It might be expected that the nanoparticle is hydrophobic, causing instability with the water percentage of the emulsion, which could be the reason of settling of material in the bottom of the vessel. However, this will need to be investigated in further work, in order to understand the behaviour of the material in more detail.

4.7 Conclusions

The new rheological modifier seems to be stable under temperature, because it was observed that the MgAl-Ada LDH maintains a flat rheology profile as temperature increases, which is desirable. However, this does not develop viscosity properties in the invert emulsion system. Therefore, the settling of particles in the bottom with MgAl-Ada LDH in the synthetic oil and emulsion indicates potential instability in comparison with Bentone 42. Also, the nanoparticles under aging treatment at 250 ˚F suffered alteration owing to conglomeration of material, then observed settled in the bottom of the vessel. The particle structure of MgAl-Ada LDH with oil is smaller than the one observed when used in the emulsion, however, the impregnation of emulsion seems to result in bigger primary particles than the Bentone exhibits. As the new rheology modifier shows some desirable characteristics, the next chapter will study its interaction with the full drilling fluid formulation in order to observe its behaviour with all the compounds of the invert emulsion.

Chapter 5

Performance of New Rheology Modifier in Drilling Fluids at Low Temperature and Low Pressure

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5.1 Introduction

This chapter describes a study of performance of the new rheology modifier, MgAl-Ada LDH, at low temperature and low pressure in model formulated drilling fluids. Throughout, the acronyms to refer to the conditions as LT for low temperature and LP for low pressure will be used for this Chapter and throughout the next chapters. Oil-based drilling fluids are complex fluids and for evaluating these systems, it is required to have previous knowledge of this topic and training to use the equipment and chemicals appropriately. For this reason, there are standardized procedures that API designed for the analysis of drilling fluids, laboratory practices and rheology hydraulics for each type of mud, as was already detailed in Chapter 2. Therefore, this Chapter starts by summarising some of the selected tests described in Chapter 3, from the list of tests that the drilling fluid should meet according to the API standards, such as rheology measurements, gel strength, filter loss and barite sag. These tests were selected because they will give a general overview should the new rheological modifier develop a good performance in the drilling fluid formulation at LT and LP.

5.1.1 Stability of oil based muds

The stability is affected by different interfacial interactions with solid materials such as the weighting agent, fluid loss control additives and drill solids[21,46]. Some of the characteristics of effective oil-base muds (OBM) in the drilling operations are: high lubricity when the bit is drilling the geological formations, low fluid loss through the wellbore, higher stability under any drilling event, superior penetration rates in some formations[94] and thin filter-cake[95]. OBM systems have become one of best candidates for drilling under HPHT conditions in comparison with WBM.

5.2 Methods

Characterization of the drilling fluid properties was conducted according to standard API test methods regarding to rheological measurements, filtration test and sag test, as described in detail in Chapter 3. As a baseline for developmental testing, a 2.2 g/cm^3 density invert emulsion formulation with a 90/10 oil/water ratio and an internal brine of a density of 1.35 g/cm^3 Calcium Chloride was formulated as shown in Table 3.5, Chapter 3. The formulations evaluated in this section are described in Table 5.1. Rheology measurements were conducted at 120 ˚F, 140 ˚F, 160 ˚F and 180 ˚F by Fann 35, before and after hot rolling for 16 hours. Thermal ageing of the fluid was initially performed at 150 ˚F. Later tests were conducted at 250 ˚F, 350 ˚F, 400 ˚F, 450 ˚F to test thermal rheology stability of MgAl-Ada LDH. Bentone 42 is used throughout as a comparison reference. Fragile gel strength measurements at very low shear rates were performed on a Brookfield viscometer to measure gel strengths at 10 seconds, 10 minutes and 30 minutes at 77 ˚F and 167 ˚F with samples aged at 350 ˚F, 400 ˚F, and 450 ˚F. The HPHT fluid loss testing was performed as per API 13B-2[89] recommendations on HPHT with the formulations aged at 350 ˚F, 400 ˚F, and 450 ˚F previously for 16 hours. Finally, formulations with the new rheology modifier and Bentone 42 with thermal ageing at 250 ˚F were conducted to develop barite sag tests at an inclination of 90^o .

Table 5.1 Formulations used for this study evaluating both rheological modifiers using the drilling fluid formulation in Chapter 3.

Formulation	Rheology modifier	Physical conditions	Before aging	After Aging	
				°F	°C
Formulation 1	Bentone 42	N/A	Yes	150	65.5
Formulation 2	MgAl Ada LDH	non-ground	Yes	150	65.5
Formulation 3	MgAl Ada LDH	ground	Yes	150	65.5
Formulation 4	Without	N/A	Yes	150	65.5
Formulation 5	Bentone 42	Product data	Base reference	-	-
Formulation 6	Bentone42	ground	yes	N/A	N/A
Formulation 7	Mg-Al Ada LDH	ground	yes	N/A	N/A
Formulation 8	MgAl Ada LDH	ground	yes	350	176.66
Formulation 9	MgAl Ada LDH	ground	yes	400	204.44
Formulation 10	MgAl Ada LDH	ground	yes	450	232.22
Formulation 11	Bentone42	ground	yes	350	176.66
Formulation 12	Bentone 42	ground	yes	400	204.44
Formulation 13	Bentone42	ground	yes	450	232.22
Formulation 14	Bentone42	ground	yes	250	121.1
Formulation 15	Mg-Al Ada LDH	ground	yes	250	121.1

5.3 Results and discussion

5.3.1 Effect of granularity for MgAl-Ada LDH at low share rate

To assess the performance of the new rheological modifier in the formulation cited in the patent already mentioned in previous Chapters, Formulation 1, Formulation 2, Formulation 3 and Formulation 4 were analysed in order to observe their rheological behaviour at low share rate, taken from the measurements made by a Fann35 viscometer BHR (before hot rolling) and AHR (after hot rolling) at 150 ˚F.

Initial tests taken within Chapter 4, using just the base oil, showed that the granularity from the new modifier was causing problems of solubility and settling on the bottom in the oil and emulsion interaction study. Therefore, the material was ground with a mortar and pestle for this study, and the influence in its rheological behaviour by using these fine particles was observed. The formulations with MgAl-Ada LDH ground, and not ground, were compared with the corresponding conventional organoclay used for HPHT conditions, Bentone 42.

Figure 5.1 shows the profile of Bentone 42 and MgAl-Ada LDH before and after hot rolling. Table 5.2 and Table 5.3 shows the dial the deflection obtained from Fann 35 at 120 ˚F, 140 ˚F, 160 ˚F and 180 ˚F. The Bentone 42 profile from the product datasheet is included as a reference point to compare the performance of both rheology modifiers.

However, the data obtained from the product data sheet is from a fluid using Bentone 42 AHR at 120°F. It could affect the comparison from the fluids used AHR at 150°F, but not for the samples BHR. As can be seen in Figure 5.1, Bentone 42 has a flat rheology profile. MgAl-Ada LDH presents slightly a higher LSRYP when ground than when not ground, before and after aging. This profile on the new rheological modifier is more noticeable before rolling as is shown in Table 5.2 and Table 5.3.

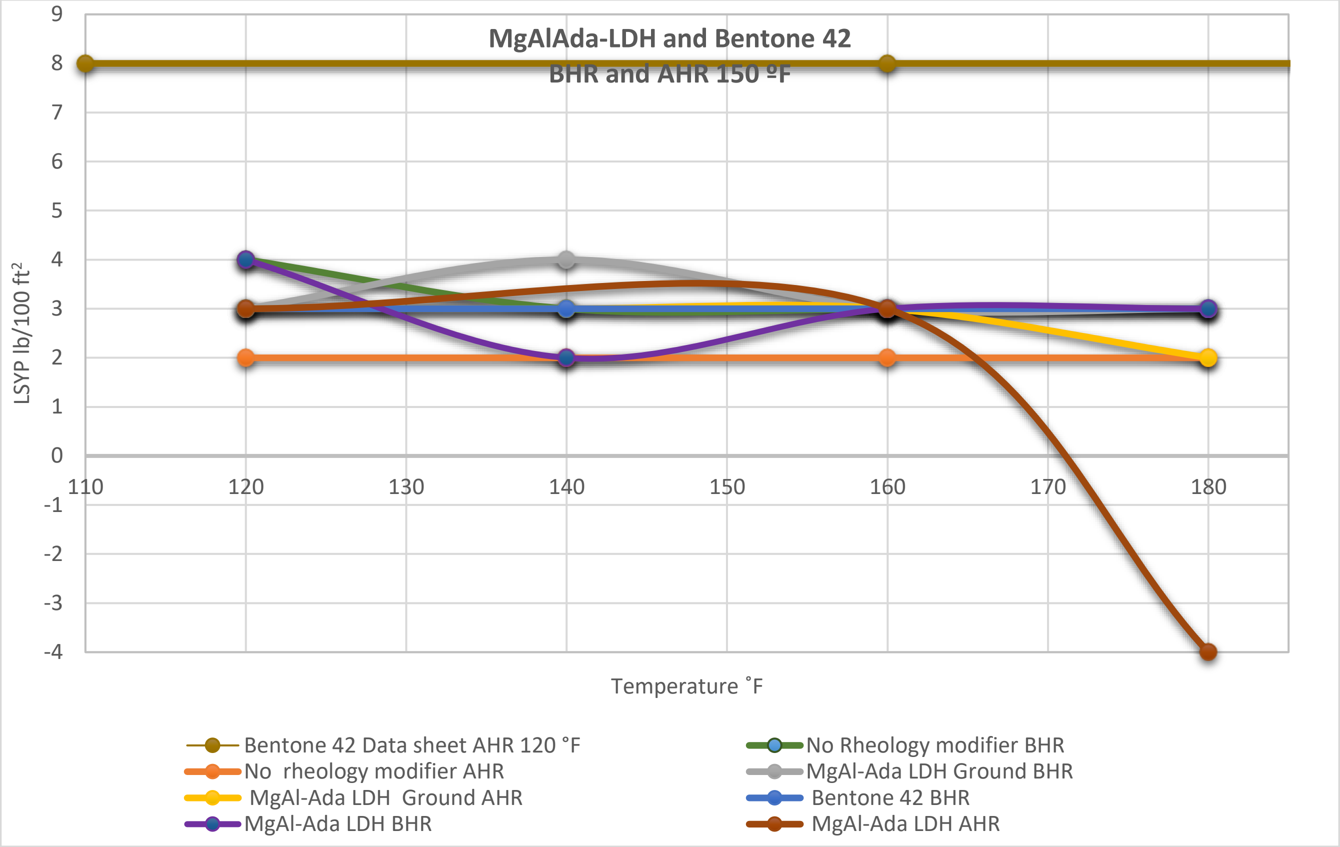

Figure 5.1 Rheology at low shear rate yield point BHR and AHR at 150˚F for the ground and not ground MgAl-Ada LDH compared to Bentone and fluids with no rheology modifier.

Table 5.2 Readings of dial deflection from Fann 35 evaluating Bentone 42, MgAl-Ada LDH, MgAl-Ada LDH grounded and without rheology modifier before hot rolling (BHR).

	Bentone 42 BHR				MgAl-Ada LDH BHR				MgAl-Ada LDH Ground BHR				No Rheology modifier			
°F	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**
°C	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
RPM																
θ600	159	128	122	105	131	105	95	92	158	116	104	97	137	112	104	92
θ300	84	69	65	55	67	55	50	47	82	59	58	49	72	58	53	46
θ200	58	48	46	39	47	39	36	35	48	41	40	35	50	41	38	32
θ100	32	23	26	22	26	22	21	21	27	23	24	20	29	24	23	19
θ6	5	5	5	5	4	4	5	5	5	4	5	5	6	5	5	5
θ3	4	4	4	4	4	3	4	4	4	4	4	4	5	4	4	4
10s/10min (lb/100ft^2)	8/11	8/15	8/14	8/14	9/13	5/13	6/9	8/9	6/7	6/7	4/8	7/8	6/7	5/8	5/7	4/5
μ_a (cP)	80	64	61	53	66	53	48	46	79	58	52	49	69	56	52	46
μ_p (cP)	75	59	57	50	64	50	45	45	76	57	46	48	65	54	51	46
τ_y (lb/100ft^2)	9	10	8	5	3	5	5	2	6	2	12	1	7	4	2	0
LSYP (lb/100ft^2)	3	3	3	3	4	2	3	3	3	4	3	3	4	3	3	3

Table 5.3 Readings of dial deflection from Fann evaluating Bentone 42,MgAl-Ada LDH, MgAl-Ada LDH grounded and without rheology modifier after hot rolling (AHR) at 150° F.

	Bentone 42 AHR 150° F	Bentone 42 Data Sheet AHR 120° F			MgAl-Ada LDH AHR 150°F			MgAl-Ada LDH Ground AHR 150°F				No rheology modifier AHR 150°F			
°F	**120**	**110**	**160**	**200**	**120**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**
°C	**49**	**43**	**71**	**93**	**43**	**71**	**93**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
RPM															
$\theta600$	184	84	50	33	144	106	92	191	122	103	94	128	105	94	88
$\theta300$	97	53	29	20	74	56	48	99	59	59	49	64	52	46	42
$\theta200$	67				52	40	35	79	42	41	34	44	37	32	30
$\theta100$	37	25	16	13	29	23	20	37	24	23	20	24	20	18	17
$\theta6$	6	10	8	8	5	5	10	5	5	5	4	4	4	4	4
$\theta3$	4	9	8	8	4	4	3	4	4	4	3	3	3	3	3
10s/10min (lb/100ft^2)	8/28				6/8	7/9	4/8	6/11	5/6	6/7	5/6	4/6	5/6	4/5	4/6
μ_a (cP)	92				72	53	46	96	61	52	47	64	53	47	44
μ_p(cP)	87	31	21	13	70	50	44	92	63	44	45	64	53	48	46
τ_y (lb/100ft^2)	10	22	8	7	4	6	4	7	-4	15	4	0	-1	-2	-4
LSYP(lb/100ft^2)	**2**	8	8	8	3	3	-4	3	3	3	2	2	2	2	2

Lower rheological performance was observed in the experiment for the Bentone 42 than the datasheet reported, as is shown in Figure 5.1. This is considered to be owing to the formulation and concentration used in the samples analysed being different to the data sheet performance. The Bentone 42 and MgAl-Ada LDH, BHR and AHR, showed almost a similar rheological profile at low shear rate yield point in this formulation, as can be seen in Figure 5.1. This might indicate that the MgAl-Ada LDH has a flat rheological profile but with low shear yield point in this formulation. MgAl-Ada LDH without grinding presented a negative point at 180° F, which might represent an error during the collection of dial deflection data, or the calibration of the equipment, or instability of material in the formulation.

5.3.2 Performance of MgAl-Ada LDH at different temperature aged.

Formulation 8, Formulation 9, Formulation 10, Formulation 11, Formulation 12 and Formulation 13 were aged to evaluate the thermal limits and subsequent rheological performance. The detail of each sample can be seen above in Table 5.1. The thermal aging was performed at 350 ˚F, 400 ˚F, 450 ˚F. The performance of the drilling fluids formulated with the new rheological modifier were compared to Bentone 42 under the same thermal aging conditions. It was observed that Bentone 42 developed an acceptable performance before hot rolling at 120 ˚F, meeting the criteria in the range of acceptable values of yield point in the order of (7-16 cP)[††††††], as was mentioned in Chapter 2, within Figure 2.2 in the rheogram regarding the density used for all the drilling formulations. As can be seen in Figure 5.2, the Bentone 42 based fluid presents higher yield rheology values after aging from 350 ˚F to 450 ˚F, in contrast to the new rheological modifier at different rheology temperatures.

The rheological values of yield point and plastic viscosity for Bentone 42 were slightly higher than the MgAl-Ada LDH. However, the increased values of yield point from 400 ° F to 450 ° F for Bentone 42 could indicate flocculation for the system at high temperatures. In comparison, MgAl-Ada LDH held low values of plastic viscosity and yield point without a noticeable effect by temperature. Table 5.4 and Table 5.5 show low LSRYP values for Bentone 42 and MgAl-Ada LDH. This might manifest as sagging, or low suspension capacity, which is related with the low shear rate yield point rheology. At a minimum, LSRYP values should be in the order of 7-15 lb/100 ft^2, [20,141] to avoid barite sag.

Table 5.4 Dial deflection measurements evaluating Bentone 42 before hot rolling (BHR) and after hot rolling at 350 ° F, 400 ° F and 450° F.

	Bentone 42 BHR				Bentone 42 AHR 350 °F				Bentone 42 AHR 400°F				Bentone 42 AHR @ 450°F			
°F	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**
°C	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82.2**
RPM																
θ600	159	128	122	105	206	213	208	206	262	230	209	210	300	274	254	234
θ300	84	69	65	55	109	121	112	119	160	122	112	113	215	159	161	156
θ200	57.5	48	46	39	76	87	81	87	123	84	77	78	163	116	125	120
θ100	32	23	26	22	42	50	45	53	82	44	42	42	100	70	79	80
θ6	5	5	5	5	5	7	6	11	47	4	4	4	26	18	26	26
θ3	4	4	4	4	3	5	4	9	46	2	2	2	21	15	22	21
10s/10min (lb/100ft^2)	8/11	8/15	8/14	8/14	6/27	7/12	7/28	11/21	41/65	4/8	5/9	6/11	42/76	25/46	29/42	30/28
μ_a(cP)	80	64	61	53	103	107	104	103	131	115	105	105	150	137	127	117
μ_p(cP)	75	59	57	50	97	92	96	87	102	108	97	97	85	115	93	78
τ_y (lb/100ft^2)	9	10	8	5	12	29	16	32	58	14	15	16	130	44	68	78
LSYP(lb/100ft^2)	3	3	3	3	1	3	2	7	45	0	0	0	16	12	18	16

[††††††] It doesn't mean that this value is acceptable at all for all oil base muds. All the operators have different parameters evaluated from its chemical products and their own drilling fluid systems. This values is just a base from Exxon criteria according with its manual[40]. Also, it dependents of other wellbore parameters as it has mentioned in previous chapters.

Table 5.5 Dial deflection measurements from Fann 35 evaluating MgAl-Ada LDH before hot rolling (BHR) and after hot rolling (AHR) at 350° F, 400° F and 450° F.

	MgAl-Ada LDH BHR				**MgAl-Ada LDH AHR 350°F**				**MgAl-Ada LDH AHR 400°F**				**MgAl-Ada LDH AHR 450°F**			
°F	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**	**120**	**140**	**160**	**180**
°C	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
RPM																
θ600	131	105	95	92	142	154	125	114	177	140	122	111	300	274	254	234
θ300	67	55	50	47	74	86	66	69	95	74	66	59	215	159	161	156
θ200	47	39	36	35	52	60	45	41	66	53	53	42	163	116	125	120
θ100	26	22	21	21	28	35	25	23	37	30	30	24	100	70	79	80
θ6	4	4	5	5	4	4	3	3	5	4	5	4	26	18	26	26
θ3	4	3	4	4	2	3	2	2	4	3	4	2	21	15	22	21
10s/10min (lb/100ft^2)	9/13	5/13	6/9	8/9	4/11	5/14	4/7	5/6	5/19	6/12	5/11	5/9	42/76	25/46	29/42	30/28
μ_a(cP)	66	53	48	46	71	77	63	57	89	70	61	56	150	137	127	117
μ_p(cP)	64	50	45	45	68	68	59	45	82	66	56	52	85	115	93	78
τ_y(lb/100ft^2)	3	5	5	2	6	18	7	24	13	8	10	7	130	44	68	78
LSYP(lb/100ft^2)	4	2	3	3	0	2	1	1	3	2	3	0	16	12	18	16

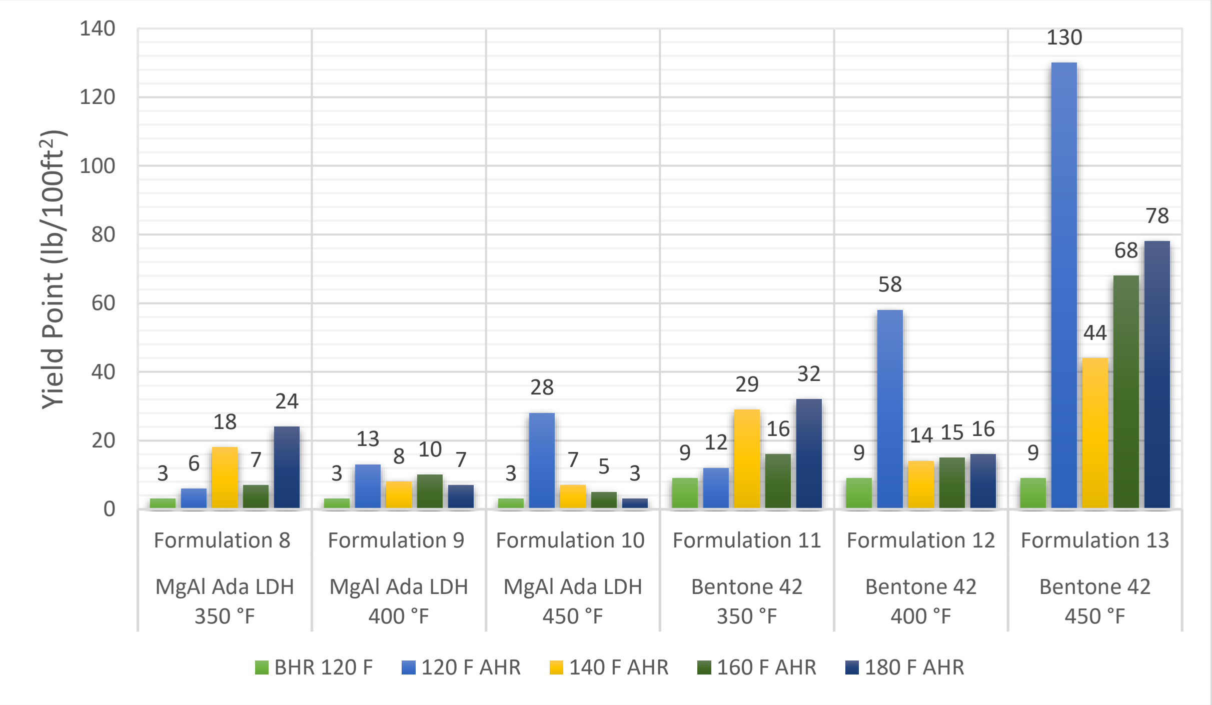

Figure 5.2 Yield point at different thermal aging and different temperature for MgAl-Ada LDH and Bentone 42.

The range of acceptability for the plastic viscosity is in the order of 35-60 cP for a drilling fluid with a density of 2.20 g/cc, as shown in Chapter 2 in Figure 2.2 .Therefore, as is shown in Figure 5.3, all the formulations tested failed to meet the ideal criteria to be a drilling fluid with good plastic viscosity values.

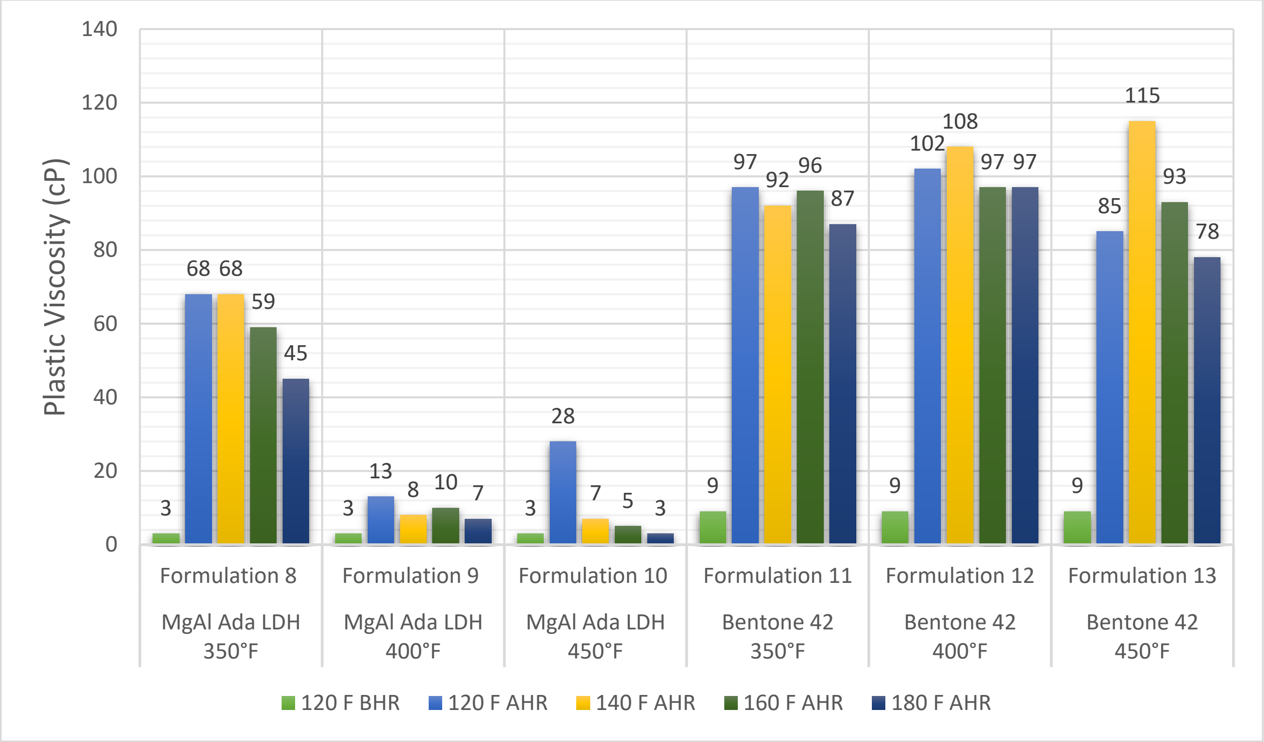

Figure 5.3 Plastic viscosity at different aging and temperatures for MgAl-Ada LDH and Bentone 42.

Overall, this analysis did not show any significant good rheological performance for both rheological modifiers in the patent's formulation evaluated. However, the plastic viscosity will be dependent on the hydraulic property optimization for the wellbore.

5.3.3 Ability of MgAl-Ada LDH to impart fragile gel.

To assess the thixotropy or gel strength, Formulation 8, Formulation 9, Formulation 10, Formulation 11, Formulation 12 and Formulation 13 were tested on a Brookfield viscometer to determine fragile gel behaviour, which is a desirable thixotropy for a drilling fluid. This thixotropy test was run assessing both rheological modifiers, the MgAl-Ada LDH and Bentone 42 aged at 350 ˚F, 400 ˚F and 450 ˚F and comparing the gel strength for 10 seconds, 10 minutes and 30 minutes at 75 °C (167 °F). This means that the sample, after being under shear stress, is held static for that time lapse. The test sequence programmed used for the equipment has already been mentioned in Chapter 3, in Table 3.8. Therefore, Figure 5.4, Figure 5.5, Figure 5.6 and Figure 5.7 shows the torque at lb/100 ft^2 versus time profile for each of the rheology modifier formulations tested. It is considered that is a gel peak of greater than 5 lb/100 ft^2 after a 30 minutes interval is a fragile gel[20].

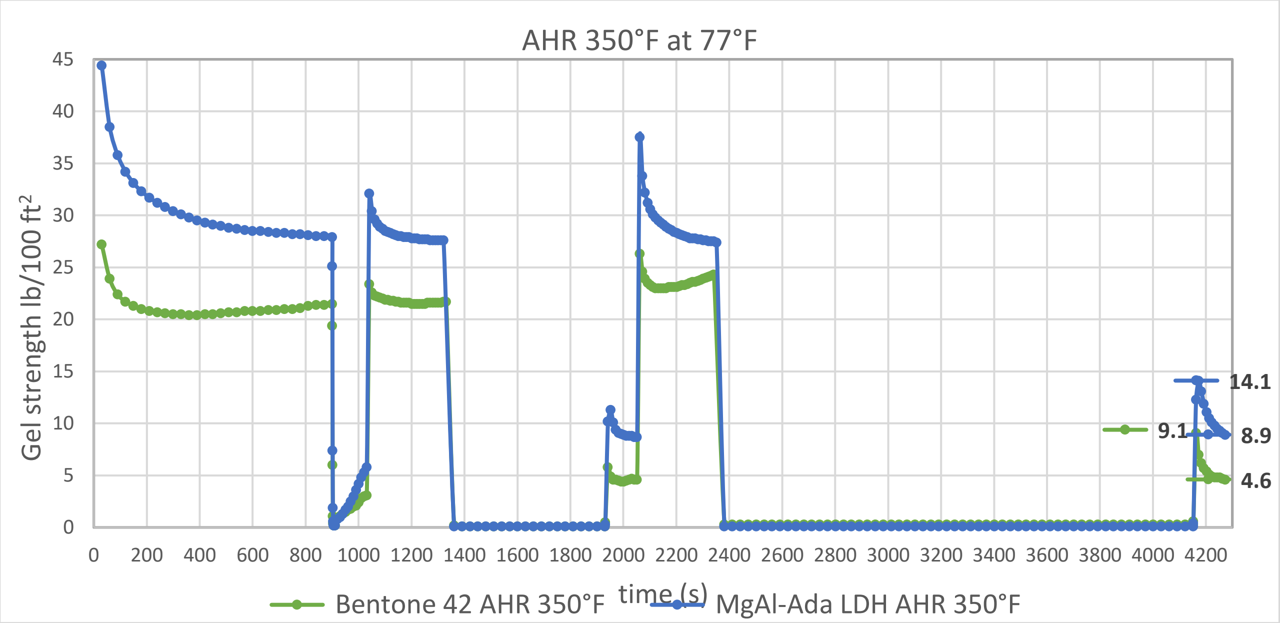

Figure 5.4 Gel strength measurements at 77 ºF of Bentone 42 and MgAl-Ada LDH AHR at 350 ˚F, showing for 10 s, 10 min and 30 min periods.

Figure 5.4 shows the gel strength measurements to 1800 s at 77 ºF aged at 350 ºF. MgAl-Ada LDH presents a peak of 14.1 lb/100 ft^2 going down to 8.9 lb/ft^2 with an interval of 5.2 lb/100 ft^2, slightly higher that Bentone 42 with a peak of 9.1 lb/100 ft^2 which falls down to 4.6 lb/100 ft^2, with an interval of 4.5 lb/100 ft^2 .This is in contrast to samples analysed at 167 ºF in Figure 5.5, where Bentone 42 followed a low flat gel of 3.1 lb/100 ft^2. This is a low value, but undesirable flat gel as is shown in Chapter 2 in Figure 2.4. Figure 5.5 shows MgAl-Ada LDH tendency of a maximum peak at 7.2 lb/100ft^2 and minimum value of 4.3 lb/100 ft^2 with an interval of 2.9 lb/100 ft^2.

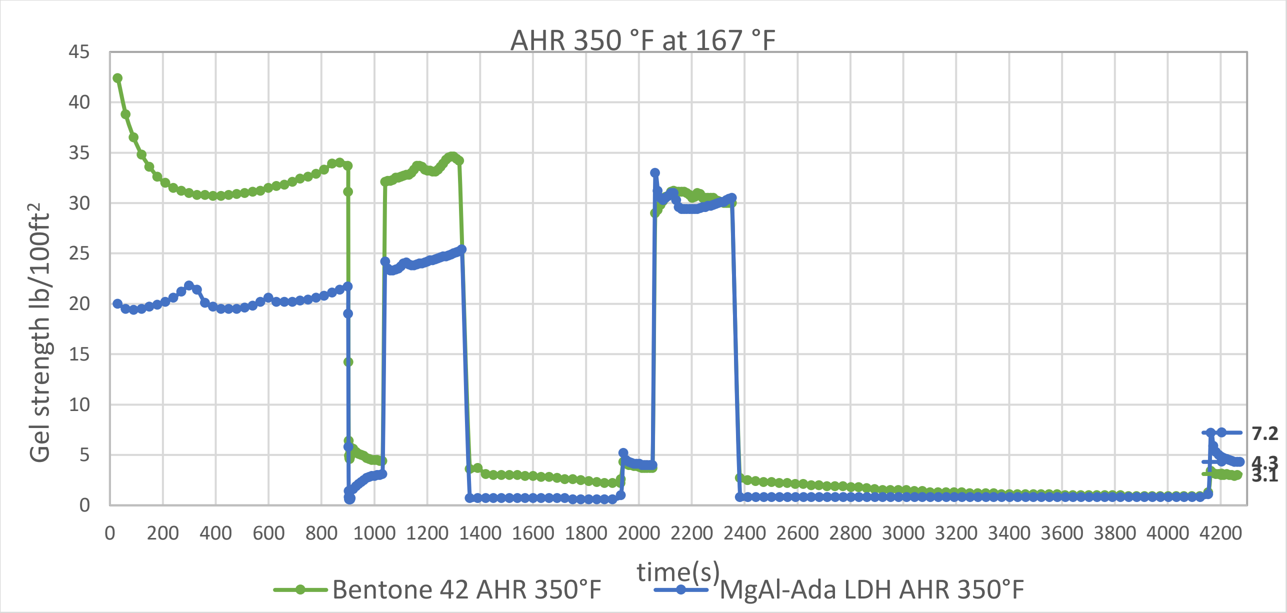

Figure 5.5 Gel strength measurements at 167 ºF of Bentone 42 and MgAl-Ada LDH AHR at 350 ˚F, showing for 10 s, 10 min and 30 min periods.

In the graph in Figure 5.6, the results are showing a desirable gel behaviour for Bentone 42 with a value in the order of 13 lb/100 ft^2 where it is considered in the fragile gel zone. However, this value fell down dramatically when the formulations were aged at 450 ˚F showing an undesirable flat gel for 1800s to both rheological modifiers.

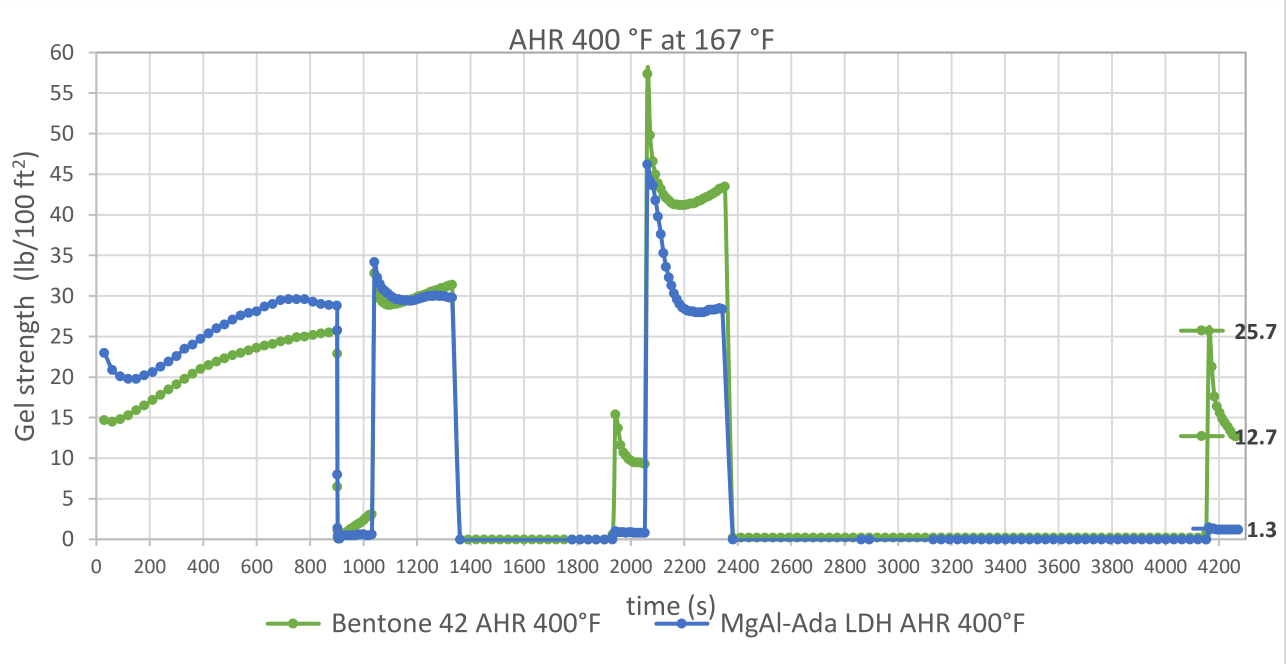

Figure 5.6 Gel strength measurements at 167 ºF of Bentone 42 and MgAl-Ada LDH AHR at 400 ˚F, showing for 10 s, 10 min and 30 min periods.

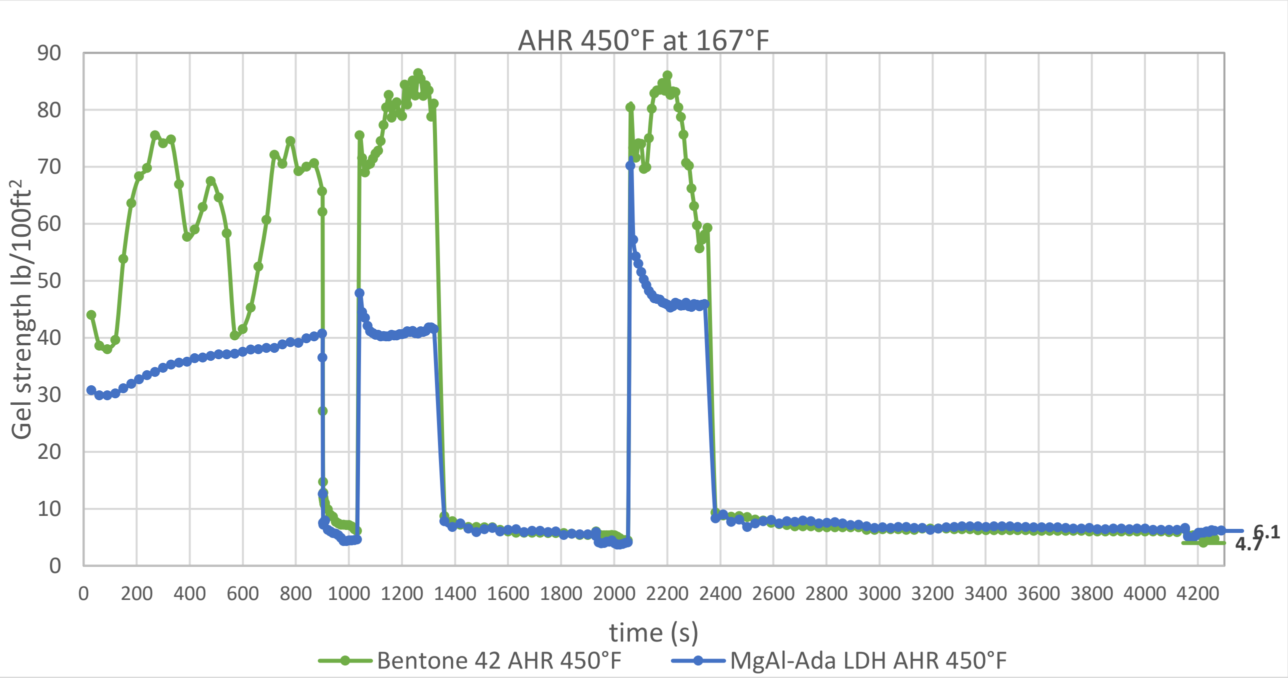

Figure 5.7 Gel strength measurements at 167 ºF of Bentone 42 and MgAl-Ada LDH AHR at 450 ˚F, showing for 10 s, 10 min and 30 min periods.

Finally, MgAlAda-LDH presented a different behaviour with the gel strength measurement at 77 ºF and aged at 350ºF, without a noticeable affect by the temperature. This is in contrast to samples aged at 400 ˚F and 450 ˚F, as is illustrated in Figure 5.6 and Figure 5.7. Although, Bentone 42 aged at 400 ºF had a good gel strength, this behaviour wasn't found for the sample aged at 450ºF. Both rheological modifiers had an undesirable flat gel strength pattern for 1800 s at this higher temperature. Also, in Figure 5.7 the progressive gel pattern during the data collection for 10 s and 600 s for both samples is noticeable, as it is shown in Figure 2.4 in Chapter 2. These results indicate failure in gel properties at high aging conditions in the formulations, with both rheological modifiers, give a clear explanation of this research, which represent an opportunity to do more further work to enhance the chemical and mechanical properties for the rheological modifiers between others compounds within the formulation, which provide the rheological properties in an invert emulsion drilling fluid.

5.3.4 Suspension weight material capacity

Sagging is mainly a settling of high density fluid weighting material. In the case of this formulation, barite is used as the weighting material. Management of sag in drilling fluids is considered as a challenge. A good performance drilling fluid must have the capacity to suspend the weighting material during all the operation conditions encountered. In this study we only evaluated the sag under vertical wellbore conditions. This sag testing was developed at 120 ˚F with Formulation 14 and Formulation 15, both aged at 250 ˚F. The method used is as stated in Chapter 3. The sag factor was calculated with Equation 3.1. As can be seen in Table 5.6, Formulation 15, the new rheology modifier has not met the criteria of a drilling fluid with a good performance, with a sag factor of 0.7. A fluid which exhibits acceptable suspension characteristics, the sag factor should be between 0.50 and 0.53. This was in contrast to Bentone 42, which presented a sag factor of 0.5. It could be considered as a good performance for the Formulation 14 in terms of suspension capacity. The volume set up to this experiment was 5.0 mL, however the volume for MgAl-Ada LDH was 6.9 mL due to the fact that the sample was too solid, and it was impossible to manage accurate quantities.

Table 5.6 Sag testing at 120 ºF

Sag testing									
Formulation	**Rheology modifier**	**Aging**	**ρ**	**Mud top**	**Mud Bottom**	**Volume**	**ρ**	**ρ**	**sag factor**
		°F	**g/cm³**	**g**	**g**	**mL**	**top g/mL**	**bottom g/mL**	
14	Bentone 42	250.0	2.3	11.4	13.2	5.0	2.3	2.6	0.5
15	MgAl-Ada LDH	250.0	2.3	7.9	20.7	6.9	1.1	3.0	0.7

5.3.5 Fluid loss test at high pressure high temperature

Filtration characteristics of an oil-based drilling fluid are affected by the quantity, type and size of solid particles and emulsified water in the drilling fluid, and by the properties of the liquid phase[89]. For this reason, the filter loss test was used to evaluate the performance of the new rheological modifier to observe if it was developing good filtration control characteristics. Formulation 8, Formulation 9, Formulation 10, Formulation 11, Formulation 12 and Formulation 13 were used to develop the measurement of filtration behaviour and filter cake characteristics, as is shown in Table 5.7. The data reveals that the MgAl-Ada LDH developed acceptable performance with the formulation aged at 350 ˚F. The other formulations aged at 400 ˚F and 450 ˚F were higher without any filtration control. In Table 5.7 the filtration values, which are shown in the filtration correction values column for the samples formulated with Bentone 42 aged at 350 ˚F and 400 ˚F, are considered as acceptable filtration control performance with values obtained at 0.4 mL and 4.4 mL respectively. However, for the sample aged at 450 ˚F, filtration correction was slightly higher at 5.6 mL. A lower filtration value was observed for the formulation with MgAl-Ada LDH aged at 350 °F with a value of 1.8 mL, the higher values obtained for MgAl-Ada LDH were for the samples aged at 400°F and 450°F with values at 13.8 mL and 10.4 mL respectively. When all of those values were compared with the values obtained for the Bentone 42, they were higher, which is undesirable for a drilling fluid. This is another indication that the drilling fluid is not stable with the reagents added in the full fluid formulation. The mud cake was weighed to calculate the thicknesses of each sample. As the mud cake was broken when taken from the cell, it cannot be consider a representative samples. For that reason, there are some variations in the weight with the temperature aged of every formulation. It was observed that the mud cake weight was higher for MgAl-Ada LDH with the samples aged at 400 °F and 450 °F. This can be correlated to the sag factor that was obtained in the sag testing mentioned above. The suspension capacity property for the drilling fluid is not being developed with the incorporation of MgAl-Ada LDH in the formulation.

Table 5.7 High Pressure High Temperature Fluid loss testing at 300 ˚F

HPHT filtrate loss					
Formulation	**Rheology modifier**	**AHR (°F)**	**(mL)**	**Filtration correction (mL)**	**Mud cake (g)**
8	MgAl-Ada LDH	350	0.9	1.8	31
11	Bentone 42	350	0.2	0.4	47.4
9	MgAl-Ada LDH	400	6.9	13.8	62.8
12	Bentone 42	400	2.2	4.4	43
10	MgAl-Ada LDH	450	5.2	10.4	48.5
13	Bentone 42	450	2.8	5.6	46.3

5.4 Conclusions

In summary, the new material was observed to have lower rheological values of plastic viscosity and yield point, lower suspension capacity of the weighting material and higher filtrate loss during all the tests thus far. Despite being a high aspect ratio organophilic nanoparticle, the MgAl-Ada LDH does not appear to develop the main function of a rheological modifier under low temperature or low pressure conditions when compared to the Bentone 42 product.

It was noted that the original small scale preparations of the new modifier had very different material handling properties relative to the scaled-up preparation from the toll manufacturer. The original samples were very talc-like, low density, soft to touch and with lubricity. The scaled-up sample was far harder and more aggregated. It is likely that the primary particle size from the manufactured product from High Force was bigger that in the initial development in the laboratory scale in the University. The conglomeration behaviour from the nanoparticle interacting with the emulsion that we mentioned in Chapter 4 may be affecting the properties for the drilling fluid formulation. It is predictable from the results of sag testing that the HGS are settling out, together with LGS, showing a high sag factor for the new fluid.

The performance of the MgAl-Adamantane LDH based rheological modifier was below that of the presently used Bentone 42, through all the tests performed in this chapter. At this point, further work is needed in the future to establish what is affecting the MgAl-Ada LDH behaviour, if it is the size of particle, the material compound, the concentration, the formulation or the mixing time.

Chapter 6

Performance of New Rheology Modifier in a Synthetic Base Fluid at High Temperature and High Pressure

6.1 Introduction

This chapter describes a study using a new rheological modifier, MgAl-Ada LDH, incorporated into a synthetic base mud (SBM) for application under high pressure and temperature drilling operations. As stated in Chapter 4, it was important to initially evaluate the nanoparticle interactions in the drilling fluid formulations at low temperature (LT) and low pressure (LP) in order to observe the behaviour of the nanoparticles with the rest of the compounds used in the formulations before attempting high pressure high temperature (HPHT) rheological experiments. The data at LT and LP obtained in the Fann 35 viscometer (Chapter 5) were necessary in order to compare the results obtained in the HPHT rheometer for the overlapping temperature regime, allowing them to be correlated between each other as an accuracy check point. As reported by other researchers, the addition of nanoparticles[24] in drilling fluid formulations has shown an improvement in rheological properties[142] and wellbore stability[143]. However, thus far the new MgAl Ada LDH has not shown improved properties within the experiments undertaken. As was mentioned in previous chapters, HPHT conditions represent a challenge for the operators, one of which is to maintain stable drilling fluids properties during drilling operations. Optimal maintenance of rheological properties are one of the most significant concerns to the operators because it can cause operational problems.

The rheological properties of a drilling fluid are required to suspend drilled solids, and to clean the wellbore. A minimum yield stress or LSRYP (7-15 lb/100 ft^2)[20,141] for oil based muds is desired[‡‡‡‡‡‡], because it implies better hole cleaning and sag control. Under HPHT conditions the conventional thickeners, such as organophilic clays, tend to become degraded at temperatures in excess of about (177 ˚C/350 ˚F) [58] .When this occurs, problems are caused in the fluid viscosity, and as a consequence the capacity for suspension of cuttings[58].Two of the most commonly encountered problems related to

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[‡‡‡‡‡‡] The range of an acceptable low shear rheology for drilling fluids will be depend on the oilfield services company. In this case, the formulation that it is being used not correspond in a marketed formulation system to know the drilling fluid behaviour. Others studies more in deep need to be investigated to specify the acceptable low share rate yield point range of this specify chemical compounds and concentrations used.

lost rheological properties are barite sag and poor hole cleaning[21,20]. The new HPHT organic rheology modifier seeks to impart optimal rheological properties to low, medium and high density synthetic base mud (SBM) at elevated temperature and pressure. This present experimental phase will be evaluated on a high density formulation to test the rheological modifier, as it was the same density used for the formulations to evaluate at low temperature and low pressure. This present study evaluates 12 formulations with a conventional rheological modifier used in the industry, Bentone 42, and compares it to the new MgAl-Ada LDH nanoparticles. Samples were aged at 121 ˚C (250 ˚F) and 177 ˚C (350 ˚F). These samples were analysed in a Grace 7500 HTHP rheometer at different temperatures, in the range 49 ˚C-204 ˚C (120 ˚F – 400 ˚F) and pressures from 5000 psi to 20000 psi. In addition, the effect of solids contamination was evaluated. Selected samples were contaminated with Hymod Prima (HMP) clay in order to simulate contamination by solids from drilling cuttings. This was undertaken to observe the rheological behaviour that simulates real situations, when the fluid is in the wellbore. This chapter shows experimental data demonstrating both the environmental and rheological performance for HTHP with MgAl-Ada LDH nanoparticle technology in a fluid with a synthetic base mud (SBM) formulated for high pressure and high temperature applications.

6.2 Methods

As a baseline for developmental testing, a 2.2 g/cm^3 density invert emulsion formulation with a 90/10 oil/water ratio and an internal brine of a density of 1.35 g/cm^3 calcium chloride was formulated. The formulation was used to prepare the oil-based drilling fluid. This approach follows the same formulation protocol reported in the patents[1,2]. The order mixing and the formulation used for both rheology modifiers used is shown in Table 3.5, in Chapter 3.This formulation wasn't verified to check the oil/water ratio because it wasn't possible to have access to the specific density value of every compound to formulate this drilling fluid of 2.2 g/cm^3 . Also, it proved impossible to analyse whether this oil/water ratio was holding BHR and AHR, because it wasn't possible to have access to retort equipment for the development of tests to know the oil, water and solids content, as it is established in the API 13 B-2[89]. Characterization of the drilling fluid properties was conducted according to standard API test methods. Rheology was measured under ambient conditions before being evaluated at HPHT conditions, at 120 °F (49 °C) and 180 °F (82.2 °C), and electrical stability was measured at 120 ˚F (48.9°C). Thermal ageing of the fluid was initially performed at 250 ˚F and 50 psi over 16 hours. Later tests were conducted at (177 ˚C) 350 ˚F to test thermal stability. The rheological characterization for HPHT conditions was conducted to develop a range of temperatures from 120 ˚F (49 ˚C) – 350 ˚F (177 ˚C) and a maximum pressure of 20,000 psi by the rheology sweep method. This method sets a determined temperature at two pressures, then alternates to set a pressure with two temperatures, and repeats this successively to reach the maximum, swapping two pressure and two temperature steps each time. The schedule for evaluation followed is shown in Table 6.1.

Table 6.1Temperature/Pressure Schedule used for High Pressure High Temperature rheology measurement of invert drilling fluid.

Schedule for evaluation HPHT conditions		
Temperature		Pressure
°F	°C	Psi
120	49	0
150	66	0
150	66	5000
250	121	5000
250	121	10000
300	149	10,000
300	149	20,000
350	177	20,000

6.3 *Results and discussions*

Formulation 1, Formulation 2, Formulation 3 and Formulation 4 shown in Table 6.2 were formulated with the main formulation given in Table 3.5 in Chapter 3. The formulations were prepared in Durham University, while Schlumberger facilities were identified to recorded them and observe the reproducibility of each samples. Table 6.2 shows a summary of the formulations that will be discussed in this results and discussion section.

Table 6.2 Summary of drilling fluid formulations, based on fluid formulation described in Chapter 3.

Formulation	**Rheological modifier**	**Reproducibility**	**Conditions**
Formulation 1	Bentone 42	Durham University	Aged 250 ˚F+ Hamilton Beach
Formulation 2	Bentone 42	Schlumberger	Aged 250 ˚F+ Hamilton Beach
Formulation 3	MgAl-Ada LDH	Durham University	Aged 250 ˚F+ Hamilton Beach
Formulation 4	MgAl-Ada LDH	Schlumberger	Aged 250 ˚F+ Hamilton Beach
Formulation 5	Bentone 42	Schlumberger	Aged 350 ˚F+ Silverson
Formulation 6	MgAl-Ada LDH	Schlumberger	Aged 350 ˚F+ Silverson
Formulation 7	Bentone 42	Schlumberger	Aged 250 ˚F+ Silverson
Formulation 8	MgAl-Ada LDH	Schlumberger	Aged 250 ˚F+ Silverson
Formulation 9	Bentone 42+HMP+5g	Schlumberger	Aged 250 ˚F+ Hamilton Beach
Formulation 10	MgAl-Ada LDH+HMP+5g	Schlumberger	Aged 250 ˚F+ Hamilton Beach
Formulation 11	Bentone 42+HMP+20g	Durham University	Aged 250 ˚F+ Hamilton Beach
Formulation 12	MgAl-Ada LDH+HMP+20g	Durham University	Aged 250 ˚F+ Hamilton Beach

6.3.1 *Performance of drilling fluid with different rheology modifier before High Pressure High Temperature testing.*

To ensure the fluid to be used for the testing would not fail the HPHT conditions, the thermal stability of the fluid was evaluated by heat aging at 121˚C (250 ˚F).The emulsion stability was evaluated at 49 ˚C (120 ˚F). Also, this study was useful in testing the rheological behaviour for the formulation, taking the rheologies at 49 ˚C (120 ˚F) BHR and 49 ˚C (120 ˚F), 82 ˚C (180 ˚F) after hot rolling in the viscometer (FANN35), assessing two rheological modifiers. The results are shown in Table 6.3 and Table 6.4.

Table 6.3 Rheology of Bentone 42 before hot rolling (BHR) and after hot rolling(AHR) at 250 °F.

Bentone 42						
Hamilton Beach	**Formulation 1**			**Formulation 2**		
Temperature °C/°F	**49**	**49**	**82.2**	**49**	**49**	**82.2**
	120	120	180	120	120	180
Density g/cm^3	2.2			2.2		
Hot Rolling/16 hours	BHR	AHR 250°F	AHR 250°F	BHR	AHR 250°F	AHR 250°F
θ600	142	141	89	134	136	84
θ300	73	74	46	72	73	44
θ200	51	53	34	51	52	32
θ100	29	31	21	30	29	19
θ6	5	6	5	6	5	4
θ3	3	5	4	5	4	3
10 s gel (lb/100ft^2)	8	7	5	7	6	5
10 min gel (lb/100ft^2)	9	8	6	8	8	8
μ_a (cP)	71	70.5	44.5	67	68	42
μ_p(cP)	69	67	43	62	63	40
τ_y (lb/100ft^2)	4	7	3	10	10	4
LSRYP (lb/100ft^2)	1	4	3	4	3	2
ES (Volts)	1000	250	-	1081	317	-

As can be seen in Table 6.3, the rheological profile obtained from Formulation 1 and Formulation 2, assessing Bentone 42, shows that these weren’t affected substantially after being aged. As shown for Formulation 1 at 120 ºF BHR, the plastic viscosity was 69 cP and 67 cP AHR, this small variation also was obtained in the Formulation 2 with a plastic viscosity BHR of 62 cP and 63 cP. Formulation 2 does not present variations in the yield point, holding a value of 10 lb/100 ft^2 in contrast to Formulation 1, which increased the yield point AHR from 4 lb/100 ft^2 to 7 lb/100 ft^2. The LSRYP obtained from both formulation were notably low, where it may predict severe suspension capacity issues for the rheological test for HPHT. The emulsion stability decreased dramatically for both formulations after aging. The reading measurement desired for the electrical stability test is in the order of >500 volts according with API standards and the worst scenario is considered as <200 volts. Therefore, the emulsion stability for both samples is considered acceptable from this test.

Table 6.4 Rheology of MgAl-Ada LDH before hot rolling (BHR) and after hot rolling (AHR) at 250˚F.

MgAl-Ada LDH						
Hamilton Beach	**Formulation 3**			**Formulation 4**		
Temperature °C/°F	**49**	**49**	**82.2**	**49**	**49**	**82.2**
	120	120	180	120	120	180
Density g/cm^3	2.2			2.2		
Hot Rolling/16 hours	BHR	AHR 250°F	AHR 250°F	BHR	AHR 250°F	AHR 250°F
θ600	114	153	74	107	101	59
θ300	58	79	34	56	50	30
θ200	40	54	23	40	37	22
θ100	22	29	12	23	20	13
θ6	3	4	2	4	4	3
θ3	2	2	1	3	3	2
10 s gel (lb/100ft^2)	5	6	3	6	5	5
10 min gel (lb/100ft^2)	7	6	4	8	5	4
μ_a (cP)	57	76.5	37	53.5	50.5	29.5
μ_p(cP)	56	74	40	51	51	29
τ_y (lb/100ft^2)	2	5	-6	5	-1	1
LSRYP (lb/100ft^2)	1	0	0	2	2	1
ES (Volts)	820	850		865	875	

Table 6.4 details the results of emulsion stability obtained from Formulation 3 and Formulation 4, evaluating MgAl-Ada LDH. We observed higher values of electrical stability, > 820 volts BHR and after hot rolling for both samples. In contrast, the rheology values for these formulations decreased dramatically after hot rolling. As can be seen from the yield point values between Formulation 3 and Formulation 4, the difference is higher after ageing. It is more noticeable for Formulation 4 where it presented a negative value from 5 lb/100ft^2 BHR at 120ºF to -1 lb/100ft^2 AHR. Formulation 3 presented negative yield point AHR but at 180ºF of -6 lb/100ft^2. These negative values could be obtained due to the calibration of the equipment or the poor suspension capacity. Those negative values from Formulation 3 and Formulation 4 with the new modifier were a sign that the fluid was showing thermal instability. It is reflected in the LSYP values which are extremely low, predicting low rheological properties.

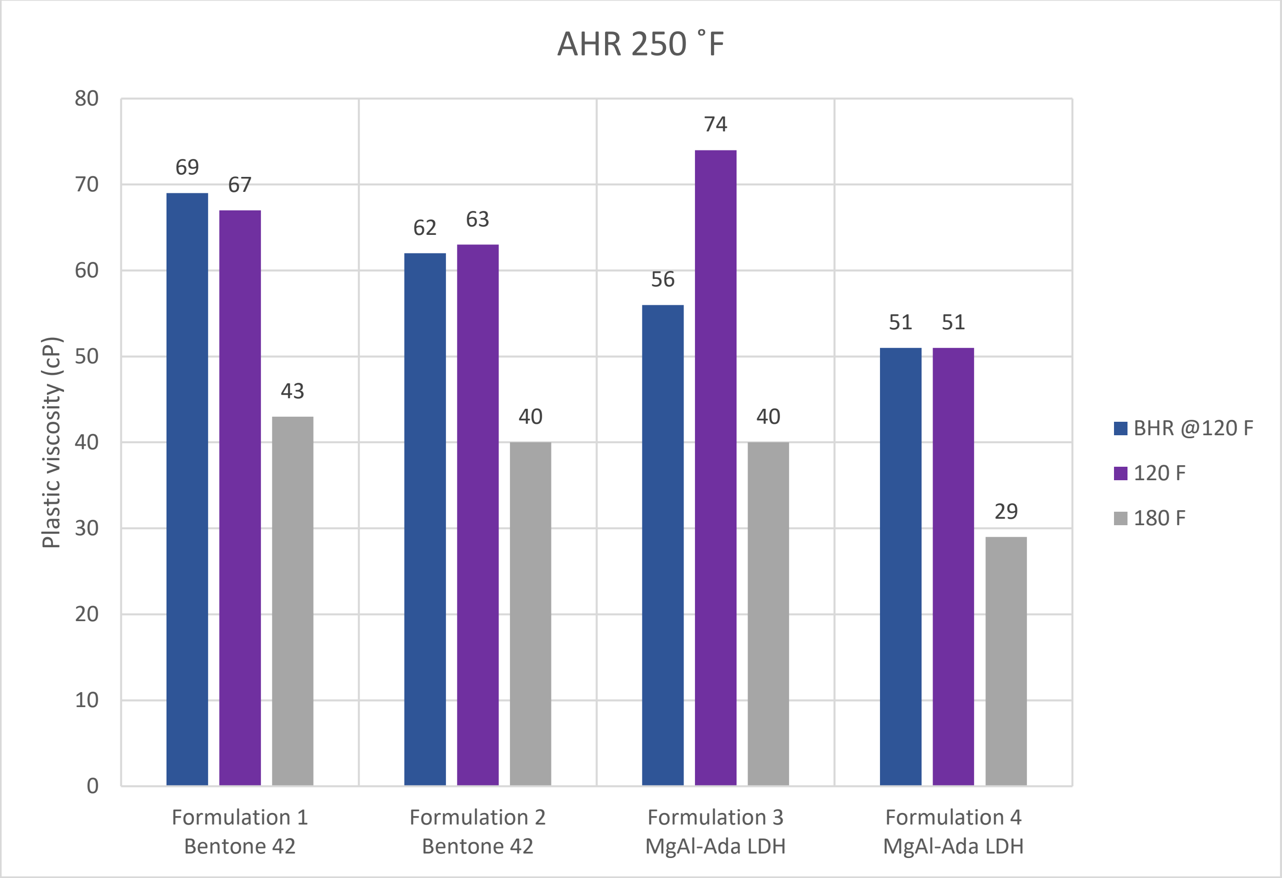

Figure 6.1 Comparison for the plastic viscosity between Bentone 42 and MgAl-Ada LDH.

Further comparison between the plastic viscosity for Formulation 1 and Formulation 2 containing the Bentone 42 did not show a significant data error in the measurements by the Fann 35. However, for Formulation 3 and 4, with MgAl-Ada LDH present, more variations between readings were noted. The plastic viscosity values obtained of 74 cP and 51 cP, respectively, meet acceptable criteria for a drilling fluid base in the rheogram mentioned in Figure 2.2 in Chapter 2. However, it will be depending on each oilfield services standards and operators requirements. The range of acceptability is in the order of 35-60 cP for a drilling fluid with a density of 2.20 g/cm^3, as was shown in Figure 2.2 in Chapter 2.

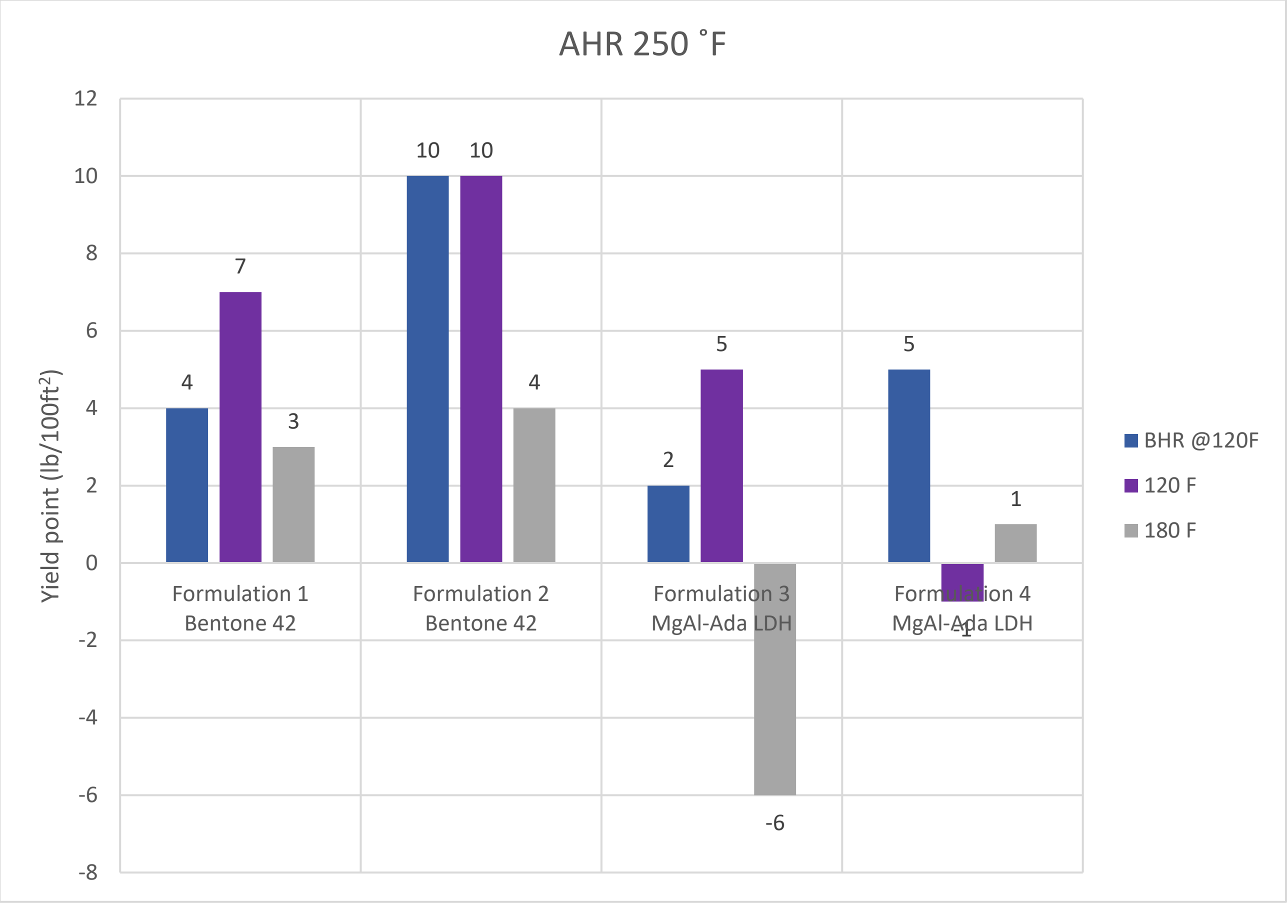

Figure 6.2 Comparison for the yield point between bentone 42 and MgAl-Ada LDH.

Figure 6.2 illustrates that the variation of yield point values in every formulation was significant, noticeably so for MgAl-Ada LDH formulations. Contrary to expectations, in Figure 6.2 it can be seen that negative values of yield point are shown in Formulation 3 and 4 when MgAl-Ada LDH is used, in comparison with Bentone 42 from Formulation 1 and Formulation 2, as was mentioned above. As it was mentioned above those negative value, it could be an indicator that the material undergoes reaction with some of the other compounds present in the drilling fluid, affecting the measurements. It could also be linked with the samples increasing the fluid temperature when it was mixing. Also, from the 0 lb/100ft^2 values of LSYP for the formulation 3 AHR, it could indicate that the drilling fluid with MgAl-Ada LDH is not correlating well with the Bingham rheological model, which is the basis of all the rheology calculations from the Fann 35. The minimum value acceptable for yield point parameter for this density of drilling fluid is between (7-16 lb/100ft^2) at 120 ˚F as it is shown in the rheogram in Figure 2.3 in Chapter 2. Therefore, the MgAl-Ada LDH did not meet these criteria of minimum and maximum of yield point at 120 ˚F either BHR or after hot rolling. These initial data from the MgAl-Ada LDH formulations thus needed to be interpreted carefully, because the formulations seem to be unstable to the conditions encountered HPHT test regime.

6.3.2 Comparison of the performance to MgAl-Ada LDH aged at 250 ˚F and 350 ˚F.

Table 6.5 shows data from a second batch of samples, Formulation 5 and Formulation 6, which were formulated with Bentone 42 and MgAl-Ada LDH aged at 350 ˚F. This was undertaken to observe the rheological parameters and thermal stability with a higher ageing temperature before further testing the MgAl-Ada LDH under HPHT conditions.

Table 6.5 Rheology of Bentone 42 and MgAl-Ada LDH before and after hot rolling at 350 ˚F.

Silverson	**Formulation 5**			**Formulation 6**		
	Bentone 42			**MgAl-Ada LDH**		
Temperature °C/°F	**49**	**49**	**82.2**	49	49	82.2
	120	120	180	120	120	180
Density g/cm^3	2.2			**2.2**		
Hot Rolling/16 hours	BHR	Hot Rolled at 350°F	Hot Rolled at 350°F	BHR	Hot Rolled at 350°F	Hot Rolled at 350°F
θ600	128	117	65	97	76	49
θ300	68	57	34	49	40	25
θ200	48	40	24	35	28	18
θ100	28	22	14	20	16	10
θ6	6	3	3	4	3	2
θ3	5	2	2	3	2	2
10 s gel (lb/100ft^2)	6	5	4	5	4	5
10 min gel (lb/100ft^2)		6	6	6	5	4
μ_a (cP)	64	58.5	32.5	48.5	38	24.5
μ_p(cP)	60	60	31	48	36	24
τ_y (lb/100ft^2)	8	-3	3	1	4	1
LSRYP (lb/100ft^2)	4	1	1	2	1	2
ES(volts)	250	249		862	307	

These tests revealed that the emulsion stability for both systems was higher for the MgAl-Ada LDH systems before and after ageing at 350 ˚F. The rheological properties for Formulation 6 with the new rheology modifier had not developed good performance at 180 ˚F. As can be observed in Table 6.5, the plastic viscosity felt down from 48 cP BHR to 36 cP AHR at 120 ºF. For the Bentone 42, this material has not showed any change AHR, it held a value of 60 cP BHR and AHR. For the yield point values MgAl-Ada LDH presented lower values than Bentone 42. However, Bentone 42 showed a yield point of -3 lb/100 ft^2 AHR at 120 ºF. Both formulations showed low capacity of suspension with the range of LSRYP between 2 lb/100 ft^2 and 1 lb/100 ft^2, they were similar values which were found for the samples aged at 250 ºF.

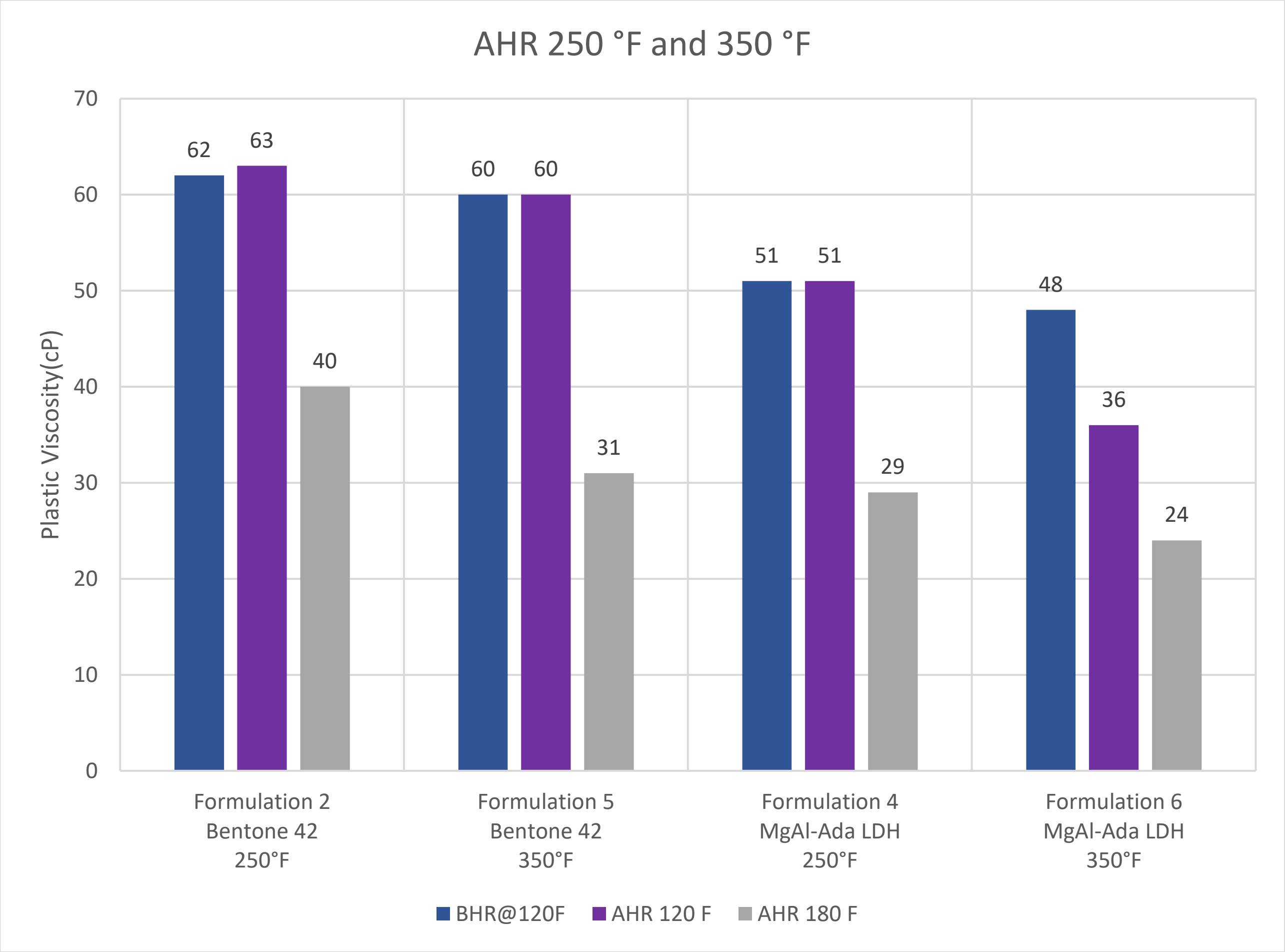

Figure 6.3 Comparison of the plastic viscosity between Bentone 42 and MgAl-Ada LDH; aged at 250 ˚F and 350 ˚F.

Formulation 2 and Formulation 5 aged at 250 ˚F were the samples most representative to compare the rheological behaviour to the same samples aged at 350˚F. Figure 6.3 shows a comparison of plastic viscosity between Bentone 42 and MgAl-Ada LDH containing formulations, where it can be seen that the values for the plastic viscosity at 180 ˚F for Formulation 5, Formulation 4 and Formulation 6 aged at 350˚F did not meet the criteria of good performance as it was mentioned above. There were significant differences between the plastic viscosity measurements obtained at 120 ˚F and 180 ˚F. This was noticeable that the rheological property as plastic viscosity at 120˚F was stable without many variations between formulations. The most notable variations were recorded for the yield point values.

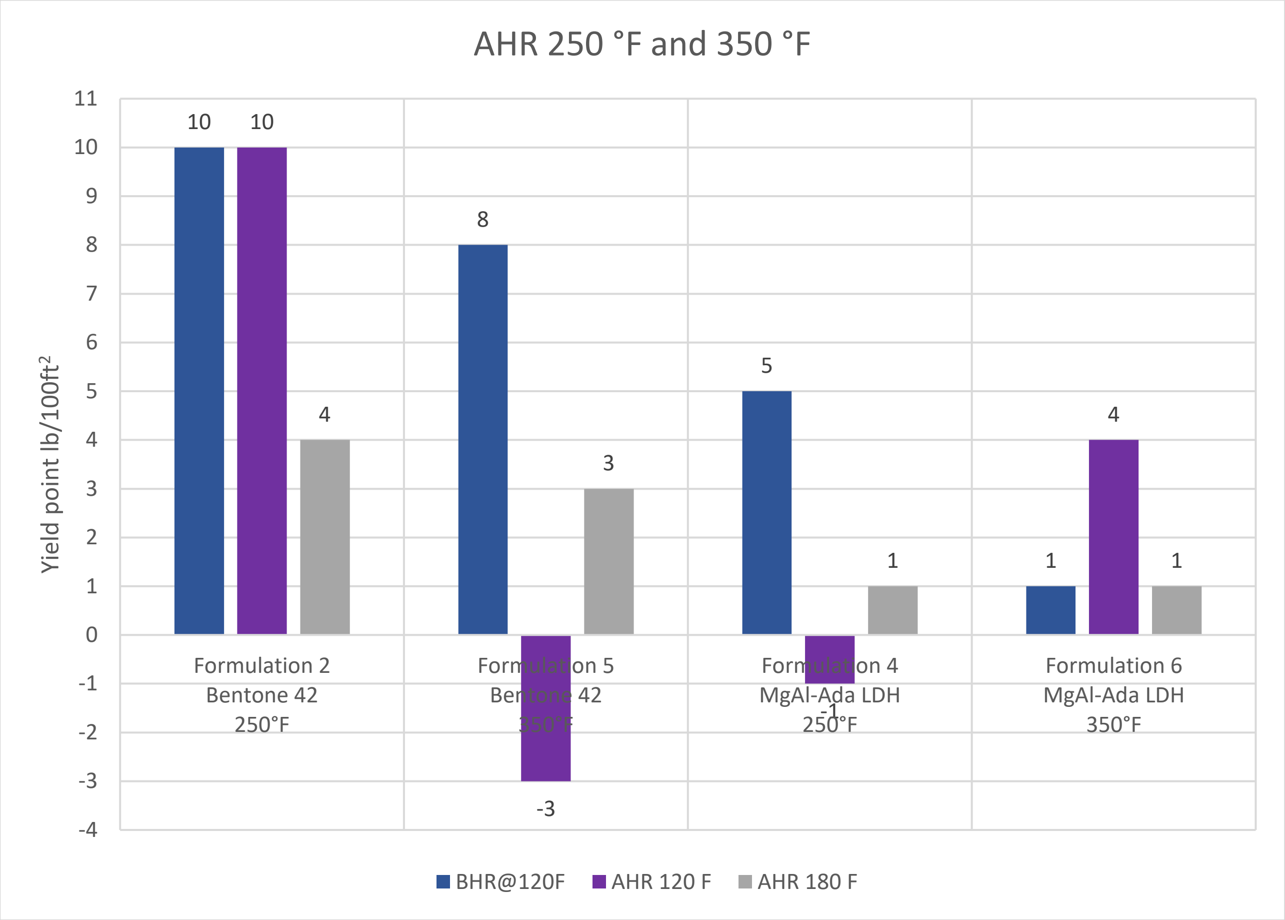

Figure 6.4 Comparison for the yield point between Bentone 42 and MgAl-Ada LDH; aged at 250 ˚F and 350 ˚F.

As can be seen in Figure 6.4, both Formulation 2 and Formulation 4 at 250 ˚F did not show minimum criteria of yield point values between (7-16 lb/100ft^2). Also, this behaviour was highlighted for Formulation 5 and Formulation 6, where the yield point values were even lower than the values at 350 ºF. It is also evident that the new rheology modifier does not meet any minimum criteria of the yield point for both aging conditions.

6.3.3 Observations from formulations with MgAl-Ada LDH

The mixing time and the preparation method used for the formulation of drilling fluids are important due to the fact that every compound has a specific chemical reaction time upon interaction with other reactants. The formulations shown in Table 6.3 and Table 6.4 had slight data variations. Therefore, it was believed that the main difference in preparation was in the use of different high shear mixers used in Durham and at the Schlumberger facilities, and this may have influenced the reproducibility of data. It seems that the shear rates of the Hamilton Beach mixers in the two locations, at low shear, were affecting the results. In addition, the two Formulations, 7 and 8, were mixed with Bentone 42 and the MgAl-Ada LDH, respectively, using the Silverson mixer. This was done to evaluate the influence of shear rate between the Hamilton Beach mixer at 3914 rpm and Silverson mixer at 6000 rpm. Table 6.6 shows the rheological profile from Formulation 7 with Bentone 42 and Formulation 8 with the MgAl-Ada LDH. These samples were prepared at different shear rates at 6000 rpm to evaluate if the rheological values shown in Table 6.3 and 6.4 were slightly influenced by the shear rate used during the formulation of the fluids.

Table 6.6 Rheology of MgAl-Ada LDH and Bentone 42 before and after hot rolling at 250 ˚F.

Silverson	**Formulation 7**			**Formulation 8**		
	Bentone 42			**MgAl-Ada LDH**		
Temperature °C/°F	**49**	**49**	**82.2**	**49**	**49**	**82.2**
	120	**120**	**180**	**120**	**120**	**180**
Density g/cm^3	**2.2**			**2.2**		
Hot Rolling/16 hours	BHR	Hot Rolled 250°F	Hot Rolled 250°F	BHR	Hot Rolled 250 °F	Hot Rolled 250 °F
θ600	128	135	75	97	107	64
θ300	68	74	40	49	56	33
θ200	48	52	29	35	39	23
θ100	28	30	17	20	22	13
θ6	6	6	4	4	4	3
θ3	5	5	3	3	3	2
10 s gel (lb/100ft^2)	6	7	5	5	5	5
10 min gel (lb/100ft^2)	7	8	8	6	7	6
μ_a (cP)	64	67.5	37.5	48.5	53.5	32
μ_p(cP)	60	61	35	48	51	31
τ_y (lb/100ft^2)	8	13	5	1	5	2
LSRYP (lb/100ft^2)	4	4	2	2	2	1
ES(volts)	250	199		862	464	

After that, Formulation 7 and Formulation 8, which were mixed with different shear rate, were observed to have slight differences between the samples shown in Table 6.3 and Table 6.4 in terms of consistency. However, dial deflection readings shown in Table 6.3, in comparison with the data in Table 6.6 did not show significant changes.

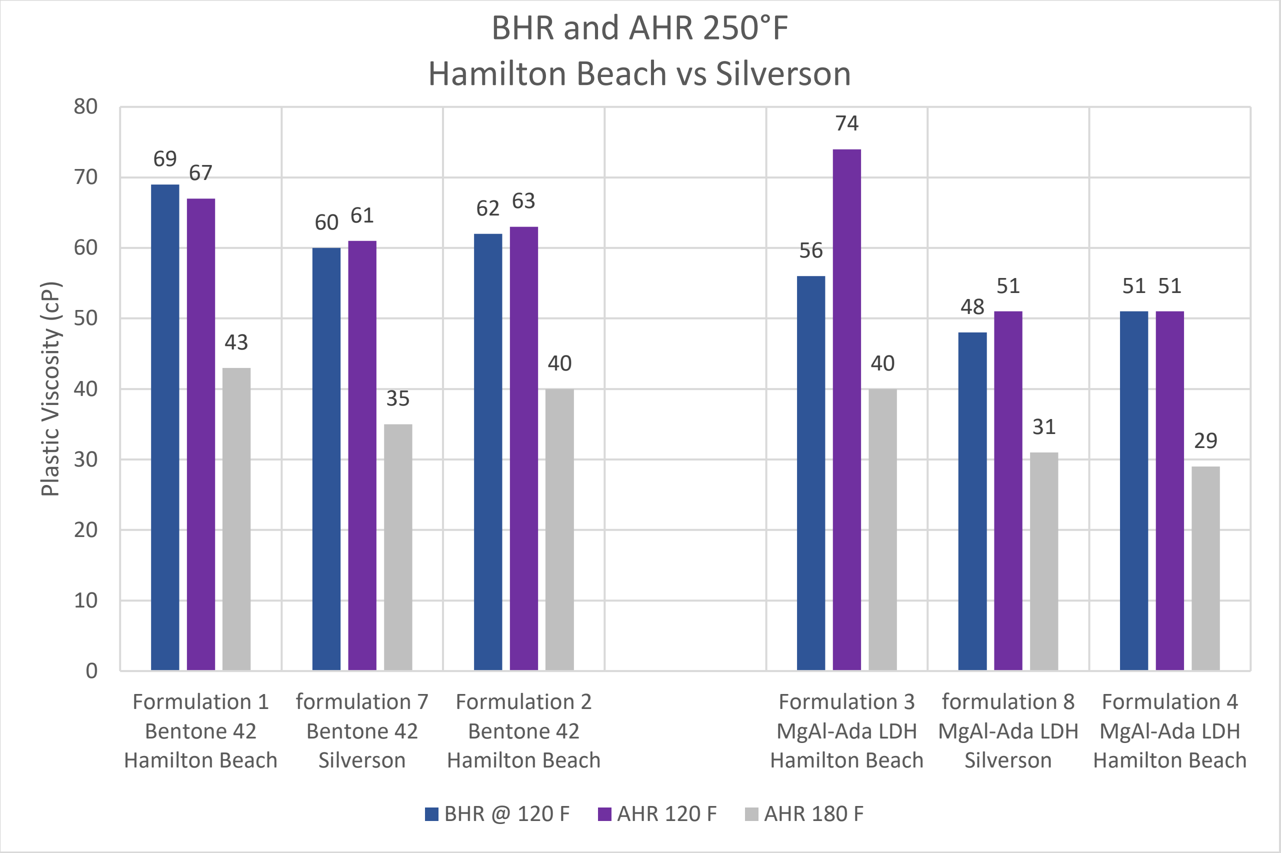

Figure 6.5 Comparison of plastic viscosity for BHR and AHR at 250ºF evaluating low shear rate and high shear rate for mixing of samples by Hamilton Beach and Silverson mixer.

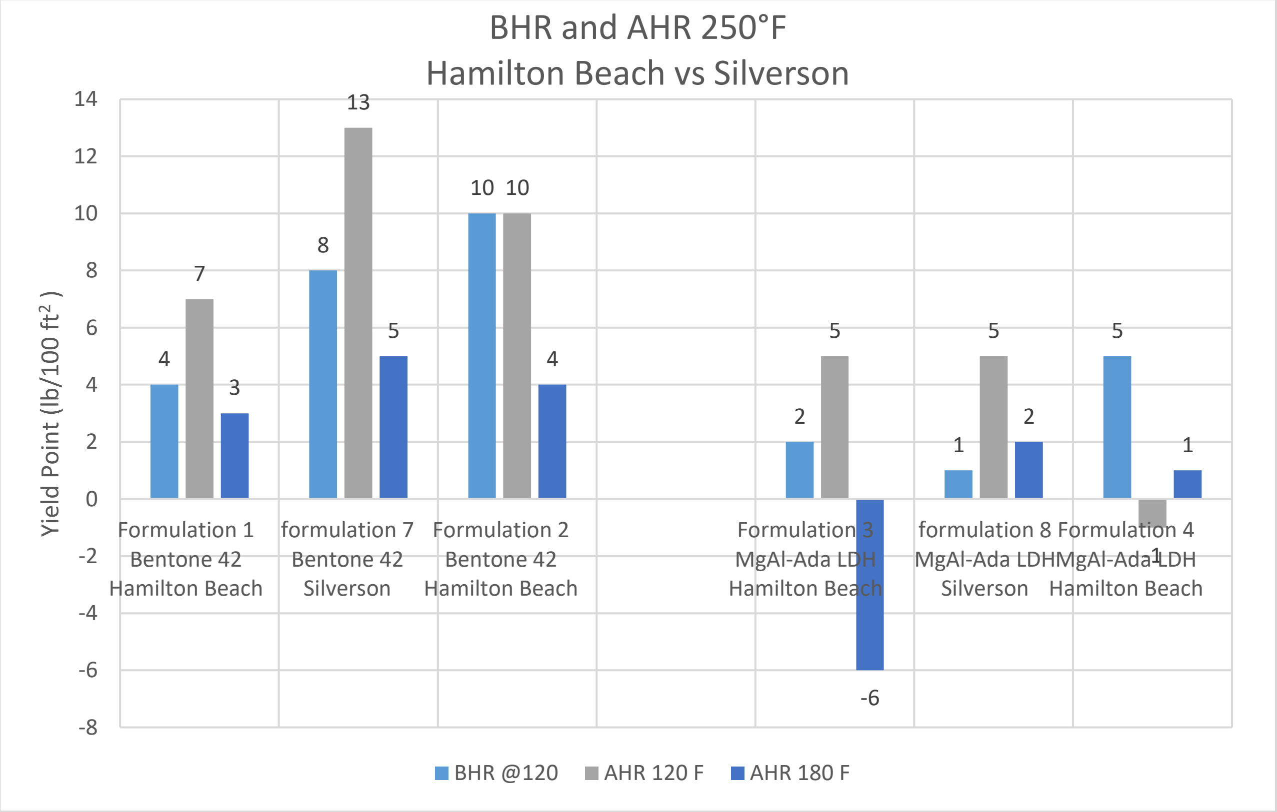

Figure 6.6 Comparison of yield point BHR for and AHR at 250ºF evaluating low shear rate and high shear rate for mixing of samples by Hamilton Beach and Silverson mixer.

Figure 6.5 and Figure 6.6 shows the comparison of plastic viscosity and yield point BHR and AHR at 250 ºF respectively. These are for formulations with Bentone 42 and MgAl-Ada LDH prepared at low shear rate with the Hamilton Beach mixer and high shear rate with the Silverson mixer. The maximum plastic viscosity value for the samples which were mixed in Hamilton Beach for Bentone 42 were 10 cP with minimum value of 3 cP in contrast to the sample mixed in the Silverson mixer with a maximum value of 13 cP and minimum value of 5 cP. The maximum values reached for plastic viscosity to MgAl-Ada LDH were 74 cP with a minimum value of 29 cP for mixing in the Hamilton Beach, in contrast to Silverson mixer which gave formulations with a maximum of 51cP and minimum value of 31cP. These range of small difference between yield points values were similar that it was obtained to the plastic viscosity. Therefore, this can be confirmed that the use of low shear rate and high shear rate not represent significant changes in the rheological behaviour for these formulations and the observed variation between samples prepared at Durham and Schlumberger must be due to another, as yet undetermined, factor.

6.3.4 Comparison of the High Pressure High Temperature performance of MgAl-Ada LDH with Bentone 42.

Any synthetic drilling fluid may become unstable if it doesn't have an accurate and optimised formulation, mixing routine and if a new additive is interacting with the rest of compounds in the formulation or the formulation has exceeded temperature limits. For this reason, it was important to evaluate the samples prepared here prior to being exposed high pressure and high temperature conditions. Though the results obtained in the analysis developed before testing the samples under HPHT conditions were not optimal for the formulation with the MgAl-ADA LDH. In other work, Portnoy et al.[58] found a rheology modifier with temperature activation at 300 °F (149 °C), as mentioned previously and thus, low temperature performance is sometimes not the best predictor of HPHT performance. Therefore, on the basis of Portnoy's findings, it was opted for following the experiments to observe if the material under high pressure and high temperature conditions was presenting an abnormal behaviour. Formulation 2 and Formulation 4, with Bentone 42 and MgAl-ADA LDH, respectively, were exposed to further testing to evaluate both its thermal limits and its performance under high pressure and high temperature.

Table 6.7 Grace 7500 results from the Formulation 2 Bentone 42.

Bentone 42 Formulation 2										
	Fann 35		**Grace Intrument 7500**							
Temperature (°F)	**120**	**180**	**120**	**150**	**150**	**250**	**250**	**300**	**300**	**400**
Pressure (psi)	**0**	**0**	**0**	**0**	**5000**	**5000**	**10000**	**10000**	**20000**	**20000**
RPM										
θ600			139	111	154	94	123	101	158	110
θ300			70	55	78	49	65	53	83	55
θ200			47	38	52	35	45	38	58	38
θ100			26	21	28	21	27	23	34	21
θ6			2	3	2	4	6	5	6	3
θ3			2	2	2	2	3	3	3	2
10 s gel strength (lb/100ft^2)			2	1	2	3	4	3	4	2
10 m gel strength (lb/100ft^2)			3	3	3	3	4	3	4	1
μ_p (cP)	0	0	69	56	76	45	58	48	75	56
τ_y (lb/100ft^2)	0	0	1	-1	2	4	7	5	8	-1
LSYP (lb/100ft^2)	0	0	2	2	1	1	1	1	1	0

Table 6.8 Grace 7500 results from the Formulation 4 MgAl-Ada LDH.

MgAl-Ada LDH Formulation 4										
	Fann 35		**Grace Instument 7500**							
Temperature (°F)	**120**	**180**	**120**	**150**	**150**	**250**	**250**	**300**	**300**	**400**
Pressure (psi)	**0**	**0**	**0**	**0**	**5000**	**5000**	**10000**	**10000**	**20000**	**20000**
RPM										
θ600			192	131	187	86	125	93	167	114
θ300			100	56	94	41	56	45	80	51
θ200			68	38	63	28	34	30	48	32
θ100			36	20	32	15	18	16	25	16
θ6			5	3	4	3	3	3	3	2
θ3			3	2	3	2	2	3	3	1
10s gel strength (lb/100ft^2)			4	3	3	2	3	2	3	1
10 m gel strength (lb/100ft^2)			4	3	3	3	3	3	3	1
μ_p (cP)	0	0	92	75	93	45	70	48	87	63
τ_y (lb/100ft^2)	0	0	8	-19	1	-3	-14	-3	-8	-12
LSYP (lb/100ft^2)	0	0	1	1	1	1	1	2	2	1

Tables 6.7 and 6.8 illustrate the results from the HPHT rheometer tests on Formulation 2 and Formulation 4. As can be seen in the tables, the temperature and the pressure applied were selected in such a way that results were obtained for each pressure at two different temperatures and for each temperature at two different pressure. This technique allowed the isolation of either temperature or pressure to study each of these parameters on the rheology, which is analysed more in detail in Figure 6.7 and Figure 6.8. The HPHT rheometer used works with the Hershel-Bulkley model, so it may be

the theory that the model is built around that results in the negative value data points. Also, this model doesn't correlate to the behaviour of these formulations. Generally, the rheometer is more accurate for the data collection. So, this seems that the negative values obtained at HPHT for yield point measurements in this equipment are related to the null suspension capacity in the formulation or the calibration of the equipment for the dial deflection readings at high shear rate, which affect directly the yield point property. In contrast to low shear rate yield point values, negative values were not observed in the HPHT rheometer.

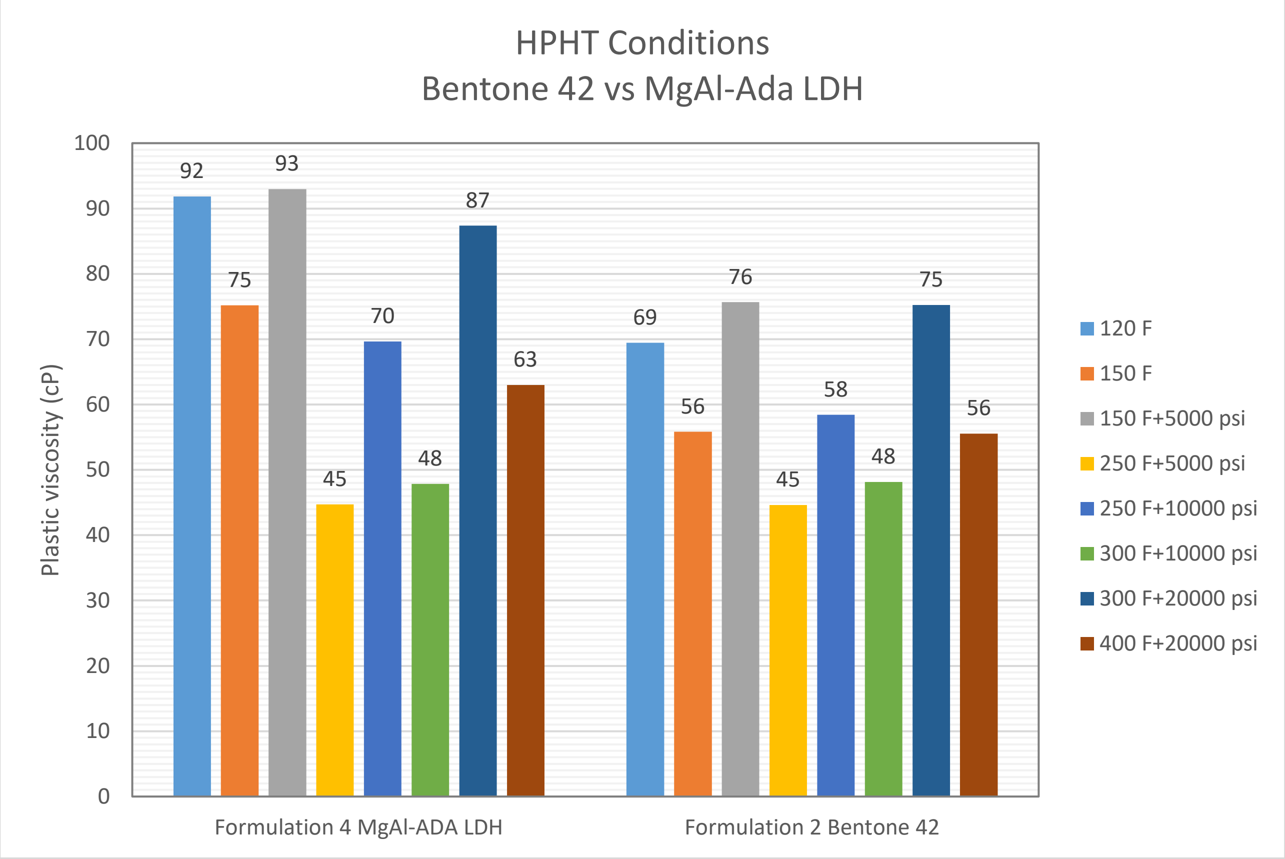

Figure 6.7 Comparison of the plastic viscosity, rheological parameter of a drilling fluid with Bentone 42 vs a drilling fluid with MgAl-Ada LDH.

Figure 6.7 shows the rheological profile for the plastic viscosity plotted across temperature and pressure variations for Formulation 2 and Formulation 4, with Bentone 42 and MgAl-ADA LDH, respectively. As it can be seen in the graph, as the pressure was increased at a constant temperature a slight increase in the plastic viscosity was observed for both samples.

The plastic viscosity measurements under HPHT for both samples did not present significant variations between those measurements at ambient conditions. However, the formulations tested at HPHT did not follow an accurate rheological profile. Although, Bentone 42 developed better performance in some temperature and pressure conditions than MgAl-Ada LDH, within the range of acceptability, which is in the order of 35-60 Cp. However, the data does not show enough consistency; therefore, it cannot indicate a good performance for both materials under HPHT in the present formulation. A reasonable conclusion, would be that be that further optimisation of the overall formulation is needed to derive better rheological profiles, with different oil/ratio formulations, densities and different concentration of some additives to define the rheological behaviour of MgAl-Ada LDH.

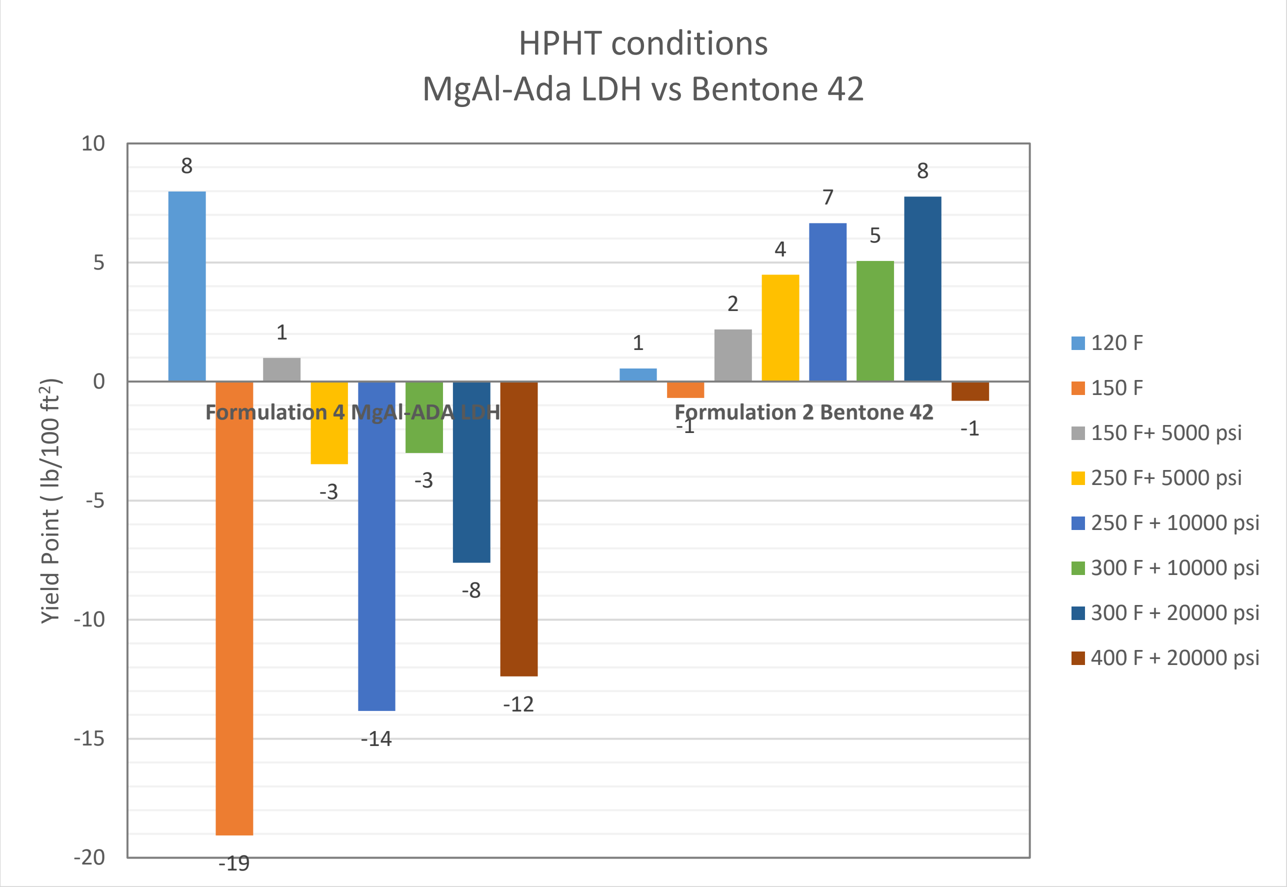

Figure 6.8 Comparison of yield point rheological parameters of a drilling fluid with Bentone 42 vs a drilling fluid with MgAl-Ada LDH.

Figure 6.8 shows the rheological profile of the yield point parameter for Formulation 2 and Formulation 4 with Bentone 42 and MgAl-ADA LDH, respectively. The results from the new rheological modifier in Formulation 4 were below expectations. However, Formulation 2 also shows low yield point values. After the test was finished, the testing cell was unassembled and cleaned for Formulation 4, however it became apparent a part from the cell of the equipment was damaged during the running. This part was an elastomer, which is a piece of the cup. The signs of wear for this elastomer were thought to be caused because the sample analysed was settling on the bottom of the vessel. The results in Figure 6.8 shows clearly that the MgAl-ADA LDH had not developed any suspension capacity during the test. Also, it can be seen in Table 6.8 the LSRYP low values are a good indicator that during the tests were developed several sagging problems, where it could have damaged that part of the equipment owing to the torque built up during the measurements. The values for LSRYP obtained between 1lb/100 ft^2 and 2 lb/100 ft^2 have not met the minimum criteria for LSRYP of (7-15lb/100 ft^2). In addition, other factors that were observed after removing and opening the cell from the rheometer were the fluid syneresis or degradation and amine smells, which was noted for both samples. This strongly suggests that certain components in the formulations tested had undergone thermal degradation.

6.3.5 Effect of solids on drilling fluids performance at ambient conditions.

Tolerance to contamination is a primary requisite of any good drilling fluid. Contamination studies were performed on Formulation 9 and Formulation 10, evaluating the tolerance of Bentone 42 and MgAl-ADA LDH, respectively. The contaminant evaluated was Hymod Prima Clay (HMP), which is a commonly used standard to simulate drilled cuttings from the wellbore in fluid tests. Therefore, this part of the study approaches operating conditions where the drilling fluid would be expected to have good stability, even with a contaminant present. The contaminant tolerance study was divided into two parts, (i) evaluating the drilling fluid at ambient conditions and (ii) under HPHT conditions. Initially, a concentration of 20 g of HMP was considered to contaminate the samples. However, it was observed that after the samples were aged with the concentration of 20 g of HMP, they showed flocculation for both Formulation 11 and Formulation 12. The dial deflection readings and rheological properties data for both samples are shown in Table 6.9 and 6.10 respectively. Therefore, it was subsequently decided to evaluate the contamination effects with 5 g of HMP as is shown in Table 6.11.

Table 6.9 Dial deflection measurements and rheological properties data to different temperatures, BHR and AHR at 250ºF for 16 hours evaluating the formulation 11 contaminated with 20g of HMP.

Bentone 42 + 20 g /bbl HMP Formulation 11								
Temperature °C/°F	49	60	71.1	82.2	49	60	71.1	82.2
	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2			
°F/hr	BHR + 20g HMP				AHR + 20 g HMP			
					AHR 250/16	AHR 250/16	AHR 250/16	AHR 250/16
θ600	222	169	144	127	210	132	169	139
θ300	119	91	79	70	115	101	93	77
θ200	82	64	56	51	82	72	66	57
θ100	46	37	33	31	47	42	39	35
θ6	7	9	9	9	9	9	9	10
θ3	6	6	6	7	7	7	8	8
10 s gel strength (lb/100ft^2)	9	10	11	9	9	9	11	11
10 min gel strength (lb/100ft^2)	10	12	14	11	11	13	10	11
μ_a (cP)	111	85	72	63.5	105	66	84.5	69.5
μ_p(cP)	103	78	65	57	95	31	76	62
τ_y (lb/100ft^2)	16	13	14	13	20	70	17	15
LSRYP (lb/100ft^2)	5	3	3	5	5	5	7	6

Table 6.10 Dial deflection measurements and rheological properties data to different temperatures, BHR and AHR at 250ºF for 16 hours evaluating the formulation 12 contaminated with 20g of HMP.

MgAl-Ada LDH + 20 g /bbl HMP Formulation12								
Temperature °C/°F	49	60	71.1	82.2	49	60	71.1	82.2
	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2			
°F/hr	BHR + 20g HMP				AHR + 20 g HMP			
					AHR 250/16	AHR 250/16	AHR 250/16	AHR 250/16
θ600	135	122	104	92	196	175	150	134
θ300	74	66	57	50	115	112	89	79
θ200	52	47	40	36	84	76	67	60
θ100	30	27	24	21	53	48	43	39
θ6	6	5	5	5	15	15	15	14
θ3	4	4	4	4	13	13	13	12
10 s gel strength (lb/100ft^2)	8	7	9	9	20	20	20	18
10 min gel strength (lb/100ft^2)	12	11	11	11	31	34	30	24
μ_a (cP)	67.5	61	52	46	98	87.5	75	67
μ_p(cP)	61	56	47	42	81	63	61	55
τ_y (lb/100ft^2)	13	10	10	8	34	49	28	24
LSRYP (lb/100ft^2)	2	3	3	3	11	11	11	10

Table 6.11 Dial deflection measurements and rheological properties data to different temperatures, BHR and AHR at 250°F for 16 hours evaluating the Formulation 9 and Formulation 10 contaminated with 5 g of HMP.

MgAl-Ada LDH + 5 g /bbl HMP Formulation 10						Bentone 42 + 5 g /bbl HMP Formulation 9		
Temperature °C/°F	**49**	**49**	**49**	**82.2**		**49**	**49**	**82.2**
	120	**120**	**120**	**180**		**120**	**120**	**180**
Density g/cm^3	2.2					2.2		
°F/hr	**BHR + 5g HMP**		**5 grs/bbl HMP**			**BHR**	**5 grs/bbl HMP**	
	BHR	**5 grs/bbl HMP**	**AHR 250/16**	**AHR 250/16**			**AHR 250/16**	**AHR 250/16**
θ600	107	111	118	72		134	134	81
θ300	56	57	61	37		72	72	44
θ200	40	40	43	26		51	52	33
θ100	23	22	24	16		30	30	20
θ6	4	4	4	4		6	6	6
θ3	3	3	3	3		5	5	5
10 s gel strength (lb/100ft^2)	6	6	5	5		7	6	5
10 min gel strength (lb/100ft^2)	8	6	6	6		8	7	8
μ_a (cP)	53.5	55.5	59	36		67	67	40.5
μ_p(cP)	51	54	57	35		62	62	37
τ_y (lb/100ft^2)	5	3	4	2		10	10	7
LSRYP (lb/100ft^2)	2	2	2	2		4	4	4
ES(volts)	865	836	639			1081	438	729

Figure 6.9 and Figure 6.10 show the plastic viscosity and yield point results for Formulation 9 and 10 contaminated with 5 g of HMP. In addition, Formulation 11 and 12 are shown, which were formulated with 20 g of HMP. Figure 6.9 and 6.10 compares the contamination loading effects on the rheological parameters such as plastic viscosity and yield point, with two contaminant dosages of 5 g and 20 g of HMP.

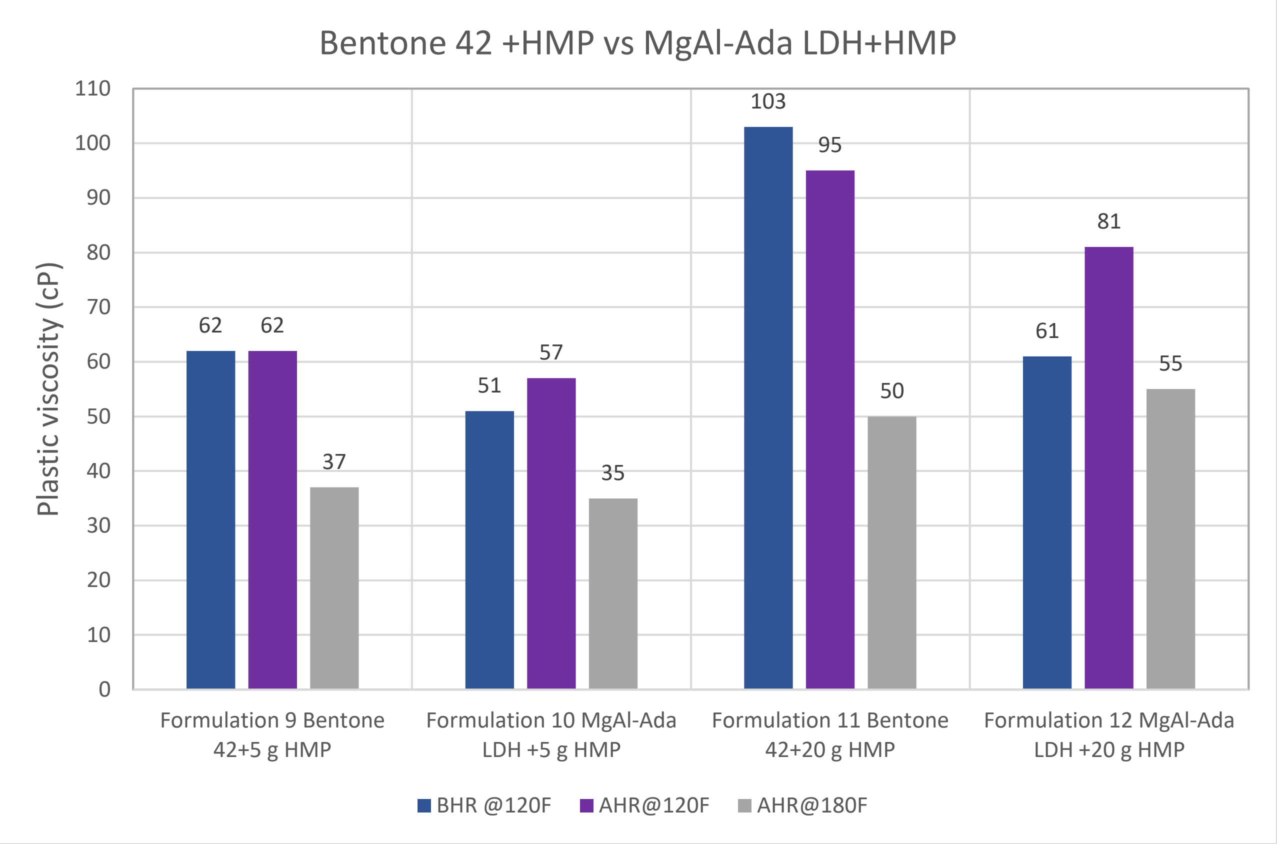

Figure 6.9 Comparison of plastic viscosity to a drilling fluid with Bentone 42+ HMP vs a drilling fluid with MgAl-Ada LDH+HMP.

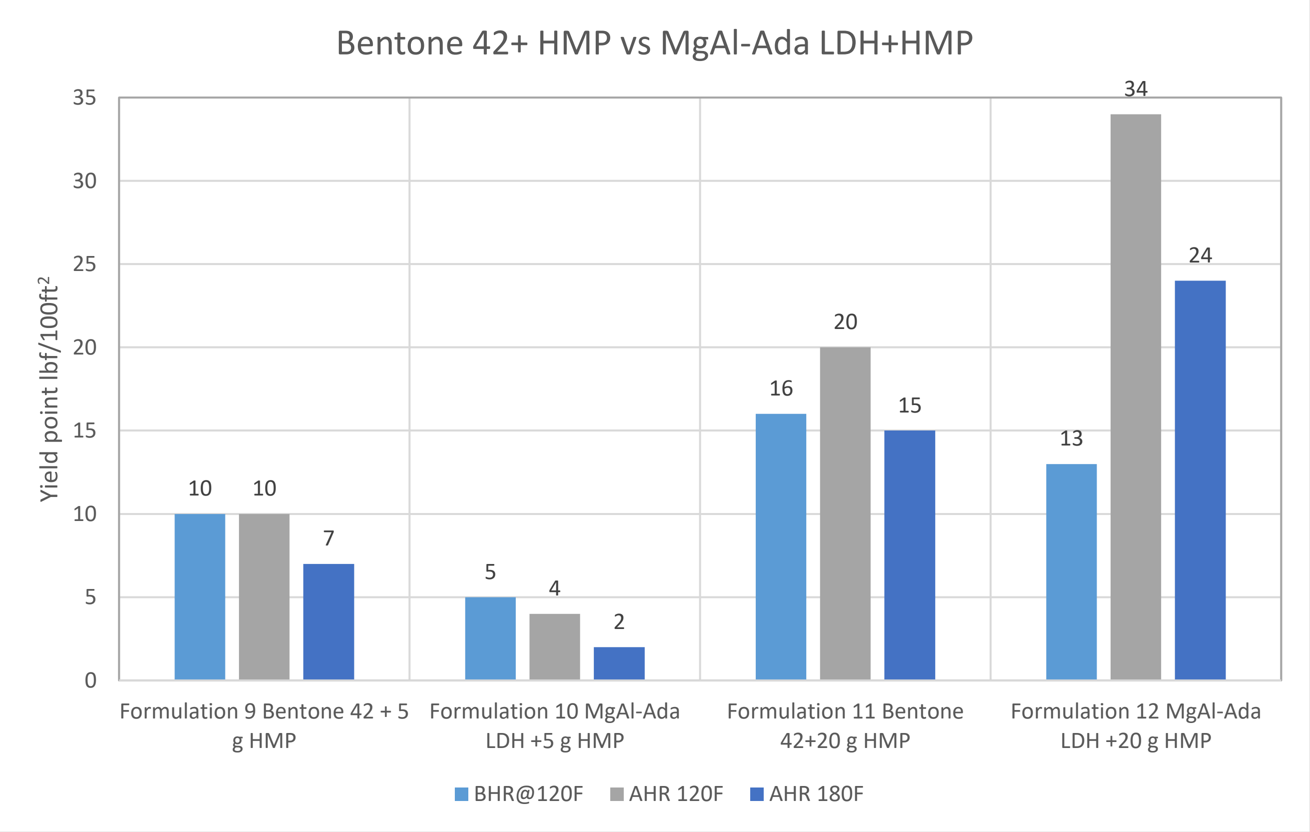

Figure 6.10 Comparison of yield point to a drilling fluid with bentone 42+ HMP vs a drilling fluid with MgAl-Ada LDH+HMP.

The results obtained demonstrated that Formulation 9, 10, 11 and 12 with HMP did not develop good performance in the rheological properties evaluated, however the samples with 5 g of HMP did not present flocculation as the formulation containing 20 gr of HMP. Although, this time with the addition of HMP in the formulation for both samples, the values obtained for the yield point viscosity were not negative such as was observed without the HMP contamination. Table 6.11 shows the LSRYP values under contamination effects of 5g HMP which are low of 2 lb/100 ft^2 for MgAl-Ada LDH, and 4 lb/100 ft^2 to Bentone 42, which would predict severe sagging issues. The Mg Al-Ada LDH in 6.10 seems to show contamination tolerance and the Bentone 42 with the concentration of 5 g HMP. It seems, that the MgAl-Ada LDH improve slightly with the addition of HMP. This also was observed that the formulation with MgAl-Ada LDH when it was under stirring and in short time after stirring, its behaviour was a thining fluid in comparison with Bentone 42. It seems if the shear rate has an influence in the drilling fluid containing MgAl-Ada LDH. This behaviour is more noticeable with HMP in the formulation. There may be synergistic effects between the anionic MgAl-Ada LDH and cationic HMP clay systems, which under yield stress makes a thining fluid.

6.3.6 Effect of solids on drilling fluids performance at HPHT conditions

After the contamination tests at ambient conditions, further experiments at HPHT conditions were developed with the dosage of contaminant held at 5 g, which were Formulations 9 and 10, with Bentone 42 and Mg-Al Ada LDH, respectively. Table 6.12 and Table 6.13 show the dial deflection to Bentone 42 and MgAl-Ada LDH contaminated with HMP. These measurements were taken from Grace Instrument 7500.

Table 6.12 Dial deflection readings and rheological properties at HPHT evaluating Bentone42+HMP

Bentone 42 HB + HMP Formulation 9										
	Fann 35		**Grace Intrument 7500**							
Temperature (°F)	**120**	**180**	**120**	**150**	**150**	**250**	**250**	**300**	**300**	**400**
Pressure (psi)	**0**	**0**	**0**	**0**	**5000**	**5000**	**10000**	**10000**	**20000**	**20000**
RPM										
θ600			136.0	115.0	151.0	97.0	133.0	101.0	148.0	134.0
θ300			71.0	60.0	81.0	48.0	69.0	51.0	77.0	68.0
θ200			49.0	42.0	56.0	34.0	46.0	35.0	52.0	46.0
θ100			29.0	24.0	30.0	18.0	26.0	19.0	28.0	24.0
θ6			3.0	4.0	4.0	3.0	4.0	2.0	3.0	2.0
θ3			2.0	3.0	3.0	2.0	2.0	2.0	1.0	0.8
10s (lb/100ft^2)			1.0	3.0	3.0	3.0	3.0	2.0	2.0	1.0
10 m (lb/100ft^2)			3.0	3.0	3.0	2.0	3.0	2.0	2.0	1.0
μ_p (cP)	0	0	65.0	55.0	70.0	49.0	64.0	50.0	71.0	66.0
τ_y (lb/100ft^2)	0	0	6.0	5.0	11.0	-1.0	5.0	1.0	6.0	2.0
LSYP (lb/100ft^2)	0	0	1	2	2	1	0	2	-1	-0.4

Table 6.13 Dial deflection readings and rheological properties at HPHT evaluating MgAl-Ada LDH+HMP

MgAl Ada LDH HB + HMP Formulation 10										
	Fann 35		Grace Intrument 7500							
Temperature (°F)	**120**	**180**	**120**	**150**	**150**	**250**	**250**	**300**	**300**	**400**
Pressure (psi)	**0**	**0**	**0**	**0**	**5000**	**5000**	**10000**	**10000**	**20000**	**20000**
RPM										
θ600			122.0	100.0	145.0	84.0	117.0	91.0	153.0	121.0
θ300			66.0	52.0	74.0	42.0	57.0	45.0	74.0	57.0
θ200			47.0	38.0	52.0	31.0	40.0	30.0	50.0	40.0
θ100			28.0	24.0	31.0	20.0	23.0	20.0	28.0	23.0
θ6			10.0	8.0	11.0	7.0	7.0	7.0	7.0	6.0
θ3			8.0	8.0	7.0	7.0	7.0	5.0	7.0	6.0
10s (lb/100ft^2)			8.0	8.0	7.0	7.0	7.0	5.0	7.0	6.0
10 m (lb/100ft^2)			8.0	8.0	8.0	6.0	7.0	6.0	6.0	6.0
μ_p (cP)	0	0	56.0	48.0	71.0	42.0	60.0	46.0	79.0	64.0
τ_y (lb/100ft^2)	0	0	10.0	4.0	3.0	0.0	-3.0	-1.0	-5.0	-7.0
LSYP (lb/100ft^2)	0	0	6	8	3	7	7	3	7	6

Table 6.12 and Table 6.13 show low shear rate yield point values for Bentone 42 and MgAl-Ada LDH, which is an indicator that during the test also was developed sagging problems for the low suspension capacity for both samples.

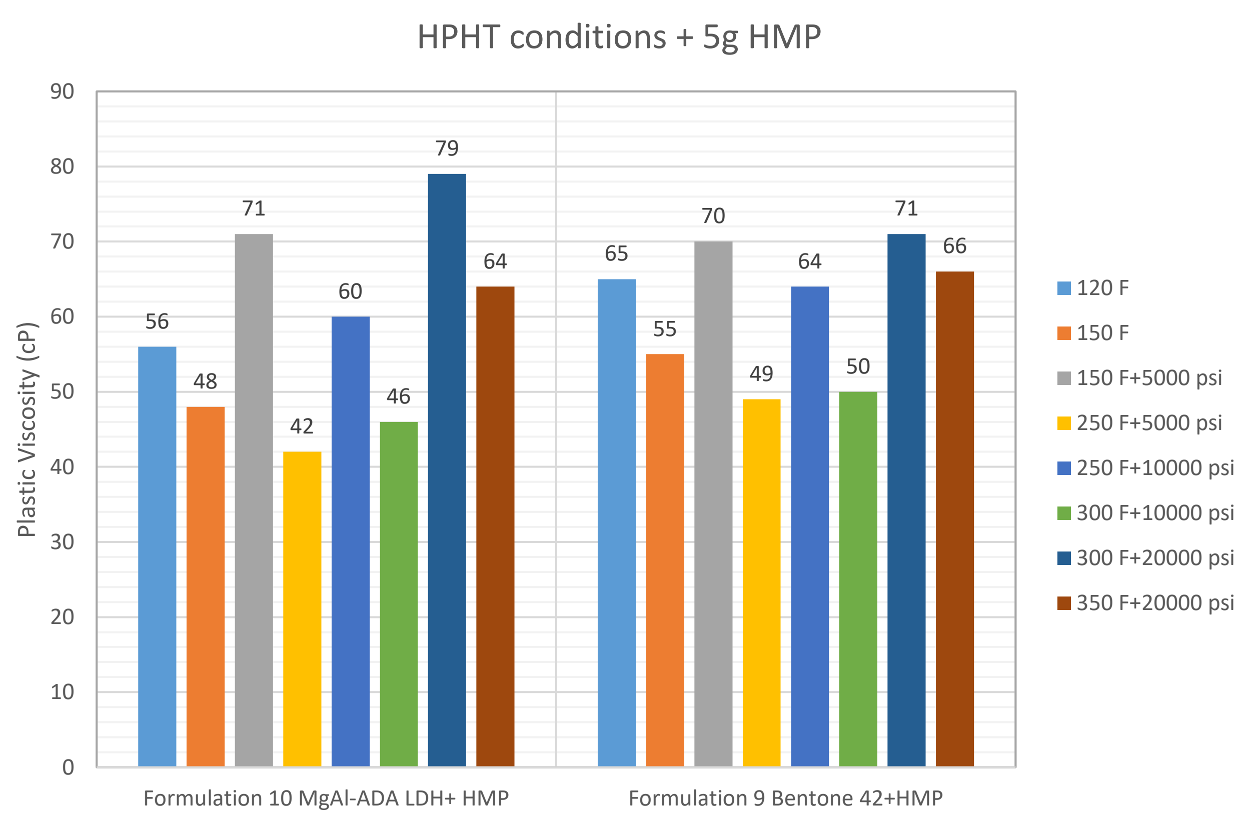

Figure 6.11 Comparison of plastic viscosity to a drilling fluid with Bentone 42 + HMP vs a drilling fluid with MgAl-Ada LDH + HMP.

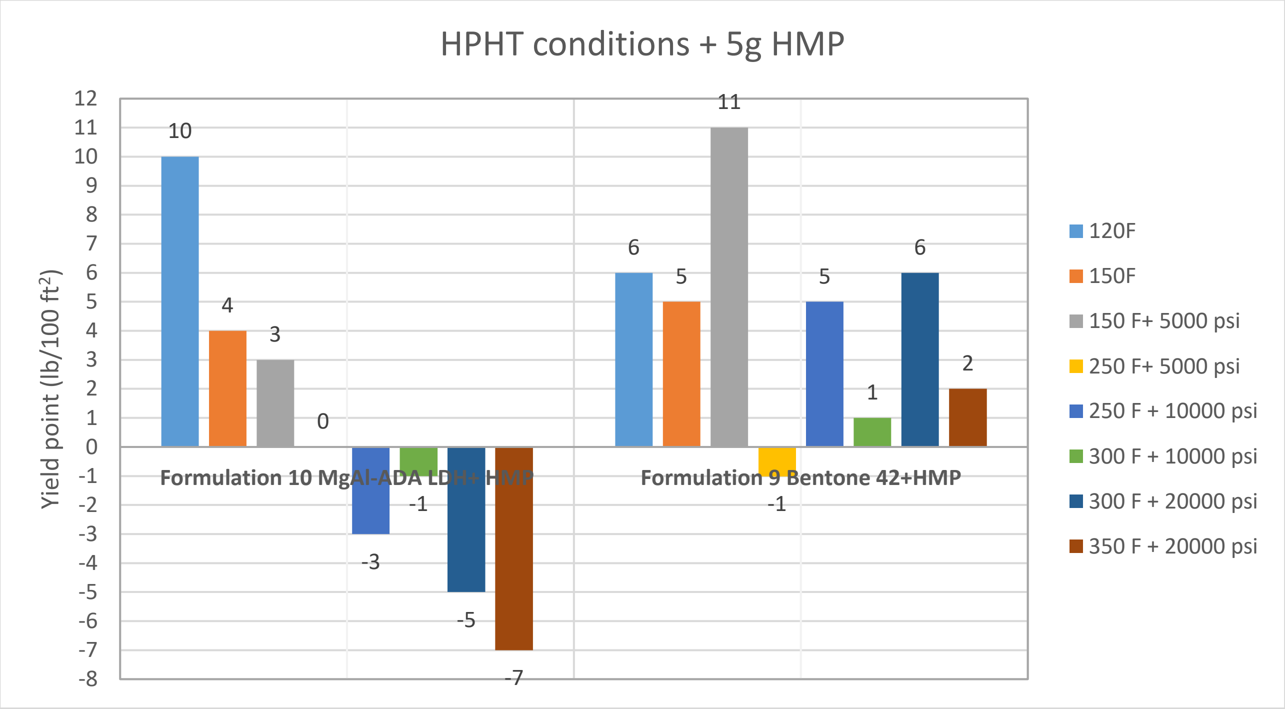

Figure 6.12Comparison of yield point to a drilling fluid with Bentone 42+ HMP vs a drilling fluid with MgAl-Ada LDH+HMP.

Figure 6.11 and 6.12 show the rheological properties comparing Formulation 9 and Formulation 10. As can be seen in the figures, the formulations contaminated with HMP, when evaluated under HPHT conditions, presented instability. It is because the plastic viscosity values shown were higher than the ambient conditions for both samples, Formulation 9 with Bentone 42 and Formulation 10 with MgAl-Ada LDH. The yield point shows negative values for the MgAl-Ada LDH under high pressure and high temperature, with an exception at 150 ˚F and 5000 psi. This might be confirming sagging, as we observed in the results of the sagging test and the initial tests at LT and LP in Chapter 5. Also the samples with Bentone 42 show lower values at yield point at HPHT in comparison with the previous samples.

To better understand the reason for the performance of MgAl-Ada LDH for the test at HPHT, and the rheological properties data with the contamination of HMP an experiment was developed with a concentration profile in order to understand if the formulation needed to have more concentration of MgAl-Ada LDH to increase the yield point values and the viscosity properties. The concentration profile revealed in Figure 6.14 that the MgAl-Ada LDH rheological modifier with a concentration of 5 g delivered a rheology slightly higher than lower concentration profiles. However, this cannot definitively state that this could be an appropriate concentration due to the fact that the concentration profile at 6 g was lower than the concentration profile of 5 g, it doesn't mean that the rheological modifier is developing good performance with that concentration due to the fact that the LSRYP keep going be too low of 4 lbf/100ft^2, it doesn't meet the minimum criteria of acceptable rheological properties even after increasing the concentration. Therefore, more studies are required in the future to better understand compatibility between the rheology modifier developed and the components used within the formulated drilling fluid.

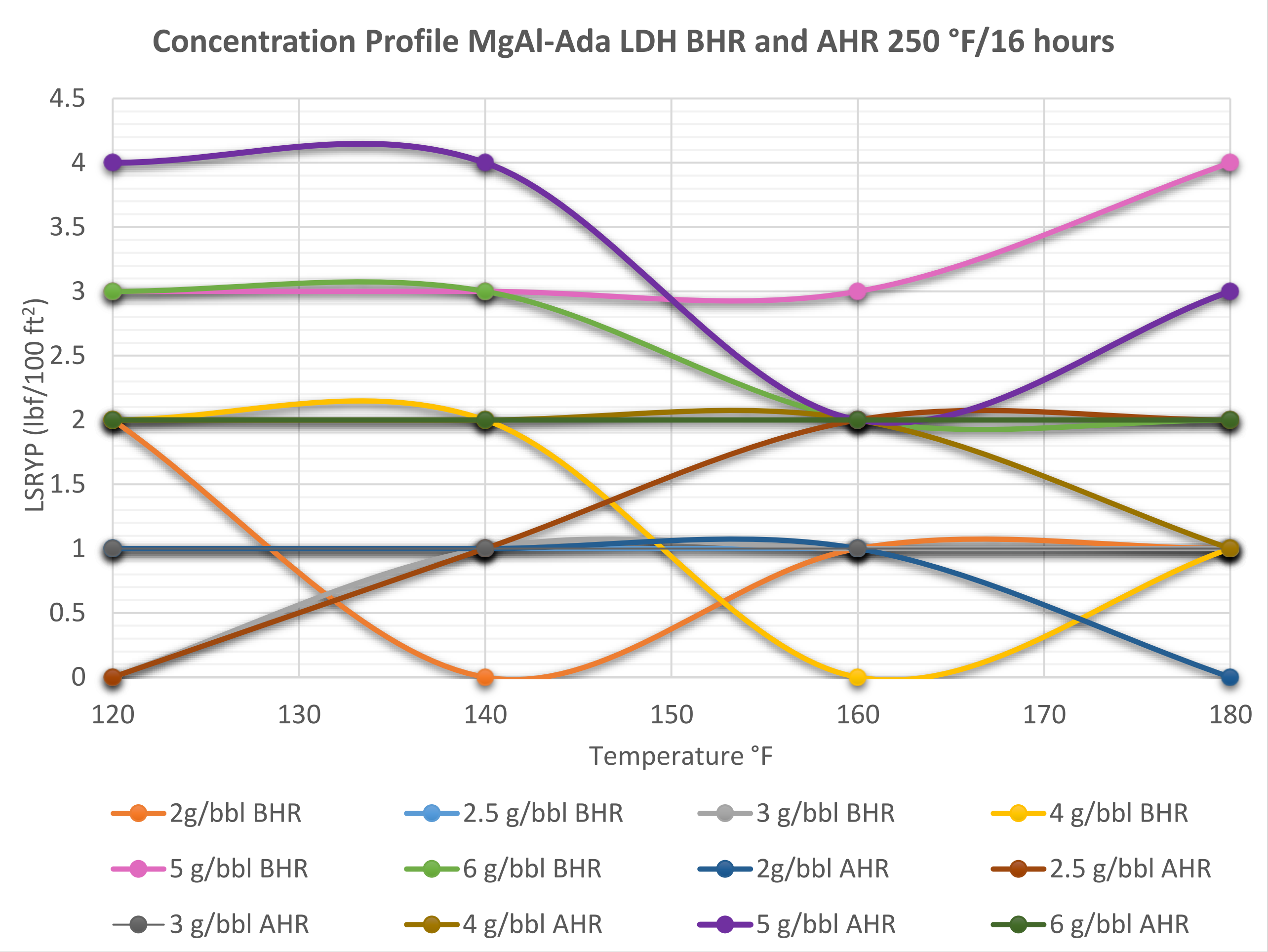

Figure 6.13 Concentration profile of MgAl-Ada LDH at different concentrations BHR and AHR at 250ºF.

6.4 Conclusions

The use of a new organophilic layered double hydroxide rheology modifier in test drilling fluid formulations under a range of temperature and pressure conditions with/without solid contaminants has been investigated. The new material has been compared in all tests with the industry best available technology, Bentone 42. The data clearly shows that the new formulations need to be further optimised. The MgAl-Ada LDH doesn´t present good rheological properties into a synthetic base mud with the formulation tested, as per the patent mentioned, despite the reported high temperature stability and organophilic nature of the particle[1,2] . It could be worth further refining the preparation of the modifier to change the formulation and the order and time of mixing the properties for the MgAl-Ada LDH to get the appropriate properties that a rheological modifier needs to develop into a HPHT drilling fluid. During the formulation preparation with MgAl-LDH a thining fluid behaviour was observed while it was stiring. However, the MgAl-Ada LDH showed serious settling problems, with significant material migrating to the bottom of the reactor after stirring. This was reflected in the yield point values from the experiments, which is an indicator of poor suspension capacity of weighting and other compounds. Also, the damage of one part of the equipment at HPHT tests evidences that the material needs to be more fully investigated and optimised before carrying out other HPHT tests during further work.

Chapter 7

Conclusions and Further Work

7.1 Conclusions

In this thesis we set out to study a new thermally stable, high aspect ratio, organophilic layered mineral rheology modifier developed and patented by Durham University. It was observed through the experiments carried out in this thesis that the particle size had an influence on the rheology properties. It appeared that with the scaled-up MgAl-Ada LDH material, in comparison to the small scale preparations used in the initial patent studies, the interaction with other compounds in the formulation was causing settling to the bottom of the reactor (sag) and the rheological properties performance were notably lower. It can be concluded that the new rheological modifier was then unable to develop any performance in the formulation of the drilling fluids trialled, as was cited in the patent. This presents instability, low rheological values, any suspension of weighting capacity, flat undesirable gel strength, high filter loss at HPHT, degradation of the system at high pressure and high temperature, and low tolerance to contamination by fines. In summary, the formulations evaluated have not developed good performance for the new rheological modifier. Thus, further development work remains to be done to establish if the new LDH based material can be offer any improved fluid performance at HPHT in a synthetic base drilling fluid.

7.2 Further Work

In summary, further experimental investigations are needed to estimate;

1. Material characterization of the bulk toll manufactured rheology modifier in depth prior to it being further evaluated in a drilling fluid, including particle size dispersion and ion exchange of the alkaline-earth diamondoid compound as the new rheological modifier.
2. Optimization for the patent's trial drilling fluid formulation, mixing time, compounds, mixing order etc.
3. Optimization for the concentrations of reagents in the fluid at different aging temperatures.

In addition, the definition of other properties of new materials which may be incorporated in a drilling fluid, some investigation are required before these may be added in a drilling fluid. Any materials used need to be optimised for working temperature range, state of flocculation, strength, and influence of molecular weight on viscosity, settling stability, ageing and dispersion. They are crucial properties which need to be known for a thorough understanding of the interactions between components in the drilling fluids and the causes of probable instability related to the materials used.

Abbreviations

ECD	Equivalent Circulating Density
ESD	Equivalent Static Density
LT	Low Temperature
LP	Low Pressure (not exceeding 300°F)
LAO	Linear Alpha Olefins
IO	Internal Olefin
SBF	Synthetic Base Fluid
OBM	Oil Base Mud
WBM	Water Base Mud
OECD	Organization for Economic Cooperation and Development
HPHT	High Pressure and High temperature conditions
PWD	Pressure While Drilling (drilling tool)
MWD	Measure While Drilling (drilling tool)
LWD	Logging while drilling
NPT	Non Productive time
HSG	High Solids Gravity
LSG	Low Solids Gravity
ROP	Rate of Penetration
HMP	Hymod Prima Clay
PV	Plastic Viscosity
AV	Apparent Viscosity
RPM	Revolution Per Minute
YP	Yield Point
LSRYP	Low Shear Rate Yield Point
LSRV	Low Shear Rate Viscosity
LSR	Low Shear Rate
HSR	High Shear Rate
BHR	Before Hot Rolling
AHR	After Hot Rolling
H-B	Herschel-Bulkley model
LDH	Layered Double Hydroxides

SEM	Scanning Electron Microscope
ES	Emulsion Stability
NADF	Non Aqueous Drilling Fluid
BEIS	Department for Business, Energy and Industrial Strategy in the UK
OCNS	Offshore Chemical Notification Scheme
CEFAS	Centre for Environment, Fisheries and Aquaculture Science
LTMO	Low Toxicity Mineral Oil
BBL	Barrel Unit

Nomenclature

Symbol	**Description**	**Units**
θ600	Viscometer reading at 600 r/min	°deflection
θ300	Viscometer reading at 300 r/min	°deflection
θ200	Viscometer reading at 200 r/min	°deflection
θ100	Viscometer reading at 100 r/min	°deflection
θ6	Viscometer reading at 6 r/min	°deflection
θ3	Viscometer reading at 3 r/min	°deflection
ROP	Rate of Penetration	m/h
ρ	Fluid density	g/cm^3
Rpm	Rotational speed from Viscometers	°deflection
μ_a	Apparent viscosity	cP
μ_p	Plastic viscosity	cP
τ_y	Yield Point (yield stress)	lb/100 ft^2
LSRYP	Low share rate yield point	lb/100 ft^2
Gel 10 s	Thixotropic at 10 s	lb/100 ft^2
Gel 10 min	Thixotropic at 10 min	lb/100 ft^2
τ	Shear Stress	lb/100 ft^2
$\dot{\gamma}$	Shear Rate	s^{-1}
n	Flow index	dimensionless
K	Consistency Index	dimensionless
Lab bbl	Lab barrel	350 ml
ES	Emulsion Stability	Volts
SG	Sag Factor	dimensionless
SG$_{\text{bottom}}$	Density of Sample at the bottom of the Cell	g/mL
SG$_{\text{top}}$	Density of Sample at the top of the Cell	g/mL
Mud Cake	Remaining Solids on the filter paper from HPHT filter test	g
Filtration correction	mL obtained from filter loss testing multiplied per 2	mL

Appendix A *Types of Drilling Fluids*

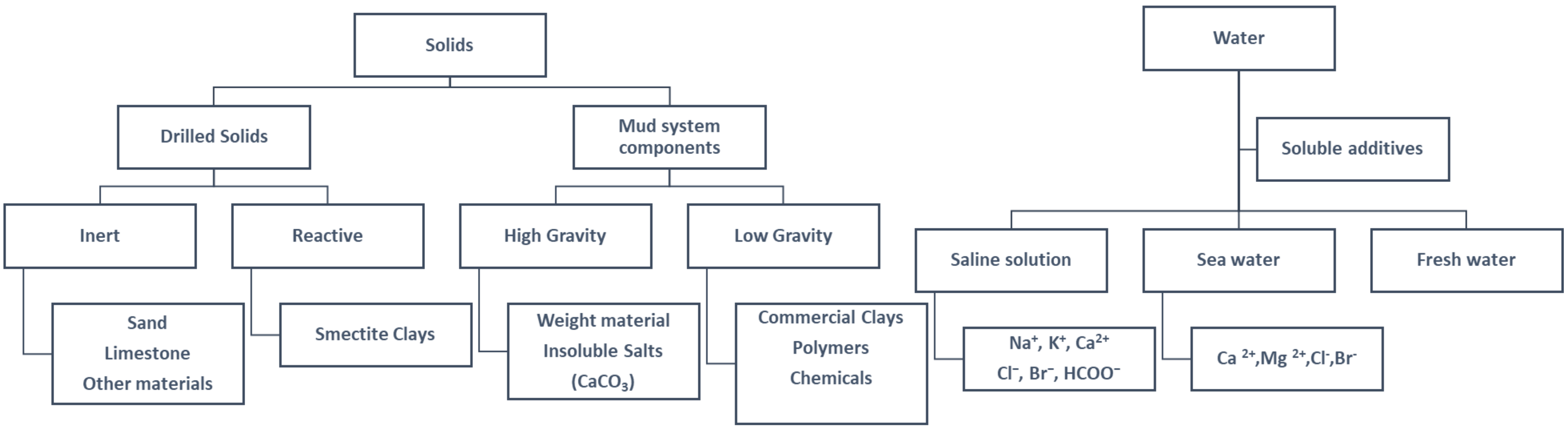

Figure A.1Type of water-based muds. Adapted from ASME shale Committee[39]

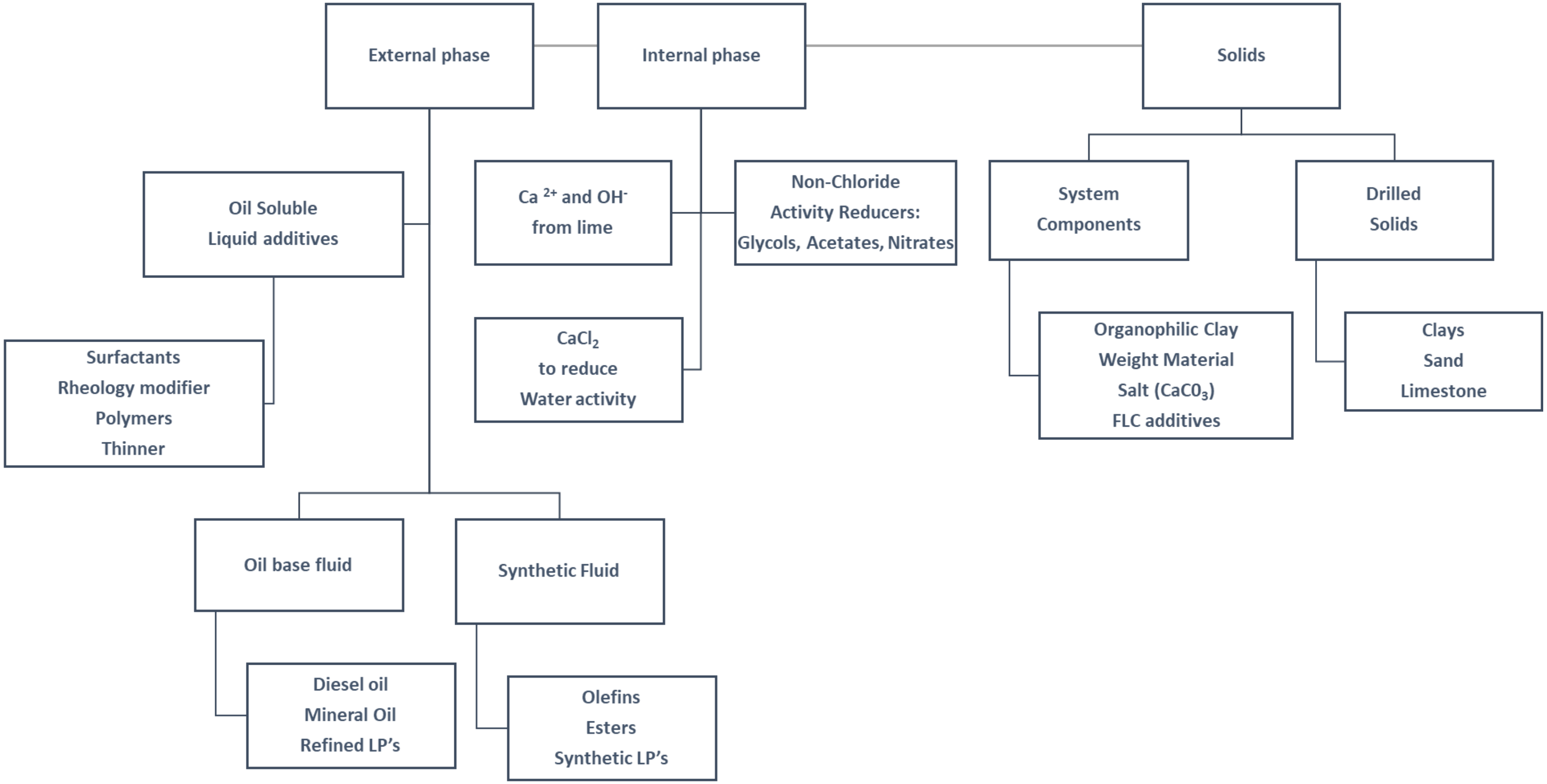

Figure A.2 Types of Invert-Emulsion. Adapted from ASME Shale Committee[39]

Table A.1Description of well requirement characteristics to select the gas-based and water-based drilling fluid. Adapted from ASME Shale Shaker Committee[39]

Classification Type of Fluids	Principal Compounds	Characteristics
Gas		
Dry Air	Dry Air	Fast drilling in dry, hard rock No water influx Dust
Mist	Air water or mud	Wet formations but little water influx High annular velocity
Foam	Air Water Foaming agent	Stable rock Moderate water flow tolerated
Water		
Fresh	Fresh water	Fast drilling in stable formations. Need large settling area flocculants, or ample water supply and easy disposal
Salt	Sea Water	Brines for density increase and lower freezing point. Limited to low permeability rocks.
Low solids muds	Fresh water Polymer Bentonite	Fast drilling in competent rocks. Mechanical solids removal equipment needed. Contaminated by cement, soluble salts.
Spud Mud	Bentonite Water	Inexpensive Narrow margin between the pore pressure and fracture pressure in deepwater drilling. Pump and dump “riserless system.

Classification Type of Fluids	Principal Compounds	Characteristics
Salt water muds	Sea water Brine Saturated salt water Salt-water clays Starch Cellulosic polymers	Drill rock salt, workovers Drilling salts other than halite may require special treatment.
Lime Muds	Fresh or brackish water. Bentonite (or native clays). Lime. Chrome lignosulfonate. Lignite. Sodium chromate and surfactant for high temperatures.	Shale drilling. Simple maintenance at medium densities. Max. temp 300 °F(150°C) with lignite added. Some tolerance for salt. Unaffected by anhydrite, cement PH11-12
Gyp Muds	Fresh or brackish water. Bentonite (or native clays). Gypsum Chrome lignosulfonate. Lignite. Sodium chromate and surfactant for high temperatures.	Shale drilling Simple maintenance Max. temp 325 °F (165°C) Unaffected by anhydrite, cement, moderate amount of salt PH 9-10
CL-CLS Muds	Fresh or brackish water. Bentonite. Caustic soda. Chrome lignite. Chrome lignosulfonate. Surfactant added for high temperature.	Shale drilling Simple maintenance Max. temp 350°F (180°C) Same tolerance for contaminants as gyp muds ph 9-10
Potassium Muds	Potassium Chloride. Acrylic. Bio or cellulosic polymer. Bentonite	Hole stability Mechanical solids-removal equipment necessary. Fast drilling at minimum solids content. Ph 7-8

Table A.2 Description of well requirement characteristics to select oil-based drilling fluid. Adapted from ASME Shale Shaker Committee[39].

OIL		
Classification **Type of Fluid**	**Principal Compounds**	**Characteristics**
Oil	Weathered crude oil Asphaltic crude Soap Water	Low-pressure well completion and workover. Drill shallow, low-pressure, productive zone. Water can be used to increase density and cutting-carrying ability
Asphaltic muds	Diesel oil. Asphalt. Emulsifier. Water 2-10%.	The composition of oil muds can be designed to satisfy any density and hole stabilization requirements and temperatures requirements to 600 °F (315°C).
Non-Asphaltic Mud(Invert)	Diesel oil Emulsifiers Oleophilic clay Modified resins and soaps, 5-40% water	High initial cost and environmental restrictions, but low maintenance cost.
Synthetic Mud	Synthetic hydrocarbons or esters.	Environmental friendly for the mineral oil base.

Appendix B

Concentrations of MgAl-Ada LDH in the formulation for drilling fluids

Table B.1 Dial deflection readings and rheological properties from Fann 35 for concentration dosage of MgAl Ada LDH of 2g/bbl, 2.5 g/bbl and 3g/bbl before hot rolling.

Mg Al Ada LDH Concentration Profile BHR												
Hamilton Beach	**2g/bbl BHR**				**2.5 g/bbl BHR**				**3 g/bbl BHR**			
Temperature °C/°F	**49**	**60**	**71.1**	**82.2**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
	120	140	160	180	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2				2.2			
	BHR				BHR				BHR			
θ600	115	96	95	78	120	96	94	75	184	114	89	76
θ300	58	50	48	37	60	49	46	36	95	57	45	38
θ200	40	35	33	26	41	34	32	26	65	39	30	26
θ100	22	19	28	15	21	18	17	14	34	21	16	14
θ6	4	4	3	3	3	3	3	3	4	3	3	3
θ3	3	2	2	2	2	2	2	2	2	2	2	2
10 s gel (lb/100ft^2)	6	5	4	5	6	4	4	6	4	4	4	4
10 min gel (lb/100ft^2)	7	6	7	6	7	6	6	7	5	5	5	4
μ_a (cP)	57.5	48	47.5	39	60	48	47	37.5	92	57	44.5	38
μ_p(cP)	57	46	47	41	60	47	48	39	89	57	44	38
τ_y (lb/100ft^2)	1	4	1	-4	0	2	-2	-3	6	0	1	0
LSRYP (lb/100ft^2)	2	0	1	1	1	1	1	1	0	1	1	1

Table B.2 Dial deflection readings and rheological properties from Fann 35 for concentration dosage of MgAl Ada LDH of 2g/bbl, 2.5 g/bbl,3g/bbl after hot rolling

Mg Al Ada LDH Concentration Profile AHR												
Hamilton Beach	**2g/bbl AHR**				**2.5 g/bbl AHR**				**3 g/bbl AHR**			
Temperature °C/°F	**49**	**60**	**71.1**	**82.2**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
	120	140	160	180	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2				2.2			
° F/ hrs	AHR 250/16				AHR 250/16				AHR 250/16			
θ600	115	105	89	84	132	183	154	127	156	128	98	81
θ300	57	52	44	40	63	97	80	65	79	65	50	41
θ200	40	36	30	26	42	67	56	46	54	45	35	28
θ100	22	20	17	14	22	36	30	26	29	24	28	16
θ6	3	3	3	2	2	5	4	4	3	3	3	3
θ3	2	2	2	1	1	3	3	3	2	2	2	2
10 s gel (lb/100ft^2)	5	5	5	5	4	6	6	7	4	5	4	4
10 min gel (lb/100ft^2)	6	6	5	3	6	9	9	9	4	4	4	4
μ_a (cP)	57.5	52.5	44.5	42	66	91.5	77	63.5	78	64	49	40.5
μ_p(cP)	58	53	45	44	69	86	74	62	77	63	48	40
τ_y (lb/100ft^2)	-1	-1	-1	-4	-6	11	6	3	2	2	2	1
LSRYP (lb/100ft^2)	1	1	1	0	0	1	2	2	1	1	1	1

Table B.3 Dial deflection readings and rheological properties from Fann 35 for concentration dosage of MgAl Ada LDH of 4g/bbl, 5 g/bbl, 6g/bbl before hot rolling.

Mg Al Ada LDH Concentration Profile BHR												
Hamilton Beach	**4 g/bbl BHR**				**5 g/bbl BHR**				**6 g/bbl BHR**			
Temperature °C/°F	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
	120	140	160	180	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2				2.2			
	BHR				**BHR**				**BHR**			
θ600	150	120	103	84	167	129	108	96	160	134	112	99
θ300	80	64	53	43	86	67	56	50	86	71	58	51
θ200	55	45	37	31	61	48	40	36	60	51	42	37
θ100	30	25	20	17	34	27	23	21	33	28	23	20
θ6	4	4	4	3	5	5	5	4	5	5	4	4
θ3	3	3	2	2	4	4	4	4	4	4	3	3
10 s gel (lb/100ft^2)	4	5	5	5	5	6	6	6	6	4	6	4
10 min gel (lb/100ft^2)	7	7	7	7	8	8	8	8	7	8	8	6
μ_a (cP)	75	60	51.5	42	83.5	64.5	54	48	80	67	56	49.5
μ_p(cP)	70	56	50	41	81	62	52	46	74	63	54	48
τ_y (lb/100ft^2)	10	8	3	2	5	5	4	4	12	8	4	3
LSRYP (lb/100ft^2)	2	2	0	1	3	3	3	4	3	3	2	2

Table B.4 Dial deflection readings and rheological properties from Fann 35 for concentration dosage of MgAl Ada LDH of 4g/bbl, 5 g/bbl, 6g/bbl after hot rolling.

Mg Al Ada LDH Concentration Profile AHR												
Hamilton Beach	**4 g/bbl AHR**				**5 g/bbl AHR**				**6 g/bbl AHR**			
Temperature °C/°F	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**	**49**	**60**	**71**	**82**
	120	140	160	180	120	140	160	180	120	140	160	180
Density g/cm^3	2.2				2.2				2.2			
° F/ hrs	**AHR 250/16**				**AHR 250/16**				**AHR 250/16**			
θ600	129	104	88	86	175	135	110	95	150	124	105	87
θ300	66	53	45	43	96	75	60	50	76	63	54	45
θ200	46	37	32	30	70	53	43	36	53	44	38	31
θ100	26	21	18	16	40	31	25	21	29	24	21	18
θ6	4	4	4	3	8	6	6	5	4	4	4	4
θ3	3	3	3	2	6	5	4	4	3	3	3	3
10 s gel (lb/100ft^2)	5/6	5/6	5/6	5/6	8	6	6	6	6	6	6	6
10 min gel (lb/100ft^2)	6	6	6	6	9	8	7	7	6	6	6	6
μ_a (cP)	64.5	52	44	43	87.5	67.5	55	47.5	75	62	52.5	43.5
μ_p(cP)	63	51	43	43	79	60	50	45	74	61	51	42
τ_y (lb/100ft^2)	3	2	2	0	17	15	10	5	2	2	3	3
LSRYP (lb/100ft^2)	2	2	2	1	4	4	2	3	2	2	2	2

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