Synthesis & Performance evaluation of Cellulose Nanocrystals as a Drilling Fluid Additive for Fluid loss and its Impact on the Fluid Rheological Properties

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

8 May 2015, Johannesburg

DECLARATION

I Sibusiso Makonjwa hereby declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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ABSTRACT

Drilling fluid/Mud constitute about 15% of the drilling process cost with a single well costing approximately $ 8.7million in 2013 according to the Petroleum Services Association of Canada. Common challenges experienced during drilling are fluid loss and the need to formulate a fluid with desirable rheological properties to withstand increasing temperature and pressure conditions. This investigation looks at using Cellulose Nanocrystals (CNCs) as an additive to reduce fluid loss and maintain or improve the fluids rheological properties. This involved the synthesis and characterisation of CNCs, CNC-Bentonite suspensions rheological properties and fluid loss tests. All rheological tests were measured using a Rheolab QC at 120°F for 6wt% Bentonite mud samples with 0, 0.1, 0.3, 0.5 and 0.8wt% CNCs concentration. It was discovered that the inclusion of CNCs into Water-Bentonite mud resulted in reduced fluid loss of significant amount within the range of 0.3-0.8% CNC concentration. Formulations with CNC concentration above 0.1wt% showed a significant increase in the mud's viscosity and gel strength. Test results indicated that CNCs can be used in drilling fluids as an additive for fluid loss control, as a viscosifier and a gel strengthening agent.

DEDICATION

To my family, my late great grandmother

Nogiye Maria Mabena, my grandmother Bathabile Martha Mkiti and my niece Nondumiso Ntombi Skhosana

ACKNOWLEDGEMENTS

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1 CHAPTER 1: BACKGROUND & MOTIVATION

A drilling fluid/mud is a complex fluid comprising of a number of additives, the type and amount of additive is added according to the type of reservoir to be drilled, drilling method employed and the wellbore conditions. Drilling fluids also known as drilling mud are used to facilitate the drilling of oil, gas and geothermal wells. The most frequently used mud types are water based mud (WBM), oil based mud (OBM) and synthetic based mud (SBM). Synthetic drilling fluids, similar to OBM in composition but the base fluid is made up of synthetic material instead of oil. SBM are more preferred compared to OBM especially on offshore operations since they are less toxic due to low aromatic content with high biodegradability (Youlin et al., 2011; Shah et al., 2010). An OBM is made of hydrocarbons mainly diesel oil as the continuous phase of which poses a disposal concern with a more complex fluid formulation compared to WBM rendering the mud more expensive. WBM is the most used type of drilling fluid both offshore and onshore with water the continuous phase and consist mainly of water, clay, polymer and chemical additives. This type of mud is said to be inexpensive with less environmental problems (Ahmed-Haras et al., 2013).

The role of a drilling fluid during drilling is to provide the sufficient hydrostatic pressure, cool and lubricate the drill bit, lift the drill cuttings to the surface, prevent the transport of fluids from the permeable formations to the drilling fluid & vice versa, withstand/ hold back the formation pressure this will help keep the wellbore stable and avoid squeezing in of the well on the drill bit which may result in the bit being stuck etc. (Fordyce & Baer., 1950). Drilling fluids are formulated with a multitude of additives each with a specific role to play or added to enhance the performance of another additive. Drilling fluid additives include weighting materials, viscosifying agents, dispersants, fluid-loss control agents, shale stabilizers, lubricants, surfactants, emulsifiers and corrosion inhibitors. Various works have been done on the use of biomass, organic & inorganic material, industrial waste and cellulose containing material as drilling fluid additives. For this research cellulose nanocrystals (CNC) are to be used as an additive in WBM to improve the fluid loss control and evaluate its impact on fluid viscosity and other rheological properties. In most WBM, Bentonite is used as the fluid loss and viscosifying agent but Bentonite has its limits thus the idea to add CNC to improve the Water-Bentonite suspension fluid loss control and viscosity.

Drilling fluids constitute about 10-15% of total drilling costs (Zhao., 2013) and help improve the drilling efficiency thus it is of vital importance that the mud is carefully formulated to lower cost and avoid consequences such as blowouts or the abandonment of the well. During drilling the formation conditions change with well depth thus the temperature and pressure of the formation increase with depth which poses a challenge. More challenges are experienced offshore through deep sea operations as the temperatures go as low as 0ºC in the riser from subsea to the surface. Fluid loss/loss circulation is when part of the drilling fluid filters into the formation depending on the formation permeability resulting in reduced drilling fluid which requires replacement.

Taking into consideration the pumping cost, it is of interest to formulate a drilling fluid that will give desired rheological properties such as low viscosity to lower strain on pumping, a fluid that will adapt to the harsh and continuously changing formation conditions with limited or no fluid loss. It is important to note that an adequately formulated drilling mud can reduce the total drilling cost by 5-15% (Bloys et al., 1994). In this project the use of CNC (Cellulose Nanocrystals) as an additive to a WBM or Water-Bentonite suspension as a viscosity modifier, fluid loss control agent together with the mud stability is investigated.

Through TEMPO (2,2,6,6-Tetramethylpiperidine) oxidation, CNCs were produced from a 3.2% Microfibrillated Cellulose (MFC) slurry then added to Spud Mud (Bentonite-Water suspension) followed by the rheological properties and fluid loss tests.

1.1 Research Questions

This research aims to determine whether CNCs can be used as an additive to drilling fluids. Thus the research intends to answer the following questions:

- Can CNCs be used in drilling fluids as a viscosifier and/ a fluid loss control additive?
- What impact will the addition of CNC on water –Bentonite suspension have on the mud rheological properties?
- Does the use of CNC as an additive for fluid loss help lower fluid loss?

1.2 Objectives

- To synthesize CNCs.
- To investigate the effect of adding CNC on the Bentonite-Water suspension Rheological properties at various CNC compositions.
- To investigate the amount of fluid loss relative to the concentration of CNC added in Bentonite-Water suspension.

1.3 Report Outline

This report is made up of five chapters. There is a background, motivation and literature review in the first two chapters. Following this there are three chapters all which give insight into the work performed, the followed procedure, the results obtained including the discussion and the conclusions made based on the obtained results.

Chapter 1; presents a background and motivation on the subject to familiarise with the challenges experienced in the industry and the proposed idea to try and solve the challenge, the research questions and objectives.

Chapter 2; presents the necessary literature on Cellulose, Cellulose Nanocrystals, Cellulose based drilling fluid additives and drilling fluids which will help discuss the obtained results.

Chapter 3; presents details on the materials used, equipment and the experimental methods employed to conduct the experimental work.

Chapter 4; presents the experimental results on fluid loss and the mud rheological properties for various mud formulations including the discussion of the obtained results.

Chapter 5; concludes the research project by suggesting that CNCs can be used as a viscosifier and a fluid loss control agent, with recommendations for future study on the subject.

2 CHAPTER 2: LITERATURE REVIEW

2.1 Oil and Gas well Drilling

Drilling a well involves the use of a drill string and a drill bit at the end of the string. In most cases rotational drilling (i.e. drilling through rotating the drill string and thus the bit rotates as it drills into the ground) is employed. When drilling deeper into the earth various rock strata is experienced and the well conditions vary with depth thus the process is subject to a number of challenges such as hard rocks, increasing temperature and pressure and formation forces. Constant friction during drilling lead to increased rate of wear on mechanical parts/ drill bit. Without removal of the drill cuttings the bit will eventually stuck bringing the process to a halt, with no pressure to balance the formation pressure a blow out of hydrocarbons to the surface uncontrollably may result.

All the mentioned challenges are matched by the use of a chemical system termed a drilling fluid/ mud, a fluid designed to get optimal results based on the well conditions. Drilling fluids are fed from the surface through the drill string by being pumped all the way through the drill bit into the annulus between the drill string and the hole before reaching the surface. Among other roles drilling fluids carry the drill cuttings to the surface, control well pressure through hydrostatic pressure, cool and lubricate the drill bit, support the well wall, keep the well stable, prevent drill pipe corrosion and create a filter cake on the walls of the well to protect permeable production formations and prevent fluid invasion into porous formation (Kosynkin., 2011; Ismail & Idris., 1997; Duhon., 1998). With the presence of drilling fluid the drill bit is allowed to rotate and drill easier with less time minimising the power costs (Forrest., 1992). The use of drilling fluids has its challenges and consequences such as handling, pumping, operation and fluid loss.

2.2 Lost Circulation & Mud Rheological Properties

2.2.1 Lost Circulation

Lost circulation also known as Fluid loss is a phenomenon where part of the drilling fluid i.e. water for water based fluids permeates into the formation due to the greater hydrostatic pressure exerted on the formation by the drilling fluid and the contact between the drilling fluid and porous formation. Some drilling fluids are expensive making fluid loss an undesirable and costly phenomenon, coupled with the environmental consequences. Fluid loss may not only result in the need for more drilling fluid to replace the lost fluid but may prove to be detrimental to the whole process in a sense that it can result in stuck pipe, poor cementing job and formation damage (Ismail & Idris., 1997). In the oil & gas industry fluid loss is a challenge not only when drilling but also during the cementing, completion, fracturing and workover operations. Fluid loss has been proven in some cases to decrease production by 20-50% as stated by a paper presented at a Society of Petroleum Engineers (SPE) in Equador’s reservoirs (Del Rio et al., 2011). According to the American Petroleum Institute (API) standards a drilling fluid should have a fluid loss of 200ml/30min or less most preferably below 50ml/30min (Raines., 1986) and 18ml/30min (Quintero., 2006; Liu et al., 2012).

Fluid loss is measured using a filter press. Various models of filter presses are used with different abilities. The commonly used models are namely, the High Pressure High temperature (HPHT) filter press and the Series 300 Low Pressure Low Temperature (LPLT) filter press. Figure 2.2.1 shows the parts of standard API filter press equipment.

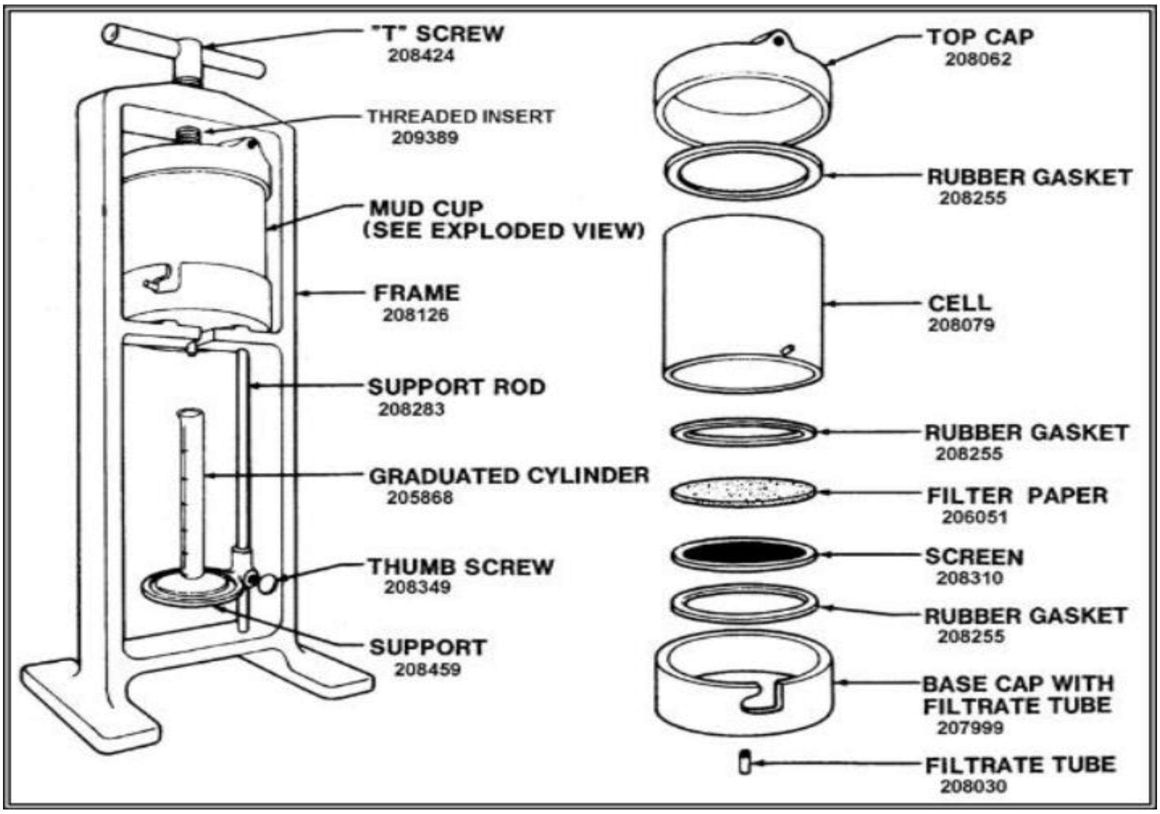

Figure 2.2.1: Standard API filter press equipment (Riverland., 2013).

Fluid loss or the filtrate is collected using a graduated cylinder with the volume measured at specific time intervals for 30min after which the test is completed.

Various cellulose based polymers have been extensively used in drilling fluids as viscosifiers and fluid loss control agents namely Carboxymethyl cellulose (CMC), Polyanionic cellulose (PAC) and Hydroxyethyl cellulose (HEC) (Melbouci & Sau., 2007). Figure 2.2.2 below depicts the ability of cellulose to absorb water.

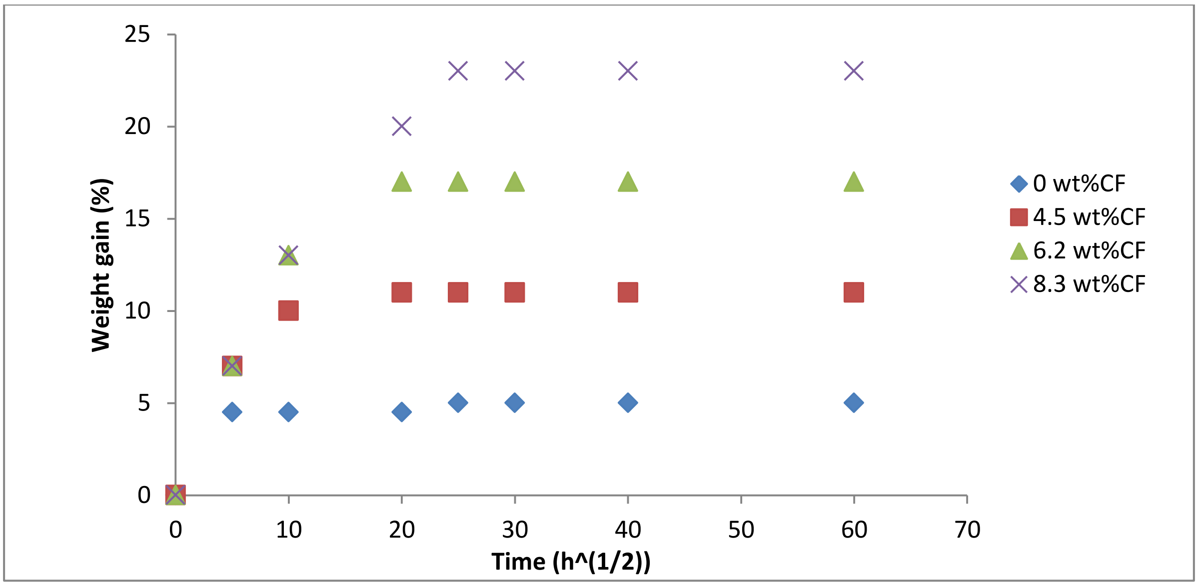

Figure 2.2.2: Water absorption behaviour of cotton fibre-reinforced Geopolymer composites at various cotton fibre (CF) concentrations (Alomayri et al., 2014).

Knowing cotton fibre contains more than 90% cellulose, figure 2.2.2 shows the ability of cellulose to absorb water as seen by an increase in weight gain with increase in cotton fibre content. It was proven by 13 cal/g heat of wetting and an adsorption & desorption test that cellulose has a high affinity for water (Hollenbeck et al., 2006).

2.2.2 Drilling Fluid Rheology

Mud rheology is an important concept when dealing with drilling fluids due to the impact and the role these properties play. Some of the most important mud rheological properties are apparent viscosity (AP), plastic viscosity (PV), gel strength and the yield point (YP). Viscosity is a property of fluid to resist motion, it is one of the important rheological properties of drilling fluids. In drilling fluids both plastic and apparent viscosities are important, while a yield point is the measure of stress to start fluid movement (Falode., 2008). According to the API standards, drilling fluids should have a viscosity of 15cP at least (Abdou et al., 2013). It is of vital importance to formulate a drilling fluid with stable viscosity characteristic to accommodate for changing temperature and pressure conditions. Below are the equations used to calculate the mentioned rheological properties using results obtained by using the standard API rotary viscometer (Ahmed-Haras., 2013).

$AV = \theta_{600}/2$ (cP) (2.1)

$PV = \theta_{600} - \theta_{300}$ (cP) (2.2)

$YP = 0.0511[\theta_{300} - PV]$ ($lb/100ft^2$) (2.3)

gel strength in drilling fluids is the measure of the strength of the gel a fluid forms after 10s, 10min and 30min of rest time after being sheared at high rates. The gel strength is the shear stress ($lb/100ft^2$) measured at 3rpm shear rate according to the API standard test method. A number of rotary viscometers are used to measure drilling fluid rheological properties but the standard API viscometer is most preferred and reliable, with the fann 35 viscometer being the most commonly used type of viscometer.

2.2.2.1 Non-Newtonian Fluids

Most drilling fluids are Non-Newtonian fluids mainly Pseudo-plastic or Bingham fluids. Figure 2.3 Below depicts a relationship of shear stress/shear rate for various types of fluids

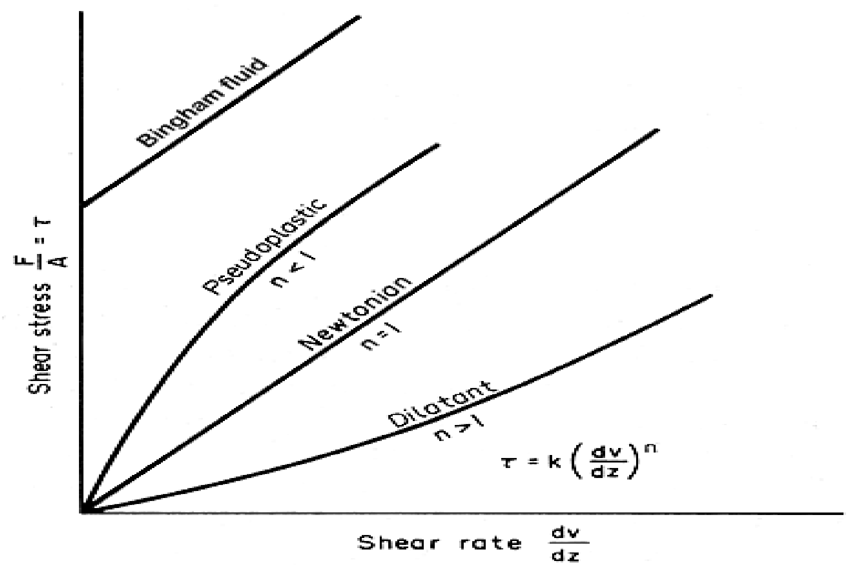

Figure 2.2.3: Shear stress/shear rate relationship in fluids (Earle & Earle., 1966).

Most Non-Newtonian fluids differ from Newtonian fluids through being dependent on shear rate/ shear history. Pseudo-plastic also known as shear thinning fluids are the most common type of drilling fluids which decrease in viscosity with increase in shear rate characteristic, meaning the fluid gets thin with shearing. Bingham fluids consist of a yield stress i.e. a minimum force required prior the fluid can be in motion, which can be depicted by the Bingham fluid curve's y-intercept, with plastic viscosity (PV) the slope of the Bingham line given as:

$$\tau = \frac{\Delta\tau}{\Delta\gamma}(\gamma) + \tau_\circ \quad (2.4)$$

Shear stress(τ), shear rate (γ) and yield stress ($\tau_\circ$).

2.3 Drilling Fluid Additives

A Drilling fluid is a chemical system made up of a number of chemicals that play a special role each, among them include weighting materials, viscosifiers, dispersants, fluid-loss control agents, shale stabilizers, lubricants, surfactants, emulsifiers and corrosion inhibitors. For this research focus is on fluid-loss control agents and viscosifiers that are made up of cellulose.

2.3.1 Bentonite

Bentonite is an inorganic drilling fluid additive, a clay rich in the mineral Montmorillonite which is the main component with varying quantities of quartz, sodium feldspar and calcium. There are two types of Bentonite i.e. Na-Bentonite which has swelling properties while Ca-Bentonite is non-swelling (Hassan & Abdel-Khalek., 1998). In most WBM the fluids are suspensions of Water-Bentonite which form a colloidal suspension that is dense fairly stable and of low viscosity. These properties make Na-Bentonite ideal for both WBM and OBM, since bentonite properties also help lift drill cuttings to the surface and show a thixotropic property ideal in case of temporary stop during drilling to prevent cuttings settling out of the mud. Due to its dense property, when Bentonite is added to drilling mud, it helps to stabilize the well and increase the well-cleaning properties (Dolz et al., 2006).

Bentonite mud can deposit a thin cake on the walls of the well which is beneficial in preventing fluid loss and preventing transport of formation fluids into the mud although this cake is often porous rendering it inefficient (Fordyce & Baer., 1950). Unfortunately, increasing the bentonite concentration in the mud leads to increase in friction during drilling (Dolz et al., 2006) whilst increasing clay solid content in mud will result in reduced penetration rate when drilling (Gatlin., 1960). Thus low concentration of Bentonite is ideal to avoid excessive torque and drag (Sharma & Manto., 2004), this means less Bentonite is required from an economical point of view. Not all bentonite clays qualify to be used as drilling fluid additive according to the API standards. The ideal Bentonite composition should constitute of the following concentrations

Table 2.1: API standard Bentonite composition (Rabah & Abdelrahman., 2012).

Compound	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	L.O.I
wt%	59.22	19.18	0.13	5.69	2.49	2.34	1.89	0.62	0.13	0.01	7.55

2.3.2 Cellulose Based Drilling Fluid Additives

2.3.2.1 Carboxymethyl Cellulose (CMC)

CMC is a derivative of cellulose formed by reaction with an alkali and chloroacetic acid. In Na-Bentonite and CMC muds CMC increases mud viscosity and reduces fluid loss. CMC is a good additive in a manner that desired mud properties can be achieved at low Bentonite concentration thus avoiding the impact high Bentonite concentrations have on the process whilst using less Bentonite and reducing cost. It is important to note that adding CMC into the mud helps maintain flow characteristics at HTHP and high salinity conditions (Abu-jdayil & Ghannam., 2014). Since Bentonite is not efficient enough to lower fluid loss due to the pores in the thin cake it forms. Starch and CMC have been employed in most cases to remedy the drilling mud to reduce/limit the transfer of fluids through these pores thus lowering the cake’s permeability. Unfortunately the use of starch is subject to bacterial attacks from the mud storage tanks, even though CMC is no subject to bacterial attack when added in amounts required for it to be effective it negatively impacts on the mud viscosity by increasing its viscosity. Increasing the mud viscosity is an undesirable characteristic which poses a strain on the pumping equipment proving to be costly or worse by blocking the drill bit. Although thinning additives can be applied but eventually the drilling cost increases (Fordyce & Baer., 1950).

A study done on the use of Lignin Graft Copolymer (LGC) as an additive to a WBM which showed how the CMC mud performed after being exposed to 200ºC for sixteen hours (Ahmed-Haras., 2013). Results show reduced stability of CMC muds at high temperatures.

Table 2.2: CMC mud rheological properties and pH prior and after stability test at 200ºC (Ahmed-Haras., 2013)

CMC composition	μ_a		μ_p		τ_y		Θ(lb/100ft^2)		pH	
	before	after	before	after	before	after	before	after	before	after
5% w/w	97.5	25	19	18	129.1	14.93	200.54	29.24	11.62	9.3

2.3.2.2 Polyanionic Cellulose (PAC)

PAC is also used as a viscosity modifier and a fluid loss additive for WBM, it can be found in two forms i.e. as a high viscosity grade or a low viscosity grade (Paul et al., 2000). Unfortunately the PAC is stable up to 149ºC after which it degrades (Plank., 1992). like CMC, PAC is not subject to bacterial degradation (Elward-berry & Darby., 1997). PAC also comes in a form of PAC-R and PAC-L with PAC-R used as a control for fluid loss and PAC-L used as a mud rheological properties modifier. (Olatunde et al., 2011). A mud stability test was conducted by subjecting the PAC-Bentonite WBM to 120ºF hot-rolling oven for sixteen hours below is the result. From table 2.3 below it can be observed that the cellulose-based (PAC, Bentonite WBM) has good stability characteristics at temperatures around 120 ºF from 0-300rpm followed by a slight difference from 300-600rpm as, compared to non cellulose-based (Gum arabic, Bentonite WBM) as depicted in table 2.2. Mud stability test comparison results after 120ºF aging temperature.

Table 2.3: Comparison of rheological properties of cellulose based (PAC-Bentonite WBM) prior and after hot rolling (Olatunde et al., 2011). BHR, AHR stands for before and after hot rolling respectively.

viscosity(cP)\ \ speed (rpm)	0	100	200	300	600
Cellulose based (PAC) BHR	3	17	26	34	65
Cellulose based (PAC) AHR	4	18	26	34	52
Non cellulose based (Gum Arabic) BHR	5	10	13	16	22
Non cellulose based (Gum Arabic) AHR	7	35	48	57	82

2.3.2.3 Hydroxyethyl Cellulose (HEC)

HEC is one of the cellulose based drilling fluid additives employed as a viscosifier. Unlike other cellulose based drilling fluid additives HEC is versatile in a sense that it is also employed during completion and work over operations. An HEC of molar substitution (M.S.) 1.1-1.6 was tested on water based drilling fluids and showed desirable fluid loss characteristics compared to HEC with M.S. of 2 or more. Previous studies have shown that the use of HEC as a drilling fluid has advantages such as increased penetration rate, longer drill bit span, and increased production rate when used as a work over fluid in Ecuador's reservoirs (Robles., 2011). One of the primary drilling fluid roles is to transport drill cuttings to the surface which requires a fluid with additives that promote good gel strength characteristics (Westland., 1994). HEC has poor gel strength characteristics which can explain the reluctance in the use of HEC in drilling fluids as compared to completion and work over fluids.

2.4 Nano Particles in Drilling Fluids

2.4.1 Nano Mud

Nano muds are drilling fluids which compose of nano materials such as carbon nanotubes, nanocrystals etc. These materials can be dispersed in liquid phase and added to drilling fluids in less volumes compared to the corresponding additives of larger sizes. Nano muds meet the desired mud properties i.e. rheological and fluid loss control properties even at HTHP conditions (Quintero et al., 2012). A study on the Bentonite WBM was conducted using normal Bentonite and synthesized nano Bentonite WBM, it was found that the normal Bentonite WBM was negatively affected by high temperatures whilst the nano Bentonite synthesized WBM retained all the desired rheological properties at elevated temperatures (Nasser et al., 2013). Table 2.4 shows the comparison in fluid loss between normal drilling mud and nano-mud. From the table it can be argued that the introduction of nano material in drilling fluids has a positive impact on fluid loss control.

Table 2.4: Fluid loss comparison for a nano mud and a normal mud (Nasser et al., 2013).

	Filtrate loss (ml)				
Time (min)	1	7	20	40	60
Normal Mud	3	45	7	10	22.5
Nano Mud	2	3.6	5.2	7.5	10.5

2.4.2 Cellulose Nanocrystals (CNCs)

2.4.2.1 CNCs in Drilling Fluids

Nanocrystalline cellulose/ cellulose nanocrystals are basically cellulose crystals of nano scale size. Cellulose is the most abundant natural polymer that is renewable, non-toxic and biodegradable (Peng et al., 2011; Chauhan et al., 2013). There are a number of ways to produce CNCs mainly the acid hydrolysis of wood to pulp and the cellulose is then removed from the pulp through a number of processes to form CNCs. Currently CNCs are used limitedly in industry due to the low thermal stability (Samir et al., 2005). Limited work has been done on the use of CNCs as an additive in drilling mud, one of the projects conducted and still in progress is that of Dr. Yaman Boluk University of Alberta where ‘the lab results show a CNC-based drilling fluid with superior fluid loss and filtration characteristics' (Boluk., 2012).

CNC dispersions have a high viscosity at low CNC concentrations (Pääkkö et al., 2007; Tatsumi et al., 2002) with shear thinning behavior as observed on dilute polymer solutions (Ryder & Yeomans., 2006). Most drilling fluids with polymer based additives have shear thinning characteristics, a desirable property in drilling fluids since it promotes increased penetration rate thus reduced rig time (Caenn et al., 2011).

2.4.2.2 CNCs Synthesis

Cellulose is also the most abundant polymer on earth found in wood pulp, cotton fibre, sugar beet pulp, bacteria and tunicin (Saito et al., 2006; Haigler et al., 2009; Habibi et al., 2009). CNCs can be produced from various methods such as acid hydrolysis and TEMPO-mediated oxidation. The acid hydrolysis method makes use of acids such as H_2SO_4, HCl, HBr and H_3PO_4 with H_2SO_4 and HCl the most employed methods. The TEMPO mediated oxidation method is said to be green and simple to apply. The physical, mechanical and thermal properties of CNCs depend on the production method and the acid used. H_2SO_4 hydrolyzed CNCs show poor thermal stability characteristic compared to HCl. HCl hydrolyzed CNCs tend to flocculate in water while H_2SO_4 hydrolyzed CNCs show good dispersion properties in water , which can be explained by the formation of sulfate esters on the surface hydroxyl groups of cellulose (Habibi et al., 2009). Different types of CNCs can be formed e.g. network, spherical and rod shaped. Figure 2.4 shows TEM images of different CNCs.

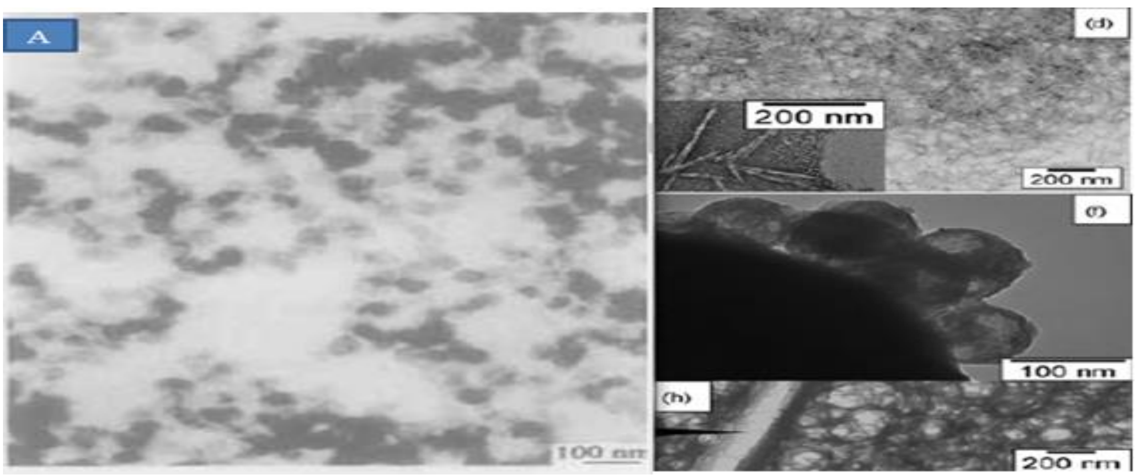

Figure 2.4 TEM images of CNCs in the forms of (A and f) spherical, (d) rod shaped and (h) network (Lu & Hsieh., 2010; Li et al., 2001).

3 CHAPTER 3: MATERIALS AND METHOD

3.1 Materials

A 3.2% microfibrillated cellulose (MFC) suspension obtained from Sappi was used as the source of cellulose, 13-15% NaClO solution (Rochelle Chemicals), 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) & Na-Bentonite (Sigma Aldrich S.A.), Nitrogen gas (AFROX), NaBr (Rochelle Chemicals), NaOH pellets together with 32% HCl were obtained from (Merck). All chemical were not diluted nor concentrated except for NaOH and HCl of which were converted to 0.5M solutions.

The Bentonite used for this research had the following composition (wt%): 66.008 SiO_2; 22.905 AI_2O_3; 0.421 Fe_2O_3; 3.388 FeO; 0.01 MnO; 2.746 MgO; 1.393 CaO; 2.506 Na_2O; 0.401 K_2O; 0.160 TiO_2; 0.06 P_2O_5; L.O.I 0.24.

3.2 Experimental Procedure

3.2.1 Synthesis of CNCs

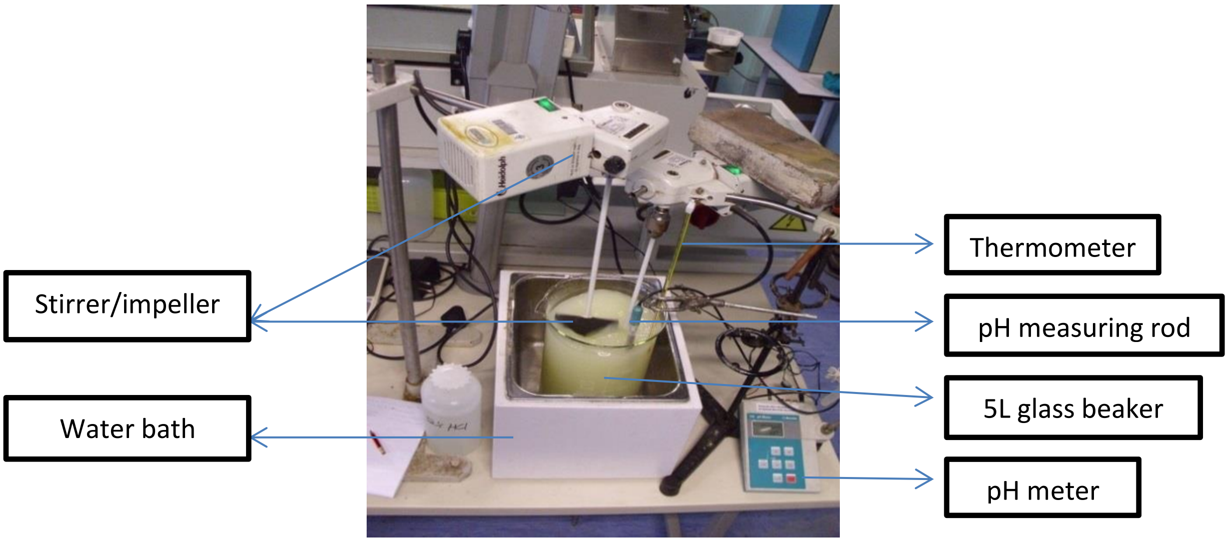

Figure 3.1: Laboratory setup of the CNCs synthesis

Procedure:

CNCs were synthesized using the setup in figure 3.1, by the TEMPO-mediated Oxidation method, 750ml of 3.2% microfibrillated cellulose (24g solids) slurry was further diluted in

3877.5ml of distilled water containing 0.369g TEMPO and 3.69g NaBr. Both the slurry and distilled water were pre stored at 9°C, the reaction was initiated by adding 172.5ml of 13-15% NaClO solution. The reaction was allowed to run for 6hrs under agitation at controlled temperature (10°C) using ice bath varying between 9°C and 11°C and pH 10. After 6hrs the reaction was halted and the contents were filtered, washed and suspended in 1000ml of distilled water prior being sonicated using an ultrasonicator (USM20) for 15min and stored at 9°C in a tightly sealed container. It is important to note that measures to avoid contamination were taken by sealing the Buchner funnel with parafilm during the filtering process and carefully transferred the CNC cake into the storage containers with clean equipment.

3.2.1 Mud sample preparation

Mud samples were prepared using distilled water as the base fluid, the required amount of CNCs was added to water and stirred using a magnetic stirrer. Bentonite was slowly added to the suspension under agitation and allowed to mix until homogeneity was achieved. 6 wt% Bentonite samples were prepared with varying CNCs concentration i.e. 0, 0.1, 0.3, 0.5 and 0.8 wt% CNCs. The prepared samples were then allowed to stand for 16hrs or longer at ambient conditions prior to any testing.

3.3 Analysis

3.3.1 CNCs characterization

An FEI Tecnai T12 TEM was used to characterize the CNC samples, drops of dilute CNC suspension were deposited on to a carbon coated copper grid and allowed to dry. The specimen was then analysed under the microscope at different magnifications.

3.3.2 Mud Rheology test

A Rheolab QC viscometer figure 3.2, from Anton Paar was used to perform the rheology tests, using a CC39 measuring bob with all tests done at 120°F (48.88°C). Prior testing the mud samples would be agitated for 10seconds in case the fluid is time dependent since

Bentonite has some time dependent properties (Balhoff et al., 2011). The mud is then poured into the measuring cup and fitted on to the viscometer.

Figure 3.2: RheolabQC viscometer from Anton Paar (South Africa).

3.3.3 Fluid loss test

Mud samples were prepared in the same manner as mentioned in Section 3.2.1, with 500g samples of 6 wt% Bentonite and varying CNCs concentration i.e. 0, 0.1, 0.3, 0.5 and 0.8wt% CNCs. The fluids were prepared and allowed to stand for 15min. using Nitrogen gas the sample was poured into the pressure cell then subjected to 100 psi (690kPa) pressure using a filter press for 30 minutes, the filtrate volume was collected using a graduated cylinder and the volume recorded after 30 minutes. Figure 3.3 shows the equipment setup for fluid loss measurements.

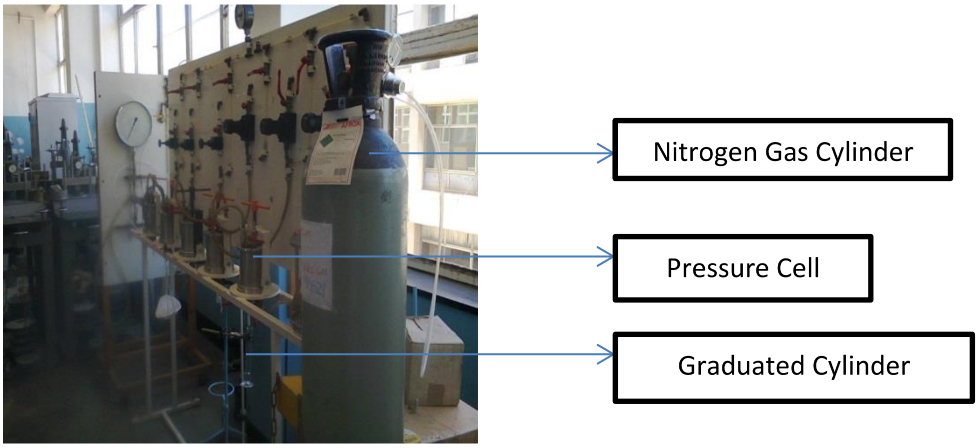

Figure 3.3: Laboratory setup of the fluid loss test equipment showing the filter press, Nitrogen gas cylinder and the graduated cylinder collecting the filtrate

4 CHAPTER 4: RESULTS AND DISCUSSION

4.1 Synthesised CNCs

The common TEMPO-mediated oxidation methodology to produce CNCs was followed but scaled up so to produce large amounts of the suspension for the subsequent stages of the experiment. The aim was to produce cellulose crystals of nanoscale size i.e. CNCs. Figure (4.1) shows the TEM results obtained.

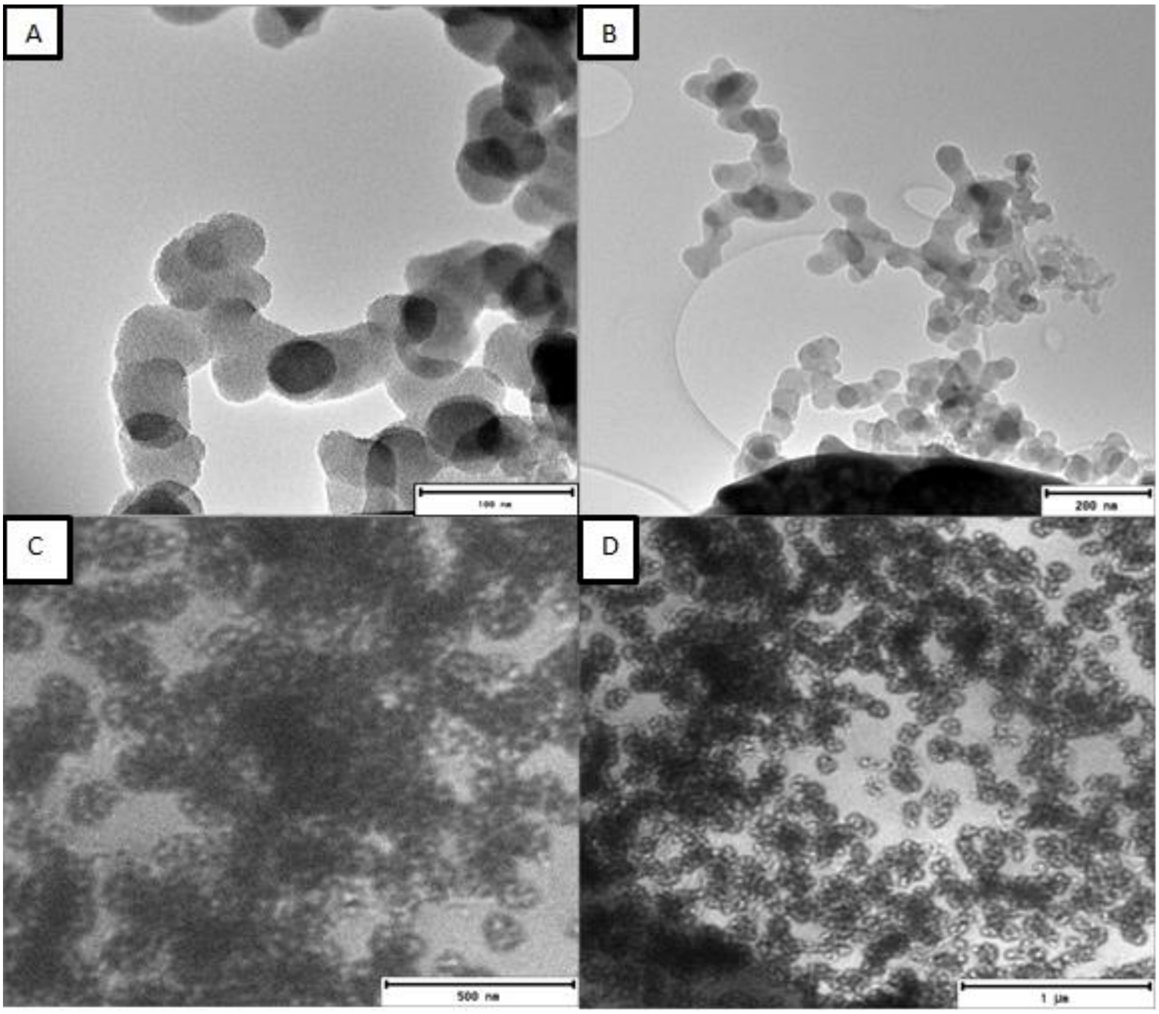

Figure 4.1: TEM images of CNCs under different magnifications with (A) under the highest magnification followed by (B),(C) then (D), respectively.

Images A and B show the cellulose polymer chains with particles size below 100nm. This behaviour can be explained by the fact that cellulose is a polymer thus the chains observed.

Images C and D show spherical particles CNCs of size below 200nm. From the images C and D, spherical cellulose crystals of nanoscale can be observed. As mentioned in the literature (Lu & Hsieh., 2010; Li et al., 2001), CNCs of spherical shape where successfully produced.

4.2 Fluid loss

Na-Bentonite from Sigma Aldrich was used to produce the Mud samples. A sample of Bentonite was analysed with XRF and the following composition (wt%) was obtained:

Composition (wt%): 66.008 SiO_2; 22.905 AI_2O_3; 0.421 Fe_2O_3; 3.388 FeO; 0.01 MnO; 2.746 MgO; 1.393 CaO; 2.506 Na_2O; 0.401 K_2O; 0.160 TiO_2; 0.06 P_2O_5 and; L.O.I 0.24wt%, which compare fairly with the results presented in Table 2.1.

Mud samples with 6wt% Bentonite and varying CNC concentrations were prepared and subjected to 100 psi pressure for 30 minutes at room temperature in a filter press. The aim was to collect & record the amount of filtrate lost after 30min and compared the performance of each formulation. Figure 4.2 depicts the relationship between fluid loss and the concentration of CNCs with fair standard deviation of 0.37, 0.91, 0.74, 0.17 and 0.62 for a 0, 0.1, 0.3, 0.5 and 0.8wt% CNC mud samples respectively.

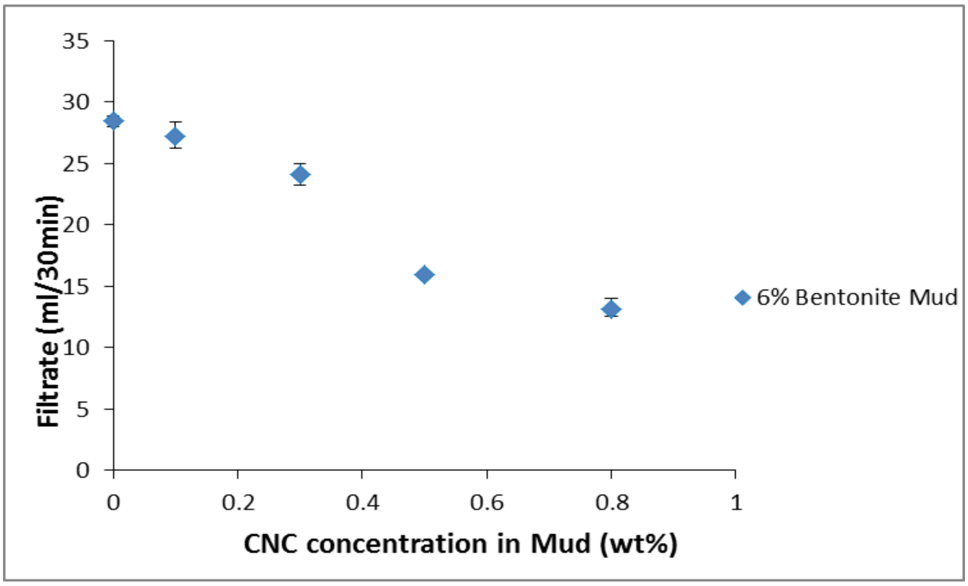

Figure 4.2: Mud fluid loss for varying Cellulose Nanocrystals (CNC) concentrations

Based on the results on Figure 4.2 fluid loss was reduced with the inclusion of CNCs to the fluid. 0.1 wt% CNCs gives a very low fluid loss control compared to 0.3, 0.5 and 0.8 wt% CNCs when compared to fluid loss for a 0wt% CNCs mud. Moving from 0.5 to 0.8wt% CNCs the difference in fluid loss was reduced compared to the difference between 0.3, and 0.5 wt% CNCs.

As seen from Figure 4.2 fluid loss was reduced with increasing CNC concentration, but further increase of CNCs may end up not giving a significant improvement in fluid loss control as seen by the difference in fluid loss between 0.5 and 0.8wt% CNCs. Thus an optimal amount of CNCs should be used to obtain significant fluid loss control to minimise cost.

The reduction of fluid loss with increasing concentration of CNCs can be explained by the cellulose's high affinity to water and its ability to absorb and hold water (Hollenbeck et al., 2006). With the cellulose size reduced to nano-scale all the CNCs have an increased surface area to volume ratio increasing the contact area between cellulose and water thus improving its fluid loss control ability.

4.3 Mud Rheology

The aim for this section was to investigate the impact of CNCs on the Mud viscosity, Shear Stress, gel strength and how the Mud will behave when sheared. Under constant shear at 600rpm, 120°F the Mud effective viscosity were measured as presented in Figure 4.3. The results show good reproducibility with a percentage deviation of zero after six minutes. It is important to mention that all rheological tests were measured at 120°F unless stated otherwise.

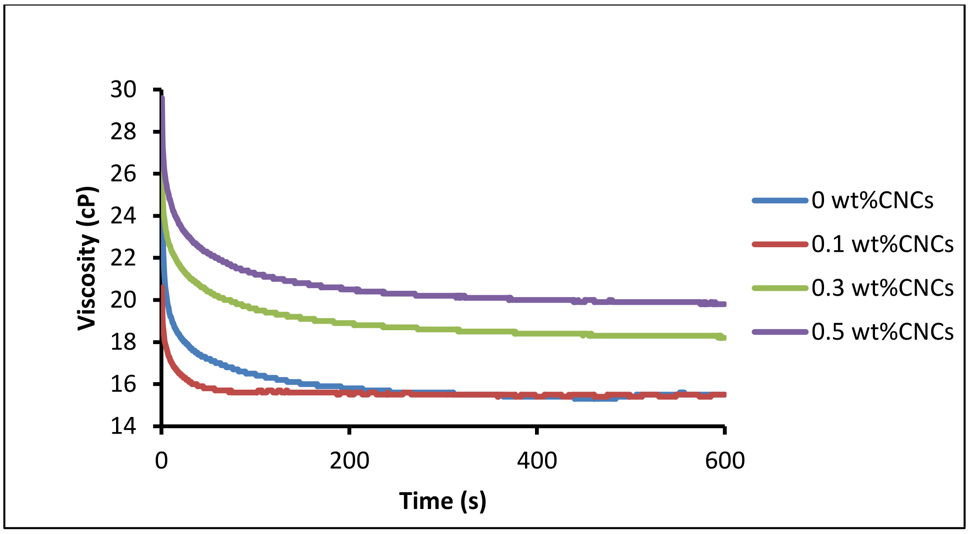

Figure 4.3: Mud effective viscosity at 600rpm, 120°F for fluids with 6wt% Bentonite at varying CNC concentrations**.**

From Figure 4.3 it can be observed that under constant shear rate the fluids slowly decrease in viscosity approaching steady state with the 0.1 wt% CNCs Mud approaching steady state faster than the other formulations. From the figure one can tell that the steady state viscosity for a pure Bentonite mud and that of 0.1wt% CNCs are very similar if not equal. This could suggest the amount of CNCs to be added in order to observe a significant impact of CNCs on the Mud viscosity as observed to be increasing with increasing the CNCs concentration. As discussed earlier in literature CNC dispersions effect high viscosity at low CNC concentration (Pääkkö et al., 2007; Tatsumi et al., 2002). This could explain the increase in Mud viscosity with the introduction of CNCs. Based on these results, CNCs can be used as a viscosifier for drilling fluids but at concentrations above 0.1wt% CNCs.

4.3.1 Mud Shear Stress

Mud shear stress data was measured against shear rate, a similar trend as that of the use of Carboxymethyl cellulose (CMC) as an additive to a Water-Bentonite Suspension (Abu-jdayil et al., 2014; Iscan & Kok., 2007) was observed. Figure 4.4 shows the relationship between the Mud shear stress and the CNC concentrations. Results in figure 4.4 can be reproduced, explained by the 0% deviation at high shear rate as seen at $250s^{-1}$ from Table A2 appendix A with % deviation reduced with increasing shear rate.

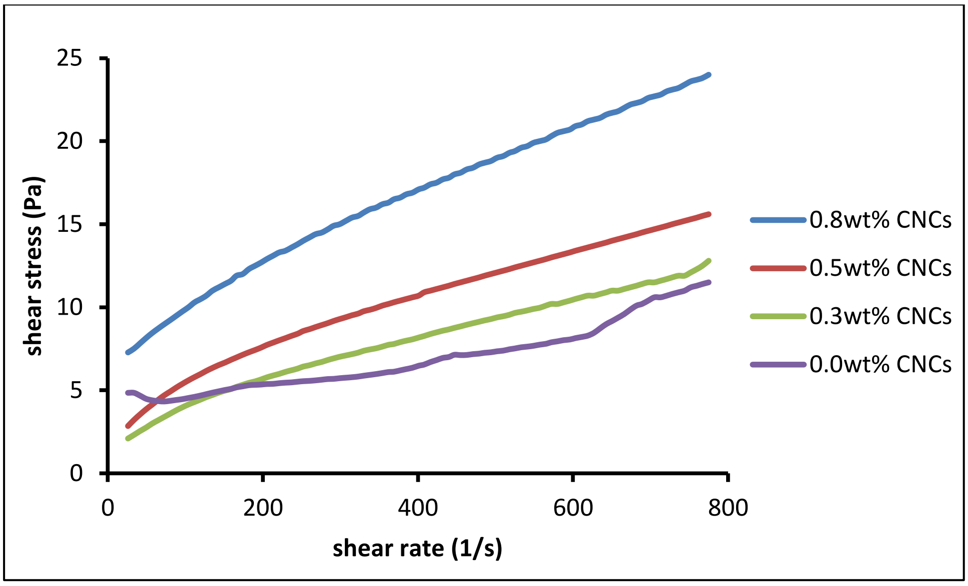

Figure 4.4: Flow curves of a 6 wt% Bentonite suspension with varying CNCs concentration.

Based on the results obtained, the CNC-Bentonite Mud /suspension shear stress substantially increases with increasing CNC concentration from 0.5 to 0.8wt% CNCs. At high shear rate Water-Bentonite suspensions have a low shear stress compared to CNC containing formulations. All the CNCs based formulations show a shear thinning behaviour different from the Water-Bentonite suspension. The 0wt% CNC mud has a pH 9.63 within the pH range of 9.5 to 10.5 known to have Bentonite particles with negative charges (Benyounes et al., 2010), thus the attraction between two particles becomes low with increase in pH (Durán et al. 2000). Due to the interaction between the polymer and the Bentonite particles thus the adsorption of the polymer on the surface of the particles (Abu-jdayil et al., 2014), may explain the change in rheology of the suspension seen with the 0wt% CNC curve not smooth as compared to CNC containing formulations. Figure 4.5 supports the shear thinning behaviour of CNCs-Bentonite suspension with a decrease in viscosity under shearing conditions. From Figure 4.5, the shear thinning degree increases with increase in CNC concentrations for CNC containing mud measured by looking at the initial viscosity relative to the steady state viscosity.

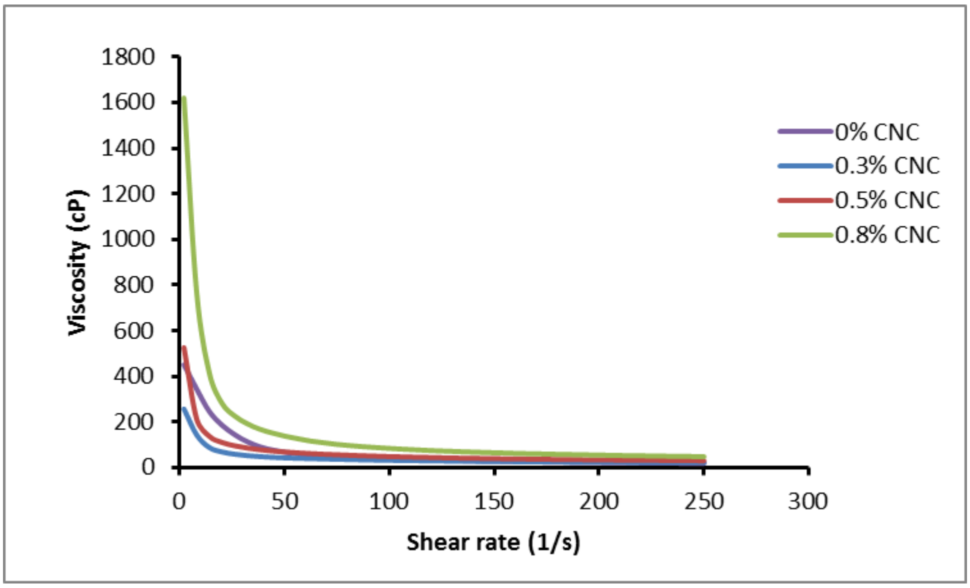

Figure 4.5: CNC- 6wt%Bentonite suspensions shear thinning characteristics

Results in figure 4.5 have a good reproducibility, with low % deviation of 0.54 for 0.5% CNC and 0 %deviation for the other formulations at $250s^{-1}$. From figure 4.5 it can be seen that at low shear rate i.e. below 100 s^{-1} the 0.3 and 0.5% CNC mud have a low viscosity compared to the 0% CNC mud but gradually become greater with increasing shear rate, approaching a similar trend to that of figure 4.3 which shows how mud viscosity is affected by the CNCs.

4.3.2 Gel Strength

Gel strength in drilling fluids is an important rheological property through the role it plays when there is no circulation. In most cases the 10s and 10min gels are measured by measuring the mud shear stress at 3rpm after the fluid has been allowed to stand for 10s after being exposed to high shear rates and further tested after 10 minutes at rest. Some methods continue to evaluate the 30 minute gel, this is done to measure the extent at which the fluid can form a gel. Figure 4.6 presents the 10s and 10min gels of CNC-Bentonite suspensions, obtained with fairly low standard deviations of (0.03; 0.11) , (0.05; 0.27) and (0.08; 1.39) for 0.3, 0.5 and 0.8wt%CNC at the 10s and 10min gel strength data respectively.

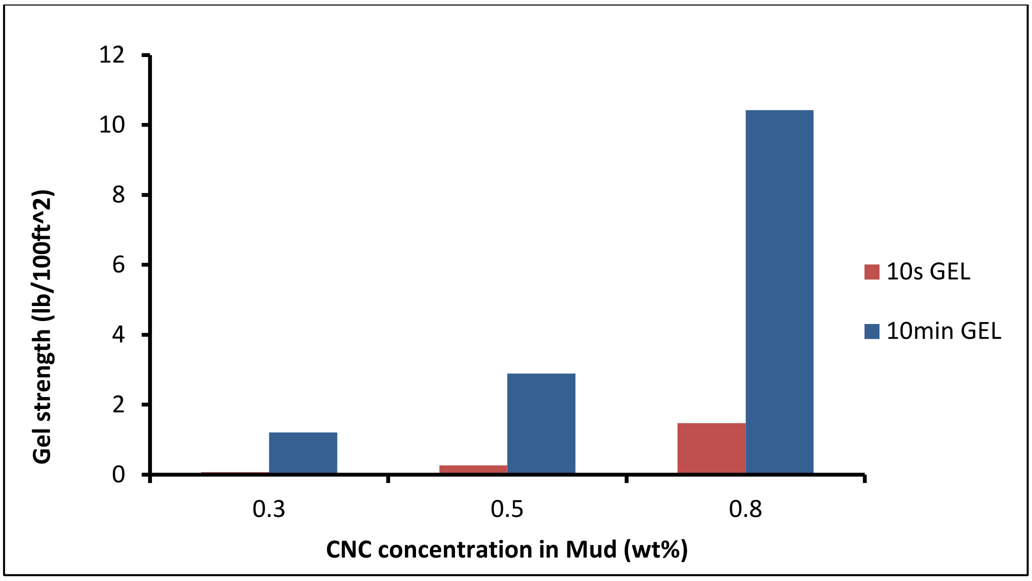

Figure 4.6: 10s and 10min gels for a 6wt% Bentonite suspension with varying CNC concentrations i.e. 0.3, 0.5 and 0.8wt%.

An increase in gel strength with increase in CNC concentrations is observed for both 10s and 10min gels. Since the ability of drilling fluids to form a gel at rest is desirable to suspend cuttings (crushed rocks) and avoid settling out of cuttings to the bottom of the well, which may result in the drill bit being stuck, the synthesised mud-CNC suspensions would have a very promising industrial application. A too strong gel is not desirable since it will result in reduced penetration rate, but for a fluid with shear thinning characteristics a strong gel is not an issue since it will quickly break as the fluid gets thinner due to shearing resulting in increased penetration rate (Caenn et al., 2011). It is important to note that although the shear rate was kept constant at $3.87s^{-1}$ there's a fluctuation in orders of magnitude see Table A.4 which can be explained by the low torque (outside the Rheolab QC operating range of 0.25-75mNm) which can be caused by low shear rate and mud viscosity.

Figure 4.7 below shows the effect of temperature on the Water-Bentonite suspension with and without CNCs at atmospheric pressure from 0°C to 98°C

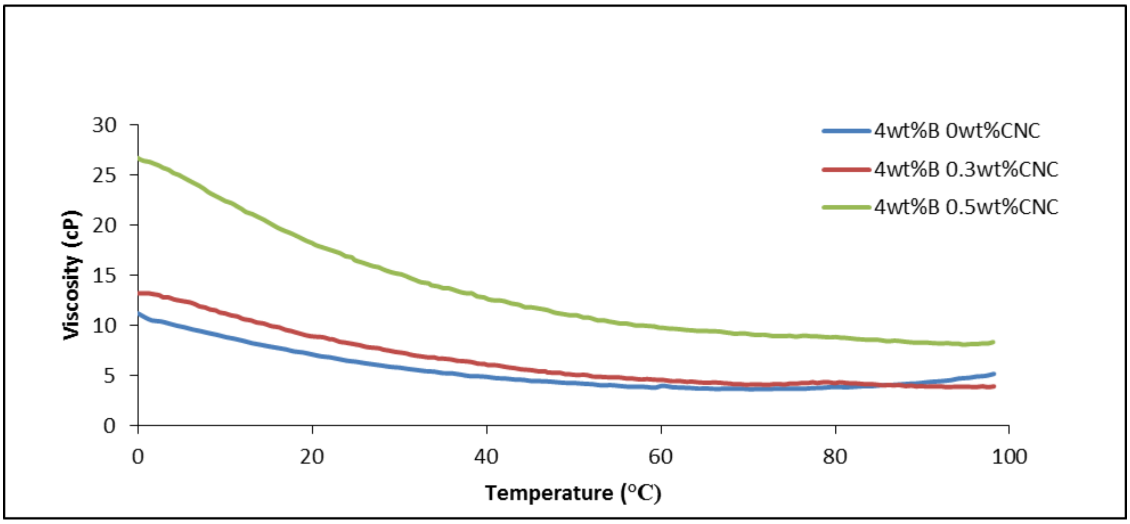

Figure 4.7: Effect of temperature on Water-Bentonite suspension with varying CNC concentration at atmospheric pressure.

From figure 4.7, it can be seen that the mud viscosity decreases with increasing temperature. Since the test were conducted at atmospheric pressure, as 100°C is approached instability results with viscosity fluctuating frequently due to water reaching its boiling point as seen with the 0wt% CNC mud viscosity increasing from 80°C and above. Based on the results, at low temperatures the CNC concentration has more effect on the mud viscosity as opposed to higher temperatures.

Compared to CNCs some additives such as Fly Ash and Xanthan are either good in terms of lowering fluid loss but with no effect on mud gel strength or vice versa (Mahto et al., 2013 ; Mahto & Jain., 2013) this gives CNCs an edge when looking to reduce cost and use less additives. Taking into account the discussed limits of alternative additives in chapter two, CNCs have the potential to be a good drilling fluid additive that can compete in the market.

5 CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The CNC-Bentonite suspensions show good gel strength and shear thinning characteristics, a relationship that may result in reduced rig time with increased penetration rate and the ability to suspend cutting during sudden stop in circulation.

The addition of CNCs into a Water-Bentonite suspension showed good fluid loss control at 0.3, 0.5 and 0.8wt% CNCs, with decreasing fluid loss with increasing CNC concentration. Although there are signs of a decrease in the impact adding CNCs will have on fluid loss above 0.5wt% CNCs

Flow curves show that adding CNCs at concentrations above 0.1wt%, CNCs have significant impact on the fluid's rheology and viscosity. CNCs tend to increase the fluid's viscosity with increasing CNC concentration.

In conclusion CNCs can be used in drilling fluids as an additive for various applications namely fluid loss control, viscosifier and gel strengthening. CNCs can further be added to reduce the amount of Bentonite normally used to limit the negative effects that come with higher Bentonite concentration.

5.2 Recommendations

The following are recommended for further studies

- For future work it would be beneficial to compare the performance of CNCs produced by acid (H_2SO_4) hydrolysis to those produced through TEMPO oxidation especially under high temperature conditions to investigate which method will produce CNCs with more desirable characteristics.
- A further study on the effect of temperature on the formulated mud fluid loss will help assess the performance of CNCs at high pressure and temperature conditions.

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NOMENCLATURE

Abbreviation's

OBM	Oil Based Mud
WBM	Water Based Mud
SBM	Syntheic Based Mud
MFC	Microfibrillated Cellulose
NCC/ CNCs	Nanocrystalline cellulose/ cellulose nanocrystals
CMC	Carboxymethyl Cellulose
PAC	Polyanionic Cellulose
HEC	Hydroxyethyl Cellulose
PV	Plastic Viscosity
AV	Apparent Viscosity
YP	Yield Point
HTHP	High Temperature High Pressure
LTLP	Low Temperature Low Pressure
LGC	Lignin Graft Copolymer
API	American Petroleum Institute
HCL	Hydrochloric Acid
H_2SO_4	Sulfuric Acid
NaBr	Sodium Bromide
TEMPO	2,2,6,6-Tetramethylpiperidin-1-oxyl
NaCIO	Sodium perchloride
HBr	Hydrobromic Acid
H3PO4	Phosphoric Acid
L.O.I	Lost on ignition (mass of moisture and volatile material)

Symbols

Ca	Calcium
Na	Sodium
μ_a	Apparent viscosity
μ_p	Plastic viscosity
$\boldsymbol{T}_y$	Yield stress
Θ (lb/100ft^2)	Gel strength in pounds/ square feet
ºF	Temperature unit measure Degree Fahrenheit
℃	Temperature unit measure Degree Celsius
γ	Shear rate
τ	Shear Stress
$\tau_{\circ}$	Yield Stress
σ	Standard deviation
Σ	Summation (sum or total)
X_m	Mean

APPENDICES

A. Rheology data

Chapter 4 Results, raw data and a summary of the calculations are presented in section A of the appendices.

Table A1 shows the effect CNCs has on the formulations viscosity i.e. the raw data for Figure 4.3 obtained using a RheolabQC at 120ºF.

Table A1: raw data showing the sample composition and rheology data at 120ºF obtained at 600rpm shear rate.

Sample	A(0%) CNCs	A2(0%) CNCs	B(0.1%) CNCs	B2(0.1%) CNCs	C(0.3%) CNCs	C2(0.3%) CNCs	D(0.5%) CNCs	D2(0.5%) CNCs
Bentonite(g)	6	6	6	6	6	6	6	6
CNCs (g)	0	0	0.1	0.1	0.3	0.3	0.5	0.5
Water (g)	94	94	93.9	93.9	93.7	93.7	93.5	93.5
Time (s)	Viscosity (cP)							
0.603	28.8	28.8	19.9	20.6	23.3	26.9	29.6	29.6
1.2	24	24	18.4	19.2	21.7	25.1	27.7	27.7
1.8	22.6	22.6	17.8	18.7	21.2	24.5	27	27
2.4	21.9	21.9	17.5	18.5	20.9	24.1	26.6	26.6
3	21.3	21.3	17.3	18.2	20.7	23.9	26.2	26.2
6	20	20	16.7	17.6	20.3	23	25.3	25.3
9	19.3	19.3	16.5	17.2	20	22.6	24.8	24.8
12	18.9	18.9	16.3	16.9	19.9	22.2	24.3	24.3
15	18.6	18.6	16.2	16.7	19.8	22	24	24
30	17.8	17.8	15.8	16.1	19.4	21.1	23	23
45	17.3	17.3	15.6	15.8	19.2	20.6	22.3	22.3
60	17	17	15.5	15.7	19	20.2	22	22
75	16.8	16.8	15.4	15.6	18.9	19.9	21.6	21.6
90	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
100	16.5	16.5	15.3	15.6	18.8	19.6	21.2	21.2
120	16.3	16.3	15.5	15.6	18.7	19.4	21	21
130	16.2	16.2	15.5	15.6	18.7	19.3	21	21
140	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
150	16	16	15.6	15.6	18.6	19.1	20.8	20.8
175	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
200	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
250	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
275	15.6	15.6	15.5	15.5	18.5	18.6	20.2	20.2
300	15.6	15.6	15.6	15.5	18.5	18.6	20.2	20.2
310	15.6	15.6	15.5	15.5	18.5	18.6	20.2	20.2

320	15.5	15.5	15.5	15.5	18.4	18.5	20.2	20.2
330	15.5	15.5	15.5	15.5	18.4	18.5	20.1	20.1
340	15.5	15.5	15.5	15.5	18.4	18.5	20.1	20.1
350	15.5	15.5	15.5	15.5	18.4	18.5	20.1	20.1
355	15.5	15.5	15.5	15.5	18.4	18.5	20.1	20.1
360	15.5	15.5	15.5	15.5	18.4	18.5	20.1	20.1
average	15.5	15.5	15.5	15.5	18.45	18.45	20.1	20.1
% Deviation	0	0	0	0	0	0	0	0

NB. The average and % Deviations were calculated after 6minutes i.e. viscosity values at 360s, assuming the average is approximately the true value.

Figure A1 and Table A2 respectively below show the diagram and data for Figure 4.4 obtained using a Rheolab QC at 120ºF for 6wt% Bentonite samples at various CNC concentrations. Figure A1 shows the effect adding CNC has on the fluids shear stress.

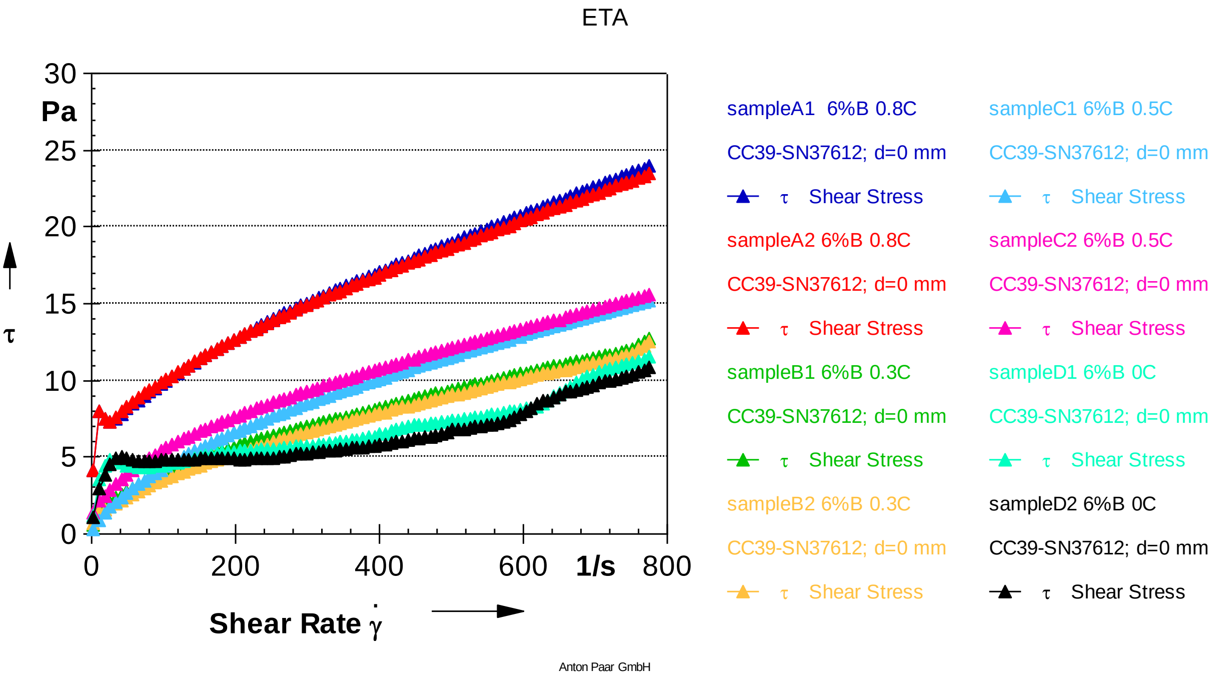

Figure A1: Relationship between shear stress and shear rate at 120ºF for 6wt% Bentonite samples at various CNC concentrations i.e. 0, 0.3, 0.5, and 0.8wt% CNC.

Table A2: Shear stress data for 6wt% Bentonite formulations at various CNC concentrations i.e. 0, 0.3, 0.5, 0.8wt% CNC with % deviations below.

Sample	A	A1	B	B1	C	C1	D	D1
	0.0 wt%CNCs		0.3 wt%CNCs		0.5 wt%CNCs		0.8 wt%CNCs	
Bentonite (g)	6	6	6	6	6	6	6	6
CNCs (g)	0	0	0.3	0.3	0.5	0.5	0.8	0.8

Water (g)	94	94	93.7	93.7	93.5	93.5	93.2	93.2
Shear rt(1/s)	Viscosity (cP)							
2	451	445	248	257	526	526	1620	1600
8.05	344	347	177	143	213	213	768	770
14.1	246	246	106	88	137	137	415	411
20.1	186	186.6	80.7	68.2	110	110	282	280
26.2	144	144.2	68.7	58.5	95.4	95.4	226	222
32.2	113	113.1	61.2	52.2	85.4	85.4	192	188
38.2	90.8	90.8	55.8	47.9	78.2	78.2	168	165
44.3	76.8	76.8	52.4	44.7	72.4	72.4	151	148
50.3	66.9	66.9	49.2	42.4	68.2	68.2	137	134
56.4	59.5	59.5	46.7	40.6	64.5	64.5	126	123
62.4	54.2	54.1	44.6	39	61.2	61.2	116	114
68.4	49.9	49.9	42.9	37.7	58.5	58.5	109	107
74.5	46.4	46.4	41.4	36.4	56	56	102	101
80.5	43.7	43.6	39.9	35.1	53.8	53.8	96.8	96.2
86.6	41.2	41.2	38.5	34	51.9	51.9	92.2	91.7
92.6	39.2	39.2	37.2	32.9	50	50	88.1	87.8
98.6	37.5	37.5	36	32.1	48.4	48.4	84.6	84.3
105	35.9	35.9	34.9	31.2	46.9	46.9	81.3	81
111	34.5	34.5	34	30.4	45.6	45.6	78.4	78.2
117	33.3	33.3	33	29.7	44.2	44.2	75.6	75.6
123	32.1	32.1	32	29	43.1	43.1	73.2	73.3
129	31.1	31.1	31.3	28.3	42	42	71	71.2
135	30.1	30.1	30.6	27.7	41	41	69.1	69.1
141	29.1	29.1	29.9	27.2	40	40	67.1	67.3
147	28.1	28.1	29.1	26.6	39.1	39.1	65.4	65.6
153	27.1	27.1	28.6	26.2	38.3	38.3	63.9	64.1
159	26.2	26.2	28.1	25.8	37.6	37.6	62.4	62.6
165	25.3	25.3	27.6	25.3	36.9	36.9	61	61.2
171	24.6	24.6	27.1	25	36.2	36.2	59.7	60
177	23.8	23.8	26.7	24.6	35.6	35.6	58.4	58.7
183	23.2	23.2	26.3	24.3	35	35	57.3	57.6
189	22.6	22.6	25.8	23.9	34.4	34.4	56.2	56.5
195	22	22	25.5	23.7	34	34	55.2	55.5
201	21.4	21.4	23.4	23.4	33.4	33.4	54.1	54.1
207	20.9	20.9	23	23	32.9	32.9	53.1	53.1
213	20.4	20.4	22.8	22.8	32.4	32.4	52.2	52.2
219	20	20	22.6	22.6	31.9	31.9	51.4	51.4
225	19.5	19.5	22.3	22.3	31.5	31.5	50.7	50.7
232	19.2	19.2	22.1	22.1	31.1	31.1	49.8	49.8
238	18.8	18.8	21.8	21.8	30.6	30.6	49.1	49.1
244	18.4	18.4	21.6	21.6	30.2	30.2	48.4	48.4
250	18.1	18.1	21.4	21.4	29.8	29.8	47.6	47.6

	shear rate (1/s)	2	50.3	250
0wt% CNC	average	451	66.9	18.1
	% Deviation	1.3	0	0
0.3wt%CNC	average	252.5	45.8	21.4
	% Deviation	1.8	7.4	0
0.5wt%CNC	average	526	68.2	29.8
	% Deviation	0	0	0
0.8wt%CNC	average	1610	135.5	47.6
	% Deviation	0.6	1.1	0

Table A3 below contains data used to construct figure showing how mud viscosity changes with response to shearing conditions.

Table A3: Viscosity data for 6wt% Bentonite formulations at 120ºF containing CNCs at various concentrations

Sample	A (0wt%) CNCs	A2 (0wt%) CNCs	B (0.1wt%) CNCs	B2 (0.1wt%) CNCs	C (0.3wt%) CNCs	C2 (0.3wt%) CNCs	D (0.5wt%) CNCs	D2 (0.5wt%) CNCs
Bentonite (g)	6	6	6	6	6	6	6	6
CNCs (g)	0	0	0.1	0.1	0.3	0.3	0.5	0.5
Water (g)	94	94	93.9	93.9	93.7	93.7	93.5	93.5
Time (s)	Viscosity (cP)							
0.603	28.8	28.8	19.9	20.6	23.3	26.9	29.6	29.6
1.2	24	24	18.4	19.2	21.7	25.1	27.7	27.7
1.8	22.6	22.6	17.8	18.7	21.2	24.5	27	27
2.4	21.9	21.9	17.5	18.5	20.9	24.1	26.6	26.6
3	21.3	21.3	17.3	18.2	20.7	23.9	26.2	26.2
3.6	20.9	20.9	17.1	18	20.6	23.7	26	26
4.2	20.6	20.6	17	17.9	20.5	23.5	25.8	25.8
4.8	20.4	20.4	16.9	17.8	20.4	23.3	25.6	25.6
5.4	20.2	20.2	16.8	17.7	20.3	23.2	25.5	25.5
6	20	20	16.7	17.6	20.3	23	25.3	25.3
6.6	19.8	19.8	16.6	17.5	20.2	22.9	25.2	25.2
7.2	19.7	19.7	16.6	17.4	20.1	22.8	25.1	25.1
7.8	19.6	19.6	16.6	17.3	20.1	22.7	25	25
8.4	19.4	19.4	16.5	17.3	20.1	22.6	24.8	24.8
9	19.3	19.3	16.5	17.2	20	22.6	24.8	24.8
9.6	19.2	19.2	16.4	17.1	20	22.5	24.7	24.7
10.2	19.2	19.2	16.4	17.1	20	22.4	24.6	24.6
10.8	19.1	19.1	16.4	17	19.9	22.3	24.5	24.5
11.4	19	19	16.3	17	19.9	22.3	24.4	24.4
12	18.9	18.9	16.3	16.9	19.9	22.2	24.3	24.3

12.6	18.9	18.9	16.3	16.9	19.8	22.2	24.2	24.2
13.2	18.8	18.8	16.2	16.8	19.8	22.1	24.2	24.2
13.8	18.7	18.7	16.2	16.8	19.8	22.1	24.1	24.1
14.4	18.7	18.7	16.2	16.8	19.8	22	24	24
15	18.6	18.6	16.2	16.7	19.8	22	24	24
15.6	18.6	18.6	16.2	16.7	19.7	21.9	23.9	23.9
16.2	18.5	18.5	16.1	16.7	19.7	21.9	23.9	23.9
16.8	18.5	18.5	16.1	16.6	19.7	21.8	23.8	23.8
17.4	18.4	18.4	16.1	16.6	19.7	21.8	23.8	23.8
18	18.4	18.4	16.1	16.6	19.7	21.7	23.7	23.7
18.6	18.4	18.4	16.1	16.5	19.6	21.7	23.6	23.6
19.2	18.3	18.3	16	16.5	19.6	21.7	23.6	23.6
19.8	18.3	18.3	16	16.5	19.6	21.6	23.6	23.6
20.4	18.2	18.2	16	16.5	19.6	21.6	23.5	23.5
21	18.2	18.2	16	16.4	19.6	21.5	23.5	23.5
21.6	18.2	18.2	16	16.4	19.6	21.5	23.4	23.4
22.2	18.1	18.1	16	16.4	19.5	21.5	23.4	23.4
22.8	18.1	18.1	15.9	16.4	19.5	21.4	23.3	23.3
23.4	18.1	18.1	15.9	16.3	19.5	21.4	23.3	23.3
24	18	18	15.9	16.3	19.5	21.4	23.3	23.3
24.6	18	18	15.9	16.3	19.5	21.3	23.2	23.2
25.2	18	18	15.9	16.3	19.5	21.3	23.2	23.2
25.8	18	18	15.9	16.3	19.5	21.3	23.2	23.2
26.4	17.9	17.9	15.9	16.2	19.4	21.2	23.1	23.1
27	17.9	17.9	15.9	16.2	19.4	21.2	23.1	23.1
27.6	17.9	17.9	15.8	16.2	19.4	21.2	23.1	23.1
28.2	17.9	17.9	15.8	16.2	19.4	21.2	23	23
28.8	17.8	17.8	15.8	16.2	19.4	21.1	23	23
29.4	17.8	17.8	15.8	16.1	19.4	21.1	23	23
30	17.8	17.8	15.8	16.1	19.4	21.1	23	23
30.6	17.7	17.7	15.8	16.1	19.4	21	22.9	22.9
31.2	17.7	17.7	15.8	16.1	19.4	21	22.9	22.9
31.8	17.7	17.7	15.8	16.1	19.3	21	22.9	22.9
32.4	17.7	17.7	15.8	16	19.4	21	22.8	22.8
33	17.6	17.6	15.7	16	19.4	21	22.8	22.8
33.6	17.6	17.6	15.7	16	19.3	20.9	22.8	22.8
34.2	17.6	17.6	15.7	16	19.3	20.9	22.7	22.7
34.8	17.6	17.6	15.7	16	19.3	20.9	22.7	22.7
35.4	17.6	17.6	15.7	16	19.3	20.9	22.7	22.7
36	17.5	17.5	15.7	16	19.3	20.9	22.7	22.7
36.6	17.5	17.5	15.7	16	19.3	20.8	22.7	22.7
37.2	17.5	17.5	15.7	16	19.3	20.8	22.6	22.6
37.8	17.5	17.5	15.7	16	19.3	20.8	22.6	22.6
38.4	17.5	17.5	15.7	15.9	19.3	20.8	22.6	22.6
39	17.4	17.4	15.7	15.9	19.3	20.8	22.6	22.6

39.6	17.4	17.4	15.7	15.9	19.3	20.7	22.5	22.5
40.2	17.4	17.4	15.6	15.9	19.2	20.7	22.5	22.5
40.8	17.4	17.4	15.6	15.9	19.2	20.7	22.5	22.5
41.4	17.4	17.4	15.6	15.9	19.2	20.7	22.5	22.5
42	17.4	17.4	15.6	15.9	19.2	20.6	22.5	22.5
42.6	17.3	17.3	15.6	15.9	19.2	20.6	22.4	22.4
43.2	17.3	17.3	15.6	15.9	19.2	20.6	22.4	22.4
43.8	17.3	17.3	15.6	15.9	19.2	20.6	22.4	22.4
44.4	17.3	17.3	15.6	15.9	19.2	20.6	22.4	22.4
45	17.3	17.3	15.6	15.8	19.2	20.6	22.3	22.3
45.6	17.3	17.3	15.6	15.8	19.2	20.6	22.3	22.3
46.2	17.3	17.3	15.6	15.8	19.2	20.5	22.3	22.3
46.8	17.3	17.3	15.6	15.8	19.2	20.5	22.3	22.3
47.4	17.2	17.2	15.6	15.8	19.2	20.5	22.3	22.3
48	17.2	17.2	15.6	15.8	19.1	20.5	22.3	22.3
48.6	17.2	17.2	15.6	15.8	19.1	20.4	22.3	22.3
49.2	17.2	17.2	15.6	15.8	19.1	20.4	22.2	22.2
49.8	17.2	17.2	15.5	15.8	19.1	20.4	22.2	22.2
50.4	17.2	17.2	15.5	15.8	19.1	20.4	22.2	22.2
51	17.2	17.2	15.5	15.8	19.1	20.4	22.2	22.2
51.6	17.2	17.2	15.5	15.8	19.1	20.4	22.2	22.2
52.2	17.2	17.2	15.5	15.8	19.1	20.4	22.2	22.2
52.8	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
53.4	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
54	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
54.6	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
55.2	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
55.8	17.1	17.1	15.5	15.8	19.1	20.3	22.1	22.1
56.4	17.1	17.1	15.5	15.8	19.1	20.2	22.1	22.1
57	17.1	17.1	15.5	15.7	19.1	20.2	22	22
57.6	17	17	15.5	15.7	19	20.2	22	22
58.2	17	17	15.5	15.7	19	20.2	22	22
58.8	17	17	15.5	15.7	19	20.2	22	22
59.4	17	17	15.5	15.7	19	20.2	22	22
60	17	17	15.5	15.7	19	20.2	22	22
60.6	17	17	15.5	15.7	19	20.2	22	22
61.2	17	17	15.4	15.7	19	20.1	21.9	21.9
61.8	17	17	15.4	15.7	19	20.1	21.9	21.9
62.4	17	17	15.4	15.7	19	20.1	21.9	21.9
63	17	17	15.4	15.7	19	20.1	21.9	21.9
63.6	16.9	16.9	15.4	15.7	19	20.1	21.9	21.9
64.2	16.9	16.9	15.4	15.7	19	20.1	21.9	21.9
64.8	16.9	16.9	15.4	15.7	19	20.1	21.9	21.9
65.4	16.9	16.9	15.4	15.7	19	20.1	21.8	21.8
66	16.9	16.9	15.4	15.7	19	20.1	21.8	21.8

66.6	16.9	16.9	15.4	15.7	19	20	21.8	21.8
67.2	16.9	16.9	15.4	15.7	19	20	21.8	21.8
67.8	16.9	16.9	15.4	15.7	19	20	21.8	21.8
68.4	16.9	16.9	15.4	15.7	19	20	21.8	21.8
69	16.8	16.8	15.4	15.7	19	20	21.8	21.8
69.6	16.8	16.8	15.4	15.7	19	20	21.8	21.8
70.2	16.8	16.8	15.4	15.7	19	20	21.7	21.7
70.8	16.8	16.8	15.4	15.7	19	20	21.7	21.7
71.4	16.8	16.8	15.4	15.7	18.9	20	21.7	21.7
72	16.8	16.8	15.4	15.6	18.9	20	21.7	21.7
72.6	16.8	16.8	15.4	15.7	18.9	20	21.7	21.7
73.2	16.8	16.8	15.4	15.7	18.9	20	21.7	21.7
73.8	16.8	16.8	15.4	15.7	18.9	20	21.7	21.7
74.4	16.8	16.8	15.4	15.7	18.9	19.9	21.6	21.6
75	16.8	16.8	15.4	15.6	18.9	19.9	21.6	21.6
75.6	16.8	16.8	15.4	15.6	18.9	19.9	21.6	21.6
76.2	16.7	16.7	15.4	15.6	18.9	19.9	21.6	21.6
76.8	16.7	16.7	15.4	15.6	18.9	19.9	21.6	21.6
77.4	16.7	16.7	15.4	15.6	18.9	19.9	21.6	21.6
78	16.7	16.7	15.4	15.6	18.9	19.9	21.6	21.6
78.6	16.7	16.7	15.4	15.6	18.9	19.9	21.6	21.6
79.2	16.7	16.7	15.3	15.6	18.9	19.9	21.5	21.5
79.8	16.7	16.7	15.3	15.6	18.9	19.8	21.5	21.5
80.4	16.7	16.7	15.3	15.6	18.9	19.8	21.5	21.5
81	16.7	16.7	15.3	15.6	18.9	19.8	21.5	21.5
81.6	16.7	16.7	15.3	15.6	18.9	19.8	21.5	21.5
82.2	16.6	16.6	15.3	15.6	18.9	19.8	21.5	21.5
82.8	16.6	16.6	15.3	15.6	18.9	19.8	21.5	21.5
83.4	16.6	16.6	15.3	15.6	18.9	19.8	21.5	21.5
84	16.6	16.6	15.3	15.6	18.9	19.8	21.5	21.5
84.6	16.6	16.6	15.3	15.6	18.9	19.8	21.5	21.5
85.2	16.6	16.6	15.3	15.6	18.9	19.8	21.4	21.4
85.8	16.6	16.6	15.3	15.6	18.8	19.8	21.4	21.4
86.4	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
87	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
87.6	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
88.2	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
88.8	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
89.4	16.6	16.6	15.3	15.6	18.8	19.7	21.4	21.4
90	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
90.6	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
91.2	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
91.8	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
92.4	16.5	16.5	15.3	15.6	18.8	19.7	21.4	21.4
93	16.5	16.5	15.3	15.6	18.8	19.7	21.3	21.3

93.6	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
94.2	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
94.8	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
95.4	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
96	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
96.6	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
97.2	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
97.8	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
98.4	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
99	16.5	16.5	15.3	15.6	18.8	19.6	21.3	21.3
99.6	16.5	16.5	15.3	15.6	18.8	19.6	21.2	21.2
100	16.5	16.5	15.3	15.6	18.8	19.6	21.2	21.2
101	16.4	16.4	15.3	15.6	18.8	19.6	21.2	21.2
101	16.4	16.4	15.3	15.6	18.8	19.5	21.2	21.2
102	16.4	16.4	15.3	15.6	18.8	19.5	21.2	21.2
103	16.4	16.4	15.3	15.7	18.8	19.5	21.2	21.2
103	16.4	16.4	15.3	15.7	18.8	19.5	21.2	21.2
104	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
104	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
105	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
106	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
106	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
107	16.4	16.4	15.4	15.7	18.8	19.5	21.2	21.2
107	16.4	16.4	15.4	15.6	18.7	19.5	21.2	21.2
108	16.4	16.4	15.4	15.6	18.7	19.5	21.2	21.2
109	16.4	16.4	15.4	15.6	18.7	19.5	21.2	21.2
109	16.4	16.4	15.4	15.6	18.7	19.5	21.1	21.1
110	16.4	16.4	15.4	15.6	18.8	19.5	21.1	21.1
110	16.4	16.4	15.4	15.6	18.7	19.5	21.1	21.1
111	16.3	16.3	15.4	15.6	18.7	19.4	21.1	21.1
112	16.3	16.3	15.5	15.6	18.7	19.4	21.1	21.1
112	16.3	16.3	15.5	15.6	18.7	19.4	21.1	21.1
113	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
113	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
114	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
115	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
115	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
116	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
116	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
117	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
118	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
118	16.3	16.3	15.5	15.7	18.7	19.4	21.1	21.1
119	16.3	16.3	15.5	15.6	18.7	19.4	21.1	21.1
119	16.3	16.3	15.5	15.6	18.7	19.4	21	21
120	16.3	16.3	15.5	15.6	18.7	19.4	21	21

121	16.3	16.3	15.5	15.6	18.7	19.4	21	21
121	16.3	16.3	15.5	15.6	18.7	19.4	21	21
122	16.3	16.3	15.5	15.6	18.7	19.3	21	21
122	16.3	16.3	15.5	15.6	18.7	19.4	21	21
123	16.2	16.2	15.5	15.6	18.7	19.3	21	21
124	16.2	16.2	15.5	15.7	18.7	19.3	21	21
124	16.2	16.2	15.5	15.7	18.7	19.3	21	21
125	16.2	16.2	15.5	15.7	18.7	19.3	21	21
125	16.2	16.2	15.5	15.7	18.7	19.3	21	21
126	16.2	16.2	15.5	15.7	18.7	19.3	21	21
127	16.2	16.2	15.5	15.7	18.7	19.3	21	21
127	16.2	16.2	15.6	15.7	18.7	19.3	21	21
128	16.2	16.2	15.6	15.6	18.7	19.3	21	21
128	16.2	16.2	15.6	15.6	18.7	19.3	21	21
129	16.2	16.2	15.6	15.6	18.7	19.3	21	21
130	16.2	16.2	15.5	15.6	18.7	19.3	21	21
130	16.2	16.2	15.5	15.6	18.7	19.3	21	21
131	16.2	16.2	15.6	15.6	18.7	19.3	20.9	20.9
131	16.2	16.2	15.5	15.6	18.7	19.3	20.9	20.9
132	16.2	16.2	15.5	15.6	18.7	19.3	20.9	20.9
133	16.2	16.2	15.5	15.7	18.7	19.3	20.9	20.9
133	16.2	16.2	15.5	15.7	18.7	19.3	20.9	20.9
134	16.1	16.1	15.5	15.7	18.7	19.3	20.9	20.9
134	16.1	16.1	15.5	15.7	18.7	19.2	20.9	20.9
135	16.1	16.1	15.5	15.6	18.7	19.2	20.9	20.9
136	16.1	16.1	15.5	15.6	18.7	19.2	20.9	20.9
136	16.1	16.1	15.5	15.6	18.7	19.2	20.9	20.9
137	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
137	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
138	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
139	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
139	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
140	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
140	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
141	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
142	16.1	16.1	15.6	15.6	18.7	19.2	20.9	20.9
142	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
143	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
143	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
144	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
145	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
145	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
146	16.1	16.1	15.6	15.6	18.6	19.2	20.8	20.8
146	16.1	16.1	15.6	15.6	18.7	19.2	20.8	20.8
147	16.1	16.1	15.6	15.6	18.6	19.2	20.8	20.8

148	16	16	15.6	15.6	18.6	19.2	20.8	20.8
148	16	16	15.6	15.6	18.6	19.1	20.8	20.8
149	16	16	15.6	15.6	18.6	19.1	20.8	20.8
149	16	16	15.6	15.6	18.6	19.1	20.8	20.8
150	16	16	15.6	15.6	18.6	19.1	20.8	20.8
151	16	16	15.6	15.6	18.6	19.1	20.8	20.8
151	16	16	15.6	15.6	18.6	19.1	20.8	20.8
152	16	16	15.6	15.6	18.6	19.1	20.8	20.8
152	16	16	15.6	15.6	18.6	19.1	20.8	20.8
153	16	16	15.6	15.6	18.6	19.1	20.8	20.8
154	16	16	15.6	15.6	18.6	19.1	20.8	20.8
154	16	16	15.6	15.6	18.6	19.1	20.8	20.8
155	16	16	15.6	15.6	18.6	19.1	20.8	20.8
155	16	16	15.6	15.6	18.6	19.1	20.8	20.8
156	16	16	15.6	15.6	18.6	19.1	20.8	20.8
157	16	16	15.6	15.6	18.6	19.1	20.8	20.8
157	16	16	15.6	15.6	18.6	19.1	20.7	20.7
158	16	16	15.6	15.6	18.6	19.1	20.7	20.7
158	16	16	15.6	15.6	18.6	19.1	20.7	20.7
159	16	16	15.6	15.6	18.6	19.1	20.7	20.7
160	16	16	15.6	15.6	18.6	19.1	20.7	20.7
160	16	16	15.6	15.6	18.6	19.1	20.7	20.7
161	16	16	15.6	15.6	18.6	19.1	20.7	20.7
161	16	16	15.5	15.6	18.6	19.1	20.7	20.7
162	16	16	15.5	15.6	18.6	19.1	20.7	20.7
163	16	16	15.5	15.6	18.6	19.1	20.7	20.7
163	16	16	15.5	15.6	18.6	19	20.7	20.7
164	16	16	15.5	15.6	18.6	19	20.7	20.7
164	16	16	15.5	15.6	18.6	19	20.7	20.7
165	16	16	15.6	15.6	18.6	19	20.7	20.7
166	16	16	15.6	15.6	18.6	19	20.7	20.7
166	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
167	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
167	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
168	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
169	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
169	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
170	15.9	15.9	15.6	15.6	18.6	19	20.7	20.7
170	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
171	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
172	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
172	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
173	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
173	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
174	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6

175	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
175	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
176	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
176	15.9	15.9	15.5	15.6	18.6	19	20.6	20.6
177	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
178	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
178	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
179	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
179	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
180	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
181	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
181	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
182	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
182	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
183	15.9	15.9	15.6	15.6	18.6	19	20.6	20.6
184	15.9	15.9	15.6	15.6	18.6	18.9	20.6	20.6
184	15.9	15.9	15.5	15.6	18.6	18.9	20.6	20.6
185	15.9	15.9	15.5	15.6	18.6	18.9	20.6	20.6
185	15.9	15.9	15.5	15.6	18.6	18.9	20.6	20.6
186	15.9	15.9	15.5	15.6	18.6	18.9	20.6	20.6
187	15.9	15.9	15.5	15.6	18.6	18.9	20.6	20.6
187	15.9	15.9	15.5	15.5	18.6	18.9	20.6	20.6
188	15.9	15.9	15.5	15.5	18.6	18.9	20.6	20.6
188	15.9	15.9	15.5	15.5	18.6	18.9	20.6	20.6
189	15.9	15.9	15.5	15.5	18.6	18.9	20.6	20.6
190	15.9	15.9	15.6	15.5	18.6	18.9	20.6	20.6
190	15.9	15.9	15.6	15.5	18.6	18.9	20.6	20.6
191	15.9	15.9	15.6	15.6	18.6	18.9	20.6	20.6
191	15.9	15.9	15.6	15.6	18.6	18.9	20.5	20.5
192	15.8	15.8	15.6	15.6	18.6	18.9	20.6	20.6
193	15.8	15.8	15.6	15.6	18.6	18.9	20.5	20.5
193	15.8	15.8	15.6	15.6	18.6	18.9	20.5	20.5
194	15.8	15.8	15.6	15.6	18.6	18.9	20.5	20.5
194	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
195	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
196	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
196	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
197	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
197	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
198	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
199	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
199	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
200	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5
200	15.8	15.8	15.5	15.5	18.6	18.9	20.5	20.5
201	15.8	15.8	15.5	15.6	18.6	18.9	20.5	20.5

202	15.8	15.8	15.5	15.5	18.6	18.9	20.5	20.5
202	15.8	15.8	15.6	15.5	18.6	18.9	20.5	20.5
203	15.8	15.8	15.6	15.5	18.6	18.9	20.5	20.5
203	15.8	15.8	15.6	15.5	18.6	18.9	20.5	20.5
204	15.8	15.8	15.6	15.5	18.6	18.9	20.5	20.5
205	15.8	15.8	15.6	15.5	18.6	18.9	20.5	20.5
205	15.8	15.8	15.6	15.5	18.6	18.8	20.5	20.5
206	15.8	15.8	15.6	15.6	18.6	18.8	20.5	20.5
206	15.8	15.8	15.5	15.6	18.6	18.8	20.5	20.5
207	15.8	15.8	15.5	15.6	18.6	18.8	20.5	20.5
208	15.8	15.8	15.5	15.6	18.6	18.8	20.4	20.4
208	15.8	15.8	15.5	15.6	18.6	18.8	20.5	20.5
209	15.8	15.8	15.6	15.6	18.6	18.8	20.5	20.5
209	15.8	15.8	15.6	15.6	18.6	18.8	20.4	20.4
210	15.8	15.8	15.6	15.6	18.6	18.8	20.5	20.5
211	15.8	15.8	15.6	15.6	18.6	18.8	20.4	20.4
211	15.8	15.8	15.6	15.6	18.5	18.8	20.4	20.4
212	15.8	15.8	15.6	15.6	18.5	18.8	20.4	20.4
212	15.8	15.8	15.5	15.6	18.5	18.8	20.4	20.4
213	15.8	15.8	15.5	15.6	18.5	18.8	20.4	20.4
214	15.8	15.8	15.5	15.5	18.5	18.8	20.4	20.4
214	15.8	15.8	15.5	15.5	18.6	18.8	20.4	20.4
215	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
215	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
216	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
217	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
217	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
218	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
218	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
219	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
220	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
220	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
221	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
221	15.7	15.7	15.5	15.6	18.5	18.8	20.4	20.4
222	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
223	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
223	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
224	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
224	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
225	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
226	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
226	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
227	15.7	15.7	15.6	15.6	18.5	18.8	20.4	20.4
227	15.7	15.7	15.5	15.6	18.5	18.8	20.4	20.4
228	15.7	15.7	15.5	15.6	18.5	18.8	20.4	20.4

229	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
229	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
230	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
230	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
231	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
232	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
232	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
233	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
233	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
234	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
235	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
235	15.7	15.7	15.5	15.5	18.5	18.8	20.4	20.4
236	15.7	15.7	15.5	15.5	18.5	18.7	20.4	20.4
236	15.7	15.7	15.5	15.5	18.5	18.8	20.3	20.3
237	15.7	15.7	15.5	15.5	18.5	18.7	20.4	20.4
238	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
238	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
239	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
239	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
240	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
241	15.7	15.7	15.5	15.6	18.5	18.7	20.3	20.3
241	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
242	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
242	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
243	15.7	15.7	15.5	15.5	18.5	18.7	20.3	20.3
244	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
244	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
245	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
245	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
246	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
247	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
247	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
248	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
248	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
249	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
250	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3
250	15.6	15.6	15.5	15.5	18.5	18.7	20.3	20.3

Average and % deviation at shear rate of $250s^{-1}$

Average (cP)	15.6	15.5	18.6	20.3
% deviation	0	0	0.54	0

The 10s and 10min gel strength were measured at 120ºF for the 0.3, 0.5 and 0.8 wt%CNC at 6wt%Bentonite concentration. It must be known that the 10s gel data obtained for the 0.3wt%CNC formulation was partly obtained at a torque below the equipment's specifications torque range thus the results with invalid points/ data of which were excluded in Table A4 below:

Table A4: 10s and 10min gel strength measurement measured as shear stress in (Pa)

shear rate	6wt%B 0.3wt%CNC		6wt%B 0.5wt%CNC		6wt%B 0.8wt%CNC	
	10s	10min	10s	10min	10s	10min
(1/s)	Pa	Pa	Pa	Pa	Pa	Pa
3.87		0.608		1.77	0.401	8.68
3.87		0.764	0.0981	1.85	0.549	9.21
3.87		0.802	0.0484	1.93	0.618	8.93
3.87	0.0293	0.842		2.05	0.577	8.6
3.87		0.844	0.0512	1.86	0.632	8.44
3.87		0.838	0.105	1.96	0.587	7.99
3.87		0.81	0.0766	1.82	0.665	7.78
3.87	0.014	0.849	0.125	1.91	0.628	7.71
3.87		0.681	0.0632	1.79	0.729	7.38
3.87		0.806	0.06	1.79	0.576	7.32
3.87	0.000995	0.663	0.0842	1.79		7.13
3.87	0.00339	0.601	0.123	1.64	0.7	6.18
3.87		0.658	0.0687	1.66	0.674	6.01
3.87	0	0.615	0.103	1.63	0.695	5.93
3.87	0.00954	0.675	0.111	1.55	0.662	5.37
3.87		0.609		1.56	0.686	5.31
3.87	0.0287	0.553	0.179	1.47	0.629	5.23
3.87	0.00732	0.655	0.142	1.52	0.703	5.17
3.87	2.67E-05	0.596	0.135	1.42	0.678	4.8
3.87		0.647	0.0874	1.46	0.69	4.82
3.87	0.00494	0.561	0.26	1.36	0.64	4.81
3.87	0.0183	0.518	0.109	1.4	0.606	4.77
3.87		0.615	0.161	1.47	0.673	4.82
3.87	0.00885	0.655	0.155	1.34	0.596	4.69
3.87		0.583	0.117	1.37	0.669	4.67
3.87	0	0.547	0.145	1.35	0.604	4.71
3.87	0.0248	0.5	0.108	1.37	0.576	4.55
3.87	0.026	0.663	0.105	1.31	0.778	4.47
3.87		0.523		1.19	0.72	4.46
3.87	0.0077	0.568	0.136	1.28	0.711	4.38
3.87		0.557	0.0893	1.21	0.754	4.34
3.87	0.0151	0.558	0.122	1.21	0.712	4.32

3.87	0.000553	0.526	0.0898	1.23	0.609	4.29
3.87	0.0184	0.473	0.111	1.25	0.821	4.25
3.87	0.106	0.505	0.106	1.33	0.671	4.17
3.87	0.0306	0.524		1.25	0.686	4.26
3.87	0.0671	0.5	0.153	1.29	0.758	4.17
3.87		0.585	0.172	1.24	0.712	4.11
3.87	0.0517	0.559	0.0991	1.2	0.784	4.15
3.87	0.043	0.473	0.116	1.19	0.728	4.12
3.87	0.0909	0.561	0.138	1.11	0.732	4.12
3.87	0.0468	0.476	0.174	1.18	0.793	4.08
3.87		0.478	0.123	1.22	0.835	4.01
3.87	0.0305	0.503	0.232	1.14	0.639	4.08
3.87	0.0124	0.528	0.113	1.08	0.762	4.03
3.87	0.000511	0.551	0.133	1.17	0.675	4.09
3.87	0.0278	0.525	0.279	1.19	0.683	4.05
3.87	0.0598	0.47	0.147	1.2	0.71	4.02
3.87	0.0304	0.454	0.192	1.08	0.689	4.01
3.87	0.00924	0.513	0.117	1.12	0.691	3.94
3.87		0.493	0.186	1.22	0.693	3.95
3.87	0.0764	0.47	0.141	1.09	0.769	3.9
3.87		0.438	0.188	1.19	0.786	3.89
3.87	0.0767		0.126	1.24	0.78	3.83
3.87	0.132	0.488	0.186	1.05	0.741	3.94
3.87	0.0559		0.14	1.1	0.778	3.92
3.87	0.0147	0.402	0.175	1.18	0.815	3.92
3.87			0.183	1.06	0.762	3.84
3.87	0.0908	0.462	0.11	1.03	0.763	3.83
3.87	0.0141	0.416	0.0608	1.1	0.756	3.71
3.87		0.464	0.141	0.996	0.701	3.76
3.87	0.0265	0.463	0.0842	1.15	0.819	3.71
3.87		0.461	0.122	1.13	0.772	3.77
3.87	0.0156	0.488	0.131	1.11	0.827	3.72
3.87	0.00911	0.406	0.159	1.13	0.76	3.73
3.87	0.0575	0.544	0.113	1.06	0.794	3.7
3.87	0.131	0.432	0.218	1.17	0.761	3.67
3.87		0.43	0.0777	1.13	0.872	3.73
3.87	0.0581		0.135	1.07	0.847	3.69
3.87	0.0813	0.399	0.079	1.05	0.774	3.67
3.87		0.515	0.14	1.05	0.833	3.59
3.87	0.0485	0.422	0.158	0.979	0.734	3.7
Average	0.035685	0.575479	0.122327	1.380571	0.704959	4.982959

Xm	0.04	0.58	0.12	1.38	0.70	4.98
σ(std dev)	0.03	0.11	0.05	0.27	0.08	1.39

The average values were then divided by the shear rate at which the shear stress was measured to express the gel strength in viscosity units. Below is the summary of the calculation and Table A5 showing the obtained 10s and 10min gel strength for the respective formulations.

$$Gel\ Strength\ (lb/100ft^2) = Average\ \tau\ \ (Pa) \times (\frac{2.08854\ lb/100ft^2}{Pa}) \qquad (5)$$

Table A5: Calculated gel strength data results

Sample	A 0.3 wt%CNCs	B 0.5 wt%CNCs	C 0.8 wt%CNCs
Bentonite (g)	6	6	6
CNCs (g)	0.3	0.5	0.8
Water (g)	93.7	93.5	93.2
Gel time	gel strength (lb/100ft^2)		
10 (s)	0.075	0.260	1.475
10 (min)	1.204	2.888	10.423

B. Fluid loss data

Fluid loss/ filtrate data for CNC, Water-Bentonite formulations obtained after subjecting the fluid to 100 psi pressure for 30minutes at room temperature is presented in Table B1 below. Table B1 data was used to construct the diagram in Figure 4.2.

Table B1: Filtrate data for 6wt% Bentonite formulations at 100psi pressure and room temperature for different CNC concentrations.

Sample	A	B	C	D	E
Bentonite (wt%)	6	6	6	6	6
Water (wt%)	94	93.9	93.7	93.5	93.2
CNC (wt%)	0	0.1	0.3	0.5	0.8
Total mass (g)	500	500	500	500	500
	Filtrate (ml/30min)				
X1	28	27	24	16	14
X2	28.5	26.2	23.2	15.7	12.5
X3	28.9	28.4	25	16.1	13
Average	28.5	27.2	24.1	15.9	13.2
	Statistical Analysis				
X_m	28.5	27.2	24.1	15.9	13.2
$(\Sigma(X_i\text{-}X_m)^\wedge 2)/3$	0.1	0.8	0.5	0.0	0.4

σ (std dev)	0.4	0.9	0.7	0.2	0.6

C. Thermal Data

Viscosity data for CNC, Water-Bentonite formulations obtained after subjecting the fluid to atmospheric pressure at varying temperature from 0-98°C is presented in Table C1 below. Table C1 data was used to construct the diagram in Figure 4.7.

Table C1: Viscosity data for 6wt% Bentonite formulations at atmospheric pressure between 0°C and 98°C temperature for 0, 0.3 and 0.5 wt% CNC concentrations.

Temperature [°C]	Viscosity [cP]		
	0 wt%CNC	0.3 wt%CNC	0.5 wt%CNC
0	11.2	13.2	39
0.283	10.8	13.2	37.1
0.825	10.5	13.2	36
1.26	10.4	13.2	35.4
1.72	10.2	13.1	34.8
2.32	9.98	13	34.3
2.93	9.81	12.8	33.8
3.52	9.79	12.8	33.3
4.14	9.75	12.6	32.9
4.69	9.73	12.5	32.4
5.12	9.65	12.4	32
5.75	8.63	12.3	31.5
6.39	9.63	12.1	31.1
7.06	9.56	11.9	30.7
7.51	9.43	11.8	30.2
8.16	9.23	11.6	29.8
8.84	9.06	11.5	29.4
9.38	8.91	11.3	29
10	8.82	11.2	28.7
10.5	8.79	11	28.3
11.2	8.51	10.9	27.9
11.9	8.42	10.7	27.6
12.6	8.3	10.6	27.2
13	8.23	10.5	26.9
13.5	7.97	10.3	26.5
14.2	7.3	10.2	26.2
14.9	7.61	9.99	25.9
15.6	7.53	9.9	25.5
16.3	7.11	9.81	25.2

16.9	7.05	9.57	24.9
17.3	7	9.44	24.7
18	7.66	9.31	24.3
18.7	7.54	9.19	24.1
19.4	7.32	9.04	23.7
20.1	7.14	8.93	23.5
20.6	7.08	8.87	23.3
21.1	6.9	8.82	23
21.8	6.83	8.63	22.8
22.5	6.72	8.61	22.6
23	6.69	8.38	22.3
23.7	6.63	8.31	22.1
24.4	6.58	8.2	21.9
24.9	6.51	8.09	21.7
25.6	6.41	8.02	21.4
26.1	6.3	7.86	21.2
26.8	6.09	7.79	21.1
27.5	6.04	7.72	20.9
28.2	6	7.6	20.7
28.9	5.93	7.5	20.5
29.5	5.85	7.37	20.4
30.2	5.8	7.29	20.1
30.6	5.72	7.21	20
31.3	5.61	7.1	19.8
32	5.56	6.99	19.7
32.7	5.5	6.91	19.5
33.3	5.42	6.81	19.4
33.7	5.38	6.82	19.2
34.4	5.31	6.69	19.1
35.1	5.25	6.7	18.9
35.8	5.22	6.62	18.9
36.3	5.2	6.48	18.8
37	5.15	6.46	18.6
37.5	5.1	6.43	18.5
38.2	4.98	6.35	18.5
39	4.84	6.19	18.3
39.4	4.79	6.17	18.2
40.1	4.72	6.04	18.1
40.8	4.69	6.06	18.1
41.3	4.65	6	18
42	4.59	5.88	17.9
42.8	4.57	5.81	17.8
43.4	4.51	5.75	17.7
43.9	4.5	5.64	17.7
44.6	4.49	5.59	17.6

45.3	4.47	5.54	17.6
45.9	4.45	5.44	17.6
46.4	4.31	5.43	17.5
47	4.3	5.32	17.5
47.7	4.26	5.28	17.5
48.4	4.26	5.27	17.5
49.1	4.23	5.15	17.5
49.6	4.21	5.15	17.5
50.2	4.18	5.06	17.5
50.8	4.17	5.08	17.5
51.5	4.15	5.06	17.5
52.2	4.14	4.91	17.5
52.7	4.14	4.89	17.6
53.4	4.13	4.86	17.6
54	4.12	4.84	17.6
54.6	4.12	4.84	17.7
55.3	4.12	4.81	17.9
56	4.12	4.72	17.9
56.5	4.1	4.72	18
57.2	4.1	4.66	18.1
57.8	4.1	4.62	18.2
58.5	4.1	4.66	18.4
59.1	4.08	4.62	18.5
59.6	4.01	4.58	18.6
60.3	3.99	4.57	18.8
61	3.96	4.46	19
61.6	3.92	4.45	19.1
62.3	3.9	4.45	19.3
62.8	3.8	4.38	19.5
63.5	3.79	4.41	19.7
64.1	3.77	4.34	20
64.8	3.77	4.3	20.2
65.3	3.72	4.29	20.4
66	3.7	4.32	20.7
66.6	3.63	4.29	21
67.2	3.63	4.23	21.3
67.9	3.64	4.21	21.6
68.6	3.64	4.14	21.9
69.3	3.64	4.14	22.3
69.8	3.64	4.09	22.6
70.4	3.64	4.13	23
71.1	3.65	4.12	23.3
71.7	3.65	4.1	23.7
72.4	3.67	4.09	24.1
72.9	3.67	4.16	24.5

73.6	3.69	4.16	24.9
74.2	3.7	4.12	25.5
74.9	3.7	4.21	26
75.4	3.71	4.19	26.5
76.1	3.72	4.26	26.8
76.7	3.74	4.26	27.3
77.4	3.76	4.35	27.8
78	3.77	4.26	28.2
78.5	3.78	4.35	28.7
79.2	3.85	4.33	29.4
79.9	3.86	4.26	29.7
80.5	3.86	4.34	30.3
81.2	3.87	4.28	30.8
81.9	3.88	4.24	31.4
82.5	3.9	4.22	31.8
83	3.91	4.18	32.3
83.7	3.95	4.14	32.7
84.3	3.96	4.14	33.2
85	4.01	4.09	33.7
85.6	4.05	4.04	34.3
86.2	4.06	4.06	34.7
86.8	4.1	4.04	35.2
87.4	4.12	4.06	35.6
88	4.16	3.96	36
88.6	4.19	4.01	36.6
89.2	4.22	3.93	37
89.9	4.27	3.96	37.4
90.4	4.32	3.91	37.9
91.1	4.4	3.92	38.4
91.7	4.44	3.91	38.9
92.3	4.46	3.91	39.3
92.8	4.51	3.86	39.8
93.4	4.55	3.88	40.4
94	4.72	3.91	40.9
94.6	4.75	3.89	41.5
95.2	4.78	3.9	45
95.8	4.85	3.87	89.6
96.4	4.91	3.87	68.3
97	4.97	3.94	57.1
97.5	5.03	3.85	67.8
98.1	5.18	3.93	80.8