EFFECTS OF NANOPARTICLES ON THE PERFORMANCE OF DRILLING FLUIDS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BERK BAL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
THE DEPARTMENT OF PETROLEUM AND NATURAL GAS ENGINEERING

SEPTEMBER 2017

Approval of the Thesis:

EFFECTS OF NANOPARTICLES ON THE PERFORMANCE OF DRILLING FLUIDS

submitted by **BERK BAL** in partial fulfillment of the requirements for the degree of **Master of Science in Petroleum and Natural Gas Engineering Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver
Dean, Graduate School of **Natural and Applied Sciences** ____________

Prof. Dr. Serhat Akın
Head of Department, **Petroleum and Natural Gas Engineering** ____________

Prof. Dr. Mustafa Verşan Kök
Supervisor, **Petroleum and Natural Gas Engineering Dept., METU** ____________

Assoc. Prof. Dr. İsmail Hakkı Gücüyener
Co-supervisor, **GEOS Energy Inc.** ____________

Examining Committee Members:

Prof. Dr. Serhat Akın
Petroleum and Natural Gas Engineering Dept., METU ____________________

Prof. Dr. Mustafa Verşan Kök
Petroleum and Natural Gas Engineering Dept., METU ____________________

Asst. Prof. Tuna Eren
Petroleum and Natural Gas Engineering Dept., Batman University ____________________

Assoc. Prof. Dr. Çağlar Sınayuç
Petroleum and Natural Gas Engineering Dept., METU ____________________

Asst. Prof. İsmail Durgut
Petroleum and Natural Gas Engineering Dept., METU ____________________

Date: 08.09.2017

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Berk Bal

Signature:

ABSTRACT

EFFECTS OF NANOPARTICLES ON THE PERFORMANCE OF DRILLING FLUIDS

Bal, Berk

M.S., Department of Petroleum and Natural Gas Engineering

Supervisor: Prof. Dr. Mustafa Verşan Kök

Co-supervisor: Assoc. Prof. Dr. İsmail Hakkı Gücüyener

September 2017, 77 pages

In this master thesis, effects of nanoparticles on the filtration and rheological properties of water-based drilling fluids are experimentally investigated. Four different silica nanoparticles are added into the lignosulfonate and bentonite based drilling fluids. By using data obtained at the end of this research, filtration and rheological properties of nanofluids are analyzed and compared with the base fluids at different temperatures.

Two groups of experiments are conducted in this research. In the first group, four water-based drilling fluids are formed by using bentonite, chrome free lignosulfonate (CFL) and carboxymethyl cellulose (CMC) in different concentrations. These fluids are selected as base fluids, and 0.5 lb/bbl of four different silica nanoparticles are added them to obtain nanofluids. The rheological properties, fluid loss amounts and mud cake thicknesses of samples with nanoparticles are investigated at 77 ºF and 120 ºF, and compared with base fluids. Results reveal that, all of the nanoparticles increase fluid loss of bentonite muds. On the other hand, reduction in fluid loss is observed for some lignosulfonate muds containing nanoparticle. Moreover, no significant change in mud cake thickness and rheological properties is seen for both drilling fluids.

In the second part, experiments are conducted to see more clearly the effects of nanoparticles in bentonite mud. Because of this reason, only bentonite is used as additive to eliminate other parameters. Since rheological enhancement were not observed at the first part, these experiments have higher concentrations of bentonite and nanoparticles than previous tests, with 7% by weight of bentonite and 0.5% and 1.5% by weight of nanoparticles. It is seen that the amount of fluid loss increases with the addition of nanoparticles in all concentrations and all sizes. The rheological analyses show that, only 15-20 nm porous nanoparticles affects the rheology negatively at 0.5 w/w %. In addition to these experiments, permeability of mud cakes are also compared using Darcy's Law. It is concluded that nanofluids form permeable mud cakes compared to base fluid.

Keywords: drilling fluid, mud, nanofluid, nanosilica, fluid loss

ÖZ

NANOPARÇACIKLARIN SONDAJ SIVISININ PERFORMANSI ÜZERİNDEKİ ETKİLERİ

Bal, Berk
Yüksek Lisans, Petrol ve Doğal Gaz Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Mustafa Verşan Kök
Eş Tez Yöneticisi: Doç. Dr. İsmail Hakkı Gücüyener

Eylül 2017, 77 sayfa

Bu yüksek lisans tezinde nanoparçacıkların su bazlı sondaj sıvılarının filtrasyon ve reolojik özelliklerine etkileri deneysel olarak araştırılmıştır. Dört farklı silika nanoparçacığı lignosülfonat ve bentonit esaslı sondaj sıvılarına ilave edilmiştir. Bu araştırmanın sonucunda elde edilen veriler kullanılarak, nanosıvıların filtrasyon ve reolojik özellikleri farklı sıcaklıklarda analiz edilmiş ve baz sıvılarla karşılaştırılmıştır.

Bu çalışmada iki grup deney yapılmıştır. Çalışmanın ilk kısmında bentonit, kromsuz lignosülfonat (CFL) ve karboksimetil selüloz (CMC)'u farklı konsantrasyonlarda kullanarak dört adet su bazlı sondaj sıvısı oluşturulmuştur. Bu sondaj sıvıları baz çamur olarak seçilmiş ve nanosıvı elde etmek için içlerine dört farklı silika nanoparçacığı 0.5 libre/varil eklenmiştir. Nanoparçacık içeren örneklerin reolojik özellikleri, sıvı kaybı miktarları ve çamur kek kalınlıkları 77 ºF ve 120 ºF'de incelenmiş ve baz sıvılarla karşılaştırılmıştır. Sonuçlar, bütün nanoparçacıkların bentonit çamurlarının sıvı kaybını arttırdığını ortaya koymaktadır. Öte yandan, nanoparçacık içeren bazı lignosülfonat çamurlarında sıvı kaybında azalma gözlemlenmektedir. Dahası, her iki sondaj sıvısı için çamur kek kalınlığında ve reolojik özelliklerde belirgin bir değişiklik görülmemektedir.

İkinci bölümde, nanoparçacıkların bentonit çamurundaki etkilerini daha net görmek için deneyler yapılmıştır. Bu nedenle diğer parametrelerin ortadan kaldırılması için katkı maddesi olarak sadece bentonit kullanılmıştır. Birinci aşamada reolojik artış gözlenmediğinden, bu deneyler önceki testlerden daha yüksek bentonit ve nanoparçacık konsantrasyonlarına sahiptir, ağırlıkça % 7 bentonit ve ağırlıkça % 0.5 ve % 1.5 nanopaçacık. Tüm konsantrasyonlarda ve her boyutta nanoparçacıkların ilavesi ile sıvı kaybı miktarının arttığı görülmüştür. Reolojik analizler, yalnızca 15-20 nm gözenekli nanoparçacıkların, reolojiyi ağırlıkça % 0.5 konsantrasyonunda negatif olarak etkilediğini göstermiştir. Bu deneylere ek olarak Darcy Yasası kullanılarak çamur keklerinin geçirgenliği de karşılaştırılmıştır. Nano sıvıların, baz sıvıya kıyasla daha geçirgen çamur kekleri oluşturduğu sonucuna varılmıştır.

Anahtar Kelimeler: sondaj sıvısı, çamur, nanosıvı, nanosilika, su kaybı

To My Beloved Family

ACKNOWLEDGEMENT

First of all, I would like to express my special thanks of gratitude to my supervisor Prof. Dr. Mustafa Verşan Kök who guided and encouraged me throughout my thesis.

Secondly, I wish to thank my co-advisor Assoc. Prof. Dr. İsmail Hakkı Gücüyener for his continuous guidance, support, patience and valuable advices.

Furthermore, this study could not have been completed without the support and opportunities given by GEOS Energy Inc. I am grateful to GEOS Energy Inc. and its employees for the time and resources they have given for me.

I owe special thanks to my friends in the department Selin Güven Erge, Öner Erge and Tuğçe Özdemir. I appreciate their devotion to this work and their encouragement. They were the ones who cheered me up when I felt down.

I also would like to include special note of thanks to Gökhan Mamak and İnanç Hıdıroğlu who provided me with unfailing support through the process of researching and writing the thesis.

I am also grateful to my family, especially to my father Avni Bal, for their patience and warm support during my studies. Most importantly, Gizem İnci who encouraged and helped me at every stage of my personal and academic life.

Finally, I thank everyone who helped me directly or indirectly during this study.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURES

LIST OF TABLES

TABLES

NOMENCLATURE

AFM	Atomic Force Microscope
API	American Petroleum Institute
CFL	Chrome Free Lignosulfonate
CMC	Carboxymethyl Cellulose
CMC-LV	Carboxymethyl Cellulose Low Viscosity
EDX	Energy Dispersive X-Ray Spectroscopy
HPHT	High Pressure High Temperature
KCL	Potassium Chloride
LPLT	Low Pressure Low Temperature
PAC	Polyanionic Cellulose
PV	Plastic Viscosity (cp)
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
YP	Yield Point (lb/100 ft^2)
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

Since the industrial revolution, non-renewable energy resources are the primary energy supply for the human life in the world. Statistics show that oil is the foremost resource with the highest percentage of 31.3. Contribution of coal and natural gas are respectively 28.6% and 21.2%. On the other hand, renewable energy resources like geothermal, solar, wind, hydro and etc. can only supply the 14.1% of the total primary energy [1].

Demand for energy is increasing day by day, and 30 years later, it is expected to rise 60%. In order to supply this amount of demand, revolutionary inventions and discoveries are needed in science and technology. When developments in alternative energy sources are carefully examined, it is expected that they will not be sufficient to meet the rapidly increasing energy demand. For this reason, it is expected that hydrocarbon fuels will remain the primary energy source in the future as it is today [2].

More drilling operations are required to meet this energy need. Aftab et al. [3] stated that 106,000 hydrocarbon wells should be drilled until 2020. Since conventional hydrocarbon reservoirs are at the depletion stage, drilling new and deeper wells could be the solution of this demand. However, drilling is a challenging operation in itself and with the increasing depth of the well makes it even more challenging.

This challenging operation requires money and time for the oil companies. In order to be able to complete the drilling operation successfully in time, the drilling fluid must be properly selected and designed. Since drilling fluids are the key elements of drilling operations, their rheological properties must be continuously controlled and kept in optimum level so that it could successfully perform its primary task, which is removing the cuttings without damaging the formation [4].

If the drilling fluid does not fulfill its tasks, problems like fluid loss, formation damage, erosion and pipe sticking could occur. These problems lead to time and money loss. Even in some cases, well may be abandoned [5]. Controlling the rheological properties like mud density, plastic viscosity, yield point, apparent viscosity, gel strength and fluid loss of the drilling fluid is one of the effective methods to overcome these problems [6].

Nanotechnology is a revolutionary invention, which could be a solution to such drilling problems. Thanks to their unique physical and chemical properties, nanoparticles are perfect candidates for adjusting the filtration and rheological properties of the drilling fluid [7]. It has begun to be tested in all sectors of the petroleum industry. In particular, researches are being conducted to improve the oil and gas well drilling. It can reduce the cost of the drilling operation by reducing the drilling fluid expense [8]. Moreover, it is more environmentally friendly and efficient compared to current operations. Therefore, it can be vital element for the future energy demand [9]. Nevertheless, there is merely enough number of field applications to adapt this new technology to the entire oil industry, which is difficult and risky [7].

CHAPTER 2

NANOTECHNOLOGY

2.1 Nanotechnology

Nanotechnology is a new trend of technology which deals with very small particles called nanoparticles whose radius are between 1 and 100 nanometers (nm). National Nanotechnology Initiative [10] simply defined nanotechnology as "*science, engineering and technology conducted at the nanoscale*". Another definition is to recreate materials with advanced properties such as electricity, strength, lightweight and thermal conductivity, or to manipulate them at the molecular level. The prefix "nano" indicates one-billionth of a meter. This distance is approximately equal to length of two to twenty atoms standing side by side [8], [11]. In order to visualize the nano size, Figure 2-1 can be used.

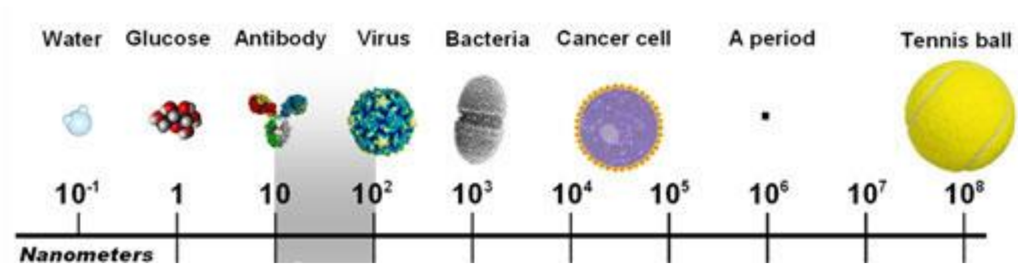

Figure 2-1: The Scale of Things in Nanometers [12]

2.2 History of Nanotechnology

In 1959, during a talk entitled "There is Plenty of Room at the Bottom", concepts and ideas behind the nanotechnology were first introduced by Richard Feynman without mentioning the term "nanotechnology" [13]. In his speech, Nobel laureate Feynman also known as the father of nanotechnology said that a few years later, precise manipulation and control of atoms and molecules would be possible. He added that machines and factories in atomic-scale would even be created [14]. Fifteen years after this speech, nanotechnology term was invented to explain accurate machining of atomic scale materials by Norio Taniguchi, a professor at the University of Tokyo. However, modern nanotechnology was begun with the invention of the scanning tunneling microscope in 1981. Thanks to this breakthrough achieved by Gerd Binnig and Heinrich Rohrer, individual atoms had been seen first time in the history [10].

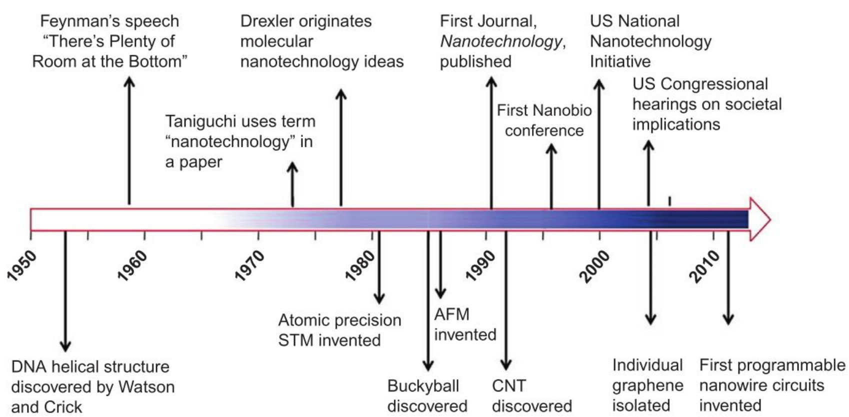

Figure 2-2: A Brief History of Nanotechnology [13]

Since the day when Gerd Binnig and Heinrich Rohrer made a great contribution to science, many studies have been done in nanotechnology. Scientists tried to find ways to produce materials at the nanoscale or reduce their sizes to nanometer. After they achieved their goal, materials have been intentionally produced at the nanoscale to enhance their properties like strength, weight, conductivity, durability and reactivity. Owing to these improved properties, nanotechnology has offered revolutionary innovations in many industries such as medical, food, transportation and energy [15].

2.3 Nanoparticles

Nanoparticles can be defined as particles, whose diameter is between 1 and 100 nm. During or after the production, they could be subjected to great variations in properties such as magnetism, internal pressure, optical absorption, thermal resistance, chemical activity, catalysis and melting point. Therefore, they may show different characteristic properties compared to their bulk material. The reason of this variations is that the periodic boundary conditions are damaged when the particle sizes approach or become less than the wavelengths of the conduction electrons [16].

As seen in Figure 2-3, these small particles have different morphologies like sphere, flake, plate, dendritic structure, tube and rod. Moreover, their structure may become complex three dimensional structure as spring, coil and brush due to manufacturing process [17].

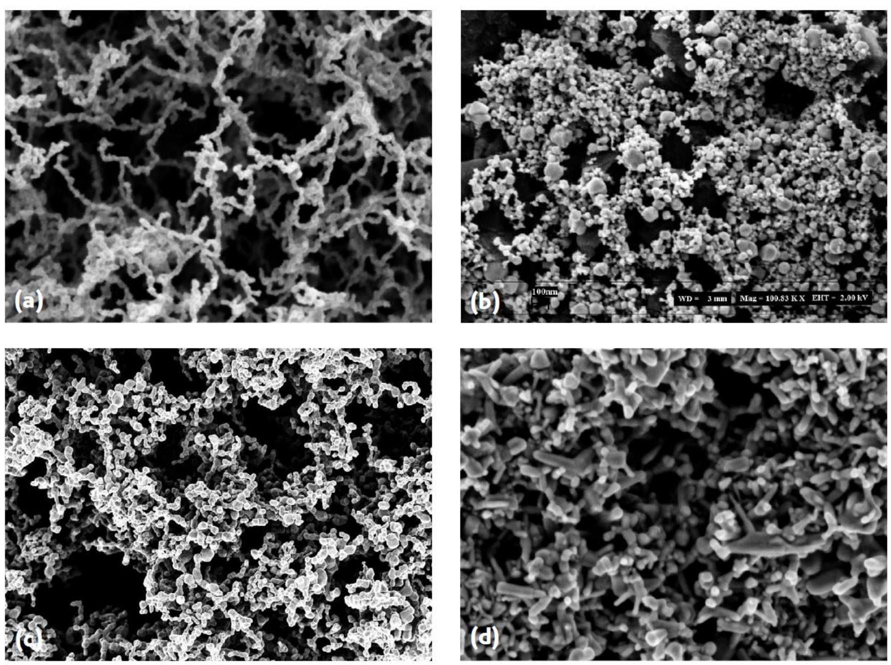

Figure 2-3: Examples of nanopowders with different morphologies: (a) Cobalt ; (b) Copper Oxide; (c) Zinc Oxide; and (d) Silver [17]

There are four different ways to manufacture nanoparticles, which are wet chemical, mechanical, form-in-place and gas-phase synthesis. In the literature, one can come across mechanical process compared to the other methods. For simplicity, this technique can be likened to the flour mills used in the past; coarse particles are converted to finer particles. Nowadays, rotary ball mills are mostly used to obtain nanoparticles with this method. In addition to having advantages such as being easy and cheap, there are disadvantages such as agglomeration of the powders, wide particle size distributions and difficulty in reaching desired sizes. Another disadvantage is the inability to use organic materials. This method is suitable for metals and inorganic materials [17].

The most important feature of these particles is the strikingly higher surface area to volume ratio. As it can be easily understood from the Figure 2-4, the surface area to volume ratio of nanoparticles is approximately 1000 times higher than the micro-sized particles. Besides, this ratio further increases with decreasing size. For instance, a football field can be squeezed within a raindrop with the interfacial area of the nanosilicates. Hence, thanks to their high surface area property, it is expected that very small quantities of nanoparticles will have a great effect on the fluid properties [17]–[19].

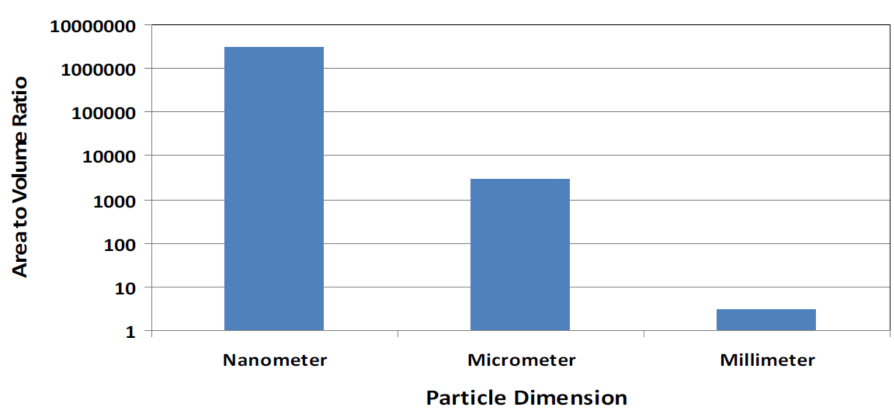

Figure 2-4: Surface Area to Volume Ratio of Same Volume of Materials [20]

As particle sizes decrease, not only the surface area but also the number of particles increase (Figure 2-5). For example, if 2 gr of spherical aluminum nanoparticles with diameter of 100 nm is taken into consideration, this amount has the number of particles equal to 300,000 times of human population on the earth [17].

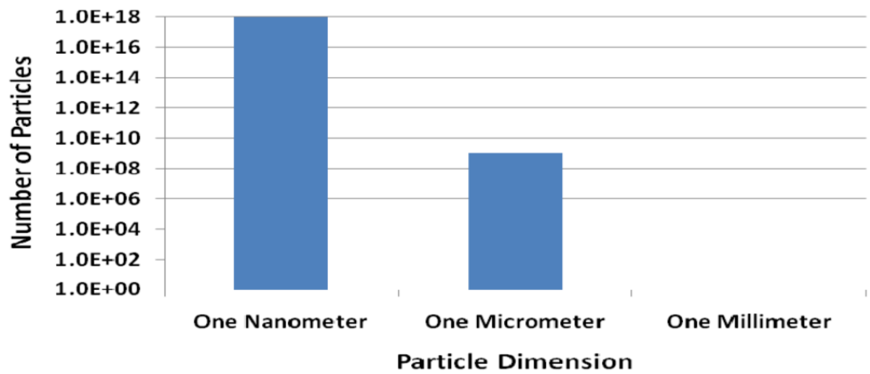

Figure 2-5: Nano and Micro Sized Spherical Particles Obtainable from a one mm Macro Sphere [20]

2.4 Nanotechnology Applications in Oil and Gas Industry

Nanotechnology has been studied by the whole oil and gas industry from exploration to drilling, completion, production, reservoir and refinery.

In 2006, Krishnamoori [21] came up with an idea that owing to the unique optical, magnetic and electrical properties of nanomaterials compared to their bulk materials, they can be used to develop new imaging sensors to explore hydrocarbons. Considering the nanoscale metals used to locate ore deposits for geochemical exploration, this idea can be implemented into the field operations [16].

In addition, by taking advantage of advanced features of nanoparticles, weight of the marine platforms can be reduced, durability can be increased, and lightweight structural materials can be produced. Not only structural materials, but also drilling equipment such as bits, drill pipes and casings can benefit from this technology [21]. For example, Chakraborty et al. [22] studied on functionalization of nanodiamond to increase the performance of polycrystalline diamond compact (PDC) bits. Furthermore, Zhang et al. [23] has achieved to increase the strength of conventional aluminum from 400 MPa to

1000 MPa and they proved that this material could be used in hydraulic fracturing operations as frac balls.

Studies also revealed that this technology could be useful for enhancing the cement properties and reduce the cost of the cement operations [24]–[26]. Results of the research carried out by Maserati et al [26] present that, nano-emulsions exhibit better performance than common ones as cement spacer. Additionally, in order to reinforce the cement, carbon nanotubes (CNT) are in the scope of investigations [25].

Lastly, nanoparticles have also proved themselves in enhanced oil recovery, especially thermal applications. Bera and Belhaj [27] stated that owing to enhanced heat capacity of nano metal oxides, they can be used in thermal heavy oil recovery applications such as steam assisted gravity drainage (SAGD), cyclic steam injection, electromagnetic heating and steam flooding. In 2015, Farooqui et al. [28] who set out the thought of heat capacity, tested metal oxide nanoparticles in cyclic steam injection. Nanoparticles improved the recovery factor by 10%.

2.4.1 Nanotechnology Applications in Drilling Fluids

There are many challenges that may be faced during drilling and production operations. Companies are concentrating on finding ways to prevent these problems rather than treat them. The reason behind this idea is the increasing expenses of drilling and production operations while decreasing the production rate. These challenges mainly caused by increasing depth which leads to harsh physical, chemical and thermal conditions and it is becoming harder to overcome these challenges due to strict environmental regulations. According to Amanullah and Al-Tahini [20], drilling fluids that contain conventional micro and macro sized additives, sometimes cannot carry out their tasks at deeper sections. With the increasing depth, physical and chemical characteristics of additives can be altered. Due to this reason, petroleum industry is searching new materials that can handle these conditions. Nanoparticles are the most promising materials for these type of conditions because of their unique characteristic properties. When they are compared with their parent materials, their chemical and thermal properties are more stable. Additionally, they are mechanically strong and environmentally degradable [20].

Nanoparticles could also be the solution of drilling problems like swelling and fluid loss. They can be used to plug the pores of shale formations physically. Since the permeability of shale formations are nanodarcy (nd), these sections prevent the formation of mud cakes and this result in increased fluid loss. An increase in fluid loss is an undesirable condition for shale formations. It leads to shale swelling and triggers wellbore instability problems [29].

There are many studies in the literature that can solve these problems and most studies are focused on drilling fluids compared to other upstream operations. These studies aim to improve the rheological properties of the drilling fluid, develop high temperature and high pressure resistant drilling fluid, reduce torque and drag, maintain wellbore stability and remove harmful gases such as hydrogen sulphide.

Drilling fluids prepared with nanoparticles are called "nanofluids" and A. I. El-diasty and A. M. S. Ragab [18] defined them for oil and gas industry as " *any fluid used in the exploration and exploitation of oil and gas that contain at least one additive with particle size in the range of 1-100 nanometers* ". They obtained by adding nano sized particles in low volumetric fractions into any liquid such as oil, water or conventional fluid mixtures. These nanofluids should not harm the environment and should be compatible with reservoir fluids. Nanoparticles, which are used to improve the properties of such fluids, have to be homogeneously mixed preventing agglomeration in the liquid [8].

Nanofluids can be both oil-based and water-based. However, oil-based drilling fluids are less preferred compared to water-based drilling fluids because they are expensive and cannot be used in all fields due to environmental regulations. For this reason, it is seen that the studies concentrate on water-based drilling fluids intensively.

Sayyadnejad et al. [30] reported one of the earliest research on nanofluids and in their study, hydrogen sulfide removal performance of nano sized zinc oxide and bulk zinc oxide were tested. Three different sizes of nanoparticles (14, 15, 25 nm) were synthesized from bulk zinc oxide by spray pyrolysis method and characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscope (AFM) and transmission electron microscope (TEM). Experimental results showed that all of the three nano-sized zinc oxide removed the hydrogen sulfide from water-based mud in 15 minutes completely. On the other hand, bulk zinc oxide removed 2.5% of total hydrogen sulfide in 90 minutes. Also, they have found out that nanoparticles with size of 14 nm showed better performance compared with others.

Pipe sticking is another undesirable problem that can occur during drilling operations. In order to find a solution to this problem, Paiaman and Al-anazi [31] studied the effects of carbon black nanoparticles on the mud cake thickness. These experiments revealed that carbon black nanoparticles reduced the mud cake thickness by 25%. Furthermore, increase in temperature continued to decrease the thickness of the mud cake. Besides, reduction in viscosity and yield point was observed.

The fact that shale formations have nanoscale pore sizes causes nanoparticles to be tested in drilling muds used in these formations. Since fluid losses in these formations lead to stability problems, the use of oil-based drilling fluids is more common. However, water-based drilling fluids that contain fluid loss additive are a better choice because oil-based drilling muds are expensive and they may pollute the environment. Sharma et al. [32] tried to solve this problem by using 20 nm silica nanoparticles in water-based drilling fluid. They tested the rheology and stability of the nanofluids and concluded that nanofluids are stable at high temperature and pressure. Moreover, fluid invasion was reduced by 10 to 100 times, which will minimize wellbore instability.

In the research of Aftab et al. [6], KCL mud was prepared with various nanoparticles (graphene nanoplatelet, silica nanoparticles and multi-walled carbon nanotubes) to examine the shale swelling and rheological enhancement. Linear swell meter was used to determine shale swelling. It was concluded that base mud increased the volume of shale 30%. An addition of 0.1 ppb multi-walled carbon nanotube and silica nanoparticles to the base mud could not effect positively and increased the volume of shale 32% and 33% respectively. On the other hand, graphene nanoplatelet revealed the best results. They achieved to change the volume of shale only 10%. Moreover, it improved the rheological properties more than other nanoparticles.

When literature is examined, one can clearly see that number of studies on fluid loss are more than other drilling problems mentioned above. In some of the studies, the researchers compared the fluid loss properties of the same materials in micro and nano dimensions. In order to achieve this, they have used a “Milling Machine” which can reduce the fluid loss additives to the desired dimensions mechanically. Since particle size varies according to the milling time and milling rate, dimensions of the particles obtained by this method need to be measured. As already understood from the experiments in the literature that the desired particle sizes have been obtained by trial and error method. The dimensions of the obtained nanoparticles were measured with the help of Scanning Electron Microscope or Particle Size Analyzer.

In 2011, Manea [33] grinded Xanthan Gum into nanoscale and compared to its original state. It was reported that since the area of the polymer increased, swelling capacity of polymer was also increased and especially in alkali medium, it enhanced the rheology and reduced the filtrate volume of the drilling fluid.

Saboori et al. [34] compared the fluid loss and mud cake thickness of two different water-based drilling fluids prepared with conventional CMC and CMC nanoparticles. CMC nanoparticles were produced by ball milling method at 500 rpm rotational velocity for approximately 1 hr to 1.5 hr. They measured average particle size of the CMC powder and CMC nanoparticles as 4.66 μm and 47 nm respectively by particle size analyzer. After filtration experiment was done by API filter press, they concluded that fluid loss and mud cake thickness decreased by the help of the CMC nanoparticles.

Fereydouni et al. [35] performed the same experiment using the same procedure for the same purpose. The only difference was the fluid loss additive. Instead of CMC, polyanionic cellulose (PAC) was used. They applied same method, ball milling, to obtain nano-sized PAC but at 400 rpm for 2 - 2.5 hours. It was observed that nanoparticles achieved to reduce fluid loss and mud cake thickness at all concentrations.

Abdo and Haneef [36] tested a new material called clay ATR. Mechanical milling method was used to reduce the size of ATR (fine grinded, $\leq 63\mu$, $\leq 21\mu$ and 30 nm) and bentonite (fine grinded, $\leq 63\mu$). 16 samples were prepared for different objectives to find an answer to these questions; effect of the size of ATR on rheology, effect of size of bentonite on rheology and best concentration for ATR nanoparticles in water-based mud prepared with regular bentonite. As a result of this detailed study, they have found out that ATR nanoparticle showed an improvement of 200% in gel strength. On the contrary, micro sized ATR did not affect rheology significantly. Unlike ATR, PV and YP of the sample decreased with the decreasing size of bentonite. Lastly, it was proven that 4 gr of nano-sized ATR is the best amount for least fluid loss when it is mixed with 40 gr regular bentonite.

Abdou et al. [37] made a comparison between bentonite and nano bentonite. Conventional bentonite was grinded to obtain nano bentonite whose size is ranging between 4 to 9 nm. Rheological and filtration properties were investigated and concluded that at nano-scale, bentonite does not exhibit desired characteristics. It did not affect the gel strength and slightly changed the PV and YP. Besides, it could not reduce the fluid loss below the acceptable amount specified by API.

Zoveidavianpoor & Samsuri [38] reduced the dimensions of starch to nano sizes like other researchers. Fluid loss and mud cake thickness comparison of micro and nano-sized starch was done for three different sizes (64μ, 7μ and 920 nm) and five different concentrations (0.5%, 1%, 1.5%, 2% and 2.5%). Best results were obtained from the sample containing 2.5% of nano starch. Reduction in fluid loss and decrease in mud cake thickness were 64.2% and 80.9% respectively at this concentration. Besides, improvement in fluid loss, viscosity, yield point and gel strengths was observed not only for LPLT conditions but also HPHT conditions.

In other studies, different sizes of purchased nanoparticles were compared with conventional fluid loss additives. Nanosilicon wires, silica nanoparticles, multi-walled carbon nanotubes, allumina nanoparticles, iron oxide nanoparticles are some of them.

In the research of Nasser et al. [39], rheological properties of water-based drilling fluids were investigated at different pressures and temperatures. Mixture of nanosilicon wires and graphite nanoparticles with the size of 40 nm and purity of 99.9% were used in this study. Density, viscosity, filtrate loss and mud friction experiments were performed to make comparison between nanofluid and base fluid. They concluded from the results that nanoparticles enhance the rheological properties. In other words, it decreased the filter loss, increased the viscosity and decreased the roughness of mud cake.

Ragab and Noah [40] conducted experiments by using potassium chloride (KCl) muds which contain conventional PAC and three different nano-sized (5-15 nm, 10-25 nm, 70-95 nm) SiO_2 to determine the optimum size and concentration for minimum fluid loss. Scanning Electron Microscope (SEM) was used to ensure the sizes and the composition of nanoparticles were verified by Energy Dispersive X-Ray spectroscopy (EDX). Firstly, they found out that mud which contains 5-15 nm SiO_2 yielded minimum fluid loss compared to conventional PAC and other nano-sized SiO_2. After finding the optimum size, the experiments were repeated by changing the concentration of the SiO_2. Between the various of concentrations, they discovered that the range between 20% - 30% wt./vol. is the most economic and effective concentration which reduced fluid loss by 47.52% - 49.01% respectively compared to PAC.

In 2016, Ragab [41] repeated his study for the same purposes. He reduced dimensions of micro-sized SiO_2 particles to nano size by milling machine. Four different concentrations (0.14 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt%) were designated for nanoparticles and compared with base mud and conventional PAC. It was found that the sample containing 0.5% of SiO_2 is most efficient with a reduction of 45% in fluid loss. In the second part of the study, bentonite added to the base mud and named as a control group. Two more samples were prepared with PAC and 0.7% SiO_2 and static filtration experiments revealed that amount of the fluid loss decreased by 20% and 44% respectively.

Ismail et al. [42] tested not only SiO_2 nanoparticles but also multi-walled carbon nanotube (MWCNT) in KCL mud at very low concentrations (0.001 ppb, 0.002 ppb, 0.01 ppb etc.). Both nanoparticles achieved to reduce the fluid loss and improved the rheology of samples.

Li et al. [43] tested SiO_2 nanoparticles in salt (KCL) treated bentonite mud in different concentrations (0.1, 0.2, 0.3 and 0.4 ppb). Like previous studies, they concluded that nanoparticles improved the rheological properties of mud and reduced the fluid loss. Additionally, significant reduction in mud cake thickness was observed.

Belayneh et al. [44] also studied salt (KCL) treated bentonite mud to investigate the effect of SiO_2 nanoparticles. They have found similar results with other researches. Nanoparticles succeeded to lower the filtration volume with the increasing concentration.

Anyanwu & Unubi [45] conducted a series of experiments to investigate the effect of particle size of mica and alumina nanoparticles on filtrate loss. In order to make a comparison between the fluid loss additives, they prepared four different muds: base mud, base mud with 60 microns mica, base mud with 40 microns mica and base mud with alumina nanoparticles. Experimental results revealed that fine mica particles decreased the fluid loss. On the other hand, alumina nanoparticles produced a mud cake with a smaler permeability and effective sealing ability compared to other muds. Based on results from API filtration experiments, amount of the fluid loses of the muds were respectively 23 ml, 20 ml, 17 ml and 13 ml. In other words, alumina nanoparticles reduced the filtration loss approximately 43%..

In the research of Javeri et al. [46], improvement of rheological properties could not be achieved by using SiO_2 nanoparticles with a size distribution of 40 – 130 nm. But, addition of 3% by volume of nanoparticles to sample reduced mud cake thickness by 34%.

Zubaidi et al. [47] tested MgO, TiO_2 and graphene nanoparticles in bentonite mud at very low concentrations (0.005, 0.01, 0.05, 0.1, 0.2 and 0.4 wt. %). It was concluded that MgO nanoparticles achieved to reduce fluid loss 35%.

Some nanoparticles have also proved themselves HPHT conditions. Unlike conventional additives, these nanoparticles can preserve their structure under these harsh environments.

Graphene oxide was experimented by Kosinkin et al. [48] to observe the fluid loss characteristics at HPHT conditions. They concluded that GO is suitable candidate for filtration control. Favorable results were got from both LPLT and HPHT experiments. Besides, shear-thinning behavior of graphene oxide was proved.

In the research of Jung et al. [49], it has been found that nanoparticles do not always have positive effects on fluid loss, and even sometimes, they have adverse effects. They investigated rheological properties of bentonite muds containing iron oxide nanoparticles at LPLT. Five weight percentage bentonite mud was selected as a control group and two different sizes of iron oxide nanoparticles, 3 nm and 30 nm, were added to bentonite mud. It has been observed that viscosity and yield stress increased with the increasing concentration of the iron oxide nanoparticles. However, this was not the case for the fluid loss. Only one of the four muds prepared with nanoparticles was able to reduce the volume of filtration. The increase in nanoparticle concentration showed a negative impact on water loss.

Barry and Lee [50] conducted the same experiment for iron oxide nanoparticles both at LPLT and HPHT conditions. They have revealed that iron oxide nanoparticles showed an adverse effect at LPLT. Unlike the LPLT conditions, it decreased filtrate volume about 28% at HPHT conditions.

Iron oxide nanoparticle was also investigated by Vryzas et al. [4]. Within the scope of this research, rheological properties of water-based drilling fluids containing iron oxide and silica nanoparticles were tested. Experiments were conducted not only at LPLT conditions but also at HPHT conditions. Three different composition (0.5, 1.5 and 2.5 wt.%) of each nanoparticle were added to bentonite mud separately and like the other studies bentonite mud selected as a control group. According to the results, iron oxide nanoparticles remarkably improved the fluid loss and filter cake quality on both API filter press and HPHT filter press. Moreover, it increased yield strength and gel strength with increasing concentration of nanoparticles. Conversely, silica nanoparticles could not decrease the mud cake permeability. It adversely affected the fluid loss and made negligible changes on drilling fluid rheology.

In 2016, Mahmoud et al. [51] also studied on iron oxide and silica nanoparticles for the same goal. They obtained similar results with Vryzas et al. [4]. Additionally, they have discovered that increasing nanoparticle concentration or using silica nanoparticles increases agglomeration, which results in permeable filter cake.

CHAPTER 3

STATEMENT OF THE PROBLEM

The main key of a successful drilling operation is the proper selection of the drilling fluid and regular monitoring and controlling of its rheological and filtration properties. This is the most general solution to avoid drilling problems such as pipe sticking, formation damage, borehole instability and poor hole cleaning.

The aim of this study is to investigate the effects of the nanoparticles on the performance of the water-based drilling fluids. For this purpose, four different silica nanoparticles are added into the lignosulfonate and bentonite muds to obtain nanofluids. Rheological and filtration properties of the nanofluids are analyzed and compared with the base fluids.

CHAPTER 4

EXPERIMENTAL SET-UP AND PROCEDURE

4.1 Sample Preparation

Within the scope of this research, two different experimental groups were tested. Bentonite, sodium hydroxide, Carboxymethyl Cellulose Low Viscosity (CMC-LV) and Chrome Free Lignosulfonate (CFL) were used to prepare the drilling fluid samples. These additives were provided by GEOS Energy Inc. Nanoparticles were purchased from NANOGRAFI Co. Ltd. Specifications of nanoparticles can be found in the APPENDIX A.

4.1.1 Experimental Group 1

The first group experiments consisted of base fluids (BF) prepared with different combinations of bentonite, CMC and CFL. Before adding other additives and nanoparticles, water-bentonite mixture was held at room temperature for 16 hours for hydration of bentonite. After that, 0.5 ppb of four different silica nanoparticles were added into the base fluids. In total 16 nanofluids (NF) were prepared and compared with the base fluids. Detailed information can be found in the following Table 4-1 and Table 4-2.

In order to simulate field conditions, instead of preparing samples separately, they were prepared as a batch. For instance, for Batch 4, 1750 cc water was poured in a container and 100 grams of bentonite was added to water slowly while mixing with FANN

Dispersator (High shear mixer) [52]. After the hydration of bentonite, 5 grams of CMC and 5 grams of CFL were added respectively. Then, sodium hydroxide in aqueous solution 25% was used to adjust the pH to 9.5. When the mixture becomes homogenous, 5 samples of 350 cc were placed in the mixer cups by the help of the graduated cylinder. Finally, nanoparticles were added to the samples and mixed.

The weights of the additives to be used to prepare the samples were measured with Precisa Balance Model 321LX [53]. Then, they were added slowly and sequentially with the aim of preventing agglomeration. The samples were stirred for 5 minutes after each additive. When the nanoparticles were added, they were mixed for a further 10 minutes. All the prepared samples were mixed in equal time.

After the prepared samples became homogenous, they were placed in FANN Aging Cells and placed in FANN Roller Oven Model 704ET [54], [55]. Roller oven was adjusted to 140 °F and samples were left there for four hours.

The samples taken from the roller were kept at room temperature for cooling. They were mixed with the help of multimixer and rheological measurements were performed at two different temperatures (77 ºF and 120 ºF). After the rheological measurements were completed, the samples were mixed again and the API Fluid Loss measurements were performed at both temperatures. The thickness of the mud cakes obtained from both experiments was measured.

Table 4-1: Compositions of Group 1 Base Fluids

Sample	BF-1	BF-2	BF-3	BF-4
Water, cc	350	350	350	350
Bentonite, ppb	20	20	20	20
CFL, ppb		1		1
CMC, ppb			1	1

Table 4-2: Composition of Experimental Group 1 Nanofluids

	Batch 1				Batch 2				Batch 3				Batch 4			
	NF-1	NF-2	NF-3	NF-4	NF-5	NF-6	NF-7	NF-8	NF-9	NF-10	NF-11	NF-12	NF-13	NF-14	NF-15	NF-16
Water, cc	350	350	350	350	350	350	350	350	350	350	350	350	350	350	350	350
Bentonite, ppb	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
CFL, ppb					1	1	1	1					1	1	1	1
CMC, ppb									1	1	1	1	1	1	1	1
SiO_2 15-20 nm porous, ppb	0.5				0.5				0.5				0.5			
SiO_2 15-20 nm nonporous, ppb		0.5				0.5				0.5				0.5		
SiO_2 20-30 nm, ppb			0.5				0.5				0.5				0.5	
SiO_2 60-70 nm, ppb				0.5				0.5				0.5				0.5

4.1.2 Experimental Group 2

For this section, base mud was prepared using only bentonite and 350 ml deionized water. Sodium hydroxide was not used because prepared water-bentonite mixture had a pH of 9.5. Unlike previous experiments, samples were prepared one by one and bentonite was allowed to hydrate after the nanoparticles were added. It was kept at room temperature for 16 hours and then experiments were conducted.

In total nine samples were prepared. Concentration of bentonite was selected as 7.0% (w/w). Four different nanoparticles were used at two different concentrations (0.5 and 1.5% by weight). During preparation, samples were mixed 20 minutes in total. Moreover, in order to obtain homogeneous samples and accurate results, they were also mixed for five minutes before each experiments.

Table 4-3: Composition of Experimental Group 2 Base Fluid and Nanofluids

Concentration of Bentonite, % (w/w)	Concentration of Nanoparticles, % (w/w)	Weight of bentonite, gr	Weight of Nanoparticle, gr
7.0	0.0	26.344	0.000
7.0	0.5	26.486	1.892
7.0	1.5	26.776	5.738

None of the samples was placed in a roller oven for aging. The rheological measurement carried out at three different temperatures (77 ºF, 104 ºF and 140 ºF). On the other hand, fluid loss experiments were performed only at 77 ºF.

Apart from these, experiments were conducted with the aim of comparing the permeability of the mud cakes. As in previous experiments, the mud cake thickness were measured. In order to obtain accurate results, measurements were taken from five different places of the mud cake.

After the water loss experiments were finished, the mud in the chamber was drained and replaced with deionized water. The water loss experiment was repeated with the same procedures and the water loss was measured. Using these obtained data and using the

Darcy's Law, permeability of the mud cakes were compared. Calculations was conducted by the following formula [56].

$$Q = \frac{kA\Delta P}{\mu L} \tag{5.1}$$

where;

Q: Flow rate, cm^3/s

k: Permeability, darcy

μ: Viscosity, cp

A: Area, cm^2

ΔP: Pressure, atm

L: Length, cm

Darcy's Law can be written as:

$$k = \frac{Q\ \mu\ L}{A\Delta P} \tag{5.2}$$

Since, viscosity of the water, area and pressure are same for all experiments, permeability ratio of two samples becomes as follows:

$$\frac{k_1}{k_2} = \frac{Q_1\ L_1}{Q_2 L_2} \tag{5.3}$$

Permeability ratio of two mud cakes can be obtained by Placing water loss values and mud cake thicknesses into the equation shown above.

4.2 Mud Additives

Bentonite, CMC, CFL and caustic soda were used as mud additives for different purposes.

4.2.1 Bentonite

Bentonite is the main additive constituting the composition of fresh water-based muds and controls the fluid loss and flow properties of the mud. The presence of sufficient and certain quantities bentonite in the system is a prerequisite for the creation of a thin, durable and impermeable cake. These cake properties are important because of the differential sticking and formation contamination. The effect of the bentonite is reduced at concentrations greater than 10,000 mg/L Cl-ion and 240 mg/L higher Ca^{+2} ion concentrations [57].

Bentonite can be classified as calcium bentonite and sodium bentonite. Since calcium bentonite does not have swelling ability, sodium bentonite is being preferred more [58]. Thanks to its swelling ability, sodium bentonite is used in this study.

4.2.2 Chrome Free Lignosulfonate (CFL)

CFL is an organic origin additive and it is successfully used in all fresh water-based muds. Moreover, it has a secondary function, which helps to control fluid loss. General dosage of 0.5 - 4 lb/bbl gives maximum effect if the pH is 9 - 10. The efficiency of the CFL begins to decrease as the wellbore temperature approaches 350 ºF. When added to the system, it causes the pH to drop [57].

4.2.3 Carboxymethyl Cellulose Low Viscosity (CMC-LV)

CMC-LV is a fluid loss control material used to provide a further reduction in fluid loss as well as bentonite in fresh water-based mud. CMC is an anionic polymer based on cellulose, the general dosage is 1-3 lb/bbl. The fluid loss control ability of CMC will be decreased if the salt concentration of the environment is higher than 50,000 ppm and the wellbore temperature reaches 300 ºF. Furthermore, the Cl^{-} concentration in excess of 30,000 mg/L and the high concentration of Ca^{+2} at 500 mg/L negatively affects the CMC [57].

4.2.4 Caustic Soda (NaOH)

Sodium hydroxide is used to adjust the pH of water-based drilling fluids [57].

4.3 Analysis of Mud Properties

With the aim of investigating the effects of nanoparticles on drilling fluids, physical and chemical analysis are performed. The procedures of the experiments mentioned in the sample preparation section are described in detail in this section.

4.3.1 Physical Analysis

In this study, in order to test the physical properties of mud, density measurement, viscosity, gel strengths (10 sec. and 10 min) and filtration experiments were conducted.

4.3.1.1 Density Measurement (Mud Weight)

For this experiment, FANN Model 140 Mud Balance was used to measure mass of a given volume of liquid. It was designed to determine the density of drilling fluid in four different units accurately by moving the counterweight along the graduated scale. In this study, unit of measure is selected as lbs/cuft [59].

Procedure of determining mud weight is as follows [59]:

1. Clean and dry the mud balance cup before pouring the sample.
2. Place the carrying case on a flat surface.
3. Pour the sample into the balance cup and tap the sides to rid trapped air.
4. Close the lid onto the balance cup and make sure that it seats firmly. Some sample should be expelled from the vent hole to free the trapped air.
5. Wipe the expelled sample from the outside of the balance cup.
6. Place the mud balance onto the carrying case and move the counter balance until the equipment is levelled.
7. Read the density and report it to the nearest 0.01 g/cm^3, 0.5 lbs/cuft or 0.1 lbs/gal.

4.3.1.2 Rheological Analysis

Evaluation of rheological analysis consists of three measurements called plastic viscosity (PV), yield point (YP) and gel strengths. Experiment is conducted by using FANN Model 35SA Viscometer that measures the shear stress caused by shear rate at six different speeds ranges from 3 rpm to 600 rpm. *"Viscometer measurements are made then outer cylinder, rotating at a known velocity, causes a viscous drag exerted by fluid. This drag creates a torque on the bob, which transmitted to a precision spring where its deflection is measured."*[60]

Procedure of determining plastic viscosity, yield point and gel strengths is as follows [60]:

1. Pour the sample into the Thermocup. (OFITE Thermocup is used for this study. [61])
2. Turn the heater and heat the sample to the desired test temperature.
3. Check the temperature of the sample.
4. Run the viscometer at 600 rpm. Record the reading when the dial reading is steady. (θ_{600})
5. Run the viscometer at 300 rpm. Record the reading when the dial reading is steady. (θ_{300})
6. For the rheological analysis, repeat the step 4 for 200 rpm, 100 rpm, 6 rpm and 3 rpm.
7. Rerun the viscometer at 600 rpm for 10 seconds and turn the motor to the OFF position for 10 seconds.
8. Operate the viscometer at 3 rpm and record the maximum dial reading as the 10-seconds gel strength.
9. Run the viscometer at 600 rpm for 10 seconds and turn the motor to the OFF position for 10 minutes.

10. Operate the viscometer at 3 rpm and record the maximum dial reading as the 10-minutes gel strength.

Necessary calculations for plastic viscosity (PV), yield point (YP) and gel strengths are listed below [60]:

$$PV\ (cp) = \theta_{600} - \theta_{300} \tag{5.2}$$

$$YP\ (lb/100ft^2) = \theta_{300} - PV \tag{5.3}$$

$$10\ sec.\,Gel\ Strength\ (lb/100ft^2) = Max.\,dial\ reading\ at\ 3\ rpm \tag{5.4}$$

$$10\ min.\,Gel\ Strength\ (lb/100ft^2) = Max.\,dial\ reading\ at\ 3\ rpm \tag{5.5}$$

4.3.1.3 Filtration

In order to measure the fluid loss and wall-building properties of the prepared drilling fluid samples, OFITE Low Pressure Low Temperature (LPLT) 6 Unit Filter Press is used for this study. Experiment is carried out according to American Petroleum Institute (API) standards, 100 psi and 30 minutes. As it is done in this study, proper 9 cm filter paper like Whatman No. 50, S & S No.576 (or equivalent) must be used for consistent results [62].

Following steps are performed for determining filtration and mud cake thickness [62]:

1. Assemble the parts starting with base cap, screen, filter paper, gasket and cell respectively.

2. Pour the sample into the assembled cell body until the empty space between sample and cell top is 0.5" or 13 mm.

3. Place the assembled cell body to the frame and close the top cap before securing the cell with the T-screw.

4. To measure the filtrate volume, place a dry and clean graduated cylinder under the filtrate tube which is located at the bottom of the test cell.

5. Close all the valves.

6. Adjust the pressure 100 ± 5 psi from pressure source and start the experiment by opening the valve which is above the cell.

7. 30 minutes after the experiment start, measure and record the volume of filtrate to the nearest 0.1 ml.

8. Close the pressure source valve and release the pressure by opening the bleeder valve.

9. Open the T-screw and take the cell body out from frame.

10. Discard the drilling fluid sample and save the mud cake carefully.

11. Clean the excess mud from the mud cake by water.

12. Measure the thickness of the mud cake and record it to the nearest 1/32" or 0.8 mm.

13. Observe the wall-building properties of mud cake such as firmness, softness, toughness etc.

4.3.2 Chemical Analysis

In this part of the study, hydrogen ion concentration was measured.

4.3.2.1 Hydrogen Ion Concentration (pH)

Two different methods, colorimetric and electrometric, can be used to measure the pH value of the drilling fluid. pH strips are used for the colorimetric method and glass electrode is used for electrometric method [63].

Since the glass electrode is more reliable than the pH strips, electrometric method is preferred for this study. Tests are done by using OACTON EcoTestr pH 2 Waterproof Pocket Tester which has a accuracy of 0.1 [64].

Measurement steps for determining the pH value is given below [64]:

1. Make sure the pH meter is calibrated.

2. Dip the pH meter into the drilling fluid sample at least 20 mm and stir it one.

3. Read and note the pH value on the device when the value is stabilized.

CHAPTER 5

RESULTS AND DISCUSSION

This section presents the results of the experiments conducted within the scope of this thesis. Experiments were carried out in accordance with the procedures as described in Chapter 4 to obtain accurate results. Detailed results can be found in APPENDIX B and APPENDIX C.

5.1 Analysis of Silica Nanoparticles Effects on Mud Properties

Four different silica nanoparticles with average sizes of 15-20 nm porous, 15-20 nm nonporous, 20-30 nm and 60-70 nm were tested for both experimental groups in different water-based muds. The physical and chemical analysis of the samples were done and the results were examined.

5.1.1 Results of the Experimental Group 1

Experimental group 1 consists of 16 nanofluids and 4 base fluids. Results are presented below.

5.1.1.1 Effects of Nanoparticles on the Rheological Properties

In this section, FANN Model 35SA 6 speed Viscometer was used to calculate plastic viscosity (PV), yield point (YP) and 10 sec/10 min gel strengths of the samples at 77 ºF and 120 ºF.

As seen in Figure 5-1 and Figure 5-2, nanoparticles have not been able to change significantly the rheology of any lignosulfonate and bentonite muds. In other words, change in PV and YP values are negligible. Because of this reason, some of the graphs have only one line. Moreover, all of the nanoparticles exhibited same rheology. It can be concluded from the test results that unlike the KCL muds mentioned in the literature [40], [41], [43], [44], nanoparticles could not affect the rheology of lignosulfonate and bentonite muds at very low concentrations.

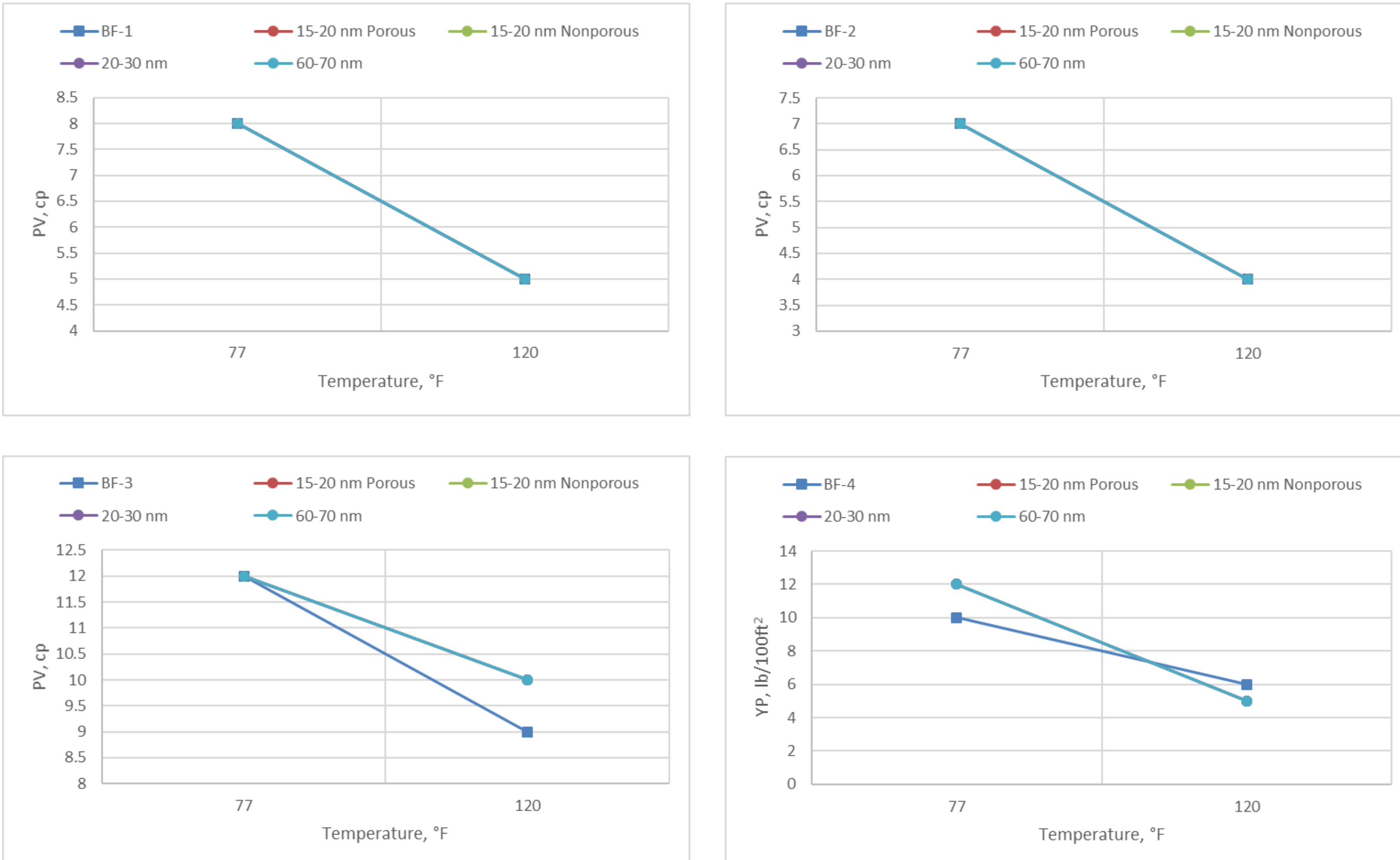

Figure 5-1: Plastic Viscosity Values of All Base Fluids and Nanofluids

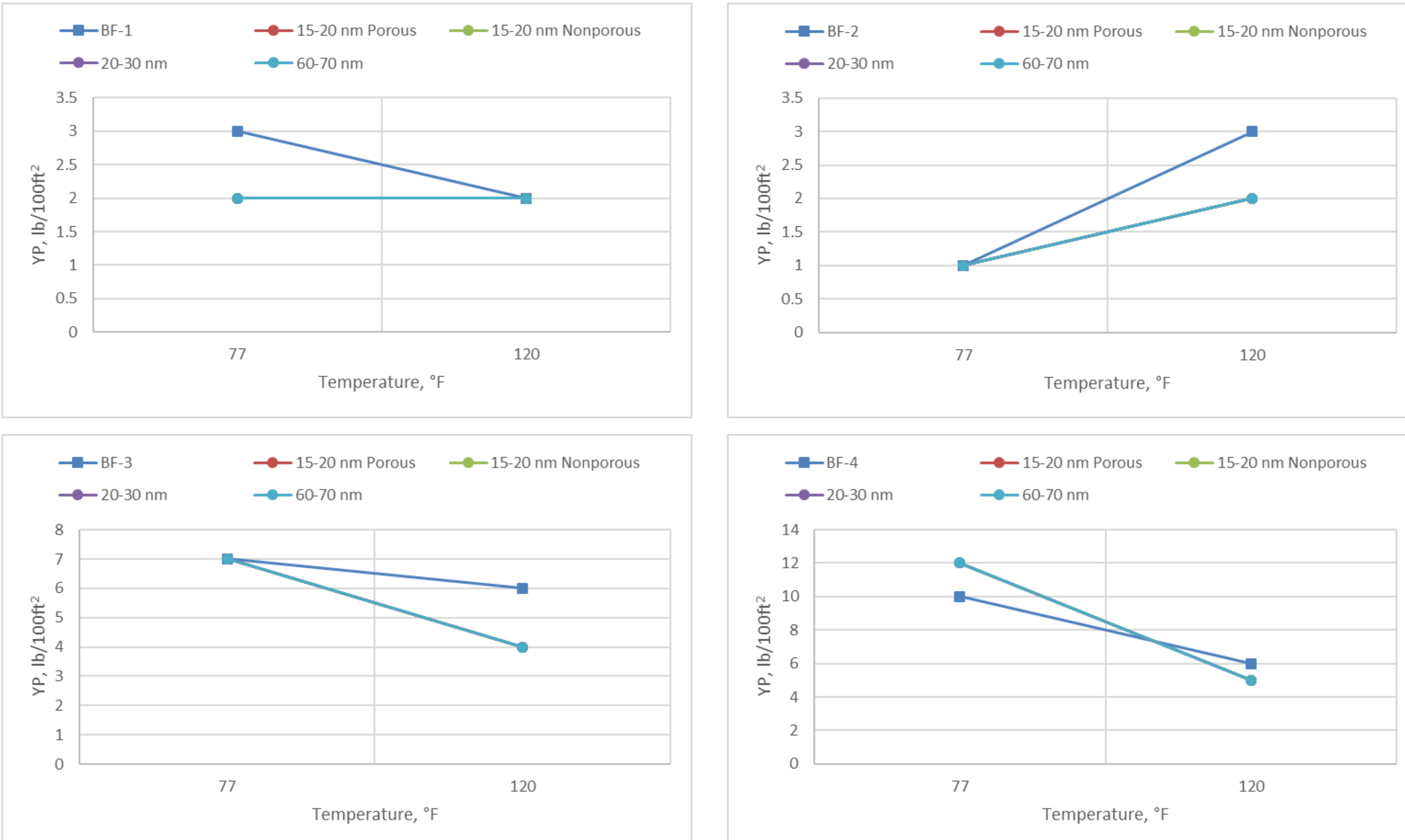

Figure 5-2: Yield Point Values of All Base Fluids and Nanofluids

5.1.1.2 Effects of Nanoparticles on the Filtration Properties

OFITE API Filter Press was operated at 100 psi to conduct fluid loss experiments. Measurements were done in two different temperature (77 ºF and 120 ºF) to see temperature effect. In order to perform the tests at 120 ºF, experiments were initiated immediately after samples were removed from the roller oven.

5.1.1.2.1 Fluid Loss

After examining the test results, it was observed that nanoparticles increased fluid losses of some base fluids. As seen in Figure 6-1 and Figure 6-3, all of the nanoparticles showed an adverse effect at both temperature in bentonite muds. On the other hand, a decrease in fluid loss was observed, especially at 77 ºF, with the addition of nanoparticles of 20-30 nm and 60-70 nm sizes to water-based drilling fluids containing CFL (Figure 6-2 and Figure 6-4). Moreover, when 15-20 nonporous, 20-30 nm and 60-70 nm nanoparticles were added into BF-4, reduction in fluid loss was observed at 77 ºF and 120 ºF. However, since there is no consistent trend for the reduction and it is not significant, solid conclusion cannot be drawn from these results. This may be caused by the lignosulfonate, which is a strong deflocculant and saturates the positive charges on the edge of the clay. Thus, the repulsive force between the clay particles increases and the system becomes deflocculated. Therefore, deflocculated samples may prevent to obtain consistent results. In addition, all samples containing 15-20 nm porous nanoparticles increased fluid loss of all base fluids at both temperatures.

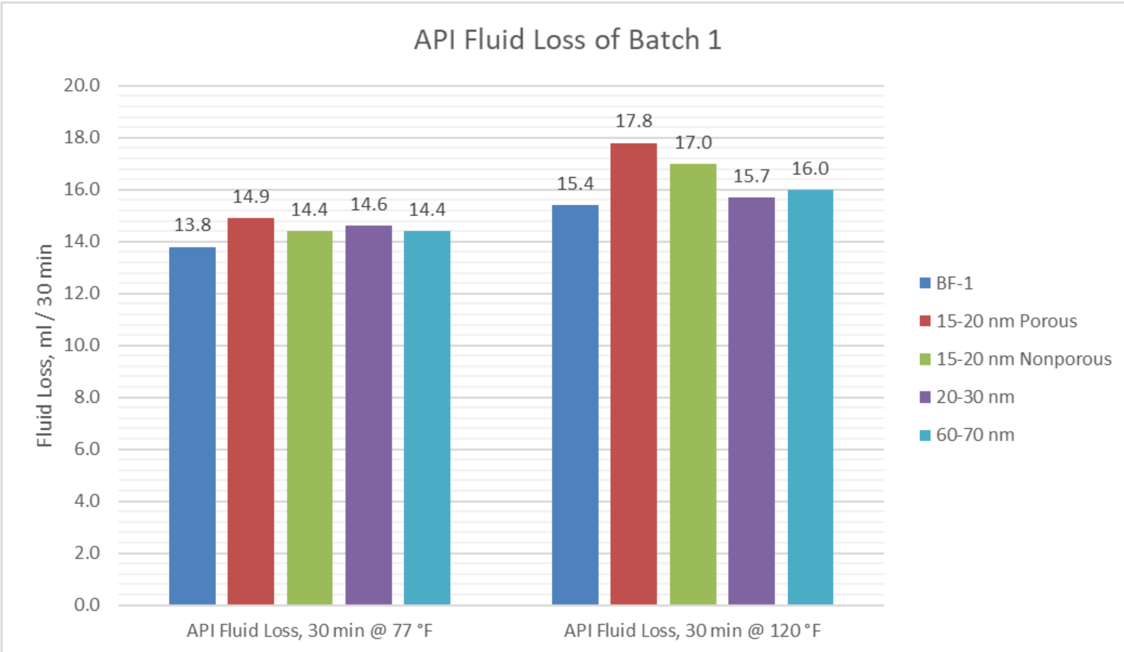

Figure 5-3: Amount of the Fluid Losses of the Batch 1 at 77 ºF and 120 ºF

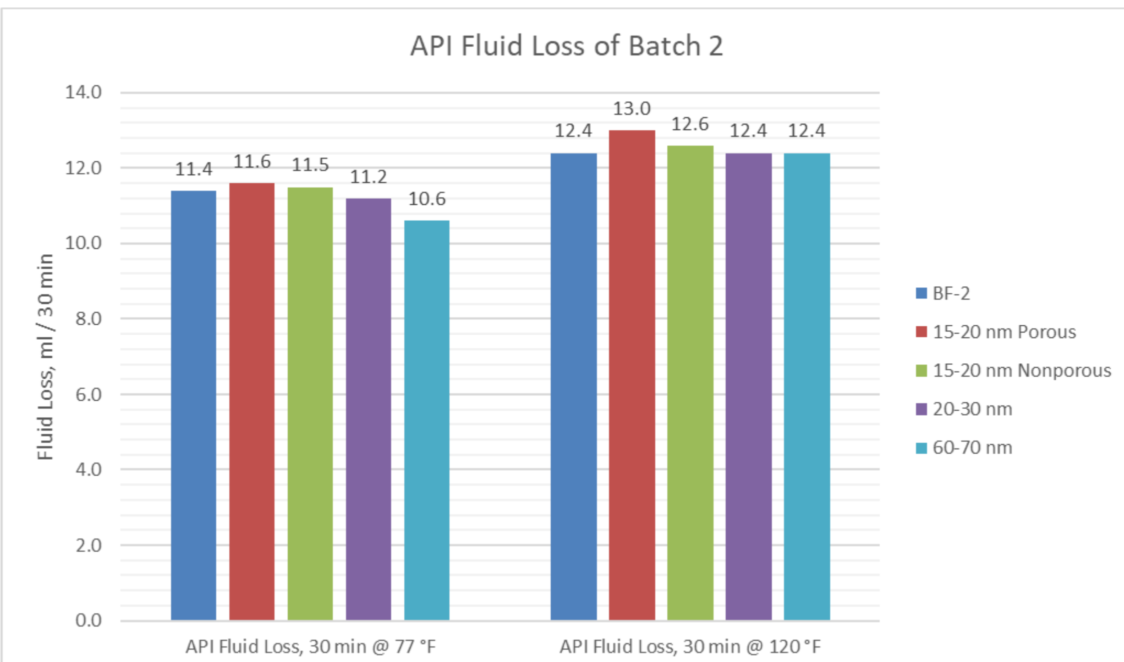

Figure 5-4: Amount of the Fluid Losses of the Batch 2 at 77 ºF and 120 ºF

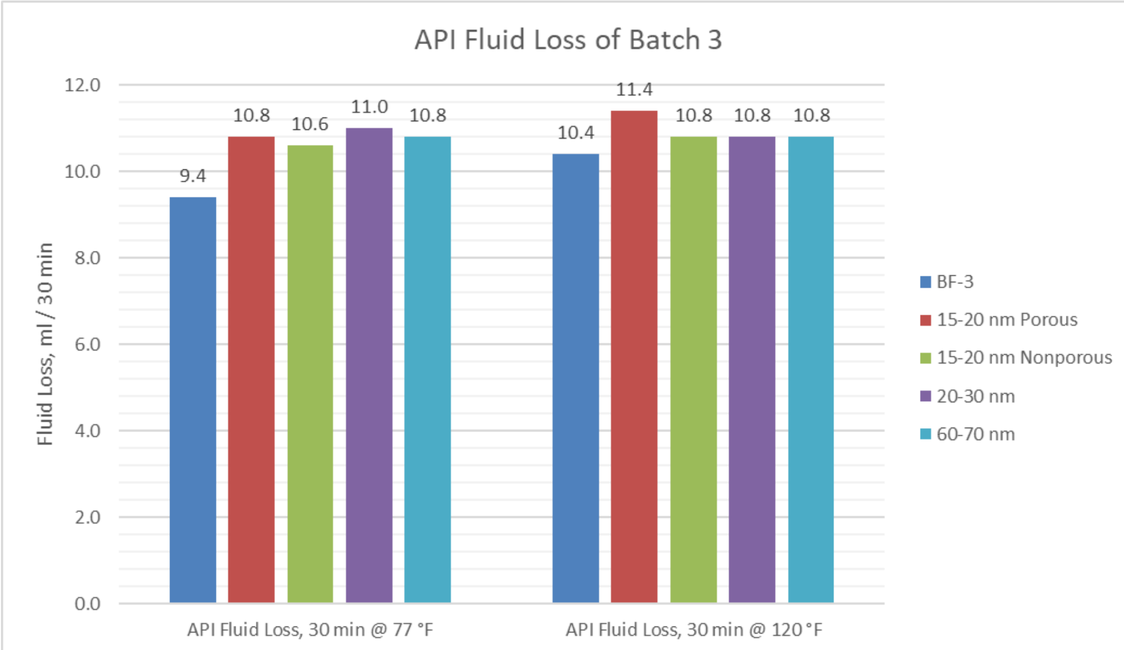

Figure 5-5: Amount of the Fluid Losses of the Batch 3 at 77 ºF and 120 ºF

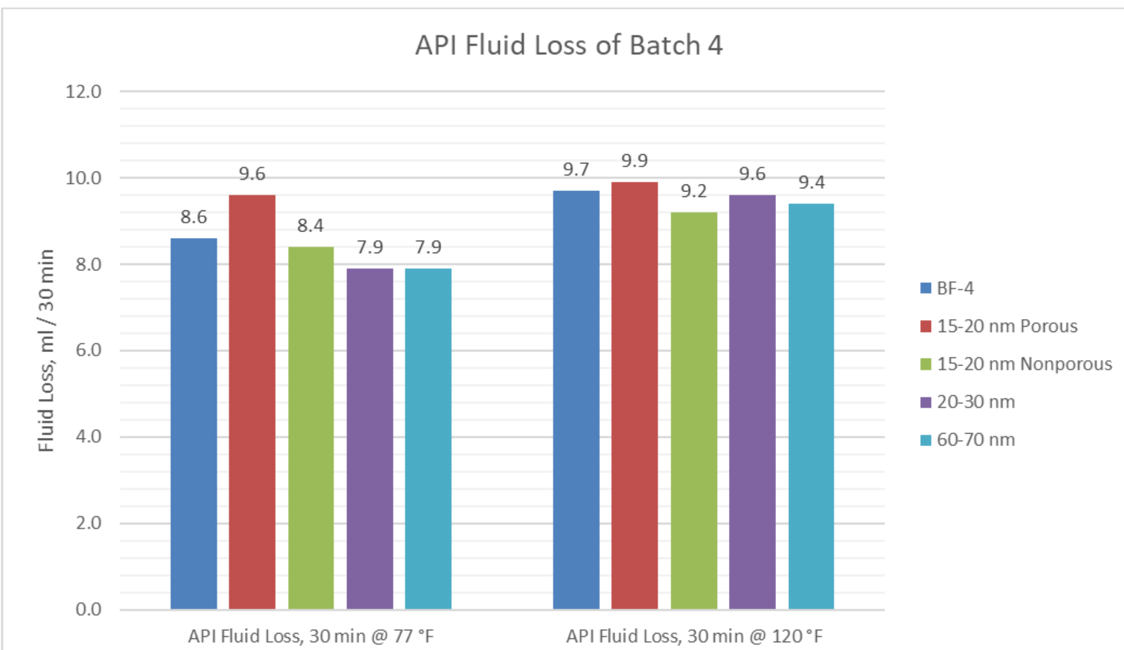

Figure 5-6: Amount of the Fluid Losses of the Batch 4 at 77 ºF and 120 ºF

5.1.1.2.2 Mud Cake Thickness

After the static filtration tests, mud cake thicknesses were measured with the ruler and reported to the nearest 1/32". When the results were examined, it was found that unlike the some studies in the literature, the addition of nanoparticles to the lignosulfonate and bentonite muds did not change the thickness of the mud cake (Figure 5-7). Li et al. [58] used very small amounts of silica nanoparticles (0.1, 0.2, 0.3 and 0.4 gr), bentonite, KCL and xanthan gum to prepare nanofluids and these fluids achieved to reduce mud cake thicknesses remarkably. Amanullah et al. [18] stated that without using highly effective surfactants or polymer, it is very hard to obtain stable nanofluids. Therefore, it can be explained by effect of xanthan gum, which may provide better stability for nanoparticles.

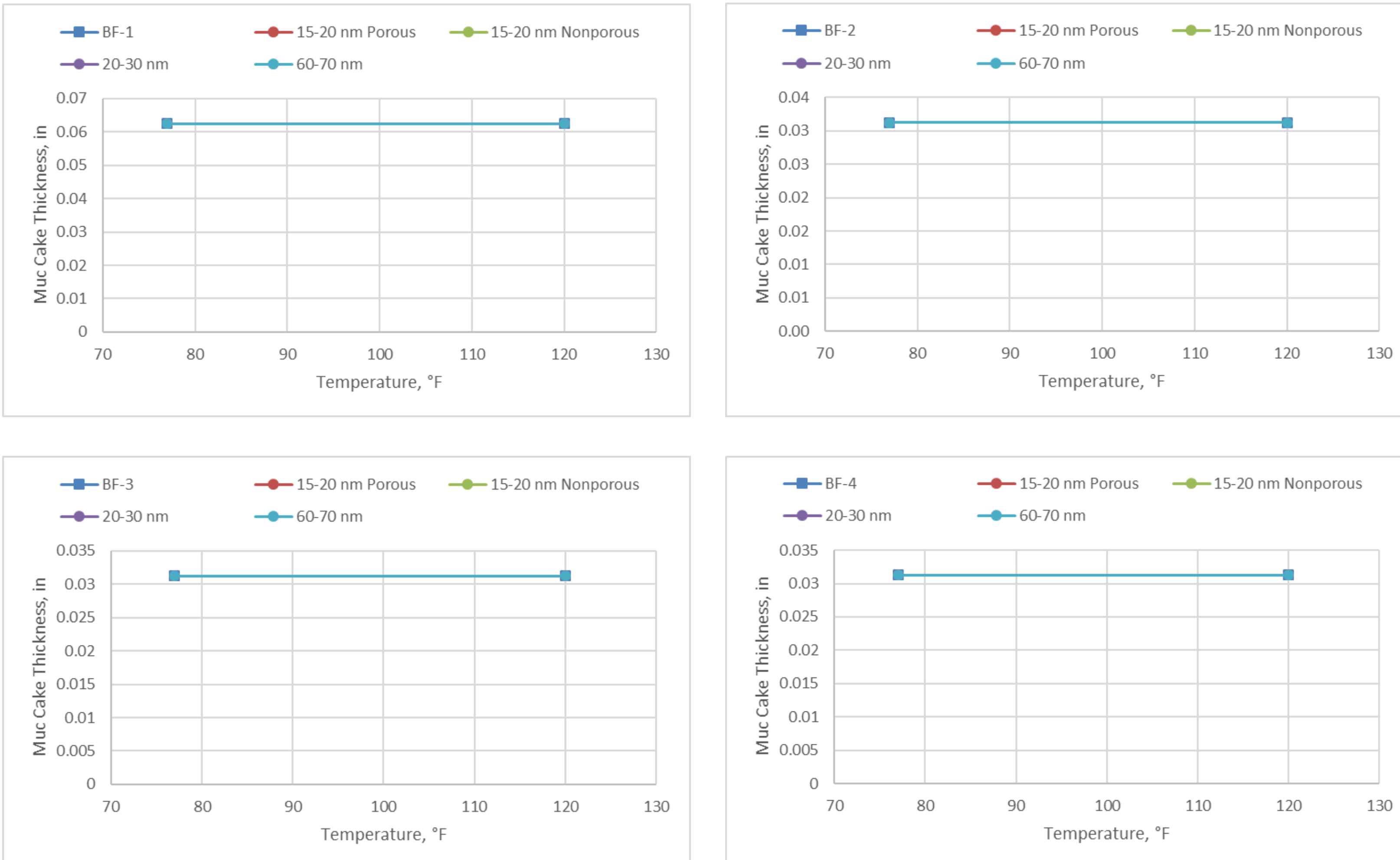

Figure 5-7: Mud Cake Thicknesses of Base Fluids and Nanofluids

5.1.2 Results of the Experimental Group 2

The amount of bentonite in the base drilling fluid were selected as 7% by weight. Moreover, nanoparticle amounts were adjusted as 0.5% and 1.5% by weight. Using these quantities, eight nanofluids were prepared to make comparison between base fluid. The test results of all samples are shown below. Detailed results can be found in APPENDIX C.

5.1.2.1 Effects of Nanoparticles on the Rheological Properties

As seen in Figure 5-8 and Figure 5-9, drilling fluids with 0.5 w/w % 15-20 nm porous nanoparticle addition have lower PV and YP values compared to base mud at 77 ºF, 104 °F, whereas, when the concentration increased to 1.5 w/w %, same nanoparticles improved the rheology when compared to base mud at all temperatures. On the other hand, 15-20 nm nonporous nanoparticles enhanced the rheology at both concentrations, and at all temperatures.

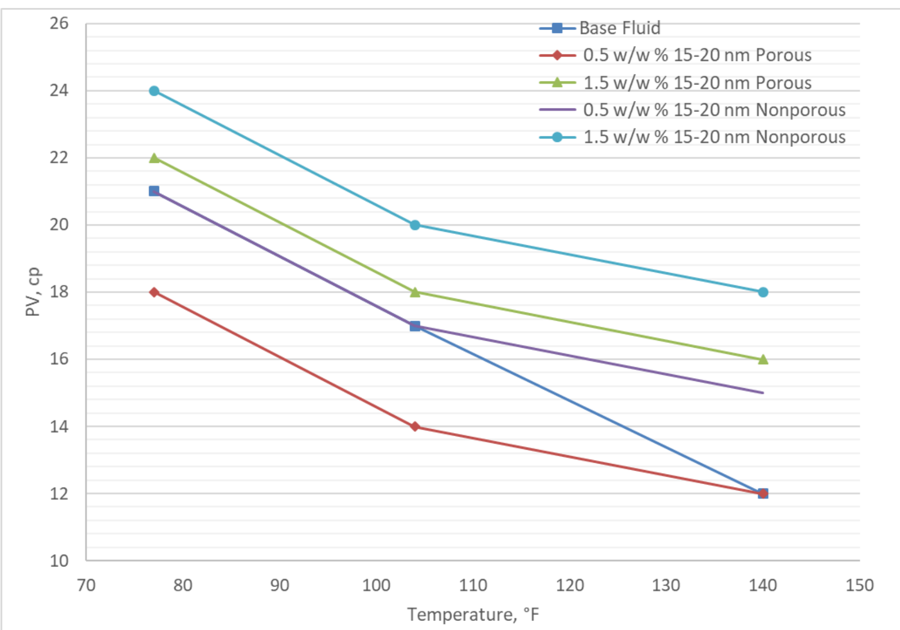

Figure 5-8: Plastic Viscosity Values of 15-20 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

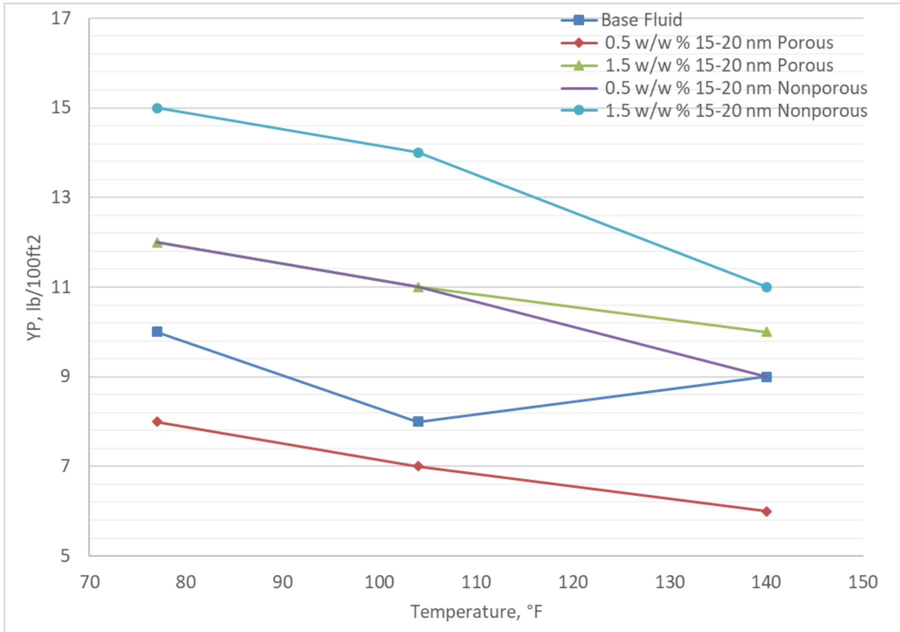

Figure 5-9: Yield Point Values of 15-20 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

20-30 nm nanoparticles with 0.5 w/w % concentration did not change the rheology of mud significantly at all temperatures, but at 104 ºF, an increase in YP is observed. On the other hand, the addition of 1.5 w/w % 20-30 nm nanoparticles form more viscous fluids at all temperatures (Figure 5-10 and Figure 5-11).

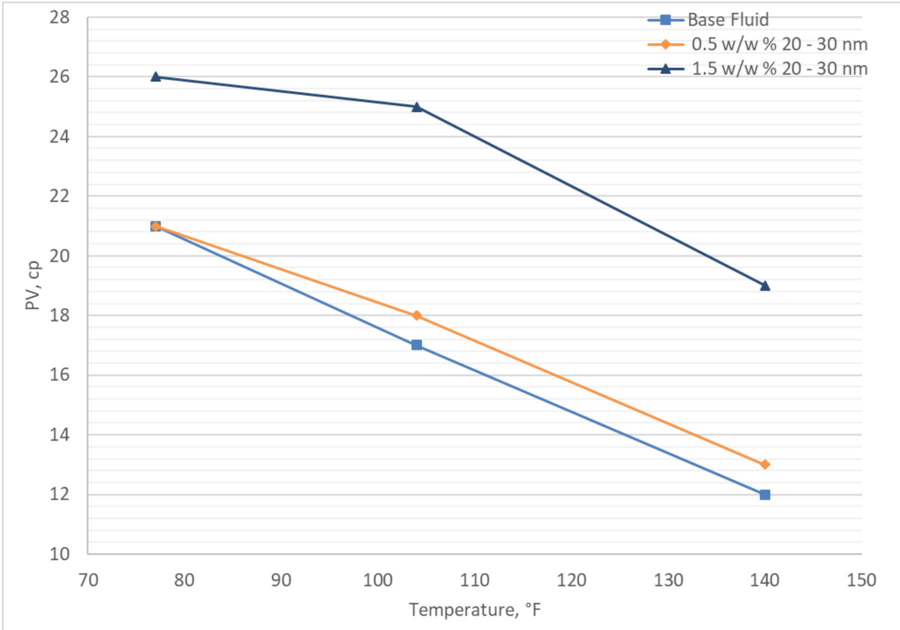

Figure 5-10: Plastic Viscosity Values of 20-30 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

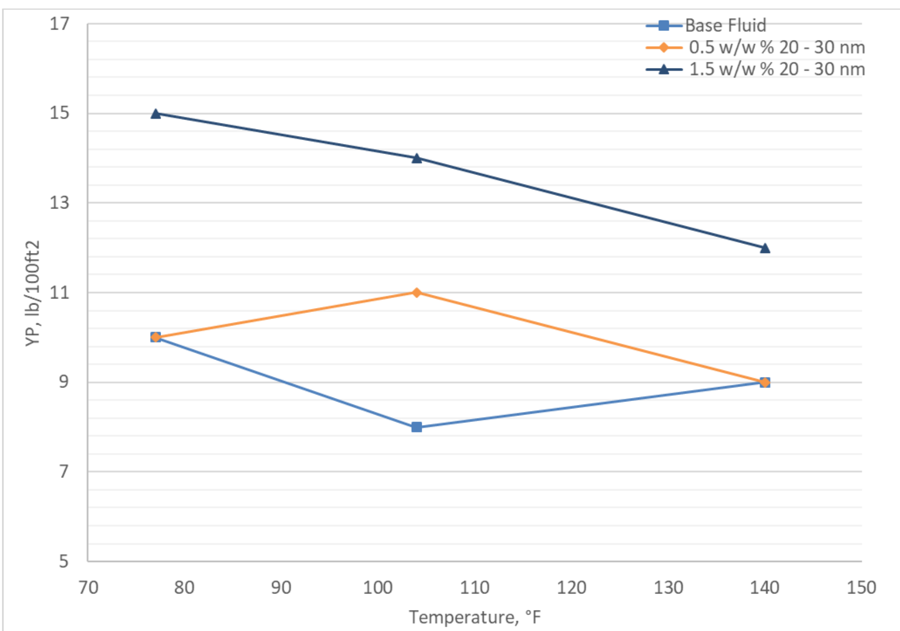

Figure 5-11: Yield Point Values of 20-30 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

Figure 5-12 and Figure 5-13 shows that addition of 0.5 w/w % 60-70 nm nanoparticles to base fluid constituted slight increase in rheological values regardless of test temperature. More pronounced improvement in rheology was observed when 60-70 nm nanoparticle addition increased to 1.5 w/w % at all temperatures.

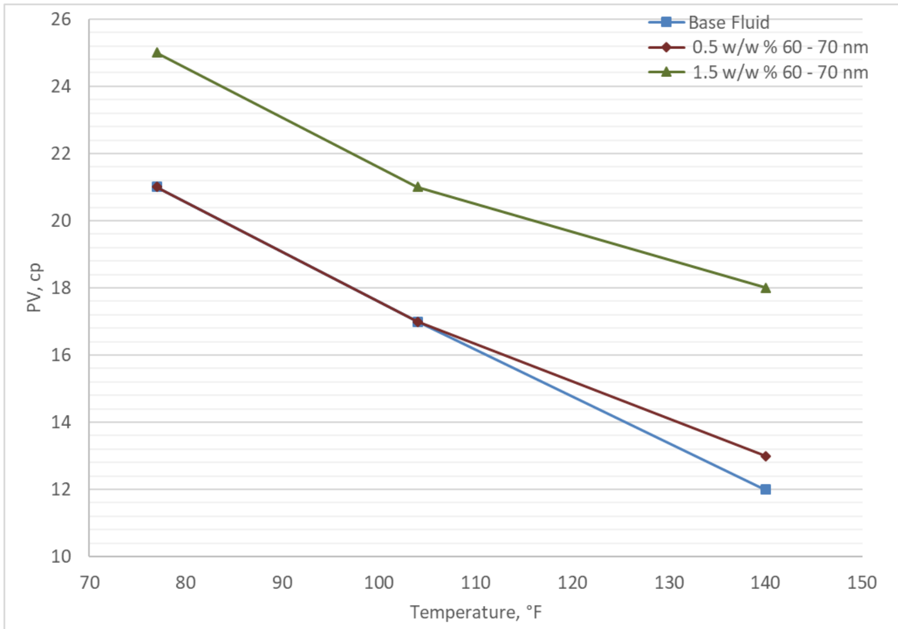

Figure 5-12: Plastic Viscosity Values of 60-70 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

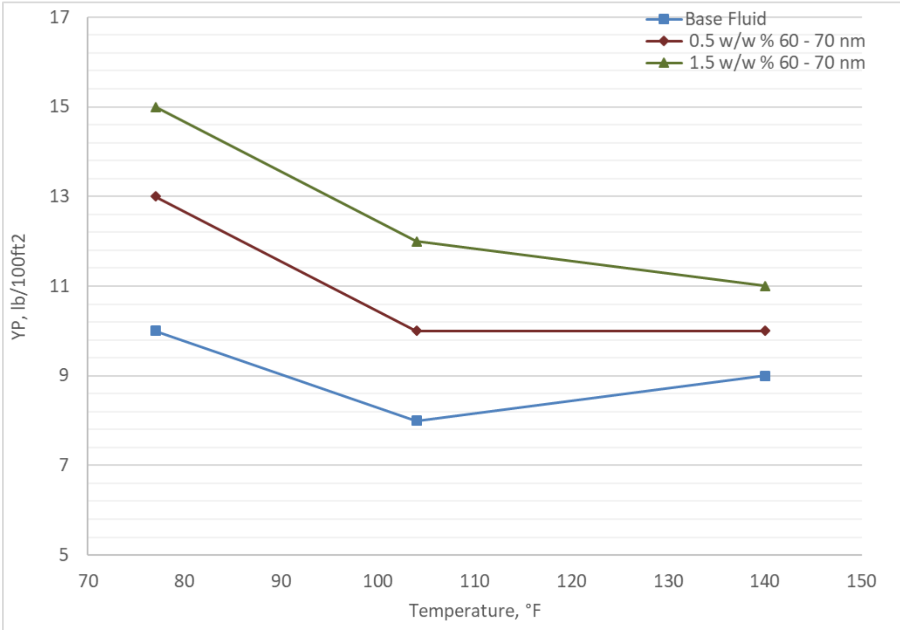

Figure 5-13: Yield Point Values of 20-30 nm Nanoparticles at 77 ºF, 104 °F and 140 ºF

In addition to the graphs given above, the change in PV and YP values depending on the nanoparticle concentration can be examined in Figure 5-14 and Figure 5-15.

Plastic viscosity, which is caused by the mechanical friction, was expected to increase. It is directly proportional to solid content of the mud. In addition, the decrease in particle size further increases the plastic viscosity [6]. Thus, addition of nanoparticles into the water-based drilling fluid enhanced the plastic viscosity. 20-30 nm nanoparticles achieved to improve plastic viscosity of water-based drilling fluids more than others at the concentration of 1.5 w/w %.

Improvement in yield point was also observed for all samples except sample containing 0.5 w/w % 15-20 porous nanoparticles which affect negatively the rheology of the water-based drilling fluid at all temperatures.

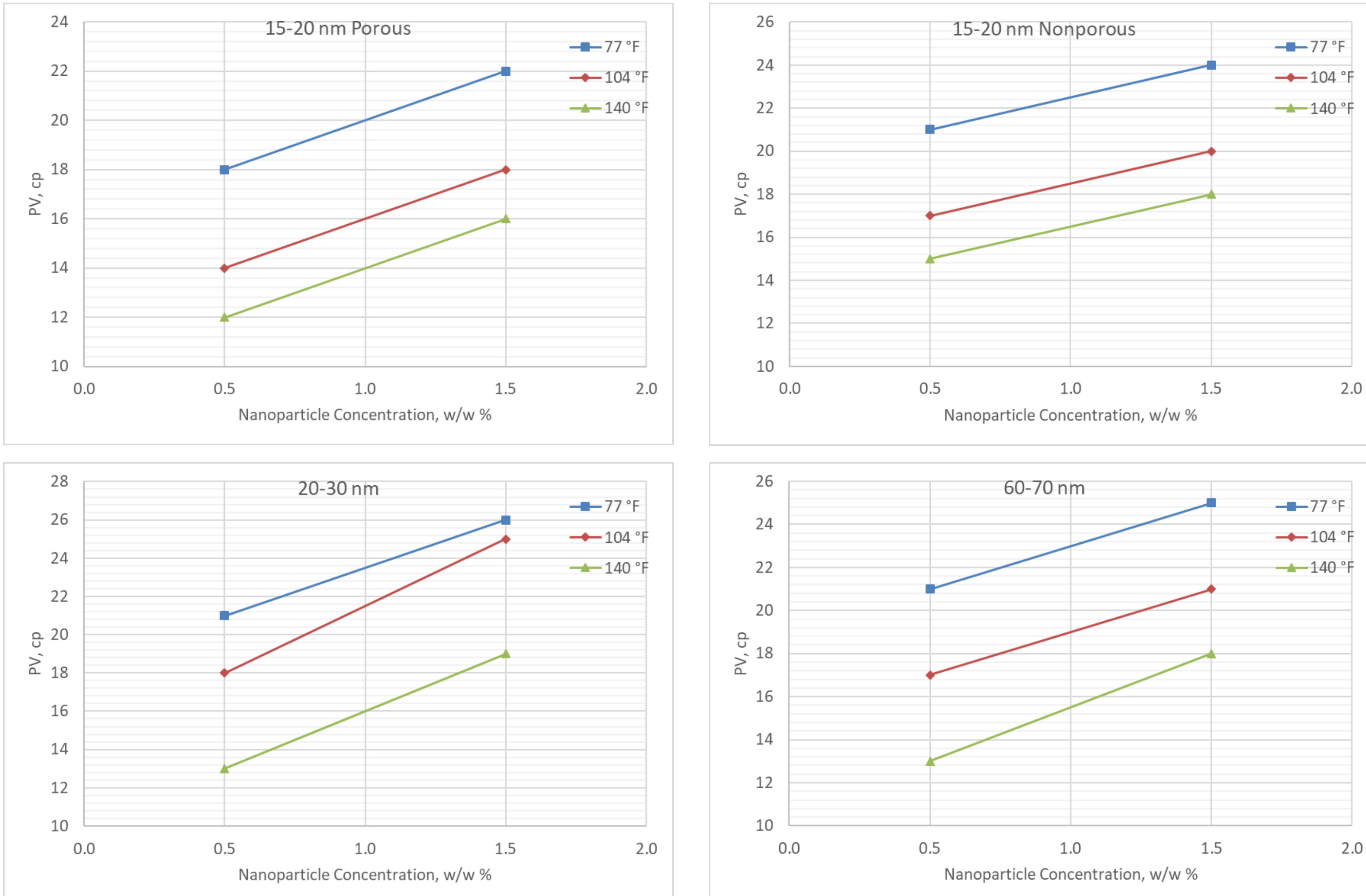

Figure 5-14: Plastic Viscosity vs Nanoparticle Concentration Graphs of All Nanofluids

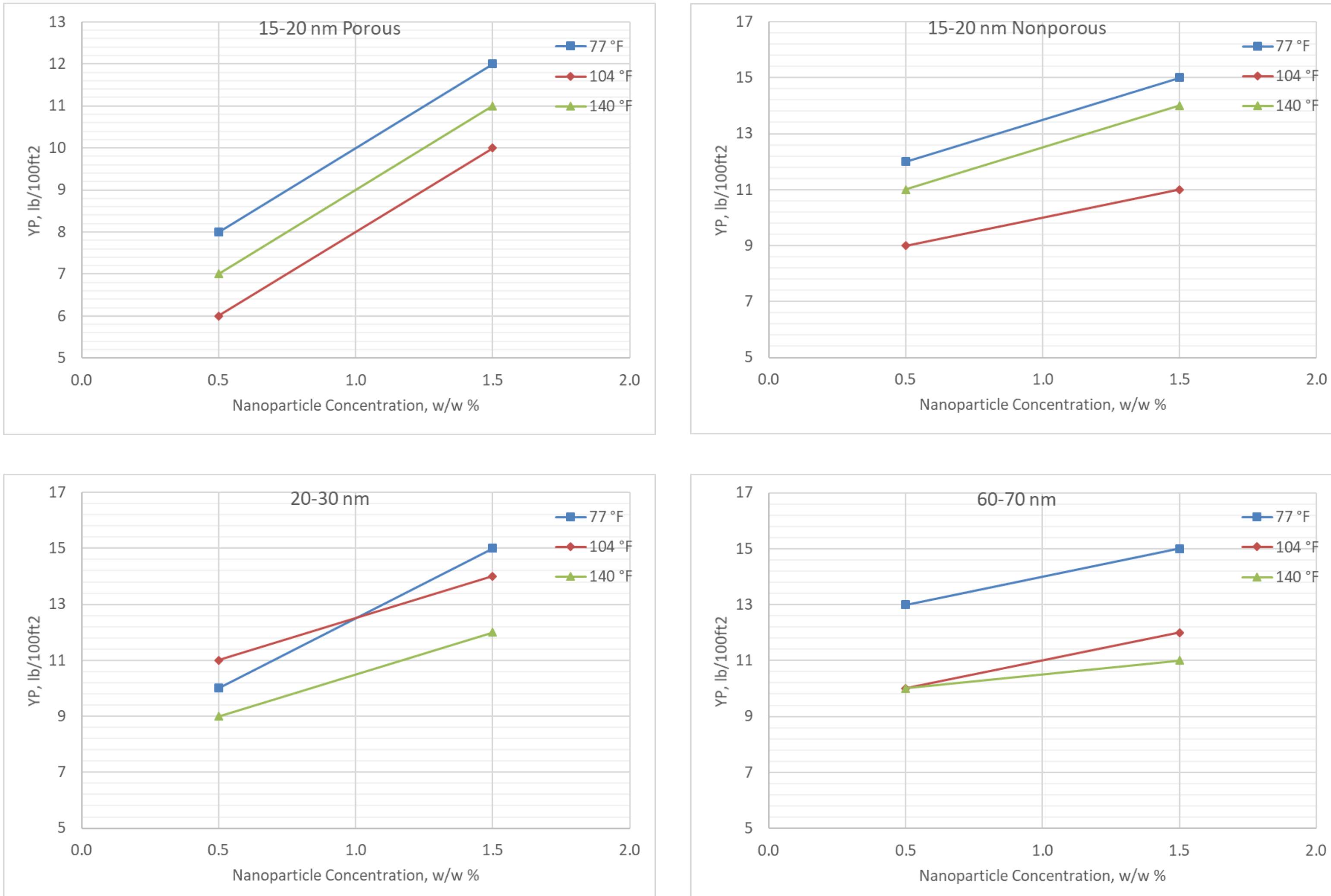

Figure 5-15: Yield Point vs Nanoparticle Concentration Graphs of All Nanofluids

5.1.2.2 Effects of Nanoparticles on the Filtration Properties

OFITE API Filter Press was operated at 100 psi to conduct fluid loss experiments at 77 ºF.

5.1.2.2.1 Fluid Loss

Figure 5-16 represents the fluid loss values of the all samples. It was observed that the addition of nanoparticles to the base mud showed negative effect on the fluid loss. The increase in the concentration of nanoparticles led to a further increase in fluid loss.

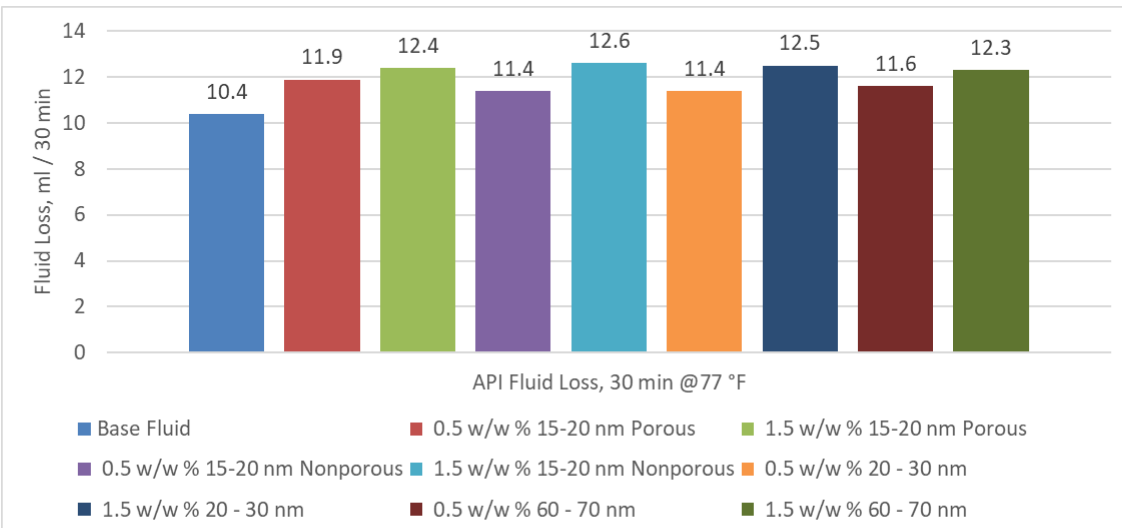

Figure 5-16: Amount of Fluid Losses of All Samples

5.1.2.2.2 Mud Cake Thickness

Increase in mud cake thicknesses was encountered for all the samples containing 1.5 w/w nanoparticles. At the concentration of 0.5 w/w %, nanoparticles did not change the thickness of mud cakes except 15-20 nm porous nanoparticle, According to Rabia [65], thickness of mud cake should be 1 to 2/32". Thickness should not exceeded 3/32" for water-based muds. However, mud cake thicknesses of the samples (1.5 w/w % nanoparticle concentration) were 3/32" and for some samples it exceeded 3/32".

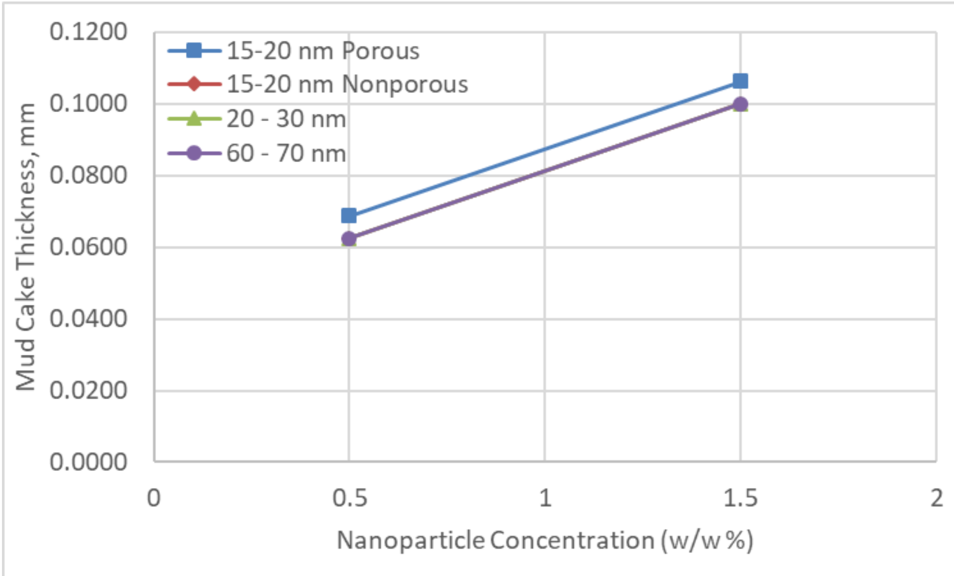

Figure 5-17: Mud Cake Thicknesses of Nanofluids

5.1.2.2.3 Mud Cake Permeability

Since fluid losses and mud cake thicknesses of bentonite mud was increased with the addition of nanoparticles, permeability of mud cakes were also investigated and compared by using Darcy's Law [56]. As shown in Table 5-1, it was found that permeability ratios are bigger than one which indicates that mud cakes of the nanofluids are permeable than mud cake of the base fluid. As can be seen from Figure 5-18, it is very hard to make a comparison between nanoparticles. However, it can be said that 15-20 porous nanoparticles had worst performance among others. Moreover, with the increasing nanoparticle concentration, permeability of mud cakes were increased.

Table 5-1: Values for Required for Permeability Comparison

	Base Mud	15-20 nm porous		15-20 nm nonporous		20-30 nm		60-70 nm	
Nanoparticle Conc., w/w %	-	0.5	1.5	0.5	1.5	0.5	1.5	0.5	1.5
Mud Cake Thickness, in	0.0625	0.0688	0.1063	0.0625	0.1000	0.0625	0.1000	0.0625	0.1000
Water Loss, ml	5.8	6.0	6.1	6.1	6.2	6.0	6.4	6.2	6.3
Permeability ratio compared to base mud (k_n/k_b)	1.000	1.139	1.789	1.052	1.710	1.034	1.766	1.069	1.738

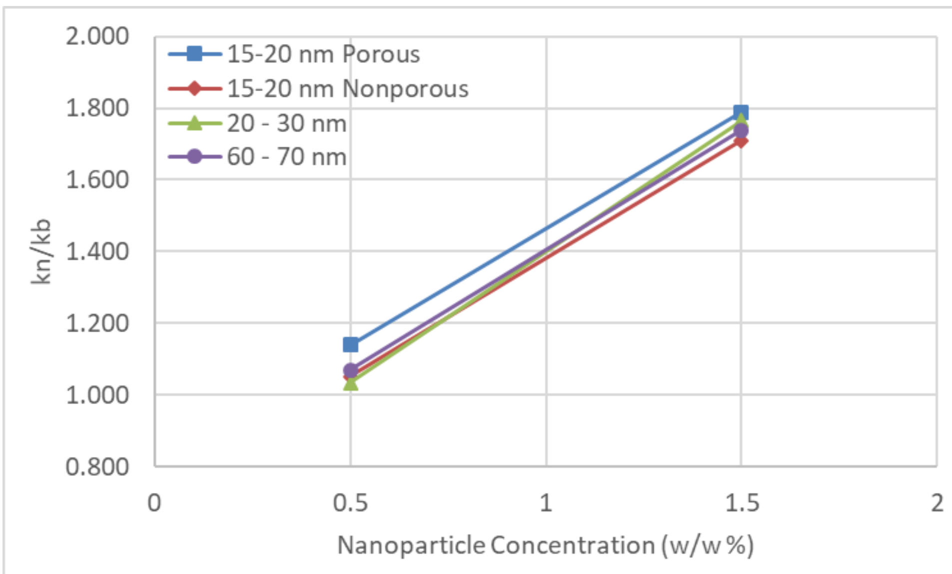

Figure 5-18: Normalized Permeability

Increase in fluid loss and mud cake thickness can be explained by these results and it can be associated with the disorientation of clay platelets, changing it from face to face, to edge to face configuration, therefore, flocculation of bentonite (Figure 5-19). Due to edge to face configuration of the platelets, thickness and permeability of the mud cakes increased. Vryzas et al. [4] concluded in their study that clay platelet configuration of bentonite is adversely affected by the silica nanoparticles. Moreover, after the zeta potential measurements, they have found out that these nanoparticles are not stable in bentonite muds because of their negative charges. Hence, flocculation of bentonite resulted in permeable mud cake and increase in fluid loss.

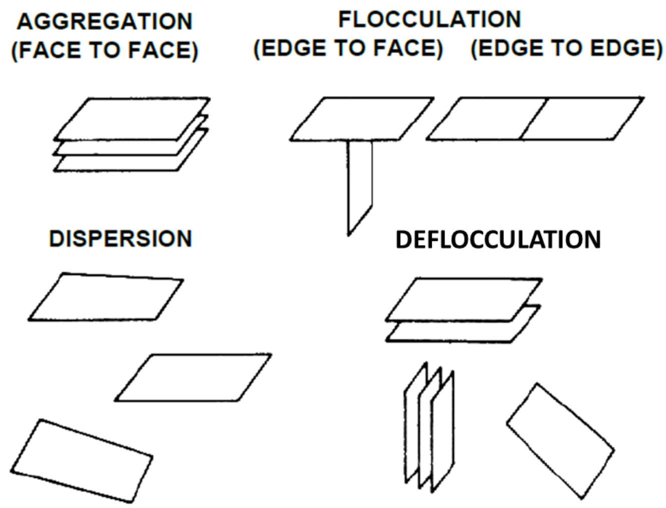

Figure 5-19: Modes of particle association in clay suspensions [66]

CHAPTER 5

CONCLUSIONS

In this study, effects of SiO_2 nanoparticles on the filtration and rheological properties of lignosulfonate and bentonite drilling fluids experimentally analyzed. From the experiment results following conclusions can be reached:

- At low nanoparticle concentrations (0.5 ppb);
  - Nanoparticles do not change the rheology of bentonite and lignosulfonate muds significantly.
  - All nanoparticles have a negative effect on fluid loss in bentonite muds.
  - Reduction in fluid loss is observed for lignosulfonate muds with addition of 15-20 nm nonporous, 20-30 nm and 60-70 nm nanoparticles. However, since there is no consistent trend for the reduction, a firm conclusion cannot be drawn.
  - 15-20 nm porous nanoparticle shows worst performance on fluid loss for bentonite and lignosulfonate muds.
  - No change in mud cake thickness is observed for all samples.
- At nanoparticle concentration (0.5 and 1.5 w/w %);

    - All nanoparticles, except 15-20 nm porous, improve the rheology of bentonite muds.
    - 15-20 nm porous nanoparticle affect the rheology negatively at the concentration of 0.5 w/w %.
    - Best rheological improvement is observed with the addition of 1.5 w/w % 20-30 nm nanoparticle into the bentonite mud.
    - Fluid loss increases with the addition of nanoparticles into the bentonite mud, regardless of size.
    - Nanoparticles, except 15-20 nm porous, do not change the mud cake thickness when added in bentonite mud at 0.5 % by weight.
    - Increase in mud cake thickness is noticed for all nanofluids contains 1.5 w/w % nanoparticle.
    - At both concentrations, addition of nanoparticles increases mud cake permeability of bentonite muds.
- Reduction in pH value is observed for all water-based drilling fluids containing silica nanoparticles.

REFERENCES

[1] International Energy Agency, “Key World Energy Statistics 2016,” *Statistics (Ber).*, p. 80, 2016.

[2] J. Abdo and M. D. Haneef, “Nanoparticles : Promising Solution to Overcome Stern Drilling Problems Mechanical and Industrial Engineering Department,” *NSTI-Nanotech 2010*, vol. 3, pp. 635–638, 2010.

[3] A. Aftab, A. R. Ismail, Z. H. Ibupoto, H. Akeiber, and M. G. K. Malghani, “Nanoparticles Based Drilling Muds a Solution to Drill Elevated Temperature Wells: A Review,” *Renew. Sustain. Energy Rev.*, vol. 76, no. January 2016, pp. 1301–1313, 2017.

[4] Z. Vryzas, O. Mahmoud, H. A. Nasr-El-Din, and V. C. Kelessidis, “Development and Testing of Novel Drilling Fluids Using Fe_2O_3 and SiO_2 Nanoparticles for Enhanced Drilling Operations,” *Int. Pet. Technol. Conf.*, 2015.

[5] J. Abdo and M. D. Haneef, “Clay Nanoparticles Modified Drilling Fluids for Drilling of Deep Hydrocarbon Wells,” *Appl. Clay Sci.*, vol. 86, pp. 76–82, 2013.

[6] A. Aftab, A. R. Ismail, and Z. H. Ibupoto, “Enhancing the Rheological Properties and Shale Inhibition Behavior of Water-Based Mud Using Nanosilica, Multi-Walled Carbon Nanotube, and Graphene Nanoplatelet,” *Egypt. J. Pet.*, vol. 26, no. 2, pp. 291–299, 2017.

[7] Z. Vryzas and V. C. Kelessidis, “Nano-Based Drilling Fluids: A Review,” *Energies*, vol. 10, no. 4, p. 540, 2017.

[8] A. Esmaeili, “Applications of Nanotechnology in Oil and Gas Industry,” in *Nanotechnology*, 2009, no. January, pp. 1–6.

[9] S. Mokhatab, M. A. Fresky, and M. R. Islam, “Applications of Nanotechnology in Oil and Gas E&P,” *J. Pet. Technol.*, vol. 58, no. 4, pp. 48–51, 2006.

[10] National Nanotechnology Initiative, “What is Nanotechnology?” [Online]. Available: http://www.nano.gov/nanotech-101/what/definition. [Accessed: 25-Nov-2016].

[11] A. I. El-Diasty and A. M. S. Ragab, “Applications of Nanotechnology in the Oil & Gas Industry: Latest Trends Worldwide & Future Challenges in Egypt,” *North Africa Tech. Conf. Exhib.*, p. 13. SPE-164716, 2013.

[12] National Cancer Institute, “The Size of Things.” [Online]. Available: https://nano.cancer.gov/objects/img_resource/size-of-things.jpg. [Accessed: 25-Nov-2016].

[13] L. Yang, “Fundamentals of Nanotechnology and Orthopedic Materials,” *Nanotechnology-Enhanced Orthop. Mater.*, pp. 1–25, 2015.

[14] R. P. Feynman, “There’s Planty of Room at the Bottom,” *Eng. Sci.*, vol. 23, no. December, pp. 22–36, 1960.

[15] S. K. Das, S. U. S. Choi, W. Yu, and T. Pradeep, *Nanofluids: Science and Technology*. 2007.

[16] X. Kong, M. M. Ohadi, and T. Petroleum, “Applications of Micro and Nano Technologies in the Oil and Gas Industry- An Overview of the Recent Progress,” *Present. SPE Int. Oilf. Nanotechnol. Conf. held Noordwijk, Netherlands*, vol. 3, pp. 1–11, 2010.

[17] M. J. Pitkethly, “Nanomaterials – the Driving Force,” *Advances*, vol. 44, no. December, pp. 20–29, 2004.

[18] M. d. Amanullah, M. K. Al-Arfaj, and Z. Al-Abdullatif, “Preliminary Test Results

of Nano-Based Drilling Fluids for Oil and Gas Field Application," *SPE/IADC Drill. Conf. Proc.*, vol. 1, no. 1965, pp. 112–120, 2011.

[19] A. Wilson, "Preliminary Test Results of Nano-Based Fluids Reveal Benefits for Field Application," *J. Pet. Technol.*, vol. 64, no. 11, pp. 104–108, 2012.

[20] M. Amanullah and A. Al-Tahini, "Nano-Technology- Its Significance in Smart Fluid Development for Oil and Gas Field Application," *SPE Saudi Arab. Sect. Tech. Symp. Exhib.*, pp. 1–12, 2009.

[21] R. Krishnamoorti, "Extracting the Benefits of Nanotechnology for the Oil Industry," *J. Pet. Technol.*, vol. 58, no. 11, pp. 24–26, 2006.

[22] S. Chakrabory, G. Agrawal, A. DiGiovanni, and D. Scott, "With Functionalization, Nanodiamonds May Increase Durability of PDC Cutters," *J. Pet. Technol.*, no. December, pp. 12–14, 2012.

[23] Z. Zhang, Z. Xu, and B. Salinas, "High Strength Nanostructured Materials and Their Oil Field Applications," *Soc. Pet. Eng.*, no. June, pp. 12–14, 2012.

[24] A. K. Santra, P. Boul, and X. Pang, "Influence of Nanomaterials in Oilwell Cement Hydration and Mechanical Properties," *SPE Int. Oilf. Nanotechnol. Conf. Exhib.*, 2012.

[25] M. Rahimirad and J. D. Baghbadorani, "Properties of Oil Well Cement Reinforced by Carbon Nanotubes," *SPE Int. Oilf. Nanotechnol. Conf.*, 2012.

[26] G. Maserati *et al.*, "Nano-emulsions as Cement Spacer Improve the Cleaning of Casing Bore During Cementing Operations," *SPE Annu. Tech. Conf. Exhib.*, pp. 1–10, 2010.

[27] A. Bera and H. Belhaj, "Application of Nanotechnology by Means of Nanoparticles and Nanodispersions in Oil Recovery - A Comprehensive Review," *J. Nat. Gas Sci. Eng.*, vol. 34, pp. 1284–1309, 2016.

[28] J. Farooqui, T. Babadagli, and H. A. Li, "Improvement of the Recovery Factor

Using Nano-Metal Particles at the Late Stages of Cyclic Steam Stimulation," *SPE Heavy Oil Conf. - Canada 2014*, pp. 1–17, 2015.

[29] K. P. Hoelscher, G. De Stefano, M. Riley, and S. Young, "Application of Nanotechnology in Drilling Fluids," *SPE Int. Oilf. Nanotechnol. Conf. Exhib.*, no. June, pp. 12–14, 2012.

[30] M. Sayyadnejad, H. Ghaffarian, and M. Saeidi, "Removal of hydrogen sulfide by zinc oxide nanoparticles in drilling fluid," *Int. J. Environ. Sci. Technol.*, vol. 5, no. 4, pp. 565–569, 2008.

[31] A. M. Paiaman and B. D. Al-anazi, "Using Nanoparticles To Decrease Differential Pipe Sticking," 2008.

[32] M. M. Sharma, M. E. Chenevert, Q. Guo, L. Ji, J. Friedheim, and R. Zhang, "A New Family of Nanoparticle Based Drilling Fluids," *SPE Annu. Tech. Conf. Exhib.*, pp. 1–13, 2012.

[33] M. Manea, "Designing of Drilling Fluids Using Nano Scale Polymer Additives," *Rom. J. Chem.*, vol. 63, no. 11, pp. 1132–1137, 2012.

[34] R. Soboori, S. Sabbaghi, D. Mowla, and A. Soltani, "Decreasing of Water Loss and Mud Cake Thickness by CMC Nanoparticles in Mud Drilling," *Int. J.Nano Dimens*, vol. 3, no. 2, pp. 101–104, 2012.

[35] M. Fereydouni, S. Sabbaghi, R. Saboori, and S. Zeinali, "Effect of Polyanionic Cellulose Polymer Nanoparticles on Rheological Properties of Drilling Mud," *Int. Journalof Nanosci. Nanotechnoly*, vol. 8, no. 3, pp. 171–174, 2012.

[36] J. Abdo and M. D. Haneef, "Nano-Enhanced Drilling Fluids: Pioneering Approach to Overcome Uncompromising Drilling Problems," *J. Energy Resour. Technol.*, vol. 134, no. 1, p. 14501, 2012.

[37] M. I. Abdou, A. M. Al-sabagh, and M. M. Dardir, "Evaluation of Egyptian bentonite and nano-bentonite as drilling mud," *Egypt. J. Pet.*, vol. 22, no. 1, pp. 53–

59, 2013.

[38] M. Zoveidavianpoor and A. Samsuri, "The Use of Nano-Sized Tapioca Starch as a Natural Water-Soluble Polymer for Filtration Control in Water-Based Drilling Muds," *J. Nat. Gas Sci. Eng.*, vol. 34, pp. 832–840, 2016.

[39] J. Nasser, A. Jesil, T. Mohiuddin, M. Al Ruqeshi, G. Devi, and S. Mohataram, "Experimental Investigation of Drilling Fluid Performance as Nanoparticles," *World J. Nano Sci. Eng.*, vol. 3, no. September, pp. 57–61, 2013.

[40] A. M. S. Ragab and A. Noah, "Reduction of Formation Damage and Fluid Loss using Nano-sized Silica Drilling Fluids," *Pet. Technol. Dev. J.*, vol. 2, no. December 2007, pp. 75–88, 2014.

[41] A. M. S. Ragab, "Innovative Drilling Fluid Design Using Nano Materials," no. April, pp. 1–19, 2016.

[42] A. R. Ismail, A. Aftab, Z. H. Ibupoto, and N. Zolkifile, "The Novel Approach for the Enhancement of Rheological Properties of Water-Based Drilling Fluids by Using Multi-Walled Carbon Nanotube, Nanosilica and Glass Beads," *J. Pet. Sci. Eng.*, vol. 139, pp. 264–275, 2016.

[43] S. Li, S. Osisanya, and M. Haroun, "Development of New Smart Drilling Fluids Using Nano-Materials for Unconventional Reservoirs Introduction and Previous Work Done on Smart Drilling Fluids Methodology," in *Spe*, 2016.

[44] M. Belayneh and B. S. Aadnøy, "Effect of Nano-Silicon Dioxide (SiO_2) on Polymer/Salt Treated Bentonite Drilling Fluid Systems," in *Volume 8: Polar and Arctic Sciences and Technology; Petroleum Technology*, 2016, p. V008T11A027.

[45] C. Anyanwu and M. M. Unubi, "Experimental Evaluation of Particle Sizing in Drilling Fluid to Minimize Filtrate Losses and Formation Damage," 2016.

[46] S. M. Javeri, Z. M. W. Haindade, and C. B. Jere, "Mitigating Loss Circulation And Differential Sticking Problems Using Silicon Nanoparticles," *SPE/IADC Middle*

East Drill. Technol. Conf. Exhib., 2011.

[47] N. S. Al-Zubaidi, A. A. Alwasiti, and D. Mahmood, “A Comparison of Nano Bentonite and Some Nano Chemical Additives to Improve Drilling Fluid Using Local Clay and Commercial Bentonites,” *Egypt. J. Pet.*, pp. 0–7, 2016.

[48] D. V. Kosynkin *et al.*, “Graphene Oxide as a High-Performance Fluid-Loss-Control Additive in Water-Based Drilling Fluids,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 1, pp. 222–227, 2012.

[49] Y. Jung *et al.*, “Effect of Nanoparticle-Additives on the Rheological Properties of Clay-Based Fluids at High Temperature and High Pressure,” *AADE , Am. Assoc. Drill. Eng.*, vol. v, pp. 1–4, 2011.

[50] M. M. Barry, Y. Jung, J.-K. Lee, T. X. Phuoc, and M. K. Chyu, “Fluid Filtration and Rheological Properties of Nanoparticle Additive and Intercalated Clay Hybrid Bentonite Drilling Fluids,” *J. Pet. Sci. Eng.*, vol. 127, no. February, pp. 338–346, 2015.

[51] O. Mahmoud, H. A. Nasr-El-Din, Z. Vryzas, and V. C. Kelessidis, “Nanoparticle-Based Drilling Fluids for Minimizing Formation Damage in HP/HT Applications,” *SPE Int. Conf. Exhib. Form. Damage Control*, pp. 24–26, 2016.

[52] FANN Instrument Company, *Multimixer and Dispersator Manual*. 2015.

[53] Precisa Gravimetrics AG, *Balance Manual*. 2013.

[54] FANN Instrument Company, *Roller Oven Manual*. 2015.

[55] FANN Instrument Company, *Aging Cell Manual*. 2016.

[56] A. Y. Dandekar, *Petroleum reservoir rock and fluid properties*. 2006.

[57] Türkiye Petrolleri Anonim Ortaklığı, *Sondaj Akışkanları Teknolojisi (Lignosulfat Çamuru)*. 2007.

[58] M. C. Li *et al.*, “Cellulose Nanocrystals and Polyanionic Cellulose as Additives in

Bentonite Water-Based Drilling Fluids: Rheological Modeling and Filtration Mechanisms," *Ind. Eng. Chem. Res.*, vol. 55, no. 1, pp. 133–143, 2016.

[59] FANN Instrument Company, *Mud Balance Model 140 Instruction Manual*. 2016.

[60] FANN Instrument Company, *Model 35 Viscometer Instruction Manual*. 2015.

[61] OFI Testing Equipment Inc., *Thermocup Manual*. 2017.

[62] OFI Testing Equipment Inc., *Multi-Unit API Filter Press Instruction Manual*. 2013.

[63] FANN Instrument Company, *pH Measurement Instructions*. 2007.

[64] OACTAN, *EcoTestr pH 2 Waterproof Pocket Tester Instruction Manual*. 2017.

[65] H. Rabia, *Oil Well Drilling Engineering: Principles and Practices*. 1985.

[66] İ. H. Gücüyener, *Drilling Fluid Engineering Course Notes*. 2016.

APPENDIX A

PROPERTIES OF NANOPARTICLES

In Appendix A, the properties of nanoparticles purchased from NANOGRAFI Co. Ltd. can be examined. All the specifications were written by using the data sheet provided by the company.

SiO_2 15 - 20 nm Porous (P-type)

Purity	: 99.5+%
Average Particle Size	: 15 - 20 nm
Specific Surface Area	: ~640 m^2/g
Color	: White
Morphology	: Porous
Bulk Density	: < 0.10 g/cm3
True Density	: 2.4 g/cm3

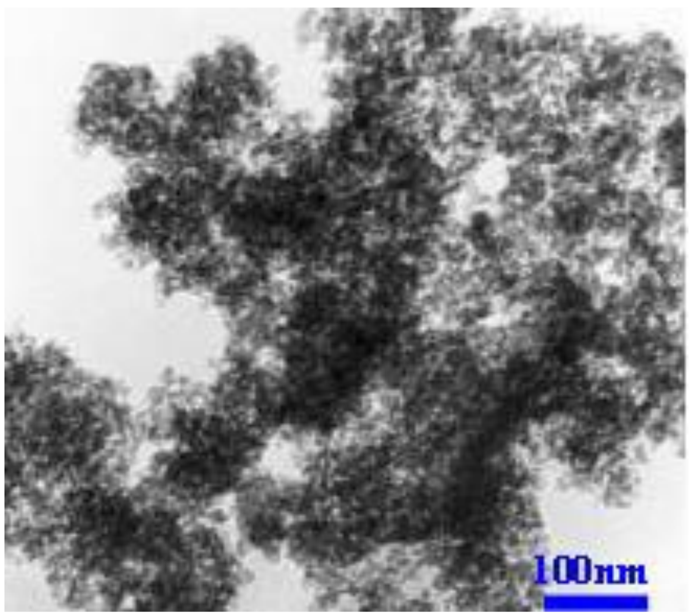

Figure A-1: TEM Imaging of SiO_2 15 - 20 nm Porous

Table A-1: Elemental Analysis of SiO_2 15 - 20 nm Porous

SiO_2	Al	Fe	Ca	Mg	Cl
> 99.5%	< 20 ppm	< 10 ppm	< 20 ppm	< 10 ppm	< 10 ppm

SiO_2 15 - 20 nm Nonporous Spherical Particles (S-type)

Purity	: 99.5+%
Average Particle Size	: 15 - 20 nm
Specific Surface Area	: 170 - 200 m^2/g
Color	: White
Morphology	: Nonporous
Bulk Density	: < 0.10 g/cm3
True Density	: 2.4 g/cm3

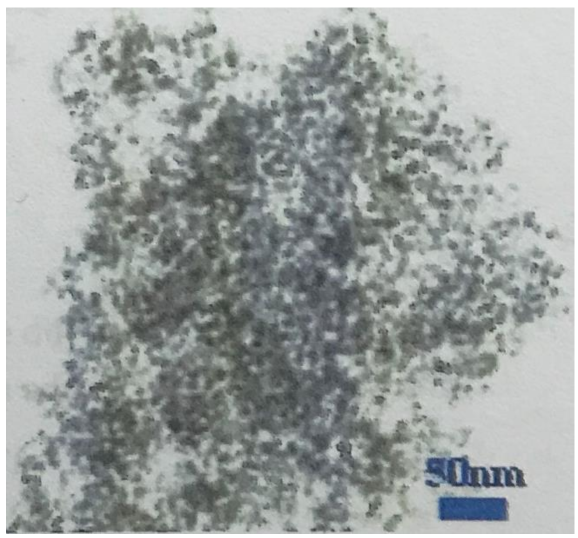

Figure A-2: TEM Imaging of SiO_2 15 - 20 nm Nonporous Spherical

Table A-2: Elemental Analysis of SiO_2 15 - 20 nm Nonporous Spherical

SiO_2	Al	Fe	Sr	Ca	Mg	Cl	Cr
> 99.5%	10 ppm	10 ppm	40 ppm	20 ppm	10 ppm	10 ppm	40 ppm

SiO_2 20 - 30 nm

Purity : 99+%

Average Particle Size : 20 - 30 nm

Specific Surface Area : 180 - 600 m^2/g

Color : White

Bulk Density : <0.10 g/cm3

True Density : 2.4 g/cm3

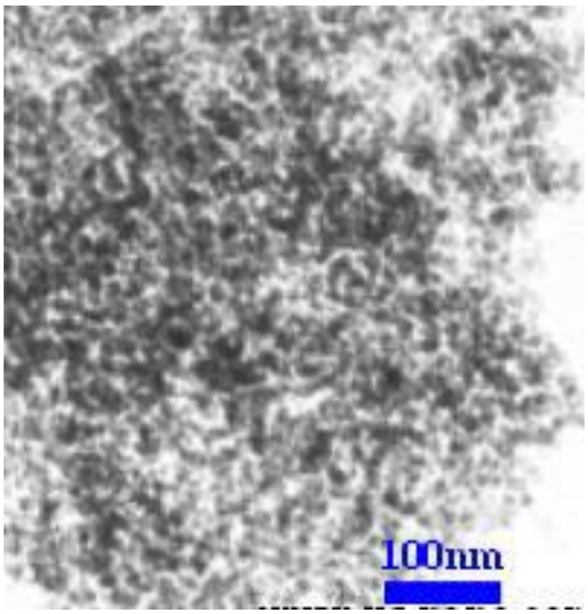

Figure A-3: TEM Imaging of SiO_2 20 - 30 nm

Table A-3: Elemental Analysis of SiO_2 20 - 30 nm

SiO_2	Ti	Ca	Na	Fe
> 99%	< 120 ppm	< 70 ppm	< 50 ppm	< 20 ppm

SiO_2 60 - 70 nm

Purity	: 98+%
Average Particle Size	: 60 - 70 nm
Specific Surface Area	: 160 - 600 m^2/g
Color	: White
Bulk Density	: < 0.10 g/cm3
True Density	: 2.4 g/cm3

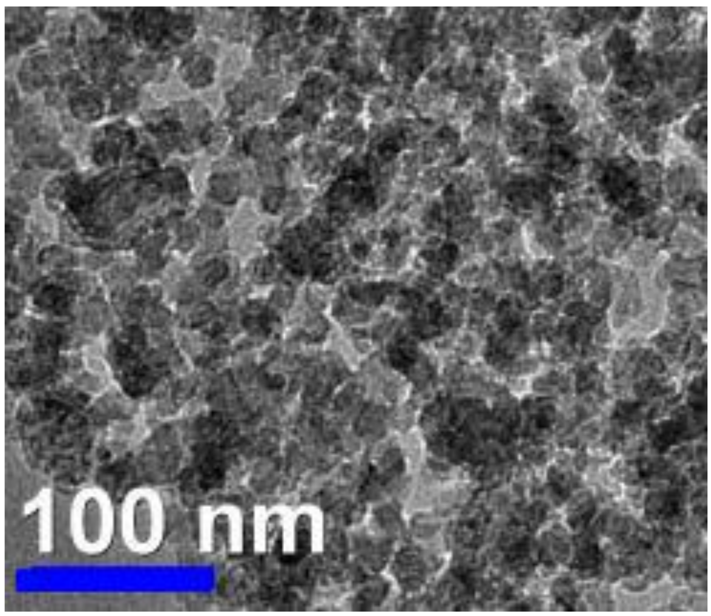

Figure A-4: TEM Imaging of SiO_2 60 - 70 nm

Table A-4: Elemental Analysis of SiO_2 60 - 70 nm

SiO_2	Ti	Ca	Na	Fe
> 98%	< 220 ppm	< 130 ppm	< 80 ppm	< 40 ppm

APPENDIX B

TEST RESULTS OF EXPERIMENTAL GROUP 1

All experimental results of group 1 are shown in detail in APPENDIX B.

Table B-5: Test Results of Batch 1

Sample	**BF-1**		**NF-1**		**NF-2**		**NF-3**		**NF-4**	
Tap Water, cc	350		350		350		350		350	
Bentonite, gr	20		20		20		20		20	
CMC, gr	0		0		0		0		0	
CFL, gr	0		0		0		0		0	
Nanoparticle, gr	0		0.5		0.5		0.5		0.5	
Aging Time, hr	4		4		4		4		4	
Aging Temperature, °F	140		140		140		140		140	
Mud Density , lb/gal	8.5		8.5		8.5		8.5		8.5	
Viscosity Measurement Temperature, °F	77	120	77	120	77	120	77	120	77	120
Viscosity, 600 rpm reading	19	12	18	12	18	12	18	12	18	12
Viscosity, 300 rpm reading	11	7	10	7	10	7	10	7	10	7
Viscosity, 200 rpm reading	8	5	7	5	7	5	7	5	7	5
Viscosity, 100 rpm reading	5	3	5	3	5	3	5	3	5	3
Viscosity, 6 rpm reading	1	1	1	1	1	1	1	1	1	1
Viscosity, 3 rpm reading	1	1	1	1	1	1	1	1	1	1
PV	8	5	8	5	8	5	8	5	8	5
YP	3	2	2	2	2	2	2	2	2	2
Gel Strength, 10 sec	1	1	1	1	1	1	1	1	1	1
Gel Strength, 10 min	2	3	1	3	1	3	1	3	1	3
API Fluid Loss, 7.5 min	6.4	7.8	6.9	9.0	6.6	8.2	6.7	7.3	6.6	7.4
API Fluid Loss, 30 min	13.8	15.4	14.9	17.8	14.4	17.0	14.6	15.7	14.4	16.0
Mud Cake Thickness, in	2/32	2/32	2/32	2/32	2/32	2/32	2/32	2/32	2/32	2/32
Mud Cake Weight, gr	2.47	3.05	2.70	3.24	2.67	3.17	2.62	3.10	2.80	3.19
pH (After Aging)	9.5		8.9		8.9		8.9		8.9	

Table B-6: Test Results of Batch 2

Sample	**BF-2**		**NF-5**		**NF-6**		**NF-7**		**NF-8**	
Tap Water, cc	350		350		350		350		350	
Bentonite, gr	20		20		20		20		20	
CMC, gr	0		0		0		0		0	
CFL, gr	1		1		1		1		1	
Nanoparticle, gr	0		0.5		0.5		0.5		0.5	
Aging Time, hr	4		4		4		4		4	
Aging Temperature, °F	140		140		140		140		140	
Mud Density , lb/gal	8.5		8.5		8.5		8.5		8.5	
Viscosity Measurement Temperature, °F	77	120	77	120	77	120	77	120	77	120
Viscosity, 600 rpm reading	15	11	15	10	15	10	15	10	15	10
Viscosity, 300 rpm reading	8	7	8	6	8	6	8	6	8	6
Viscosity, 200 rpm reading	6	4	6	4	6	4	6	4	6	4
Viscosity, 100 rpm reading	4	3	3	3	3	3	3	3	3	3
Viscosity, 6 rpm reading	1	1	1	1	1	1	1	1	1	1
Viscosity, 3 rpm reading	1	1	1	1	1	1	1	1	1	1
PV	7	4	7	4	7	4	7	4	7	4
YP	1	3	1	2	1	2	1	2	1	2
Gel Strength, 10 sec	1	1	1	1	1	1	1	1	1	1
Gel Strength, 10 min	1	1	1	1	1	1	1	1	1	1
API Fluid Loss, 7.5 min	4.6	5.2	5.1	5.7	4.9	5.1	4.8	5.5	4.6	5.2
API Fluid Loss, 30 min	11.4	12.4	11.6	13.0	11.5	12.6	11.2	12.4	10.6	12.4
Mud Cake Thickness, in	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32
Mud Cake weight, gr	2.89	3.12	2.9	3.36	3.04	3.25	2.93	3.26	2.93	3.25
pH (After Aging)	8.8		8.4		8.4		8.4		8.4	

Table B-7: Test Results of Batch 3

Sample	BF-3		NF-9		NF-10		NF-11		NF-8	
Tap Water, cc	350		350		350		350		350	
Bentonite, gr	20		20		20		20		20	
CMC, gr	1		1		1		1		1	
CFL, gr	0		0		0		0		0	
Nanoparticle, gr	0		0.5		0.5		0.5		0.5	
Aging Time, hr	4		4		4		4		4	
Aging Temperature, °F	140		140		140		140		140	
Mud Density , lb/gal	8.5		8.5		8.5		8.5		8.5	
Viscosity Measurement Temperature, °F	77	120	77	120	77	120	77	120	77	120
Viscosity, 600 rpm reading	31	24	31	24	31	24	31	24	31	24
Viscosity, 300 rpm reading	19	15	19	14	19	14	19	14	19	14
Viscosity, 200 rpm reading	14	11	14	10	14	10	14	10	14	10
Viscosity, 100 rpm reading	9	7	9	6	9	6	9	6	9	6
Viscosity, 6 rpm reading	2	2	2	2	2	2	2	2	2	2
Viscosity, 3 rpm reading	1	1	1	1	1	1	1	1	1	1
PV	12	9	12	10	12	10	12	10	12	10
YP	7	6	7	4	7	4	7	4	7	4
Gel Strength, 10 sec	2	2	2	2	2	2	2	2	2	2
Gel Strength, 10 min	6	8	3	4	3	4	3	4	3	4
API Fluid Loss, 7.5 min	4.0	5.0	4.6	5.4	4.4	5.0	5.0	5.0	5.6	5.2
API Fluid Loss, 30 min	9.4	10.4	11.0	11.4	10.6	10.8	10.8	10.8	10.8	10.8
Mud Cake Thickness, in	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32
Mud Cake weight, gr	1.44	1.41	1.51	1.54	1.54	1.57	1.52	1.47	1.55	1.57
pH (After Aging)	9		8.8		8.8		8.8		8.8	

Table B-8: Test Results of Batch 4

Sample	**BF-4**		**NF-13**		**NF-14**		**NF-15**		**NF-16**	
Tap Water, cc	350		350		350		350		350	
Bentonite, gr	20		20		20		20		20	
CMC, gr	1		1		1		1		1	
CFL, gr	1		1		1		1		1	
Nanoparticle, gr	0		0.5		0.5		0.5		0.5	
Aging Time, hr	4		4		4		4		4	
Aging Temperature, °F	140		140		140		140		140	
Mud Density , lb/gal	8.5		8.5		8.5		8.5		8.5	
Viscosity Measurement Temperature, °F	77	120	77	120	77	120	77	120	77	120
Viscosity, 600 rpm reading	42	28	40	27	40	27	40	27	40	27
Viscosity, 300 rpm reading	26	17	26	16	26	16	26	16	26	16
Viscosity, 200 rpm reading	19	13	20	11	20	11	20	11	20	11
Viscosity, 100 rpm reading	12	8	13	7	13	7	13	7	13	7
Viscosity, 6 rpm reading	3	2	4	2	4	2	4	2	4	2
Viscosity, 3 rpm reading	2	1	3	1	3	1	3	1	3	1
PV	16	11	14	11	14	11	14	11	14	11
YP	10	6	12	5	12	5	12	5	12	5
Gel Strength, 10 sec	3	2	3	2	3	2	3	2	3	2
Gel Strength, 10 min	6	9	5	4	5	4	5	4	5	4
API Fluid Loss, 7.5 min	4.0	4.2	4.4	4.3	4.7	4.2	3.2	4.2	3.2	4.2
API Fluid Loss, 30 min	8.6	9.7	9.6	9.9	8.4	9.2	7.9	9.6	7.9	9.4
Mud Cake Thickness, in	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32	1/32
Mud Cake weight, gr	1.29	1.42	1.35	1.49	1.37	1.43	1.34	1.42	1.38	1.43
pH (After Aging)	8.7		8.5		8.5		8.5		8.5	

APPENDIX C

TEST RESULTS OF EXPERIMENTAL GROUP 2

All experimental results of group 2 are shown in detail in APPENDIX C.

Table C-9: Test Results of 15-20 nm Porous Silica Added to Water-Based Mud

Sample	**Base Fluid**			**15-20 nm Porous**			**15-20 nm Porous**		
Deionized Water, cc	350			350			350		
Bentonite, gr	26.344			26.486			26.766		
Nanoparticle, gr	0			1.892			5.738		
Mud Density , lb/gal	8.6			8.6			8.6		
Viscosity Measurement Temperature, °F	77	104	140	77	104	140	77	104	140
Viscosity, 600 rpm reading	52	42	33	44	35	30	56	47	42
Viscosity, 300 rpm reading	31	25	21	26	21	18	34	29	26
Viscosity, 200 rpm reading	23	19	15	19	16	14	25	21	20
Viscosity, 100 rpm reading	14	12	10	11	9	8	15	13	12
Viscosity, 6 rpm reading	2	2	2	2	2	2	3	2	2
Viscosity, 3 rpm reading	1	1	1	1	1	1	2	1	1
PV	21	17	12	18	14	12	22	18	16
YP	10	8	9	8	7	6	12	11	10
Gel Strength, 10 sec	2	2	2	2	2	2	2	2	2
Gel Strength, 10 min	3	3	3	2	2	2	4	4	5
API Fluid Loss, 7.5 min @ 77°F	4.5			4.6			5.5		
API Fluid Loss, 30 min @77 °F	10.4			11.9			12.4		
Mud Cake Thickness, in	0.0625			0.0688			0.1063		
Mud Cake Weight, gr	1.83			2.12			2.82		
pH	9.5			9.0			8.7		
API Fluid Loss (Water), 7.5 min @ 77°F	1.5			1.8			1.8		
API Fluid Loss (Water), 30 min @ 77°F	5.8			6.0			6.1		

Table C-10: Test Results of 15-20 nm Nonporous Silica Added to Water-Based Mud

Sample	Base Fluid			15-20 nm Nonporous			15-20 nm Nonporous		
Deionized Water, cc	350			350			350		
Bentonite, gr	26.344			26.486			26.766		
Nanoparticle, gr	0			1.892			5.738		
Mud Density , lb/gal	8.6			8.6			8.6		
Viscosity Measurement Temperature, °F	77	104	140	77	104	140	77	104	140
Viscosity, 600 rpm reading	52	42	33	54	45	39	63	54	47
Viscosity, 300 rpm reading	31	25	21	33	28	24	39	34	29
Viscosity, 200 rpm reading	23	19	15	25	21	18	29	25	22
Viscosity, 100 rpm reading	14	12	10	15	13	11	17	15	14
Viscosity, 6 rpm reading	2	2	2	3	2	2	3	3	2
Viscosity, 3 rpm reading	1	1	1	2	1	1	2	2	1
PV	21	17	12	21	17	15	24	20	18
YP	10	8	9	12	11	9	15	14	11
Gel Strength, 10 sec	2	2	2	3	3	2	3	3	3
Gel Strength, 10 min	3	3	3	4	4	3	4	4	5
API Fluid Loss, 7.5 min @ 77°F	4.5			4.8			5.7		
API Fluid Loss, 30 min @77 °F	10.4			11.4			12.6		
Mud Cake Thickness, in	0.0625			0.0625			0.1000		
Mud Cake Weight, gr	1.83			2.18			3.29		
pH	9.5			9.8			8.9		
API Fluid Loss (Water), 4 7.5 min @ 77°F	1.5			1.7			1.8		
API Fluid Loss (Water), 30 min @ 77°F	5.8			6.1			6.2		

Table C-11: Test Results of 20-30 nm Silica Added to Water-Based Mud

Sample	Base Fluid			20 - 30 nm			20 - 30 nm		
Deionized Water, cc	350			350			350		
Bentonite, gr	26.344			26.486			26.766		
Nanoparticle, gr	0			1.892			5.738		
Mud Density , lb/gal	8.6			8.6			8.6		
Viscosity Measurement Temperature, °F	77	104	140	77	104	140	77	104	140
Viscosity, 600 rpm reading	52	42	33	52	47	35	67	64	50
Viscosity, 300 rpm reading	31	25	21	31	29	22	41	39	31
Viscosity, 200 rpm reading	23	19	15	23	22	16	31	29	24
Viscosity, 100 rpm reading	14	12	10	15	13	10	19	18	15
Viscosity, 6 rpm reading	2	2	2	3	3	2	3	3	3
Viscosity, 3 rpm reading	1	1	1	2	2	3	2	2	2
PV	21	17	12	21	18	13	26	25	19
YP	10	8	9	10	11	9	15	14	12
Gel Strength, 10 sec	2	2	2	3	3	2	3	3	3
Gel Strength, 10 min	3	3	3	4	4	3	4	5	6
API Fluid Loss, 7.5 min @ 77°F	4.5			5.0			5.5		
API Fluid Loss, 30 min @77 °F	10.4			11.4			12.5		
Mud Cake Thickness, in	0.0625			0.0625			0.1000		
Mud Cake Weight, gr	1.83			2.26			2.68		
pH	9.5			9.2			8.9		
API Fluid Loss (Water), 7.5 min @ 77°F	1.5			1.6			2.2		
API Fluid Loss (Water), 30 min @ 77°F	5.8			6.0			6.4		

Table C-12: Test Results of 60-70 nm Silica Added to Water-Based Mud

Sample	Base Fluid			60 - 70 nm			60 - 70 nm		
Deionized Water, cc	350			350			350		
Bentonite, gr	26.344			26.486			26.766		
Nanoparticle, gr	0			1.892			5.738		
Mud Density , lb/gal	8.6			8.6			8.6		
Viscosity Measurement Temperature, °F	77	104	140	77	104	140	77	104	140
Viscosity, 600 rpm reading	52	42	33	55	44	36	65	54	47
Viscosity, 300 rpm reading	31	25	21	34	27	23	40	33	29
Viscosity, 200 rpm reading	23	19	15	25	20	17	30	25	22
Viscosity, 100 rpm reading	14	12	10	15	12	11	17	15	13
Viscosity, 6 rpm reading	2	2	2	3	2	2	3	3	2
Viscosity, 3 rpm reading	1	1	1	2	1	1	2	2	1
PV	21	17	12	21	17	13	25	21	18
YP	10	8	9	13	10	10	15	12	11
Gel Strength, 10 sec	2	2	2	3	3	2	3	3	3
Gel Strength, 10 min	3	3	3	4	4	3	4	4	5
API Fluid Loss, 7.5 min @ 77°F	4.5			5.1			5.3		
API Fluid Loss, 30 min @77 °F	10.4			11.6			12.3		
Mud Cake Thickness, in	0.0625			0.0625			0.1000		
Mud Cake Weight, gr	1.83			2.28			2.64		
pH	9.5			9.2			9.1		
API Fluid Loss (Water), 7.5 min @ 77°F	1.5			2.2			1.8		
API Fluid Loss (Water), 30 min @ 77°F	5.8			6.2			6.3		