Zisis Vryzas

Synthesis and Development of Smart Drilling Fluids Using Nanoparticles to Tailor their Transport Properties for Enhanced Drilling Operations

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Examination Committee:
Prof. V. Zaspalis, Supervisor
Prof. V. Kelessidis, Co-Supervisor
Prof. D. Gournis, Co-Supervisor
Prof. H. A. Nasr-El-Din, Examiner
Prof. S. Yiantsios, Examiner
Assoc. Prof. A. Aggeli, Examiner
Dr. L. Nalbantian, Examiner
‘Synthesis and Development of Smart Drilling Fluids Using Nanoparticles to Tailor their Transport Properties for Enhanced Drilling Operations’
Abstract

Drilling deeper to discover new oil and gas reservoirs in hostile environments, extended horizontal sections and multi-fractured zones, necessitates the improvement of the existing drilling fluids or the design of new ones in order to meet the technological demands. The key challenge in developing such drilling fluids is to ensure stable filtration and rheological properties, but also to enable their judicious customization, particularly for high pressure-high temperature (HP/HT) applications. Thus, the search is under way to develop smart drilling fluids to address the severe technological challenges. Smart drilling fluids are novel water-based fluids having the potential of increasing the efficiency of drilling operations with a substantial minimization of lost circulation issues and differential sticking problems along with a simultaneous reduction in the environmental footprint. Nanomaterials are available commercially at affordable prices and they are considered as the best candidates for smart drilling fluids due to their unique properties stemming from their extremely high surface-to-volume ratio.

This study aimed to develop specifically engineered water-based drilling fluids for optimum drilling performance and minimal environmental impact by using commercial (C) hematite (Fe₂O₃) nanoparticles (NP), commercial (C) magnetite (Fe₃O₄) nanoparticles (NP), custom-made (CM) bare (CM-B) and citric-acid coated (CM-CA) Fe₃O₄ NP and C nanosilica (SiO₂) as drilling fluid additives. A 7 wt% water-bentonite suspension was used as the base fluid and the different NP were added at different concentrations (0.5 wt%, 1.5 wt% and 2.5 wt%). A range of physico-chemical techniques were employed to characterize the NP such as, X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), N₂ sorption, a superconducting quantum interference device (SQUID) magnetometer and High Resolution Transmission Electron Microscopy (HRTEM). A freeze granulation -freeze drying (FG-FD) technique of bentonite suspensions containing different nanoparticles was implemented in order to capture effectively the associated microstructures at the different temperatures prior to physicochemical characterization. The rheological measurements were performed at different temperatures (up to 70°C) and ambient pressure using a Couette type viscometer. The Herschel- Bulkley (HB) model was used to describe the rheological behavior of all samples at the different tested temperatures. Filtration characteristics were determined at elevated pressures and temperatures using a HP/HT filter press (at 21 bar and 176°C). Filter
The cake surface morphology was evaluated using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS).

The findings confirm that the association of the nanoparticles with the bentonite platelets in different configurations plays a critical role in the rheological characteristics of aqueous bentonite suspensions. The charge and nature (e.g. magnetic, coated or not) of the added nanoparticles are also important factors in determining the magnitude of the effects observed. Addition of C Fe$_3$O$_4$ NP as well as CM (both bare and citric acid coated) Fe$_3$O$_4$ NP affected the rheological profile of bentonite-based drilling fluids up to 70°C by increasing yield stress and viscosity. SiO$_2$ NP adversely affected the rheology of water bentonite suspensions by decreasing the yield stress. Aging at 176°C/350°F for 16 hours showed that the CM-CA (citric-acid coated) Fe$_3$O$_4$ NP remained stable with minor changes in rheological properties. Optimum concentration of NP was determined at 0.5 wt%. At this concentration the CM-CA Fe$_3$O$_4$ NP yielded maximum filtration reduction by 40% at HP/HT conditions compared to that of the base fluid, and was even greater (-43%) after thermal aging. These results indicated that the newly developed nano-enhanced drilling fluids can significantly reduce the fluid loss which in turn leads to great cost savings. On the other hand, SiO$_2$ NP increased the filtration volume. Through extensive microscopic analysis of the filter cakes with Scanning Electron Microscopy (SEM), it was determined that using optimum concentration of NP resulted in a rigid and low permeability filter cake giving superior filtration characteristics.

In addition, this research revealed the interfacial phenomena taking place and the modes of interaction between bentonite particles and nanoparticles that lead to such superior properties using Transmission Electron Microscopy (TEM) technique. Based on the research findings, a model of the interactions evolving in water Na$^+$-bentonite suspensions containing different nanoparticles at 25°C and 60°C in alkaline pH is suggested. The effect of an external magnetic field on the rheological properties of a drilling fluid containing superparamagnetic citric acid coated Fe$_3$O$_4$ NP-tailored to meet specific downhole and environmental demands with tunable rheological properties- was also examined. The results indicated that all tested fluids exhibited a typical monotonic increase in shear stress and apparent viscosity with increasing magnetic field strength, which was attributed to the strong chain-like structures between the superparamagnetic NP that were formed at high magnetic flux densities.

This research has shown that nano-based drilling fluids can offer unprecedented potential for enhanced drilling operations. Due to their unique features compared to the parent materials and their ease of manipulation to perform certain functional tasks, nanomaterials can retain
their properties over a wide range of operating conditions. A comprehensive characterization approach was adopted, combining micro- and macro- measurements, which enabled the exploitation of the improved microstructure qualities of such suspensions. Engineering high performance drilling fluid systems with excellent rheological and filtration characteristics at HP/HT environments can help operators run at peak efficiency by achieving the reservoirs’ highest potential, while eliminating the use of aggressive and potential damaging chemicals and minimizing non-productive time and formation damage risks.
Dedication

To my family,
Stergios
Katerina
Antonia
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Nomenclature

\( K = \) consistency index, Pa s^n
\( n = \) flow behavior index (dimensionless)
\( R^2 = \) regression coefficient (dimensionless)
\( t = \) time of filtration, s
\( V_A = \) van der Waals attractive energy
\( V_R = \) interparticle double layer repulsive energy
\( V_T = \) total interaction energy
\( V_f = \) cumulative filtrate volume, m^3

Greek Letters

\( \dot{\gamma} = \) shear rate, s^{-1}
\( \Delta p = \) pressure drop across the filter cake, psi or Pa
\( \zeta = \) zeta potential, mV
\( \mu = \) viscosity of the filtrate, cP
\( \mu_p = \) plastic viscosity, cP
\( \tau = \) shear stress, Pa
\( \tau_o = \) yield stress, Pa
\( \tau_{HB} = \) Herschel Bulkley yield stress, Pa
\( \Sigma Q^2 = \) sum of square errors, Pa^2
List of Acronyms

API = American Petroleum Institute
ASCH = Aluminosilicate clay hybrid
AV = Apparent viscosity
Bent SPN = Bentonite suspension
BF = Base fluid
BHT = Bottom hole temperature
BTWDFs = Bentonite water-based drilling fluids
C = Commercial
CM = Custom-made
CM-B = Custom-made bare
CM-CA = Custom-made citric acid coated
CMC = Carboxymethyl cellulose
CNC = Cellulose nanocrystals
CNP = Cellulose nanoparticles
CT = Computed tomography
CTAB = Cetrimonium bromide
CTN = Computed tomography number
ECD = Equivalent circulation density
ERD = Extended reach drilling
FD = Freeze dried
FG = Freeze granulated
FTIR = Fourier transform infrared spectroscopy
GO = Graphene oxide
HB = Herschel-Bulkley
HP/HT = High-pressure/high-temperature
HR-TEM = High Resolution Transmission Electron Microscope
HV = High viscosity
ICH = Iron oxide clay hybrid
ICP-OES = Inductively Coupled Plasma-Optical Emission Spectrometry
JCPDS = Joint Committee on Powder Diffraction Standards
<table>
<thead>
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<th>Definition</th>
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<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LCM</td>
<td>Lost circulation material</td>
</tr>
<tr>
<td>LFGO</td>
<td>Large flake graphene oxide</td>
</tr>
<tr>
<td>LP/LT</td>
<td>Low-pressure/low-temperature</td>
</tr>
<tr>
<td>LV</td>
<td>Low viscosity</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
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<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>NF</td>
<td>Nano-based fluid</td>
</tr>
<tr>
<td>NWBF</td>
<td>Nano-enhanced water-based drilling fluid</td>
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<tr>
<td>OBM</td>
<td>Oil-based mud</td>
</tr>
<tr>
<td>PAC</td>
<td>Poly anionic cellulose</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PGO</td>
<td>Powdered graphene oxide</td>
</tr>
<tr>
<td>PV</td>
<td>Plastic viscosity</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root mean square error</td>
</tr>
<tr>
<td>ROP</td>
<td>Rate of penetration</td>
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<tr>
<td>SBM</td>
<td>Synthetic-based mud</td>
</tr>
<tr>
<td>SDFL</td>
<td>Hydrophobic associated polymer based nano-silica composite with core-shell structure</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>Scanning electron microscopy-energy dispersive spectroscopy</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>WBM</td>
<td>Water-based mud</td>
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<tr>
<td>XG</td>
<td>Xanthan gum</td>
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<tr>
<td>XPS</td>
<td>X-ray photospectrometry</td>
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<tr>
<td>XRD</td>
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<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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<td>Yield point</td>
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Chapter 1. Introduction

1.1 General background and problem statement

Drilling for oil and gas is one of the most expensive operations in the search for hydrocarbons. Drilling provides a corridor from surface to potential bearing hydrocarbon formations. Once a hole (wellbore) is drilled, well logging and testing confirms or not the presence of hydrocarbons in a reservoir.

A successful drilling operation depends strongly on the effectiveness of the drilling fluid (mud) in use (Figure 1). Drilling for oil and gas involves the drilling of a telescopic hole from surface to the reservoir which can be kilometers away from the surface. Drilling is accomplished with the use of a drilling bit connected to a long string of drill pipe. Applying weight and rotation on the bit, the bit crushes the rock into small fragments, the cuttings. Drilling fluid is considered the “blood” of the well and is circulated downhole from surface, through the drill pipe to the bit face, it lifts the generated cuttings and brings them to surface via the annulus between the formation and the drill pipe, where separation equipment removes the cuttings from the drilling fluid. The clean drilling fluid is circulated back to the wellbore with the help of powerful pumps.

![Figure 1. Schematic representation of the drilling process.](image)

Drilling fluids perform several additional functions besides cuttings transport to the surface. They control subsurface pressures, stabilize the exposed rock, prevent contamination of subsurface formation hydrocarbon fluids, provide buoyancy, and cool and lubricate the bit. Such fluids must be engineered so that they can perform efficiently in harsh environments and it must be ensured that they do not damage the formations which are drilled. The many
functions performed by the drilling fluid require that some minimum properties of the fluids are maintained. Such properties are, density, viscosity, fluid loss control, gel strength, pH, lubricity, solids content and chemical composition. These properties are affected by factors including temperature, pressure, fluid composition, and fluid shear history. The rheological characteristics, specifically the yield stress, which is the stress that must be applied to a material to make it to start flow and viscosity, which indicates the resistance of a fluid to flow, of a drilling fluid have one of the largest effects on drilling operations. These rheological properties have a major impact on the hydraulics system’s objectives which are to maintain acceptable pressure control in the annulus and to clean the cuttings from the wellbore. In addition, fluid loss, which is defined as the leakage of the liquid phase of drilling fluid containing solid particles into the formation matrix, is considered as one of the major sources of capital expenditures during drilling operations. Thus, it should be carefully controlled in order to minimize formation damage and to ensure the economic viability of a well. Figure 2 presents the different formations (highly permeable formations, induced or natural fractures and cavernous formations) in which drilling fluid losses can occur.

![Image of formations for drilling fluid losses](image-url)

**Figure 2.** Formations for drilling fluid losses (Alsaba et al., 2014).

Formation damage by definition refers to the impairment of the permeability of any oil or gas producing formation imparted by various adverse processes and can occur at any time
during the life of a well from drilling to production, to stimulation and to workover operations. Minimization or mitigation of formation damage is considered vital for the efficient exploitation of oil and gas reservoirs (Energy Highlights 1990). Formation damage can be triggered by one or a combination of several factors, such as solids plugging, clay-particle swelling or dispersion, wettability reversal, emulsion blockage, aqueous-filtrate blockage, fines migration, deposition of paraffins or asphaltenes and condensate banking. If it is not prevented or efficiently mitigated, it can lead to significant decrease in the productivity of reservoirs turning them into non-economically feasible reservoirs.

Mud filtrate invasion is one of the most common causes of formation damage (Amaefule et al. 1988). Such an invasion can result in significant formation damage around the wellbore and decrease well productivity and subsequently reservoir fluids recovery. Control of formation damage through enhanced drilling fluid properties is a key element for the successful development of oil- and gas reservoirs. During drilling, the resultant - normally positive- differential pressure between wellbore pressure and reservoir fluid pressure causes fluid loss into the formation (Hoberock and Bratcher 1998). A filter cake (or mudcake) is formed on the formation face due to the build-up of the mud solids (Civan 1994) (Figure 3). Filter cake properties, such as thickness, structure, particle size distribution, texture and permeability are essential factors that should be carefully identified and optimized (El Katatny et al. 2012; Mahmoud et al. 2017). An improved (low) fluid loss value and the deposition of a high quality, thin and impermeable, mudcake can aid significantly the mitigation of excessive formation damage issues (Zakaria et al. 2012; Contreras et al. 2014; Mahmoud et al. 2016).

Figure 3. Filter cake in a wellbore with particle and filtrate invasion (Civan 1994).
Exploration of new hydrocarbon fields in complex subsurface environments under high pressure and high temperature (HP/HT) conditions, requires the development and use of exceptional drilling fluids, which maintain their properties even in such hostile environments. Failure to adequately address drilling fluid related concerns could lead to excessive well costs, unscheduled trouble time, unnecessary high risk activities, and poor performance. Currently there are a variety of definitions that exist for a high temperature and high pressure (HP/HT) well. Generally oil and gas industry follows the definition that was introduced by the Department of Trade Industry for the United Kingdom Continental Shelf (UKCS). The UKCS defines a HT/HP well as one “Where the undisturbed bottom hole temperature (BHT) at prospective reservoir depth is greater than 149°C (300°F) and the maximum anticipated pore pressure of any porous formation to be drilled through exceeds a pressure of 690 bar (10,000 psi).” Maldonado et al. (2006) breaks it up into three tiers as shown in Figure 4. According to this classification Tier I wells are characterized by wells with reservoir pressures up to 1034 bar/15,000 psi and temperatures up to 176°C/350°F. Tier II wells are what is referred to as “extreme” HT/HP (XHT/HP) wells and are characterized by reservoir pressures up to 1379 bar/20,000 psi and temperatures up to 204°C/400°F. Tier III wells are referred to “ultra” HT/HP (UHT/HP) wells and are characterized by reservoir pressures up to 2068 bar/30,000 psi and temperatures up 260°C/500 °F. Some studies that show the effectiveness of drilling fluids under the three different tiers are: Eldoy et al. (1995) for Tier I, North et al. (2000) and Liwei et al. (2016) for Tier II, Charnvit et al. (2014) for Tier III.

Figure 4. Classification of HP/HT wells (Maldonado et al., 2006).
Depending on the base fluid, drilling fluids are classified as water-based fluids or muds (WBM), oil-based muds (OBM) containing diesel oil and synthetic-based muds (SBM) containing linear chain hydrocarbons. Each drilling fluid system has advantages and disadvantages and are chosen based on their applicability to effectively assist in drilling a specific well. Bland et al. (2002) states that “the undesirable characteristics of WBMs include the ability to impede hydrocarbon flow through porous rocks, hydration/plasticization and/or disintegration of cuttings, loss of wellbore support in certain formations (e.g. shales) through pore pressure elevation, and the ability to dissolve salt and corrode metals. Alternatively the desirable characteristics of oil/synthetic fluids include better lubrication, higher boiling points, and lower freezing points.” Although OBM’s desirable characteristics have distinct advantages especially when drilling into HP/HT formations their cause for concern with respect to environmental awareness, economic considerations, and well control issues have led to an increase use of WBMs in higher temperature environments. Due to the environmentally unfriendly nature of OBMs there has been an increase in regulations around the world that explicitly prohibit the drilling and discharging of OBM and SBM cuttings and any by-products. Most environmental concerns are directed to the contamination of the ecological systems near offshore drilling platforms than that of onshore drilling operations. Although onshore drilling operations have less of contamination problems, OBMs and SBMs can often contaminate the ground in and around an onshore drilling operation thus increasing environmental concerns. However, the additives of WBMs deteriorate at HP/HT conditions (with temperature to be the main factor that affect drilling fluids performance and to a lesser extent by pressure). Hence, there is a great need to improve their properties and extend their use at extreme downhole conditions by using thermally stable additives.

WBMs consist of clays and some organic additives in order to provide the required rheological and filtration properties. Some weighing agents such as barite are also added to increase the density of the mud when needed. In the interest of well safety, there is a natural trend to keep the mud density above that actually required to control the pressure of the formation fluids, but it has some disadvantages. First of all, excessive mud density may increase the borehole pressure and induce fracturing of the borehole wall. In this scenario, mud is lost into the formed fracture with adverse impact on well safety and cost. In addition, excessive mud densities may have an adverse impact on drilling rate while high overbalance pressures increase the risk of sticking the drill pipe. Finally, it increases the mud cost not only by the initial cost of the barite, but also by the increased cost of maintaining suitable flow properties due to increase in viscosity.
Bentonite is a montomorillonite clay used in conventional WBM systems for viscosity and filtration control. Bentonite can be classified into either Na-bentonite with high swelling capacity or Ca-bentonite that quickly generates colloids in water as a non-swelling clay (Abu-Jdayil 2011). The montomorillonite particles have a plate-like structure with layers consisting of a central octahedral sheet sandwiched between two tetrahedral sheets (Van Olphen 1977). Due to its inherent, well-performing rheological properties and its ability to contribute to the formation of a thin and low permeability filter cake (Mahto and Sharma 2004), bentonite is used widely for drilling oil and gas wells. However, montomorillonite begins to chemically break down at temperatures higher than 120°C (250°F) (Kelessidis et al. 2006), causing significant increase in the fluid loss and reduction of the effective carrying capacity of cuttings (Bourgoyne et al. 1991), which make these fluids ineffective in HP/HT conditions.

Operating in HP/HT environments needs extensive planning with special attention being paid to the drilling fluid in use. In recent years various additives have been developed to improve HP/HT performance of bentonite drilling fluids. Accurate knowledge of drilling fluid behavior under actual conditions is required to maximize operational efficiency and to minimize cost and drilling fluid related risks on extreme HP/HT wells. HP/HT wells require a higher density fluid which typically requires high solids loading. High solids loading, the resulting higher pressures, combined with the competency of rock at depth, lead to low penetration rates, extending time on location and added drilling costs (Bland et al. 2006).

Nanotechnology has come to the forefront of research and has already contributed significantly to technological advances in various industries, including the energy industry. The drilling industry could not be an exception to this norm. Nanoparticles (NP) possess enhanced physico-chemical properties compared to macro and micro-sized materials, which can be attributed to their tiny size along with their extremely high surface-to-volume ratio. Such properties make NP the most promising materials for the design of smart drilling fluids with tailor-made properties that can meet the requirements of the demanding downhole environments (Amanullah et al. 2011).

The drilling industry can thus significantly benefit from nanotechnology. NP are used in drilling fluids in order to formulate smart drilling fluids to give them optimal properties under a wide range of operating conditions. Furthermore, the potential to manufacture custom-made nanoparticles may play a vital role for the development of nano-based drilling fluids, because custom-made fluids can be developed that can meet the needs of each operator to deal with different specific conditions. Hence, the application of nanoparticles to formulate high
performance drilling fluids has the potential to overcome current as well as future technical challenges encountered by the drilling industry.

Over the last few years the need for improved drilling fluids has led researchers to examine the development of enhanced drilling fluids, using various NP as additives. While most of the reported work is lab work, there are however two studies reporting full-scale field testing of nanoparticle-based drilling fluids (Borisov et al. 2015; Taha and Lee, 2015). Brief overviews of the application of nanotechnology to drilling fluid formulation has also been provided in the literature (Friedheim et al. 2012; Hoelscher et al. 2013; Vryzas and Kelessidis 2017).

From all the above, it can be deduced that there is a huge need for the development of improved drilling fluids which will be able to maintain the fluid properties at various demanding downhole environments of high temperatures in excess of 176°C and high pressures in excess of 1034 bar and nanoparticles could evolve potentially as the best drilling fluid additives to formulate drilling fluids with exceptional properties. This is the aim of this work, to develop/choose the best nanoparticles that can provide stable rheological and good filtration properties of bentonite drilling fluids at HP/HT conditions.

1.2 Brief background of clay minerals

Clay minerals and their suspensions have long been of great scientific as well as industrial interest with a wide range of applications from absorbents (Lagaly, 1994) to drilling fluids (Gray and Darley 1988; Kelessidis et al., 2006) and nanocomposites (Pinnavaia and Beall, 2001). The basic structure of clay minerals is a two-dimensional array formed by sheets of silica tetrahedron (T) and sheets of alumina octahedron (O). Clay minerals present a TO configuration (e.g. kaolinite), which means one silica tetrahedra sheet binds with one alumina octahedra sheet, or a TOT configuration (illite and montmorillonite) in which one alumina octahedra sheet is shared by two silica tetrahedra sheets. A schematic representation of the atom arrangements in a unit cell for a three-layer clay such as montmorillonite is shown in Figure 5. The montmorillonite structure is classified as dioctahedral, having two thirds of the octahedral sites occupied by trivalent cations. Dioctahedral montmorillonite has its structural charge originating from the substitution of Mg$^{+2}$ for Al$^{+3}$ in the octahedral sheet (see Figure 5). The structural formula for montmorillonite is $M_y^+nH_2O(AI_{2y}Mg_y)Si_4O_{10}(OH)2$. The negative charge is balanced by cations intercalated between the structural units and these cations may be alkaline earth ions (Ca$^{+2}$ and Mg$^{+2}$) or the alkali metal Na$^+$. When Na$^+$ cations are
exclusively in exchange with the montmorillonite surface, the clay is known as Na+-montmorillonite.

The surface charge of clay particles arises from both the basal plane and the clay edge. The basal plane of clay minerals has a permanent negative charge due to isomorphic substitution, while the charge of the edge is pH-dependent because of the exposed >Al-OH and >Si-OH groups (Luckham and Rossi, 1999). The point of zero charge (PZC) is often used to determine the charge of the edge under the pH condition of interests. The PZC represents the value of pH under which the edge of a clay mineral is neither negatively nor positively charged. The edge is positively charged when the pH is below the PZC and negatively charged when pH is above the PZC. For example, the PZC of kaolinite and montmorillonite is in the range of 6.0 – 6.5, while it is around 3.5-4.5 for illite. When the pH is below the PZC of a clay mineral, a small amount of electrolyte can disturb the stability of clay colloids which aggregate between negatively charged edge and oppositely charged basal plane. However when the pH is above the PZC, higher concentrations of electrolyte are needed to change stability because both the edge and basal of the clay particles are negatively charged. The charge of the edge is also significant for determining the predominant interaction of clay minerals such as edge-to-edge (EE), edge-to-face (EF), and face-to-face (FF) (Figure 6). It will also be reflected in interactions that occur between the clay and NP.
Clay particles in suspension owe their stability to mutual repulsion when their interacting diffuse electrical double layers interact on approach (Luckham and Rossi, 1999). A theoretical analysis of the interaction between colloidal particles has been developed by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). The fundamental feature of what is known as the DLVO Theory is that the total interaction energy ($V_T$) is determined by a combination of the interparticle double layer repulsion energy ($V_R$) and the Van der Waals attractive energy ($V_A$). Colloidal stability may be explained by means of the superposition of both energies. More details regarding DLVO theory and its applicability in clay particles can be found in Derjaguin and Landau (1941); Verwey and Overbeek (1948); Luckham and Rossi (1999).

Clay particles interact with each other through different modes leading to different flow behavior. These interactions are mostly electrostatic in nature and this can be attributed to the state of charge on the two distinct surfaces that make up each clay platelet. Generally, there are four states of clay particle association (Figure 6):

- **Aggregation** refers to face-to-face particle linking (along the large planar surfaces). This leads to the formation of large packets of clay and reduces the total number of particles in suspension.
- **Dispersion** produces the opposite effect of aggregation. Clay platelets are separated from one another, interspersed by the suspending medium (water in our case).
- **Flocculation** results from either edge-to-edge or edge to face association of clay platelets in what is commonly referred to as a house of cards structure. This causes an increase in viscosity due to the formation of interlinked flocs.
- **Deflocculation** is the reversal of the flocculation process leading to a reduction in viscosity. The edge-to-edge association is weakened by the action of chemicals due to decrease in the electrochemical forces holding the house of cards together.
Higher concentrations of clay promote flocculation which in turn causes the formation of a continuous gel structure instead of individual flocs. Deflocculation of bentonite dispersions can be achieved by addition of thinners such as polyphosphate, lignosulfonate or lignite (Kelessidis et al. 2007a), polysaccharides, cellulosics, starches with polyglycols (van Oort et al. 1997), synthetic polymers (Tehrani et al. 2009), or the use of metal complexes (Burrafato et al. 1995). Luckham and Rossi (1999) reported that the gel structures build up slowly with time, as the particles orient themselves towards positions of minimum free energy under the influence of Brownian motion. Van Olphen (1951 and 1958) suggested that the formation of gel structures in clay suspensions is a result of the attraction between the edges and the faces of the clay platelets, which leads to a microstructure network known as house of cards structure. On the other hand, Rand et al. (1980) advocated the existence of FF and EE associations in Na\(^+\) montmorillonite suspensions within a pH range 4-11. Norrish (1954) proposed that the gel structure in montmorillonite suspensions was a result of the repulsive forces caused between the interacting double layers.

Elevated temperatures adversely affect the rheological properties of water-bentonite suspensions. Luckham and Rossi (1999) determined that the origin of the flocculation behavior at higher temperatures is not entirely clear, but suggested that this may be due to modification of the electrical double layer surrounding clay platelets by temperature. Kelessidis et al. (2007) contemplated that the reasons behind this phenomenon are not entirely known.

This study is devoted to shed some additional light into the mechanisms of the bentonite inter particle interaction in high temperature environments, by combining macroscopic measurements (rheological measurements) with microscopic measurements (i.e. HRTEM) which can aid our understanding of the interactions of the particles in the microcosmos of such dispersions.

### 1.3 Background of nanoparticles and nanofluids

Over the last decade, application of nanotechnology in different industries such as electronics, medicine, biomaterials and renewable energy production has already brought new technological advances. However, due to the great risk of adapting new technologies, their application in oil and gas industry is still limited.

Nanoparticles refer to particles in the range of 1 to 100 nm which are made of inorganic or organic chemicals and they exist as particulate dispersions or solid particles. This size range (from 1–1000 nanometers) allows the creation and use of structures, systems and devices that
have novel properties with atomic-level control. They can be classified into different classes based on their properties, shapes or sizes. The different groups include metal NP, ceramic NP, and polymeric NP. Nanoparticles (NP) possess enhanced physico-chemical properties when compared to macro and micro-sized materials, which can be attributed to their tiny size along with their extremely high surface-to-volume ratio (Figure 7).

Figure 7. Surface area to volume ratio of the same volume of materials (source: adapted from Amanullah et al. 2009).

Two approaches have been known in the preparation of ultrafine particles from ancient times. The first is the breakdown (top-down) method by which an external force is applied to a solid that leads to its break-up into smaller particles. The second is the build-up (bottom-up) method that produces nanoparticles starting from atoms of gas or liquids based on atomic transformations or molecular condensations as shown in Figure 8. These approaches can be further divided into various subcategories based on the operation, reaction condition and adopted protocols. The advantages and disadvantages of each method has been extensively reported by Yu and Xie (2012).
When nanoparticles are added to a base fluid, the mixture becomes a nanofluid. Nanofluids are dilute liquid suspensions of nanoparticles with at least one of their dimensions smaller than 100 nm. The base fluid can be water, ethylene glycol, surfactant-based fluids, polymeric fluids, engine oil, mixture of two or more liquids, etc. Nano-fluids have distinctive properties and offer unprecedented potential for applications in various sectors such as the energy, cosmetic, aerospace and biomedical industries.

In recent years, nanotechnology is becoming increasingly popular in the oil and gas industry. Nanofluids find applications in drilling, completion, stimulation, and enhanced oil recovery. Studies are ongoing, in different areas of the oil and gas industry, to address several challenging issues. This research focuses on the use of various NP as drilling fluid additives in water-bentonite suspensions in order to achieve improved rheological and filtration properties.

In binary nanoparticle-bentonite systems, nanoparticles can be fully or partly intercalated or exfoliated relative to bentonite platelets. Each of these processes affect differently the flow behavior of the system, leading to major changes in their rheological profile. An effective strategy to reveal properties in such complex binary component systems, is firstly to understand the behavior of each component, as single system and then to analyze their interactions with other components in aqueous environments. Adopting such an approach may reveal how different nanoparticles associate in clay suspensions under different conditions and their subsequent effect on the rheological behavior of the system. Zhou et al. (2012) suggested that coagulation rates between montmorillonite and nanoparticles of Ag (negatively charged) or
TiO$_2$ (positively charged) are mostly affected by the pH and ionic strength of the solution. They observed that clay platelets form agglomerates mainly through FF associations, rather than EF and EE. Their stability is governed by the amount of clay in the suspension and the ions in the solution. Jung et al. (2011) noticed that bentonite particles cross-link to form well-oriented porous structure upon addition of iron oxide nanoparticle clay hybrids in bentonite suspensions. They attributed this behavior to the development of positively charged edge surfaces in the iron oxide nanoparticle clay hybrids that leads to strengthening of the gel structure of bentonite suspensions.

In spite of the reported tremendous advantages, nanoparticles have some limitations that should be taken into consideration in order to take full advantage of their properties. Their small size and large surface area can lead to particle aggregation, making physical handling of nanoparticles difficult in liquid and dry forms. Controlling the size, shape and stability of NP is a challenging task. For example, magnetic iron oxide NP have a large surface-to-volume ratio and therefore have high surface energies. This is the main reason for their tendency to aggregate as they are trying to minimize their surface energies (Wu et al. 2008).

Aggregation is one of the most important challenges when someone is dealing with nanofluids. In general, aggregation of colloidal particles occurs when physical processes bring particle surfaces in contact with each other and short-range thermodynamic interactions allow for particle–particle attachment to occur. The rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision. When contact occurs, it can result in attachment or repulsion. There are two types of aggregation relevant to manufactured NP in the environment: homoaggregation and heteroaggregation. Homoaggregation refers to aggregation of two similar particles (i.e., NP–NP attachment). Heteroaggregation refers to aggregation of dissimilar particles (e.g., NP–clay particle attachment) (Hotze et al. 2009).

Nanomaterials are commonly manufactured with surface coatings (e.g., surfactants, polymers, and polyelectrolytes) to enhance dispersion stability or to provide specific functionality (Phenrat et al. 2008; Saleh et al. 2008; Hotze et al. 2009; Faure et al. 2013). Adsorbed or covalently bound surfactants prevent aggregation and enhance dispersion stability of NP by increasing surface charge and electrostatic repulsion or by reducing interfacial energy between particle and solvent (Rosen, 2004).
1.4 Rheology of drilling fluids

Monitoring and controlling the rheological properties of the mud is indispensable part for successful oil and gas well drilling. Precise prediction of frictional losses is heavily dependent on the accurate knowledge of drilling fluid rheology (Gavignet and Wick 1987). As the fluids travel through the wellbore, their rheological profile undergoes significant alterations. The fluid is exposed to a wide range of shear rates ranges from around 1000 s$^{-1}$ in the drillstring to approximately 50000-100000 s$^{-1}$ when the fluid passes through the bit nozzles, and lower shear rates between 0-102 s$^{-1}$ in the annulus while carrying the drill cuttings to the surface (Tehrani 2008).

The flow behavior of any system is described in terms of the relationship between the shear stress, $\tau$, and the shear rate, $\dot{\gamma}$. The shear rate is defined as the change of shear strain per unit time, and the shear stress as the tangential force applied per unit area. The ratio of shear stress to shear rate is called viscosity, $\eta$, hence viscosity is a measure of the resistance to flow of the fluid.

Fluids can be divided into two main groups depending on their response to shearing: Newtonian and non-Newtonian. The first group shows a direct proportionality between shear stress and shear rate, the other does not. Most drilling fluids are non-Newtonian fluids, with viscosity decreasing as shear rate increases. Non-Newtonian fluids are separated further into subcategories defined by various models. The models of most interest in drilling fluid technology are the Bingham plastic, power-law and Herschel-Bulkley models (Table 1). The Bingham plastic model is widely used in the oil and gas industry for rheological characterization of drilling fluids. It assumes a linear relationship between the shear stress and the shear rate. Fluids that exhibit Bingham plastic behaviour do not flow until the shear stress exceeds a critical value known as the yield stress. Once the yield stress is reached, changes in shear stress and shear rate are proportional. The slope of the curve is termed the plastic viscosity (PV). Drilling fluid industry used for many years 2 points for PV and yield point (YP) determination as can be seen in Equations 1 and 2. PV and YP can be calculated by:

PV = Reading at 600 rpm ($\theta_{600}$) – Reading at 300 rpm ($\theta_{300}$), .........................................................(1)

YP = Reading at 300 rpm ($\theta_{300}$) – PV, ..............................................................................................(2)

where PV is the plastic viscosity (cP) and YP is the yield point (lb/100 ft$^2$ or Pa).
However, it should be noted here that taking into consideration only two points in a rheogram can lead to misleading results and thus, the full rheogram should be taken into account when someone wants to calculate the rheological profile of a drilling fluid.

Unlike the Bingham plastic model, the power-law model assumes a non-linear relationship between the shear stress and the shear rate, but does not have a yield stress. For power-law fluids, the shear stress increases as a function of the shear rate raised to a constant exponent. The Herschel-Bulkley model combines the models of Bingham plastic and power-law; the model is applied to fluids that have a yield stress and a non-linear relationship between the shear stress and the shear rate. Most drilling fluids are described very well by the Herschel-Bulkley model and this is the one used in this study.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bingham plastic</td>
<td>( \tau = \tau_y + \mu_p \dot{\gamma} )</td>
</tr>
<tr>
<td>Power Law</td>
<td>( \tau = K \dot{\gamma}^n )</td>
</tr>
<tr>
<td>Herschel-Bulkley</td>
<td>( \tau = \tau_{\text{HB}} + K \dot{\gamma}^n )</td>
</tr>
</tbody>
</table>

Where, \( \tau \) - shear stress (lb/100 ft\(^2\) or Pa)

\( \dot{\gamma} \) - shear rate (s\(^{-1}\))

\( \mu_p \) - plastic viscosity (cP)

\( \tau_y \) - yield stress (lb/100 ft\(^2\) or Pa)

\( \tau_{\text{HB}} \) - HB yield stress (lb/100 ft\(^2\) or Pa)

\( K \) - fluid consistency index (lb. s\(^n\)/100 ft\(^2\) or Pa s\(^n\))

\( n \) - fluid behavior index (dimensionless)

The rheological profile of water-bentonite suspensions have been extensively studied by many researchers and is closely linked with the structural association (3-D network) of bentonite particles. It is strongly dependent on pH conditions, cations and types of ionic additives due to their effect on the diffuse double layers surrounding bentonite particles (Abend and Lagaly, 2000; Kelessidis et al., 2007b). It is well known that Na-bentonite suspensions exhibit thixotropic behaviour (Tombacz and Szekeres, 2004) meaning there is change in rheological behaver with time. Thixotropy (from Greek words “thixis” which means stirring/shaking and “trepo” which means turning/changing), is originated by any shear-
induced change in suspensions microstructure and is underpinned by the break-down due to flow stresses and the build-up due to in-flow collisions and Brownian motion (ten Brinke et al., 2008). Kretser (1998), stated that thixotropy in clay suspensions is mainly attributed to the random coagulation rather than internal mutual flocculation effects. Normally in drilling industry we do not take into account thixotropy as the effective shearing of drilling fluids during flow eliminates any thixotropic effects (Kelessidis et al. 2008).

Drilling fluids are complex multi-component systems containing many additives to achieve specific functions. Water-soluble polymers such as Polyanionic-cellulose (PAC) (Li et al. 2016), Carboxymethyl-cellulose (CMC) and Xanthan-Gum (XG) (da Luz et al. 2017) and most recently various nanoparticles (NP) (Mahmoud et al. 2016) have been used as rheological or filtration control agents. Defining accurately the flow behaviour of such complex fluids and understanding the inter-particle interactions evolving in such suspensions, is crucial towards the development of high-performance drilling fluids which can significantly improve the efficiency of drilling operations.

Drilling fluids have always a basic pH and thus, the amphoteric edge sites of montmorillonite lamellae are negatively charged as are the faces. In acidic environments, the edge-face (EF) heterocoagulated network is created due to the attraction of oppositely charged edges and faces of montmorillonite platelets, which in turn promote higher degree of thixotropy (Abend and Lagaly, 2000). Edge-face (EF) or edge-edge (EE) association leads to card-house like structures, while, face-face (FF) association leads to thicker and larger flakes (tactoids), but the mechanism of formation of tactoids between negatively charges surfaces is still elusive. Till now, the full dissociation of bentonite platelets upon dispersion in water is questioned by several researchers. Benna et al. (1999) argue that, at alkaline pH, bentonite particles are associated in card-house like structures based on repulsion. McBride and Baveye (2002) suggested that the flocculation occurs due to the attraction between like-particles and this attraction is responsible for the flocculation of the bentonite particles even at alkaline pH values, however the nature of this attractive force is still questioned. Recent studies (Kelessidis et al., 2007b; Mouzon et al., 2016) attempted to enlighten this phenomenon and found that the existence of only one type of association (EE, EF, FF) in clay suspensions is very idealistic. Mouzon et al. (2016) have shown that Na⁺-montmorillonite particles, derived from Swy-2 Wyoming bentonite are forming stack of layers or tactoids with different length scales, leading to FF associations while some of the platelets connected in EF arrangement, creating associations of Y-type.
Drilling fluids are typically characterized as shear-thinning solutions, exhibiting viscosity that decreases at higher shear rates (Livescu, 2012). During non-drilling periods (making connections, tripping pipe, running casing, etc.) the drilling fluid can stay stagnant in the hole for hours or even days. Excessive settling of solids can occur while the fluid is static, which may induce many problems. For this reason, bentonite acts as a viscosifier allowing the formation of a well structured network that breaks down on applying a shear stress but quickly re-builds on the cessation of flow (this is commonly called the yield stress). In a lab scale, this inactive period of the drilling fluids at downhole conditions can be simulated by conducting both static and dynamic thermal aging (typically at 177°C (350°F) for 16 h) (Gray and Darley 1988).

The combined effect of temperature, pressure, time- and shear- history dependence of the rheological properties makes the characterization and forecasting of drilling fluids rheological profile a complex task. Accurate determination of the rheological characteristics of complex fluids necessitates very good understanding of the base fluid properties, especially the contribution of the associated microstructure mechanisms on the flow properties. Annis (1967) investigated the effect of temperature (up to 149°C (300°F)) on the rheological properties of aqueous bentonite suspensions. He concluded that high temperature causes flocculation of bentonite particles, which results in high yield points and high viscosity values at low shear rates. Alderman et al. (1988) stated that high shear viscosity decreases for higher temperatures (up to 130°C (266°F)) and yield stress values are independent of pressure variations. Kelessidis et al. (2007a) identified that water-bentonite suspensions thicken substantially upon exposure to high temperatures (after thermal aging) developing high yield stress with small effect on plastic viscosity. Vryzas et al. (2016b) showed that yield stress and viscosity of 7 wt% water-bentonite suspensions are highly sensitive to elevated temperatures (tested up to 70°C), which can be attributed to the flocculation of bentonite particles.

**1.5 Fluid loss issue in drilling operations**

Fluid loss during drilling operations has been one of the major problems for drillers. Figure 9 shows a schematic pattern of drilling fluid loss in operation. Loss of circulation is defined as the uncontrolled flow of drilling mud into a formation. Loss of circulation has a tremendous impact on the cost of the drilling process. It has been estimated to cost the drilling industry over one billion dollars annually in rig time, materials and other financial resources. Invasion of foreign fluids, such as drilling mud filtrate, into the newly exposed formations, is one of the
most common causes of formation damage, leading to costly stimulation treatments and even loss of production. This problem has been known for decades as a major contributor to the abnormal decline in productivity or injectivity in most reservoirs. During drilling, the fluid loss into the formation occurs due to the normal resultant positive differential pressure between wellbore pressure and reservoir pressure, as in most cases and for safety reasons, wells are drilled overbalanced, i.e., with higher wellbore pressures than formation fluid pressures. It is very desirable that a filter mud cake is formed on the formation face from the build-up of the mud solids to minimize fluid invasion. Satisfactory fluid loss values and the deposition of thin, impermeable filter cake can mitigate the problems of excessive formation damage (Mahmoud et al. 2016).

![Diagram of fluid loss in drilling operation.](www.gumprodf.com)

**Figure 9.** Schematic pattern of fluid loss issue in drilling operation (source: www.gumprodf.com).

Fluid loss during drilling operations is a typical filtration problem. Filtration can be carried out under static or dynamic conditions. Static filtration refers to the filtration that occurs when mud circulation stops. It is also known as dead-end filtration. During this type of filtration, the thickness of mud cake around the inner side of the filter gradually increases and the rate of filtration diminishes. On the other hand, dynamic filtration takes place when the drilling fluid is circulated continuously and the formed mud cake is partially swept away and reformed over time. The growth of the filter cake is limited by the erosive action of the drilling mud flow. This type of filtration is also called cross-flow (tangential) filtration. Dynamic filtration rates and fluid loss volumes are much higher than the static ones due to higher fluid invasion to the formations. The type of filter cake is also different in dynamic versus static filtration. Static
filter cakes consist of soft surface layers, while dynamic filter cake surfaces are more eroded due to the hydrodynamic forces of the mud flow stream.

1.6 Research aims and objectives

This dissertation proposes an original research work focused on the development of enhanced water-based drilling fluids containing various commercial and custom-made nanoparticles (Fe₃O₄ and SiO₂). The main objectives of this work are:

- Study the rheological performance of 7 wt% aqueous bentonite suspensions (used as base fluid-BF) at different temperatures (up to 70°C).
- Study the effect of addition of various nanoparticles such as commercial (C) iron oxide (C Fe₂O₃ and C Fe₃O₄) and nanosilica (C SiO₂), custom-made bare (CM-B) and citric acid coated (CM-CA) Fe₃O₄ at different NP concentrations (0.5 wt%-2.5 wt%) to the base fluid.
- Assess the effect of dynamic thermal aging on the rheological characteristics of the developed suspensions.
- Acquire a profound understanding of the behavior, beneficial properties and functions of nanoparticles in such suspensions.
- Synthesize custom-made Fe₃O₄ nanoparticles (bare and coated), have comprehensive characterization and assessment as additives.
- Characterize raw materials by employing various techniques such as XRD, XRF, FTIR and TEM.
- Establish the optimum concentration of nanoparticles in the suspensions in terms of their rheological and fluid loss characteristics.
- Investigate the use of the above NP as a fluid loss control additives.
- Determine the filtration reduction trends as a function of NP concentration at HP/HT conditions.
- Study the effect of NP on filter cake characteristics.
- Reveal the particle-to-particle interactions between bentonite particles and nanoparticles at different temperatures (25°C and 60°C) using an array of microscopic techniques (i.e. TEM).
- Explore the rheological properties of drilling fluids containing magnetic nanoparticles under the application of an external magnetic field.
1.7 Thesis outline

This dissertation is divided into seven chapters that cover the analysis of the development of enhanced drilling fluids utilizing commercial and custom-made nanoparticles.

Chapter 1 is an introduction to the work that justifies the research performed, states the research objectives, provides the background for clay minerals and nanoparticles as well as gives fundamental aspects for the rheology of drilling fluids.

Chapter 2 presents a literature review on nano-based drilling fluids. It focuses on reported results on the use of nanoparticles for the enhancement of drilling fluid properties which can be modified with addition of nanoparticles. Of the above mentioned drilling fluid properties, the ones readily modifiable by the nanoparticles are rheology and fluid loss control, wellbore and shale stabilization, wellbore strengthening, magnetic properties of such smart drilling fluids, cuttings suspension and thermal properties. The challenges for the use of nanofluids are also presented.

Chapter 3 describes the materials and methods used in this research. Preparation of samples, physicochemical characterization techniques, rheological, magnetorheological and fluid loss tests and experimental protocols are extensively discussed and presented.

Chapter 4 presents the experimental results of this study. Extensive rheological and filtration measurements are presented along with appropriate rheological modeling. Optimum NP concentration identified. Description of the precise micro-mechanisms involved in water-bentonite suspensions containing different types of Fe₃O₄ and SiO₂ NP, for like-charged systems at alkaline pH, by combining macroscopic measurements (rheological measurements) with microscopic measurements (i.e. TEM) is given.

Chapter 5 presents the conclusions of this thesis.

Chapter 6 describes the contribution of this study to the knowledge and potential beneficiaries.

Chapter 7 presents suggestions for future research as were arisen from this study.

Appendix A shows supplementary HR-TEM images of the produced suspensions at 25°C and 60°C.

Appendix B presents supplementary SEM images of the produced filter cakes.
Chapter 2. Literature Review

2.1 Rheology and fluid loss control of nano-based drilling fluids

Monitoring and controlling the rheological properties of the drilling fluid is an integral part of the drillers efforts for successful oil and gas well drilling. Good prediction of frictional losses needed for wellbore stability and safety is strongly dependent on accurate knowledge of drilling fluid rheology. As the fluids move through the wellbore, their rheological profile undergoes significant changes. The combined effect of temperature, pressure, time- and shear-history on the rheological properties makes the characterization and forecasting of drilling fluids rheological profile a complex task. Accurate determination of the rheological characteristics of complex fluids necessitates deep understanding of the base fluid properties, especially the contribution of the associated microstructure mechanisms on the flow properties.

Beyond rheology, which is a key property that needs to be optimized for the development of any stable and effective drilling fluid, fluid loss to the formation drilled is another property that drillers should minimize in order to promote safer and less expensive drilling activities. Fluid loss has been analyzed in a previous section (see 1.5).

Several researchers attempted to incorporate different NP into drilling fluids for rheological and filtration control instead of using common polymer additives. Amanullah et al. (2011) discussed the formulation and preliminary test results of three nano-based drilling fluids. The initial mud formulation indicated that development of a functionally viable, physically stable and homogeneous and also stable over a long period of time nano-based drilling fluid is difficult using water or salt water as the fluid phase. The preparation of a homogeneous and stable nanofluid with adequate time stability was very difficult without the use of highly effective surfactants, chemicals or polymers with high shielding or neutralizing capabilities. The test results indicated also that the developed nano-based drilling fluid produced suitable high and low end rheological properties. Furthermore, they noticed a significant decrease in spurt and fluid loss upon addition of the NP with a deposition of a thin and compact mudcake, which in turn can lead to major decrease in differential pipe sticking in highly permeable formations.

Zakaria et al. (2012) developed in-house a new class of nanoparticles to be used as loss circulation material to control fluid loss in porous media with very small pore size, such as shale formations. The authors tested two different approaches, in-situ and ex-situ, of
nanoparticle formation when using an oil-based drilling fluid. The authors observed a slight decrease in apparent viscosity at all tested shear rates upon addition of both types of NP. The rheograms followed a non-linear trend at low shear rates while approaching linearity at high shear rates. They tested also the fluids for their filtration characteristics (LP/LT filtration test) and they found that more than 70% reduction in fluid loss was achieved compared to 9% reduction in fluid loss in the presence of typical lost circulation materials. They reported a thin filter cake which indicates high potential for reducing the differential pressure sticking tendency as well as reducing formation damage. Moreover, there was no impact of the NP addition on the viscosity and stability of the drilling fluid for more than 6 weeks.

Contreras et al. (2014) investigated the use of in-house prepared iron-based and calcium-based nanoparticles with glide graphite as a conventional lost circulation material (LCM) -used to mitigate fluid losses- into the formation in oil-based mud in order to minimize formation damage in porous media. The rheological properties were measured at 120 °F and atmospheric pressure. They noticed that the samples containing calcium NP moderately increased their plastic viscosity. The samples containing iron NP caused a reduction in the yield point especially at high graphite concentration. The authors concluded that addition of NP and LCM did not significantly affect the rheological properties and thus NP can be used without requiring additional rheological additives. Both HP/HT filter press at 34.5 bar (500 psi) differential pressure and 121°C (250°F) and LP/LT filter press were used to investigate the behavior of NP and graphite enhanced drilling fluids under different conditions. Ceramic discs of 775 mD were used as filter media in the HP/HT filtration experiments. The results indicated that all the produced nanofluids were capable of reducing the fluid loss compared to the values obtained with the control sample. More specifically, iron-based NP gave higher reduction in the fluid loss value especially at low concentrations under HP/HT conditions, while calcium based NP yielded significant reduction at high concentration under HP/HT conditions.

Several researchers have used nanosilica (SiO₂) as drilling fluid additive. Mao et al. (2015) developed a hydrophobic associated polymer based nano-silica composite with core-shell structure (SDFL) via inverse micro emulsion polymerization and sol-gel preparation. The results revealed that the composite showed excellent thermal stability, lubricity, rheological and fluid loss properties. More specifically, addition of 0.5 wt % of the SDFL in a fresh water-based drilling fluid decreased the fluid loss by 69% at HP/HT conditions. The authors concluded that the developed fluid has great potential to stabilize the borehole and protect the reservoir. Li et al. (2016) formulated a water-based drilling fluid using common drilling fluid materials such as bentonite, KCL and XC-polymer and added nanosilica NP. Addition of silica
nanoparticles improved the fluid loss properties of the produced fluid achieving a maximum reduction 32% compared to that of the base fluid. Moreover, a thin and well textured mud cake was formed. They performed also a cost analysis that showed the economic feasibility of the use of such new fluid.

Anoop et al. (2014) examined the rheology of mineral oil-SiO$_2$ nanofluids (1% and 2%) at HP/HT conditions. They noticed that the tested nanofluids exhibited non-Newtonian characteristics at elevated pressures and temperatures. They concluded that nanofluid viscosity values increased with an increase in the particle concentration as well as at higher pressures. Temperatures higher than 100°C caused a decrease in viscosity, while the most appropriate rheological model was that of a power law for all cases. But for temperatures below 100 °C, there was no substantial reduction in viscosity values of their fluids. Changes of the viscosity values were attributed to chemical alteration of the nanofluids at HP/HT conditions, as observed by infrared spectroscopy analysis.

Ismail et al. (2016) studied the applicability of multi-walled carbon nanotube (MWCNT) and nanosilica as drilling fluid additives for improving the rheological and filtration characteristics as well as the lubricity of water-based drilling fluids. The results showed that addition of MWCNT and nanosilica improved the rheological properties by increasing the yield point by 20% on average compared to that of the base fluid. Furthermore, they found that the maximum fluid loss reduction was achieved upon addition of 0.00285 wt % (0.01 ppb) of nanosilica and MWCNT.

Abdo and Haneef (2013) tested the use of clay nanoparticles to stabilize the drilling fluid rheology at HP/HT conditions. In this work, they used palygorskite (Pal, a natural hydrous clay mineral with a fibrous rod-like microstructure), which was purified, characterized, functionalized, and tested in nano-form (10–20 nm diameter) for its effectiveness to tailor the rheology of drilling fluids. The authors reported that the elongated needle shape of Pal (Figure 10a) results in unique colloidal properties, especially in terms of the resistance to high concentrations of electrolytes. The added nanoparticles were found to provide stable drilling fluid rheology at HP/HT environment (Figure 10b). Montmorillonite alone was not stable at the tested HP/HT conditions, but adding small concentration of Pal nanoparticles solved the problem. They concluded that Pal NP can be used as effective rheology modifiers and thus eliminate the use of other expensive drilling fluid additives.
Kosynkin et al. (2012) examined the use of graphene oxide (GO) as a high-performance fluid loss control additive in water-based drilling fluids. They concluded that GO performed very well as a filtration additive in water-based fluids at concentrations of 0.2 wt % by carbon content. They performed LP/LT filtration tests on aqueous dispersions of GO and xanthan gum. They determined that a combination of large flake GO (Figure 11a) and powdered GO in a 3:1 ratio performed best in filtration tests, with an average fluid loss of 6.1 mL (Figure 11b) and filter cake thickness of 20 µm. They compared these results with standard drilling fluids used by oil industries containing ~12 g/L of clays and polymers, which gave an average fluid loss of 7.2 ml (+18%) and a filter cake with ~280 µm thickness. They also observed that GO solutions exhibited shear thinning behavior and higher temperature stability compared to clay-based fluid loss additives, thus showing a great potential to be applied for HP/HT wells. They concluded that GO has the potential for industrial scalability through production from abundant graphite sources and common reagents and can be proved as an effective fluid loss control additive for the drilling industry.
situations at 2 g/L carbon-content concentrations in 2.9 g/L (0.75 lbm/bbl) xanthan gum solution (Kosynkin et al. 2012).

Nasser et al. (2013) developed a nanofluid using nanographite and nanosilicon wires as additives. The authors concluded that the nanomud retained all the desired rheological properties at high temperatures (up to 90 °C). The viscosity of the nanomud was higher than that of the normal mud at all tested temperatures. Finally, they proposed that the cost feasibility of NP should be assessed in future work.

Li et al. (2015a) investigated the addition of cellulose nanocrystals (CNC) and polyanionic cellulose (PAC) as additives in bentonite water-based drilling fluids. They showed that the presence of bentonite and CNCs significantly improved the rheological properties of PAC/CNC/bentonite water-based drilling fluids, whereas the effect of PAC was relatively less (Figure 12 a,b). Finally, they noticed that the API fluid loss of PAC/CNCs/bentonite water-based drilling fluids remarkably decreased as the concentrations of bentonite and PAC increased, while CNCs had little impact on the fluid loss of the PAC/CNC/bentonite fluid.

Li et al. (2015b) explored the effectiveness of cellulose nanoparticles (CNPs), including microfibrillated cellulose (MFC) and CNCs in enhancing the rheological and filtration performance of bentonite water-based drilling fluids. They found that addition of MFC and CNCs increased the rheological properties of bentonite water-based drilling fluids, including the viscosity and yield point, demonstrating their capability on improving cuttings transport capacity. Moreover, they suggested that the improved viscosity, the core-shell structure as well as the formation of CNC polymer films remarkably reduced the fluid loss volume and the thickness of filter cake for CNC/bentonite fluids. On the other hand, MFC had little impact on

Figure 12. Plots of (a) viscosity; and (b) shear stress as a function of shear rate for PAC/CNC/BTWDFs at various bentonite concentrations (Li et al. 2015).
the fluid loss and yielded thicker filter cakes, which can cause serious problems such as differential pressure sticking and stuck pipe.

William et al. (2014) investigated the preparation of nanofluid-enhanced water-based drilling muds (NWBM). They used CuO and ZnO nanoparticles (with sizes less than 50 nm) in a base fluid which was a 0.4 wt % xanthan gum aqueous solution. The nanofluids were prepared using nanoparticle concentrations of 0.1, 0.3 and 0.5 wt %. An ultrasonication tank was used, and sonication for one hour was used. The WBM was formulated with 5 cP prehydrated bentonite slurry and adding xanthan gum (XG) as a viscosifier, polyanionic cellulose (PAC-L) as a fluid loss control agent, KCl for inhibition and KOH to establish a pH range of 9.0–9.5. A biocide (formaldehyde) was added to ensure that the natural polymers do not degrade due to bacterial action. The authors observed that NWBM showed improved thermal and electrical properties by about 35% compared to WBM. Increasing the concentration of nanoparticles enhanced the electrical and thermal properties of drilling fluids even more. The NWBM with CuO NP was found to show improved thermal properties and were more resistant to HP/HT conditions than the ZnO-based NWBM. High pressure and high temperature rheological studies were conducted on NWBM at different temperatures (25, 70, 90 and 110 °C) and pressures (0.1 MPa and 10 MPa). The Herschel Bulkley model was observed to be the best fit-model for describing the rheological behavior of NWBM. The results showed better rheological stability in the case of NWBM. The authors reported that the most significant role that the nanofluids play was in stabilizing the viscosity at higher temperatures. The effect of pressure on the rheology of NWBM was found to be more significant at higher temperatures.

Aftab et al. (2016) explored the effects of zinc oxide NP-acrylamide composite (ZnO-Am) on rheological and shale swelling behavior of conventional water-based drilling fluid. Results revealed that the rheological properties were slightly increased upon addition of the ZnO-Am composite over the tested temperature range (up to 65.5°C/150 °F). API fluid loss (LP/LT) was reduced by 14%, while HP/HT fluid loss was only slightly reduced. Shale swelling was decreased from 16% to 9%.

Li et al. (2015c) studied the utilization of a commercially available soy protein isolate (SPI) as fluid loss additive in bentonite-water based drilling fluids. The results indicated that at low SPI concentrations (0.5, 1.0, 1.5 wt %), strong aggregations were formed, resulting in the formation of thick, high-porosity and high-permeability filter cakes giving non-desirable high fluid loss values. On the other hand, at higher concentrations of SPI (3.0, 4.5, 6.0 wt %), intercalated structures were created that led to the formation of thin, compact and low-porosity
and low-permeability filter cakes, which had superior filtration characteristics compared to the base fluid. A critical concentration was determined (3 wt %), above which addition of SPI led to significant reduction in the fluid loss of the tested fluids. The authors attributed this behavior to the fact that the attachment of SPI on the surface of bentonite and the alteration of microstructure of bentonite in suspension from ‘house of cards’ to agglomeration or intercalation were responsible for these phenomena.

2.2 Field applications

All the above studies have been carried out in laboratories. However, it is important to evaluate nanofluids in real conditions. To the best of author’s knowledge there are only two studies in the literature that highlight the successful application of novel nanofluids in the field. Borisov et al. (2015) presented results from a field application of nanoparticle-based invert emulsion drilling fluids (an oil-based drilling fluid). They emphasize that drilling fluids that combine LCM with nanoparticles can significantly reduce fluid loss and create a thinner filter cake, compared to fluids containing LCM alone. Due to their superior properties, NP have the ability to fill the gaps between the micron-sized rock particles, which leads to lower permeability and decreased filtrate flux (Figure 13). They concluded that their attempt to scale up the NP synthesis was successful. Total mud losses were reduced by 22–34% in the presence of 0.5 wt % calcium NP, which agreed with what was obtained in the lab.

Taha and Lee (2015) studied the application of a nanofluid containing a blend of proprietary surfactants engineered with nano graphene to improve drilling fluid performance. They tested the developed nanofluid in one well in the field, a HP/HT onshore well, and they
saw a significant improvement in the drilling fluid thermal stability as well as in its lubricity. They also observed a 30% reduction in fluid loss compared to conventional muds. Furthermore, they obtained an improved rate of penetration (ROP) by 125%, actual reaming torque reduction of 20% and more than 75% increase in the bit’s life span.

2.3 Other applications of nanoparticles in drilling fluids

2.3.1 Shale and wellbore stability

Results from several studies have been reported which examine the use of various nanoparticles for the reduction of shale permeability of the wellbore walls by plugging the pore throats, building an internal mud cake and thereby reducing the fluid invasion into the shale. Sensoy et al. (2009) performed tests using an apparatus called Shale Membrane Tester for two different shales (Atoka and Gulf of Mexico shales). It was concluded that a concentration of at least 10 wt % of 20 nm NP should be used for successful shale plugging. Scanning Electron Micrographs were used to visualize the type of plugging that was taking place. It was concluded that the nanoparticles plugged primarily the pores that fit their size. However a group of nanoparticles could in some cases aggregate together to plug a bigger pore throat. Finally, four field muds were studied with and without the addition of nanoparticles. It was found that the addition of nanoparticles reduced the fluid penetration into Atoka shale by 16 to 72% and into the Gulf of Mexico shale by 17 to 27%.

Hoelscher et al. (2012) studied the application of water-based drilling fluids in unconventional shale formations using silica nanoparticles. They aimed to minimize shale permeability through physically plugging the nanometer-sized pores instead of chemical inhibition to impede water flow between the wellbore and formation, thus eliminating swelling of the shales and reducing the formation of fractures. The nanoparticles used were 5–100 nm in size. The 10–30 nm diameter nanoparticles were found to have the lowest amount of fluid loss. After that, the samples of the desired size and surface treatment were analyzed with cryo-transmission electron microscopy (c-TEM) and X-ray photospectrometry (XPS) to assure that there were no major contaminants in the samples. The authors used the Shale Membrane Tester to better understand the plugging mechanism of shale pores without taking into consideration any modifications of the rock itself. The results confirmed that the silica nanoparticles can physically plug shale at low loading levels in a water-based drilling fluid while being environmentally friendly and cost effective.
Sharma et al. (2012) developed and tested a new family of water-based drilling fluids that can be applied to a much broader range of shales. They used silica nanoparticles with uniform 20 nm diameter. They found that the formulated drilling fluids were quite stable at elevated pressures and temperatures and had a wide range of rheological properties, providing also good lubricity. The authors also conducted tests to measure the extent of invasion of water into shales when they are exposed to nanoparticle based drilling fluids. They found that the invasion into the shale was reduced by 10 to 100 times. Tests were also conducted on fractured gas shale samples. They found that the nanoparticles alone can effectively plug pores in shales without microcracks.

Taraghikhah et al. (2015) examined nanosilica as an additive in water-based drilling fluid for improving shale stability. They determined that the optimal concentration of nanosilica is <1 wt% and stated that the nano-drilling fluid had an acceptable shale recovery in comparison with ordinary shale swelling inhibitors. SEM images of collected shales after performing the shale recovery test, revealed the pore plugging as a physical shale inhibition mechanism. In addition to its improved inhibition characteristics, the developed nanofluid proved to be an efficient lubricant and gave improved rheological profiles with minor changes in fluid loss characteristics.

Akhtarmanesh et al. (2013) used NP to reduce the fluid penetration into the Gurpi shale which could promote wellbore stability. They tested three different fluids with different additives with and without NP. It was concluded that for successful shale plugging, a concentration of at least 10 wt% of 35 nm NP was needed. The fluid with the NP reduced the fluid penetration into the Gurpi shale up to 68% in comparison with control mud.

Kang et al. (2016) developed and evaluated water and oil-based drilling fluids containing silica nanoparticles for shale stability by running tests such as spontaneous imbibition, swelling rate and acoustic transit time. Results showed that, for the water-based drilling fluids, nanoparticles resulted in higher PV and YP, and lower API-filtration. Moreover, because pore throats of shale can be plugged by nanoparticles, imbibition amount, swelling rate, and Young's-modulus reduction of shale were all reduced significantly. However, the oil-based drilling fluids with nanoparticles did not have such good performance and resulted in some negative effects such as higher filtration and larger Young's modulus reduction. The authors attributed this behavior to the fact that silica nanoparticles can easily disperse in the water-based fluids, and effectively prevent the filtrate from invading into shale by plugging pore throats. But, it is difficult for the NP to disperse in oil-based fluids, thus decreasing their effectiveness.
2.3.2 Wellbore strengthening

One of the leading causes of non-productive time in drilling is wellbore instability. This may lead to lost circulation and stuck pipe. It can create significant problems particularly when drilling through depleted formations (i.e. with formation fluids at low pressures) or in deep water environment where operational drilling windows may be very small. To prevent formation fracturing while drilling, a good practice that has evolved over the past years is a preventive technique, usually called wellbore strengthening. This involves the pumping of material downhole, with the aim to have the material enter or block, either the entrance of the subsurface fractures (Figure 14a), or enter inside the fracture and block the fracture itself (Figure 14b). In either way, they are stopping any potential fracture from propagating, achieving this by isolating it from the wellbore (Shahri 2015; Growcock 2010). Several types of nanoparticles have been tested as wellbore strengthening materials with good results so far, including field applications.

Figure 14. A fracture is quickly sealed by wellbore strengthening material isolating it from the wellbore, either (a) at the entrance of the fracture (Shahri 2015); or (b) by entering the fracture (Growcock 2010).

Nwaoji et al. (2013) introduced a new lost circulation material (LCM) drilling fluid blend. They aimed at testing the ability of the blend to achieve wellbore strengthening by running hydraulic fracture experiments on Roubidoux sandstone and impermeable concrete cores. Optimum concentration of standard LCM (graphite) and in-house prepared nanoparticles (Iron III hydroxide and calcium carbonate) were established. The authors concluded that the optimum blend of iron III hydroxide nanoparticle and graphite increased the fracture pressure by 1668 psi or by 70% over the unblended water based mud. These additives had moderate impact on drilling fluid rheology. They also found that the optimal blend by using calcium carbonate nanoparticles and graphite increased the fracture pressure by 586 psi or by 36% over the unblended invert emulsion (diesel oil) mud with moderate impact on mud rheology. A 25%
increase in fracture pressure over the unblended mud was achieved in impermeable concrete core thus confirming the applicability of the designed fluid in shale wellbore strengthening. Finally, four field muds were tested with and without the addition of nanoparticles. It was found that the addition of nanoparticles reduced the fluid penetration into Atoka shale by 16–72% and into Gulf of Mexico shale from 17 to 27%.

Contreras et al. (2014) applied in-house prepared different NP (NP1 and NP2) and used them at low concentrations together with graphite aiming at wellbore strengthening. They have tested the materials in shale and in sandstone cores. The results indicated that wellbore strengthening reached a maximum value of 30% when NP2 and graphite were used in shales, while the maximum fracture pressure was increased by 20% upon addition of NP1 and graphite. In sandstone cores using NP2 and graphite resulted in a maximum wellbore strengthening value of 65% whereas a maximum fracture pressure increase of 39% was observed upon use of NP1 and graphite. The differences for their performances in both cases were attributed to the different capabilities in decreasing the filtration between the two NP as well as due to the viscosity of the resulting blends. The predominant wellbore strengthening mechanism was identified and attributed this to the tip resistance by the development of an immobile mass. The authors also noticed that a thin seal was created along the fracture plane with a homogeneous NP distribution, while the bulk of the shale formation was not found as being invaded by NP.

These are some of the few attempts aiming at using nanoparticles as wellbore strengthening materials, with good results so far. What it remains to be done is to identify the best nanoparticles which offer effective wellbore strengthening under severe downhole conditions and their effectiveness in field tests.

2.3.3 Cutting lifting capacity and cuttings suspension

One of the most important functions of mud in drilling operations is to transport the drilled cuttings to the surface through the well bore annulus which is termed as lifting or carrying capacity of the drilling fluid. There are several factors that affect the mud lifting capacity including the rheological profile and flow rate of the mud, particle settling velocities, particle size and size distribution, geometry, orientation and concentration of the particles, penetration rate, rotary speed, mud density, annulus inclination, drill pipe position in the well bore (eccentricity) and axially varying flow geometry (Kelessidis and Bandelis, 2004; Samsuri and Hamzah, 2011). Effective cuttings transport remains a major problem especially in vertical and inclined wells, where the cuttings tend to settle at the bottom side of the borehole due to gravitational force.
Samsuri and Hamzah (2011) investigated the using of multiwall carbon nanotubes (MWCNTs) as an additive to increase the carrying capacity of water-based mud. They studied the effects of, different concentrations of MWCNTs used, cutting size and mud annular velocity on the mud lifting capacity. They found that the lifting capacity increased as the amount of MWCNTs increases. They observed that low concentrations of MWCNTs (0.001–0.003% by volume) had minimal impact on the cuttings recovery. For example, the cutting recovery increased about 5–15% when 0.005% of volume MWCNTs was added to the water based mud, depending on the cutting size and annular velocity. For 0.01% of volume MWCNTs added, the cutting recovery increased by 5–21%. They attributed this enhancement to the fact that the MWCNTs improved the stability of the wellbore walls compared to the base mud, since surface forces balanced the gravity force resulting in the increase of drag force acting on the drill cuttings, which leads to easier cutting lifting to the surface. They also concluded that the multiwall carbon nanotubes improved the viscosity which significantly increased the carrying capacity of the mud.

Many drilling fluids are thixotropic, i.e. they have the ability to form a gelled structure over time when not subject to shearing and then to liquefy when agitated. This gelling behavior aids the suspension of cuttings while fluid motion is stopped. A drilling fluid must be able to transport the cuttings under dynamic conditions and suspend them under static conditions, which occurs often when drilling, for e.g. when making drill pipe connections. Gel strength is one of the most important drilling fluid properties because it reveals the ability of the drilling mud to suspend drilling cuttings and weighting materials when circulation is ceased. It is typically measured with a viscometer at different static conditions (generally after 10 s and 10 min of fluid movement cessation).

Although gel strength is a crucial property for optimal drilling operations, it is ultimately a compromise; it should be carefully monitored since it is directly related to the pressure is needed to break the gel when fluid circulation is reestablished. Excessive gel strength can also lead to retention at the surface, which in turn can cause severe drilling problems such as ineffective solids control, fracturing of the formation, and fluid loss. Low gel strength values indicate that the fluid will not efficiently suspend the cuttings leading to the build-up of the cuttings bed within the bore path resulting in an increased possibility for stuck drill pipe.

Several researchers have examined the gel strength values of various nano-enhanced drilling fluids in order to evaluate their capacity to suspend the cuttings. Amanullah et al. (2011) tested three nano-based drilling fluids against bentonite mud and they observed that the nano-based drilling fluids exhibited a flat type gel strength profile compared to the progressive
type gel strength of the micro-sized bentonite-based drilling mud (Figure 15). They concluded that the superior functional behavior of nano-based drilling fluids in terms of the development of adequate gel strength will allow homogeneous and distributed suspension of the cuttings within the fluid column without causing any accumulation of drill cuttings in critical borehole areas. They also stated that the flat type gel strength of the nano-based fluids will also ensure the requirement of lower circulation pressure to restart the drilling operation and thus will aid the reduction of the Equivalent Circulation Density (ECD), defined as the sum of static and frictional at a given depth in the annular or the pipe, induced loss of circulation and other drilling problems.

Abdo and Haneef (2012) studied the effectiveness of reducing the particle size distribution of clay material (ATR) and its incorporation as drilling fluid additive. They performed gel strength measurements in the fluids containing different concentrations of ATR nano (2 g, 4 g, 6 g and 8 g) and they noticed that the newly developed nanofluids displayed optimal gel strength values, which is essential for avoiding many severe drilling problems. At low concentrations of ATR nano (2 g) they showed an increase between the 10 s and 10 min gel strength values of 88%, while they observed maximum increase of the gel strength value upon addition of 8 g of ATR nano (+280%).

Contreras et al. (2014) investigated the gel strength values of an oil based-mud containing 0.5 wt %, 1 wt % and 2.5 wt % calcium and iron nanoparticles using also different concentrations of glide graphite as a conventional lost circulation material (0.5 wt % and 2 wt %). They noticed that the samples containing calcium NP almost doubled their gel strength values compared to the control sample at 10 s and 10 min, while the samples with iron NP showed tremendous increases in the gel strength values of 10 min with almost no change in the values obtained at 10 s. Finally, they stated that addition of slide graphite did not significantly impact the gel strength of the fluids containing iron NP, while it had a moderate impact in the fluids containing calcium NP.
Ismail et al. (2014) examined the gel strength values of water-based and ester-based drilling fluids upon the addition of different concentrations of multi-walled carbon nanotubes (MWCNTs) at different temperatures. The results revealed that in water-based drilling fluid, the gel strength was not much affected by different concentrations of MWCNTs. In ester-based drilling fluid, gel strength was slightly increased as MWCNTs concentration increases. They also noticed the significance of temperature at the rheological properties of the produced samples. They found that the gel strength in water-based fluid was decreased with an increase in temperature. However, the ester-based drilling fluid showed the opposite behavior with increased gel strength values as temperature increases. They concluded that optimal rheological as well as filtration properties were obtained at higher concentrations of MWCNTs (0.1 ppb = 0.0285 wt %).

2.3.4 Thermal properties

Designing stable drilling fluid systems with high thermal conductivity and optimal cooling properties for drilling in deep oil and gas reservoirs under extreme downhole conditions (HP/HT) is a major challenge. Drilling fluids with optimal heat transfer properties are highly desirable as drilling operations cause excessive heat due to friction between drilling bit and the rock surface. Overheating of equipment can lead to severe drilling problems with direct impact in the cost and efficiency of drilling operations. Therefore, it is required to formulate drilling muds with excellent heat transfer capabilities.

The thermal properties of nanofluids that can be used in various industrial applications as well as the associated mechanisms contributing to the enhancement in thermal conductivity,
including the role of Brownian motion, interfacial resistance, morphology of suspended nanoparticles and aggregating behavior, have been well reported in other studies (Yu et al. 2011; Angayarkanni and Philip 2015) and will not repeated here. Here we will review efforts made by several researchers over the last years related to the investigation of the thermal properties of various newly formulated drilling fluid systems containing different nanoparticles.

William et al. (2014) examined the effect of addition of CuO and ZnO nanoparticles on the thermal and electrical properties of water-based drilling fluids. The nano-enhanced drilling fluids were prepared at various NP concentrations (0.1, 0.3 and 0.5 wt %) in a xanthan gum aqueous solution (0.4 wt %) as base fluid. The authors observed that the nano-enhanced water-based mud (NWBM) showed improved thermal and electrical properties by about 35% compared to WBM. Increasing the concentration of nanoparticles enhanced the electrical and thermal properties of drilling fluids even more. The NWBM based on CuO nanofluids were found to show improved thermal properties and were more resistant to HP/HT conditions than the ZnO-based NWBM. The increase in thermal conductivity of the ZnO nanofluids was found to be from 12% to 23%, while the CuO nanofluids showed an enhancement in the thermal conductivity by 28% to 53%. The authors also stated that the increased thermal conductivity of the nano-based drilling fluids indicates the ability of the mud to cool faster as it moves up to the surface, which is really significant when dealing with HP/HT environments.

Ponmani et al. (2016) developed nano-enhanced water-based drilling fluid containing CuO and ZnO nanoparticles at various concentrations (0–0.5 wt %) and in various base fluids, such as aqueous dispersions of xanthan gum, polyethylene glycol (PEG-600), and polyvinylpyrrolidone (PVP). The results were compared to microfluid-enhanced drilling mud in order to reveal the effect of particle size (Figure 16). The authors observed that enhanced thermal conductivity properties were achieved when nanoparticles were added compared to the micron-sized materials and that higher concentrations of nanoparticles promoted better thermal conductivity properties. The authors also noticed that the system contained PEG-600 showed low thermal conductivity compared to other materials and this was attributed to the fact that PEG-600 is highly viscous in nature, and nanoparticles may get entrapped in its microstructure network-forming aggregates.
Figure 16. Variation of thermal conductivity of nano-enhanced water-based mud (NWBM) and microfluid-enhanced water-based mud (MWBM) for (a) CuO particles; and for (b) ZnO particles. Unfilled symbols: NWBM, filled symbols: MWBM (Ponmani et al. 2016).

Sabbaghi et al. (2015) synthesized TiO$_2$ nanoparticles with the sol-gel method and incorporated them into a bentonite base fluid in order to enhance its heat transfer properties. The TiO$_2$ NP were characterized with a particle size analyzer, X-ray diffraction, scanning electron microscopy and fourier transform infrared spectroscopy and showed an average size of 20 nm. The stabilization of the nano-enhanced drilling fluid was optimized using cetrimonium bromide (CTAB) surfactant and by changing the pH. It was visually examined with sedimentation tests which revealed that the titania nanofluid was stable after one month. The authors also observed that addition of NP increased the thermal conductivity by about 150% compared to that of the base fluid. They also indicated that at increasing concentrations of nanoparticles (0.1–0.3 wt %), the thermal conductivity increased moderately.

Fazelabdolabadi and Khodadadi (2015) developed nano-based drilling fluids using functionalized CNTs. CNTs functionalization was performed by applying hydrophilic functional groups onto the surface of the nanotubes via acid treatment. The time evolution of thermal conductivity was examined. The thermal conductivity was significantly increased by 23.2% in 1 vol % functionalized CNT-water-based fluid at ambient temperature. It improved even further by 31.8% at 50 °C. In the case of oil-based fluids the thermal conductivity was improved by 40.3% (unfunctionalized) and 43.1% (functionalized) at 1% volume fraction of CNT.

Ho et al. (2014) investigated the incorporation of carbon NP at different concentrations (up to 1 wt %) as drilling fluid additives for thermal conductivity enhancement. They used an ultrasonic bath for the dispersion of NP into the base fluid. They concluded that the carbon NP enhanced the viscosity of the base fluid as well as its thermal conductivity. Thermal conductivity of nanofluid increased nonlinearly with increasing mass fraction of nanoparticles.
They also focused on the impact of size of nanoparticles on nanofluid’s thermal conductivity. They stated that the ball milled nanoparticles had sizes of 4 μm on the average. However, the authors explained that large particles do not possess Brownian motion anymore as the particles approach micrometre size, thus leading to lower thermal conductivity enhancements. In addition, the results showed that 0.2 wt % of these particles showed higher thermal conductivity than 0.4 wt % and 0.6 wt % respectively due to larger distance between particles. Finally, higher nanoparticle volume fractions gave higher thermal conductivity improvement but induced higher settlement of nanoparticle cluster sizes in the end.

Li et al. (2010) developed self-assembled silver nanoparticles with an average diameter of 5 nm and they incorporated them in kerosene-based fluids. They carried out thermal conductivity measurements at three different temperatures (25, 40 and 50 °C). They concluded that the thermal conductivity of each silver nanofluid was higher than that of its base fluid and increased nonlinearly with increasing the concentration of the nanoparticles. In addition, the enhancement of the thermal conductivity was greater at higher temperatures which was explained by the fact that an increase in temperature led to enhanced Brownian motion of the particles, which improved the rate of heat transfer. They suggested that the capping of the surfaces of the nanoparticles with oleic acid significantly impacted the thermal conductivity as the oleic acid layer capped on the silver cores tended to change so that the bare part of the surfaces was enlarged at higher temperatures.

2.4 Effect of magnetic field

Engineering a drilling fluid tailored to meet specific downhole and environmental demands with tunable rheological properties can revolutionize the drilling industry. Such fluids, containing magnetic nanoparticles, could potentially offer in-situ control of the drilling fluid viscosity and yield stress, under the application of an external magnetic field. They can thus provide a great potential for drillers to formulate drilling fluid systems with instantaneous responses to continuously changing drilling environment, leading to enhanced well control and contributing to decreased non-productive time and costs.

Lee et al. (2009) investigated the performance of drilling fluids containing magnetic iron oxide (Fe₂O₃) nanoparticles that can offer possibility for in-situ control of viscosity under the application of a magnetic field. They tested two different drilling fluids, one based on hybrid nanoparticles where the NP are embedded in the interlayer space of bentonite particles and the other based on a simple mixture of nanoparticles and bentonite particles. The results indicated
that both tested fluids have the capability to increase the viscosity by one order of magnitude upon application of 0.7 T magnetic field.

### 2.5 Challenges for nano-based drilling fluids

From all the above studies, one can easily understand that nano-based drilling fluids have tremendous capabilities and can help variously the drilling industry to overcome stern drilling problems which lead to decreased productivity and higher costs. However, there are some challenges that the researchers should address before they can be fully implemented in drilling applications.

Firstly, the stability of NP dispersions remains a technical challenge and is one of the basic requirements to apply such fluids in the field. Furthermore, the process used to disperse nanoparticles in a liquid, is a critical factor for an effective dispersion. Researchers have reported various pieces of equipment that can be used to disperse solid, dry nanoparticles such as ultrasonic baths, magnetic stirrers, high-shear mixers and homogenizers. However, even after high shearing, where nanoparticles are broken to their primary size they tend to re-agglomerate due to the strong van der Waals attractive forces, which limits their advantages stemming from their high surface area. Electrostatic repulsion or steric hindrance are necessary to overcome such attractive forces and form stable dispersions (Wen et al. 2009). This can be achieved by adding certain surfactants which are able to create steric barriers between nanoparticles. Lack of surfactants can have a negative effect on the stability of nanofluids, as can be seen in Figure 17. It can be observed that aqueous nanofluids containing Al₂O₃ nanoparticles (20 nm) at 0.5 wt % without any surfactant, completely separated after 5 h (Wen et al. 2009).

The primary factors that affect the stability of such nanofluids are particle surface properties, size and morphology of the nanoparticles. Sidik et al. (2014) presented a review on the challenges of nanofluids and stated that it is impossible to achieve stable nanofluids without the addition of surfactants or without surface modification of the suspended particles. Choi et al. (2008) stated that addition of surfactants should be done with extreme care as excessive quantities may adversely affect the viscosity and chemical stability of the nanofluids.
It is well established that NP affect the rheological properties of drilling fluids at relatively low concentrations (<0.5 wt %). It is thus critical to find out the optimal nanoparticle mass fraction, which will give optimal rheological and filtration properties leading to less expensive and more efficient drilling operations. The low concentrations of NP may eliminate the use of potentially harmful chemicals, currently used in drilling fluids, thus enhancing the environmental footprint of drilling, from the use of the improved nanofluids.

Another challenge is the field scale applications of the appropriately developed nano-drilling fluids, with the use of the identified in the literature nanoparticles. This can reveal their full advantages and also identify challenges in real conditions making possible for developers to focus on specific properties and problems of such fluids. Furthermore, the cost of some nanoparticles can be an obstacle that may hinder the application of such fluids in specific operations in oil and gas industry. However, many types of nanoparticles are already commercially available at affordable prices (e.g., iron oxide, which is abundant in the nature in various forms) that can be used instead of many chemicals that are currently used by many oil and gas companies. There are numerous research groups that are currently working on scaling up the synthesis of various types of nanoparticles in order to render this process economically viable (Tighe et al. 2013; Charitidis et al. 2014).

Preparation and measurement protocols that were followed by researchers when dealing with the formulation and testing of nano-based drilling fluids are critical challenges as well. Such information is obscure in the literature. The American Petroleum Institute (API) procedures and specifications (API 2003, 2010) were developed in order to establish common procedures but sometimes these specifications do not deal with newer additives or newer requirements that are used or are needed in different mud formulations that perform difficult tasks under varying conditions (Clark 1995). So, it is very difficult to compare results from different researchers and laboratories because mixing and preparation protocols are almost
never the same. Factors such as the pre-shearing time, the hydration of additives, the raw materials, the mixing time and the order of adding the different additives are crucial that can significantly affect the reported results. Caution should thus be taken when comparing results of drilling fluid samples among different, but also even within same, laboratories, because preparation and measurement procedures are vital for producing consistent results and this is another challenge facing researchers and oil companies in order to take full advantage of such superior drilling fluids.

2.6 Literature review summary

The application of nanotechnology in the oil and gas industry is on the rise as evidenced by the numerous studies carried out over the past ten years. The quest to develop more game-changing technologies that can address the challenges currently faced by the industry has spurred this growth. Several nanoparticles, of different sizes and at different concentrations, have been used in many studies. Due to their unique properties, nanoparticles can significantly advance the drilling fluid technology. Nano-based drilling fluids can play an important role in improving mud cake quality and rheological characteristics, reducing friction, eliminating differential pipe sticking, maintaining borehole stability, protecting reservoir, and enhancing oil and gas recovery. Their use offer many potential solutions to resolving drilling problems that cannot be solved with traditional approaches and it can enable to push the limits of the existing drilling technology and endow with economically and technically viable drilling operations.

This review allowed us to present results reported by previous researchers using various nanoparticles as drilling fluid additives for rheological and fluid loss control, for enhancing shale stability and for wellbore strengthening. Suitable nanoparticles include, but are not necessarily limited to, iron oxide (Fe₂O₃ and Fe₃O₄), nanosilica, nano magnesium oxide, nanocopper oxide, nano-zinc oxide, nano-nickel oxide, nano-alumina, carbon black, nano-graphene, carbon nanotube, polymer-based nanoparticles, and combinations of these, as well as a surfactant if required in an amount effective to suspend the nanoparticles in the base fluid.

Taking into account the various available nanoparticles, this study focused on commercial iron oxide nanoparticles (Fe₂O₃ and Fe₃O₄) as well as on commercial nanosilica, as having good reported results, being cheaper and abundant compared to other nanoparticles. Furthermore, the choice of these nanoparticles is stemming also from the fact that there are some studies in the literature which show the great potential of iron oxide nanoparticles and
nanosilica as drilling fluid additives, but there is a gap and lack of the explanation regarding their exceptional behavior. This study aims to cover such aspects by examining in depth and at different conditions the effect of these nanoparticles as additives on drilling fluid properties. The ability to synthesize tailor-made nanoparticles to achieve specific functions and the main challenge associated with nano-based fluids, which is the stability of NP dispersions are issues that were identified in the literature and led us to synthesize custom-made citric acid coated iron oxide nanoparticles which proved to outperform the commercial one, showing the potential for the development of improved drilling fluids. All in all, future drilling operations are likely to face even greater technical challenges due to the economical exploitation of technically challenging oil and gas resources such as unconventional reservoirs and deep water resources (HP/HT wells) and thus there will be a huge need for the development of novel drilling fluids able to withstand such harsh environments.
Chapter 3. Materials and Methods

3.1 Materials

3.1.1 Na-based bentonite

The Wyoming Na\(^+\) bentonite (Bent) (Aquagel-Gold Seal) was supplied by Halliburton in powder form. It has relative density of 2.6 and it is without any polymer additives, according to vendor specifications. It is tan in color with a pH range 8–10 and mean particle size (d\(_{50}\)) of 68 μm, as determined by sieve analysis (Figure 18). X-Ray Diffraction (XRD) (Figure 19) confirmed that the major mineralogical component of the samples is sodium-montmorillonite. Minor phases like illite, muscovite, quartz, cristobalite, plagioclase (albite), gypsum and clinoptilolite zeolite are also present. Its composition, as percent oxides, determined by X-ray Fluorescence (XRF), is presented in Table 2. Figure 20 shows a picture from SEM at 20μm resolution and reveals the particle size of the bentonite, being composed of single platelets with an average length of 20μm.

![Figure 18. Particle Size Analysis (PSA) of Na-bentonite.](image)
Figure 19. X-Ray diffraction (XRD) of raw Wyoming Na-bentonite.

Table 2. X-Ray Fluorescence (XRF) elemental analysis (%) of raw Na-bentonite.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, wt %</td>
<td>65.30</td>
<td>20.30</td>
<td>5.75</td>
<td>2.38</td>
<td>2.24</td>
<td>1.30</td>
<td>1.16</td>
<td>0.66</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Figure 20. SEM image at 20μm from Na-bentonite powder. It reveals the particle size of the bentonite, being composed of single platelets with an average length of 20μm.
3.1.2 Nanoparticles

The ferric oxide (Fe$_2$O$_3$) NP (molecular weight =159.69 g/mol) were supplied by Sigma Aldrich (Product Number: 544884) in powder form. Particles have a dark brown color with a spherical shape and diameter of <50 nm. The surface area of these nanoparticles was 50-245 m$^2$/g with a purity of > 97% and without any coating, as per manufacturer specifications.

The commercial iron oxide (Fe$_3$O$_4$) nanoparticles (C Fe$_3$O$_4$ NP), supplied by Sigma Aldrich (Product Number: 637106), in powder form, with dark brown color, surface area >60m$^2$g$^{-1}$, density 4.8-5.1 g/mL at 250°C, purity of > 97% and without any coating, as per manufacturer specifications. They have a spherical shape with a diameter of 20-50 nm, as determined by High Resolution Transmission Electron Microscopy (HR-TEM) (Figure 21).

![Figure 21. Transmission Electron Microscope (TEM) image of the commercial magnetite NP (C Fe$_3$O$_4$ NP).](image)

The custom-made bare magnetite nanoparticles (CM-B Fe$_3$O$_4$ NP) were synthesized at the Chemical Process & Energy Resources Institute (CPERI) lab in the Centre for Research and Technology Hellas (CERTH) by a chemical co-precipitation method (Massart 1981; Nalbandian et al., 2016). The synthesis was carried out at 25 °C, under N$_2$ flow, to ensure anaerobic conditions, with continuous and vigorous mechanical stirring to ensure reagent homogeneity. The precipitation agent, concentrated NH$_4$OH 25%, was first added to deionized water. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O) and ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O) were dissolved in deionized water (concentration ratio Fe$^{3+}$:Fe$^{2+}$ =2:1) and added dropwise to the ammonia solution. Magnetite precipitates according to the reaction:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (3)$$
Vigorous mechanical stirring was applied for thirty more minutes and, subsequently, the black precipitate was separated from the dispersion medium by means of a permanent magnet and washed with deionized water, 4-5 times, until complete removal of all remaining NH$_4^+$ and Cl$^-$ ions.

It was decided to coat the CM-B NP to reduce chances of aggregation and we proceeded as follows: the prepared NP were redispersed in deionized water and ultra-sonicated for 30 min. A citric acid solution was added dropwise, in a period of 5-6 minutes, and left to react for at least 30 min, to obtain the citric acid coated magnetite nanoparticles (CM-CA Fe$_3$O$_4$ NP). After that the nanoparticles were washed 2-3 times with deionized water in order to remove the excess citric acid and finally dispersed in deionized water. The prepared suspension was stable and could be stored for more than two months, away from light sources.

The XRD pattern of the CM-CA Fe$_3$O$_4$ NP (performed at CPERI) showed peaks corresponding to pure crystallites of magnetite with no impurities (Figure 22). The size and morphology of the synthesized CM-NP (CM-B and CM-CA) were determined by High-Resolution Transmission Electron Microscopy (HR-TEM). As shown in Figure 23 both CM-NP (bare and coated) had spherical shape with a mean diameter of 6-12 nm. Their surface area, as determined by nitrogen adsorption-desorption isotherms at liquid nitrogen temperature of 77K, was 100-120 m$^2$/g. Magnetic property measurements, with a commercial Superconducting Quantum Interference Device (SQUID) magnetometer, proved that the CM-CA Fe$_3$O$_4$ nanoparticles displayed superparamagnetic behavior with saturation magnetization of 60 emu/g at 300K (Figure 24).

![Figure 22. X-ray diffractogram (XRD) of the synthesized (CM-CA) Fe$_3$O$_4$ nanoparticles.](image)
Figure 23. Transmission Electron Microscope (TEM) image of the (a) bare CM magnetite NP (CM-B Fe₃O₄ NP), and (b) citric acid coated magnetite NP (CM-CA Fe₃O₄ NP).

Figure 24. Magnetization curve of pure CM-CA Fe₃O₄ nanoparticles at 300K obtained by SQUID.

Silica nanoparticles (C SiO₂ NP) were supplied by Sigma Aldrich (Product Number: 718483), in powder form with a spherical shape, purity of >99.5% and without any coating, as per vendor specifications. They had a spherical shape with an average diameter of 12nm as shown in High Resolution Transmission Electron Microscopy (HR-TEM) images (Figure 25).
3.2 Sample preparation

The preparation of the bentonite suspensions (Bent SPN) was carried out following American Petroleum Institute Standards (API, 2003). Wyoming Na⁺-bentonite (45.16 g) (Figure 26a) was added to 600 ml of deionized water to give 7.0% mass concentration and mixed at high speed in a Hamilton Beach mixer for 20 min as per API procedures (Figure 26b). The dispersion was left to hydrate for 16 h in covered plastic containers (Figure 26c). After hydration of bentonite, different concentrations of the nanoparticles were added slowly in the water-bentonite suspension, while agitating at high speed for 20 minutes in a Hamilton Beach mixer. The pH range of all samples was between 8.0 and 8.3. All rheological measurements were taken one day after the initial sample preparation. Prior to the rheological measurements the samples were stirred for 5 min in the Hamilton Beach mixer in order to achieve the same shear history for each sample (API, 2010). The preparation and measurement protocols for each sample were followed strictly, in order to ensure consistency and to minimize any biases of our results. Table 3 presents a list of materials and suspensions developed in this study along with their abbreviations.
The sample preparation procedure - The weight of each material is measured out first (a), then mixed with de-ionized water in the Hamilton Beach mixer for 20 minutes (b). The sample is then left to hydrate for 24 hours in a closed plastic container (c).

Table 3. List of all materials and suspensions used in this study and their abbreviations.

<table>
<thead>
<tr>
<th>Materials &amp; Suspensions</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial hematite nanoparticles (bare)</td>
<td>C Fe₂O₃ NP</td>
</tr>
<tr>
<td>Commercial magnetite nanoparticles (bare)</td>
<td>C Fe₃O₄ NP</td>
</tr>
<tr>
<td>Custom-made bare magnetite nanoparticles</td>
<td>CM-B Fe₃O₄ NP</td>
</tr>
<tr>
<td>Custom-made citric acid coated magnetite nanoparticles</td>
<td>CM-CA Fe₃O₄ NP</td>
</tr>
<tr>
<td>Commercial silica nanoparticles (bare)</td>
<td>C SiO₂ NP</td>
</tr>
<tr>
<td>Bentonite suspension/Base Fluid (BF) - (7 wt% bentonite)</td>
<td>Bent SPN</td>
</tr>
<tr>
<td>BF with commercial Fe₂O₃ nanoparticles</td>
<td>Bent SPN with C Fe₂O₃ NP</td>
</tr>
<tr>
<td>BF with commercial Fe₃O₄ nanoparticles</td>
<td>Bent SPN with C Fe₃O₄ NP</td>
</tr>
<tr>
<td>BF with custom-made bare Fe₃O₄ nanoparticles</td>
<td>Bent SPN with CM-B Fe₃O₄ NP</td>
</tr>
<tr>
<td>BF with citric acid coated Fe₂O₃ nanoparticles</td>
<td>Bent SPN with CM-CA Fe₃O₄ NP</td>
</tr>
<tr>
<td>BF with commercial SiO₂ nanoparticles</td>
<td>Bent SPN with C SiO₂ NP</td>
</tr>
</tbody>
</table>

The effect of dynamic thermal aging on the rheological and filtration properties of selected samples were also investigated in order to examine the ability of the developed fluids to maintain their properties under such extreme conditions (Kelessidis et al. 2007b). The samples were put in an aging cell and pressurized at 20.7 bar/300 psig. Then the cell was placed in the rolling oven at 176°C for 16 h. After cooling down the samples were recovered and the appropriate rheological or filtration measurements were made.

The same sample was used to run firstly the rheological measurements and afterwards the fluid loss measurements. For all the tested samples, the rheological and fluid loss measurements were conducted after one day and two days after the initial preparation of the samples, respectively. Before any rheological measurement and filtration measurements, the samples
were mixed at high shear for five and ten minutes, respectively. The sample preparation procedure for each sample was followed strictly in order to ensure consistency.

### 3.3 Physicochemical characterization

X-Ray Diffraction (XRD) (performed at CPERI lab) was employed to reveal the mineralogical composition of the bentonite (Bent) and for phase identification of the synthesized nanoparticles. Powder XRD patterns were recorded with a Siemens D 500 X-ray diffractometer, with an autodivergent slit and graphite monochromator using CuKa radiation, with a scanning speed of 2°min⁻¹. The characteristic reflection peaks (d-values) were matched with JCPDS data files and the crystalline phases are identified.

The elemental analysis of the Bent powder was carried out using a Rigaku ZSX Primuss II wavelength dispersive X-ray Fluorescence (XRF) spectrometer (WD-XRD) (Central Materials Lab at TAMUQ). The powder sample was loaded on an aluminium cup and a pellet is prepared using 20T power press without adding any binder.

The presence of functional groups on the surface of the nanoparticles was studied by Fourier Transform Infrared (FTIR) spectroscopy (CPERI lab). The FTIR spectra were obtained on a Bruker FTIR spectrophotometer (Model Tensor 27) under ambient conditions. Typical scans were obtained at a resolution of 4 cm⁻¹ in the range 400-4000 cm⁻¹. In order to record the spectra, the nanoparticles were dispersed in KBr (ratio 10:90).

Specific surface area, pore volume and pore size distribution were determined by nitrogen adsorption-desorption isotherms at liquid nitrogen temperature (77 K) using a Micromeritics Tristar apparatus (CPERI Lab). The samples were degassed at room temperature for at least 48 h prior to the N₂ sorption measurement.

Core particle characterization of all samples was performed by High-Resolution Transmission Electron Microscopy (HRTEM) in a JEOL JEM 2010 microscope operating at 200 kV and equipped with an Oxford Instruments INCA EDS detector (CPERI Lab-CERTH). In order to prevent eventual agglomeration, the sample was mixed with pure ethanol in an ultrasonic apparatus and was superimposed on a lacey carbon film supported on a 3 mm Cu grid.
Before physicochemical characterization, selected suspensions were heated at the desired temperature (25°C and 60°C), freeze-granulated (FG) using the (home-made) freeze granulator shown in Figure 27, and subsequently freeze-dried (FD) using a Lyovac GT-2 (SRK Systemtechnik GmbH) freeze-dryer. During freeze granulation, the suspension was injected into the liquid nitrogen in the form of small droplets which freeze immediately. This system for freeze granulation is preferred instead of the more commonly used spray granulation technique in order to avoid any additional shear stresses to the bentonite particles and nanoparticles, due to the high pressure during spraying, which could alter their microstructure and produce misleading results. During the next step, the frozen droplets were evacuated to pressures lower than 0.006 atm and subsequently heated to ~25–30°C so that sublimation occurs (Kogias et al., 2012). Special attention was given to the final water content of the dried samples, which was in all cases 5±1 wt%. It was observed that variations in the final water content can lead to very different physicochemical characteristics of the dried bentonite samples. Adopting this procedure allowed us to better understand the microstructure networks and the connectivity between bentonite platelets and nanoparticles developing in such suspensions, which has direct impact on their rheological properties.
3.4 Rheological measurements

Rheological measurements were performed at various temperatures (25°C, 40°C, 60°C and 70°C), at ambient pressure, using a Couette type viscometer (Grace M3600-Figure 28) (Drilling Engineering, Multiphase Flow and Production Lab at TAMUQ). Selected samples were tested at 69 bar and up to 120°C (248°F) using a Chandler Ultra HP/HT viscometer (Figure 28).

For the Grace M3600 viscometer, the radius of the fixed cylinder is 17.245 mm and of the rotating outer cylinder is 18.415 mm, thus giving a gap of 1.170 mm and an outer to inner diameter ratio of \( \delta = 1.068 \). The fixed cylinder had a height of 38.0 mm. Viscometric data were obtained at fixed speeds of 600, 300, 200, 100, 60, 30, 6, 3 rpm, which give Newtonian shear rates of 1021.38, 510.67, 340.46, 170.23, 102.14, 51.069, 10.21 and 5.11 s\(^{-1}\), respectively (Kelessidis and Maglione, 2008). The yield stress is estimated from the obtained rheograms after extrapolating the shear stress – shear rate curve to zero shear rate and fitting an appropriate rheological model. The readings were taken from high to low speeds, while rotation lasted for 60s at each rotational speed, with readings being recorded every 10s, thus giving six measurements for each rotational speed with a total duration of 8 min per cycle. These six values were averaged and recorded. The rheological parameter estimation was performed according to the Herschel-Bulkley (HB) model (Herschel and Bulkley, 1926),

\[
\tau = \tau_y + K(\dot{\gamma})^n
\]  

(4)

where \( \tau, \dot{\gamma} \) are the shear stress and shear rate respectively, and the three Herschel-Bulkley rheological parameters are, the yield stress, \( \tau_y \), the flow consistency index, \( K \) and the flow behavior index, \( n \). The Herschel-Bulkley rheological model has proven to give the most accurate fitting results for water-bentonite suspensions (Kelessidis et al., 2006). The Herschel-Bulkley rheological parameters were determined using non-linear fitting subroutines from Solver™ statistical package, using least squares fittings routines, and two statistical indicators, the coefficient of determination, \( R^2 \), and the sum of squared errors, \( SQ^2 \), given by:

\[
SQ^2 = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2
\]  

(5)

Where \( y_i \) is the actual value and \( \hat{y}_i \) is the estimated value.
Temperature was controlled using a circulating water bath capable of maintaining the desired temperature with an accuracy of ±0.5 °C (Figure 28 left). The water bath allowed the water to circulate around the viscometer cup while performing the rheological measurements. Preceding each test, we started the circulating water bath and waited until the desired temperature was reached. The gradual increase of temperature was performed at a rate of ~1 °C/min. Once the desired water temperature was achieved, the sample was stirred for 5 min using the high speed mixer (Hamilton Beach) prior to each measurement, in order to achieve the same shear history. Then, the sample was poured into the measuring cup and the experiment started immediately, with an initial step of rotation at 600 rpm for 200 s, before recording any values. This step was added in the experimental procedure in order to achieve a temperature equilibration of the sample. The temperature of the samples during the experiments was monitored with a temperature sensor embedded into the viscometer cup. Before starting the experiment the exact temperature of the sample inside the viscometer cup was also measured with an external thermometer in order to double check temperature accuracy.

Dynamic aging of the base fluid (Bent SPN) as well as of the sample containing 0.5 wt% CM-CA Fe₃O₄ NP in a roller oven for 16 h at 177°C (350°F) was performed using a 500 ml aging cell in order to assess the capability of the developed fluids to maintain their rheological properties under dynamic conditions. The samples were placed inside the aging cell which was then pressurized to 300 psig by nitrogen gas at room temperature. Then the cell was placed in the oven. After 16 h, the aging cell was cooled down. Before rheological analysis, the fluids were agitated at high shear for 5 minutes in the Hamilton Beach mixer to make them homogeneous and obtain the same shear history.

Gel strength measurements were also performed. The gel strength is the shear stress measured at low shear rate after the drilling fluid has set quiescently for a period of time (10
seconds and 10 minutes as per API 2003). The gel strength demonstrates the ability of the drilling mud to suspend drill solid and weighting material when circulation is ceased.

3.5 Magnetorheological measurements

Rheological measurements under the presence of an external magnetic field were performed at 25 ± 1°C for water-bentonite suspensions containing 0.5 wt% and 1.0 wt% CM-CA Fe₃O₄ NP, using a strain-controlled rheometer (Anton Paar, MCR 302) (Figure 29) in the parallel-plate configuration (Drilling Engineering, Multiphase Flow and Production Lab at TAMUQ). The rheometer is equipped with the MRD70/1T magnetorheological cell capable to generate a magnetic field from 0 to 1.0 T perpendicular to the shear flow direction. The diameter of the parallel-plate is 20 mm, while the gap was set at a constant distance of 0.5 mm.

The readings were taken from high to low shear rates and rotation lasted for 60s at each rotational speed, with readings recorded every 10s. Before making the rheological measurements the samples were stirred for five minutes in the Hamilton Beach mixer in order to achieve the same shear history for each sample. After that, the samples were loaded and were presheared at a rate of \( \dot{\gamma} = 102 \text{ s}^{-1} \) for 60 s. The preparation and measurement protocols for each sample was followed strictly, in order to ensure consistency and to minimize any biases of our results. The rheological parameter estimation was performed according to the Herschel-Bulkley (HB) model.

![Anton Paar MCR 302 Rheometer, parallel plate geometry and application of magnetic field.](image)

Figure 29. Anton Paar MCR 302 Rheometer, parallel plate geometry and application of magnetic field.
3.6 Fluid loss measurements

Filtration properties of the fresh as well as of the thermally aged samples were obtained following the API procedures (API 2003; API 2010). Data were collected using a standard LTLP filter press (OFITE-Figure 30a) with a regulated air pressurization system and standard 3.5-in. diameter filter paper (differential pressure of 100 psi and atmospheric temperature) and a HP/HT filter press (OFITE-Figure 30b) operating at 300 psi differential pressure (400 psig top pressure and 100 psig bottom pressure) and temperature of 121°C (250°F). The apparatus includes a 500 ml cell which was furnished with a standard cell inlet cap, four 200-watt heaters, and a scribed outlet cap for the ceramic filter disks, used as the filter medium. The ceramic discs have 0.25-in. thickness and 2.5-in. diameter. They had permeability of 15 D and a mean pore throat of 50 μm, according to manufacturer specifications (OFITE). The samples were poured into the cell and the cell was then sealed and put in the heating jacket. A controlled pressure nitrogen source was used to adjust the pressures at the desired values. The filtration volume was recorded as a function of time for 30 minutes. The thickness of the filter cake was immediately measured at the end of filtration period using a digital caliper. The filter cakes (Figure 30c) were examined for their morphology and particle-to-particle interactions using SEM-EDS analysis (SEM analysis was performed the same day or the day after the filtration experiments). The test mimics the phenomena occurring when drilling and a good drilling fluid is one that produces minimal amount of filtrate and a thin and compact filter cake.

Figure 30. (a) LP/LT filter press (b) Static HP/HT filter press, and (c) filter medium (ceramic disc-bottom) and the produced filter cake (top) from HP/HT filter press.
3.7 Formation damage potential

Appropriate drilling fluid additives which can build effective filter cakes are key components to minimize formation damage. Today there exists no effective and quantitative technique which can assess the formation damage minimization potential of any novel drilling fluid. This study provides the methodology for such a technique, by integrating HP/HT fluid loss data, derived from a static HP/HT filter press, with filter cake quality and filtrate penetration depth, derived by Nuclear Magnetic Resonance (NMR) (NMR spectrometer 600 MHz) and Magnetic Resonance Imaging (MRI) (BenchTop MRI) techniques (NMR and MRI measurements) performed in Instrumental Analysis Lab in TAMUQ.

3.7.1 NMR theory (Spin-spin \( T_2 \) relaxation time measurements)

NMR is a unique tool for oil reservoir exploration. The main advantage of the NMR method is that oil, gas, and water possess different NMR properties: spin-lattice relaxation \( T_1 \), spin-spin relaxation \( T_2 \), self-diffusion coefficient \( D \) and chemical shift \( \delta \). Therefore, all different kinds of fluids present in rock reservoirs can be distinguished quantitatively on the basis of the NMR signal intensity corresponding to each \( T_1 \), \( T_2 \) or \( D \) component (Matenoglou et al. 2016).

\( T_2 \) in fluid saturated rocks is controlled by three relaxation mechanisms: (a) Relaxation due to bulk molecular motion, (b) surface relaxivity, due to fluid-pore wall interaction, and (c) molecular diffusion in the internal magnetic field gradients. The three mechanisms act in parallel, therefore the spin-spin relaxation time of fluids in a porous system is given by (Straley et al. 1994; Kleinberg et al. 1994):

\[
\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surf}}} + \frac{1}{T_{2,\text{diff}}} \quad (6)
\]

In our study we focus mainly in the \( T_2 \) value to evaluate the pore size distribution in our samples. \( T_2 \) is relative to the size of the pore:

\[
T_2 \sim r, \quad (7)
\]

where \( r \) is the radius of the pore inside the porous medium.
3.7.2 MRI Theory

Analysis of petrophysical properties of rock core samples can be done with two MRI methods: micro-imaging and flow imaging. Micro-imaging methods can provide information for the internal structure of a porous medium and distribution of various fluids inside the medium. Flow imaging is usually performed at a slightly poorer spatial resolution and it gives images of the flow field within the porous medium (Matenoglou et al. 2016).

In this study we managed to acquire saturation images of various filter cakes and their substrates (ceramic discs), in order to evaluate the formation damage from the drilling fluids used with a benchtop MRI equipment available in TAMUQ (Instrumental Analysis Lab, TAMUQ) (Figure 31). This was achieved with a fast spin echo pulse sequence. This pulse sequence follows the same principals from NMR spin-spin relaxation technique (Matenoglou et al. 2016).

Figure 31. BenchTop MRI equipment (source: http://www.mrsolutions.com/)
Chapter 4. Results

4.1 Physicochemical analysis

Physicochemical analysis was performed for selected samples of base fluid (Bent SPN) (7 wt% bentonite suspension) containing 0.5 wt% of the different nanoparticles (Bent SPN with C Fe₃O₄ NP, Bent SPN with CM-CA Fe₃O₄ NP and Bent SPN with C SiO₂ NP). In Figure 32 the XRD diffractograms of bentonite suspension (Bent SPN) after FG-FD, of bentonite suspension with 0.5 wt% citric acid coated magnetite nanoparticles (Bent SPN with CM-CA NP) after FG-FD, and of CM-NP nanoparticles are compared. Peak identification confirms that the major mineralogical component of the bentonite sample is Na-montmorillonite, while minor phases like illite, muscovite, quartz, cristobalite, plagioclase (albite), gypsum and clinoptilolite zeolite are also present, as already reported elsewhere. The XRD pattern of CM-CA Fe₃O₄ NP showed that the only crystalline phase formed is pure magnetite (FeFe₂O₄ [19-629], also shown in Figure 32) with no impurities, while the peak broadening indicates the nanocrystallinity of the NP. The XRD pattern of the Bent SPN with 0.5 wt% CM-CA Fe₃O₄ NP sample is the superposition of the corresponding XRD’s of pure bentonite and plain CM-NP nanoparticles, which shows that the bentonite as well as the nanoparticles are not structurally altered due to the interaction.
Table 4 presents the specific surface area of the four water-bentonite suspensions as well as of the pure nanoparticles, after freeze granulation and freeze drying (FG-FD). In Table 4 the surface area of the plain nanoparticles are also included, for clarity purposes. The Bent SPN with C Fe$_3$O$_4$ NP sample has a surface area 12.5 m$^2$g$^{-1}$, greater than that of bentonite suspension (Bent SPN). The increased surface area is possibly due to the mixing with the nanoparticles which have surface area of 37 m$^2$g$^{-1}$. The Bent SPN with CM-CA Fe$_3$O$_4$ NP sample has a surface area 34.4 m$^2$g$^{-1}$, significantly greater than that of the bentonite suspension containing commercial Fe$_3$O$_4$ NP (Bent SPN with C Fe$_3$O$_4$ NP). In this case, the increase in surface area cannot be solely attributed to the mixing of the nanoparticles, although the CM-CA Fe$_3$O$_4$ NP have relatively large surface area, 100 m$^2$g$^{-1}$. However, this contribution is not enough, since if the total surface area of the bentonite samples was the result of simple mixing, the SSA of the Bent SPN with CM-CA Fe$_3$O$_4$ NP should be 17 m$^2$g$^{-1}$. Since the measured SSA of the Bent SPN with CM-CA NP sample is almost twice this value, it can be inferred that besides simple mixing, other effects also occur when mixing these components.

In Figure 33 the N$_2$ adsorption – desorption isotherms obtained from the same samples are shown. From the isotherms it is obvious that, while the Bent SPN and the Bent SPN with C Fe$_3$O$_4$ NP samples have no mesoporosity, the Bent with CM-CA Fe$_3$O$_4$ NP sample presents a clear “hysteresis” loop, starting at relative pressure ($P/P_0$)$\approx$0.4, denoting the occurrence of mesopores. From pore size distribution analysis with the BJH method, it is determined that the diameter of the pores is in the range 1-6 nm. This mesoporosity could be due to the partial dissociation of the clay platelets, induced by the addition of the CM-CA Fe$_3$O$_4$ nanoparticles.
Figure 33. N$_2$ adsorption – desorption isotherms of pure bentonite suspension (Bent SPN), bentonite suspension with 0.5 wt% commercial Fe$_3$O$_4$ nanoparticles (Bent SPN with C-NP), bentonite suspension with 0.5 wt% citric acid coated Fe$_3$O$_4$ nanoparticles (Bent SPN with CM-CA Fe$_3$O$_4$ NP), and bentonite suspension with 0.5 wt% commercial silica nanoparticles (Bent SPN with C SiO$_2$ NP).

The SSA of the Bent SPN with C SiO$_2$ NP sample, the water-bentonite suspension containing 0.5 wt% silica nanoparticles, has a surface area, 41.7 m$^2$g$^{-1}$, the largest measured. The SSA that would be obtained by simple mixing the SiO$_2$-NP is 12.03 m$^2$g$^{-1}$, substantially smaller than the measured value. Thus, also in this case, there is an effect on the microstructure of the clay platelets because of nanoparticles addition. This is also evident from the “hysteresis” loop of the adsorption – desorption isotherm, shown in Figure 33. As has been observed also from the TEM images, to be presented in next section, the SiO$_2$-NP interact very strongly with the clay platelets, thus increasing their separation. This could possibly explain the observed increase in SSA and the occurrence of mesoporosity (pores of a size between 2 and 50 nanometres).

Figure 34 shows the FTIR spectrum of the Bent SPN, after freeze granulation and freeze drying (FG-FD). The peak at 1046 cm$^{-1}$ is related to Si-O-Si stretching, the 465 cm$^{-1}$ peak is connected to Si-O-Si deformation. The 798 cm$^{-1}$ peak is due to Si-O deformation, the peak at 523 cm$^{-1}$ is connected to Si-O-Al deformation and the 621 cm$^{-1}$ peak is related to Al-O and Si-O stretching. The peak at 3631 cm$^{-1}$ is O–H stretching, the 3423 cm$^{-1}$ is due to stretching of
hydrogen-bonded water H–O–H and the peak of 1639 cm\(^{-1}\) is H–O–H deformation. The obtained spectrum is very similar to the bentonite FTIR spectra presented in the literature (Tandon et al. 2013; Hashemian et al. 2015; Soliemanzadeh and Fekri 2017) and no alterations can be observed due to the followed freeze drying process.

![FTIR spectrum of bentonite suspension (Bent SPN), after freeze granulation and freeze drying.](image)

The FTIR spectra of the bentonite samples with commercial magnetite and silica nanoparticles (Bent SPN with C Fe\(_3\)O\(_4\) NP and Bent SPN with C SiO\(_2\) NP), were superposition of the spectra of bentonite suspension and of the spectra of the corresponding nanoparticles, C Fe\(_3\)O\(_4\) NP and C SiO\(_2\) NP. However, this was not the case for the bentonite samples with citric acid coated nanoparticles.

In Figure 35a the FTIR spectrum of Bent SPN is compared to the spectrum of Bent SPN with CM-CA Fe\(_3\)O\(_4\) NP. The spectrum of pure CM-CA Fe\(_3\)O\(_4\) NP, which is also shown in the Figure 35 (CM-CA), has been interpreted elsewhere (Nalbandian et al. 2016). In brief, the wide absorption band centered at 1590 cm\(^{-1}\) corresponds to the 1730 cm\(^{-1}\) peak of pure citric acid, assignable to the stretching vibration of C=O from the COOH group, which shifts towards smaller wavenumbers in CM-CA Fe\(_3\)O\(_4\) NP. This reveals that carboxylate groups of citric acid complex with the magnetite surface and render a partial single bond character to the C=O bond,
weakening it, and shifting the stretching frequency to a lower value. The peak at 1400 cm\(^{-1}\) in CM-CA Fe\(_3\)O\(_4\) NP corresponds to the symmetric stretching of COO\(^-\) group of citric acid.

The spectrum of the Bent SPN with CM-CA NP sample however, is not a superposition of the spectra of the individual components. Although all the bands of pure bentonite are present, some of the CM-CA Fe\(_3\)O\(_4\) NP peaks are shifted. A new peak seems to appear at 1434 cm\(^{-1}\) while the shape of the 1639 cm\(^{-1}\) peak looks slightly modified. In order to reveal the exact differences between the spectra of Bent SPN and that of Bent SPN with CM-CA NP, a difference spectrum is calculated, in the wavenumber range 1200-1800 cm\(^{-1}\), and is presented in Figure 39b together with the spectrum of CM-CA Fe\(_3\)O\(_4\) NP in the same range. New bands appear in the difference spectrum, a single one located at 1434 cm\(^{-1}\) and a double peak at 1598 and 1665 cm\(^{-1}\). The new bands correspond to the two bands of the CM-CA NP at 1400 and 1590 cm\(^{-1}\), slightly shifted towards higher frequencies. This could be attributed to the partial weakening of the covalent bond between the magnetite NP and the citric acid, possibly due to the presence of bentonite.

Figure 35. (a) Comparison of FTIR spectra of Bent SPN, of pure citric acid coated Fe\(_3\)O\(_4\) nanoparticles (CM-CA Fe\(_3\)O\(_4\) NP), and of bentonite SPN with 0.5 wt% CM-CA Fe\(_3\)O\(_4\) NP, (b) Comparison of FTIR spectra of pure CM-CA Fe\(_3\)O\(_4\) NP and the difference between the spectra of Bent SPN and Bent SPN with 0.5 wt% CM-CA Fe\(_3\)O\(_4\) NP.
4.2 Rheological measurements

4.2.1 Consistency of sample preparation and measurement methodology

Any colloidal dispersion exhibits peculiar flow characteristics and the rheological behavior depends strongly on prior shear history. The flow/rheological behavior of aqueous bentonite dispersions are governed by colloidal system chemistry fundamentals (van Olphen, 1977; Luckham and Rossi, 1999). The order of addition of agents in forming the dispersion is quite significant (Au and Leong, 2013). For example, water dispersions will have different properties if salt is added to water before or after the addition of bentonite. The physical state of the additives (liquid or solid) also influences the properties of the dispersion. In addition, mixing and preparation procedures such as, hydration, time of mixing, temperature, aging, are all significant influencing factors for the final properties of these dispersions.

It is very important to conduct experiments under similar conditions, if a comparison is to be made on results from different samples and between different laboratories, because of shear and time dependence of rheological properties of clay dispersions. The American Petroleum Institute (API) procedures and specifications (API Spec 13A, 2010; API Spec 13I, 2000; API Spec 13B-1, 2003) were developed in order to establish common procedures but sometimes these specifications do not deal with newer additives or newer requirements that are used or needed in different mud formulations that perform difficult tasks under varying conditions (Clark, 1995).

It is often very difficult to compare results from different investigators because mixing and preparation procedures are almost never the same. From a review of the literature and in order to have consistent results, it is evident that the important parameters are (Vryzas et al. 2017b): (1) the raw materials, (2) the mixing procedure of water and bentonite, (3) the mixing time, (4) the mixing energy, (5) the hydration of bentonite (static or dynamic), (6) the mixing procedure of any additive, (7) the hydration of any additive (static or dynamic), and (8) any pre-shearing done before measurement. Information about these procedures was sought in the literature and a non-exhaustive list of procedures that were followed is presented in Table 5. Wherever information is not indicated, it means that no actual reporting was made in the relevant reference.
Table 5. Sample preparation methodology comparison (Vryzas et al., 2017b).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Mixing</th>
<th>Mixing time</th>
<th>Bentonite hydration</th>
<th>High temperature</th>
<th>Pre – shearing</th>
<th>Time of pre – shearing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alderman et al., 1988</td>
<td>High speed</td>
<td></td>
<td></td>
<td>Hot roll, 100 °C, 48 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alderman et al., 1991</td>
<td>High shear</td>
<td>Roll 100 RPM, 3 hrs</td>
<td>16 hrs</td>
<td>Cold roll, 100 RPM</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td>API</td>
<td>High shear</td>
<td>total 15 min (5 + 10)</td>
<td>24 hrs</td>
<td>high shear</td>
<td>5 min</td>
<td></td>
</tr>
<tr>
<td>Benna et al., 1999</td>
<td>Sonicate</td>
<td>Roll 24 RPM, 24 hrs, leave for 13 days</td>
<td>sonicate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Briscoe et al., 1992</td>
<td>High shear</td>
<td>&gt; 1 day, static</td>
<td></td>
<td>Restir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hilscher &amp; Clements, 1982</td>
<td></td>
<td>Slow roll, 65.5 °C, 16 hrs</td>
<td></td>
<td>High shear</td>
<td>5 mins</td>
<td></td>
</tr>
<tr>
<td>Khandal, and Tadros, 1988</td>
<td>High shear</td>
<td>5-10 min, depending on clay concentration</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Laribi et al., 2006</td>
<td>Overhead mixer (low shear)</td>
<td>12 - 15 h</td>
<td>5 days</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Miano et al., 1996</td>
<td>Vigorously, Hamilton beach mixer</td>
<td>16 hrs</td>
<td>Hot roll, 16 – 24 hours, 17 RPM</td>
<td>Low speed</td>
<td>10 mins</td>
<td></td>
</tr>
<tr>
<td>Nyland et al., 1988</td>
<td>Stirring</td>
<td>1 hr</td>
<td>Hot roll 21 hrs, 121 °C</td>
<td>Stirring</td>
<td>1 hr</td>
<td>ultrasound</td>
</tr>
<tr>
<td>Penner &amp; Lagaly, 2000</td>
<td>Ultrasound</td>
<td>72 hr shaking</td>
<td></td>
<td></td>
<td></td>
<td>ultrasound</td>
</tr>
<tr>
<td>Ramos-Tejada et al., 2001</td>
<td></td>
<td></td>
<td></td>
<td>For 30s with 10 Pa shear stress</td>
<td>measure after 3 mins</td>
<td></td>
</tr>
<tr>
<td>Rossi et al., 1997</td>
<td>High shear</td>
<td>sufficient (not stating specific time)</td>
<td>up to 24 h</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Singh &amp; Sharma, 1991</td>
<td></td>
<td></td>
<td>24 – 48 h</td>
<td>204-232 °C, static, 16 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhang &amp; Yin, 2002.</td>
<td>10,000 RPM</td>
<td>20 min</td>
<td>24 hrs</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the inspection of the list it is evident that there is no consensus on the procedures of preparation of water-bentonite dispersions, and this is true for the listed works covering a period of >15 years. Drilling fluid industry appears to follow more ‘common – API’
procedures, though not fully, while ‘bentonite or colloidal industry’, if we can call it that, seems to follow less common and less standardized procedures. Caution should thus be exercised when comparing results of bentonite/colloidal dispersions among different, but also even within same, laboratories, because preparation procedures are very important for producing the desired rheological properties.

This work was based on API procedures. Following API procedures, and most importantly the procedure of preshearing, consistency in measurements is ensured, so that cross-comparison of results can be made with more certainty. Møller et al. (2006) have also recognized the importance of controlling the aging history of colloidal samples by large preshearing in getting reproducible results.

The consistency of the results, following API procedures and methodologies described above, is proven from the results presented in Figure 36, where the rheograms of four different 7 wt% water-bentonite dispersions are plotted. These samples were prepared in four different batches (the same day) and measured at 25 °C (a day later). The exact replication of these rheograms is, if anything else, remarkable. Data fitting to the Herschel-Bulkley rheological model, gave the results shown in Table 6.

It is worth noting the following: (a) the excellent fit of the data to the Herschel-Bulkley rheological model, with extremely small error square values; (b) the remarkable repeatability of the flow behavior index, (n), hovering around 0.82, and (c) the very good repeatability of the yield stress at 3.36–3.44 Pa, with a standard deviation of only 1.1% of the mean value.
Figure 36. Rheograms of four different samples of 7% wt% Wyoming sodium bentonite water suspensions, prepared the same day and measured a day later, as per preparation methodology.

Table 6. Herschel-Bulkley rheological parameters of the four samples of Figure 36.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_s, Pa)</th>
<th>(K, Pas^n)</th>
<th>(n)</th>
<th>(R)</th>
<th>(SQ^2, Pa^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.36</td>
<td>0.0563</td>
<td>0.822</td>
<td>0.9992</td>
<td>0.35</td>
</tr>
<tr>
<td>S2</td>
<td>3.36</td>
<td>0.0582</td>
<td>0.817</td>
<td>0.9994</td>
<td>0.29</td>
</tr>
<tr>
<td>S3</td>
<td>3.40</td>
<td>0.0580</td>
<td>0.818</td>
<td>0.9990</td>
<td>0.47</td>
</tr>
<tr>
<td>S4</td>
<td>3.44</td>
<td>0.0600</td>
<td>0.815</td>
<td>0.9993</td>
<td>0.31</td>
</tr>
<tr>
<td><strong>Mean value</strong></td>
<td></td>
<td>3.39</td>
<td>0.0580</td>
<td>0.818</td>
<td></td>
</tr>
<tr>
<td><strong>St. dev/mean</strong></td>
<td></td>
<td>1.1%</td>
<td>2.8%</td>
<td>0.4%</td>
<td></td>
</tr>
</tbody>
</table>

4.2.2 Na-bentonite suspension (base fluid)

Figure 37, shows the rheograms of 7 wt% water Na-bentonite suspension (base fluid-BF) at different temperatures (25, 40, 60 and 70°C). The fluid exhibited a yield stress, followed by a shear thinning behavior with higher shear stress values at increased temperatures. Furthermore, there are larger differences of the stress values at ambient temperature at lower shear rates compared to higher shear rates. More specifically, at low shear rates (5.1-170 s\(^{-1}\)), the sample has almost double the shear stress values at all tested temperatures. This can be plausibly attributed to the microstructural network and gel-like structure of bentonite suspensions, which is broken at higher shear rates, while becomes stronger at lower shear rates, giving rise to the build-up of an interconnected network structure in the aqueous suspension.
Figure 37. Rheograms of 7 wt% water-bentonite suspension at different temperatures.

Figure 38 compares the apparent viscosity of the BF at the different tested temperatures (25°C-70°C). It can be seen that higher temperatures cause an increase of the apparent viscosity at all shear rates, with shear thinning characteristics. This is in contrast to the base fluid (water) behavior, where high temperatures cause a decrease in viscosity values. A possible explanation for this behavior is that exposure of the suspensions at higher temperatures has caused a better dispersion of the bentonite, therefore increasing the number of individual platelets in suspension. The results are in good agreement with those presented by Annis (1967), who observed a significant increase in the viscosity for higher temperatures and argued that high shear rate viscosities are mainly due to mechanical interaction of the solids and the liquid. The low shear rate viscosities are greater than the viscosity at higher shear rates. This can be possibly attributed to the fact that particle aggregates were broken down into smaller flow units by the applied forces, leading to lower viscosity values at higher shear rates. Under high shear rates the fluid is not able to build a strong inter-particle network which arises from the gelation of water-bentonite suspensions upon exposure at high temperatures and thus giving lower apparent viscosity values.
Figure 38. Apparent viscosity of 7 wt% water-Na bentonite suspension as a function of shear rate at different temperatures.

Table 7 presents the Herschel-Bulkley (HB) rheological parameters at different temperatures for the Na-bentonite water suspension (BF). It can be clearly seen that there is an excellent fit of the HB model because of the very high regression coefficient ($R^2$) values and the very small variation of the sum square errors ($\Sigma Q^2$) achieved, with $R^2$ to be higher than 0.99 in all cases and the range of $\Sigma Q^2$ between 0.35–1.43 Pa$^2$.

Table 7. Herschel-Bulkley (HB) Model parameters fitted at different temperatures for 7 wt% water Na-bentonite suspensions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\tau_y$ (Pa)</th>
<th>$K$ (Pa s$^n$)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$\Sigma Q^2$ (Pa$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.38</td>
<td>0.097</td>
<td>0.747</td>
<td>0.9990</td>
<td>0.45</td>
</tr>
<tr>
<td>40</td>
<td>4.92</td>
<td>0.050</td>
<td>0.833</td>
<td>0.9992</td>
<td>0.35</td>
</tr>
<tr>
<td>60</td>
<td>7.36</td>
<td>0.026</td>
<td>0.907</td>
<td>0.9972</td>
<td>0.88</td>
</tr>
<tr>
<td>70</td>
<td>8.19</td>
<td>0.022</td>
<td>0.931</td>
<td>0.9985</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Figure 39a presents the yield stress versus temperature (up to 70°C) for the 7 wt% water Na-bentonite suspension. It can be clearly seen the increase in yield stress values for increasing temperatures. The highest yield stress value was obtained at 70°C giving a final yield stress value of 8.19 Pa, which is 142% larger than the one obtained at 25°C (3.38 Pa). It is interesting
also to notice that this increase follows a linear pattern up to the highest tested temperature (70°C) and can be described by an equation as can be seen in Figure 39a. In Figure 39b it can be seen the variation of flow consistency (K) and flow behavior (n) indices across the temperature range of 25°C - 70°C, for the BF sample. One observes the decrease in K as the temperature increases, which probably represents the decrease of water viscosity. The flow behavior index (n) showed an increase which dictates that the fluids tend to become Bingham plastic at high shear rates.

Figure 39. a) Yield stress as a function of temperature for the 7 wt% water Na-bentonite suspension (BF). b) Variation of Herschel-Bulkley flow consistency (K) and flow behavior (n) index with temperature for the BF sample.
The rheological stability of the BF under different aging times was evaluated by testing the BF sample at fresh conditions (1 day), after 30 days and after 60 days at 25°C. The sample kept static in a plastic container (for 30 and 60 days) and was stirred for 10 min in the Hamilton Beach mixer before making the rheological measurements. Table 8 gives the HB parameters and Figure 40 presents the rheograms. It is observed that there is a small increase in the yield stress after 30 and 60 days with a value of 3.69 Pa and 3.76 Pa, respectively, compared to its initial value of 3.41 Pa. This can be attributed to the formation of a stronger particle network due to an enhanced clay platelet dispersion over time. The variations in K and n are small, while $R^2$ is higher than 0.99 in all cases. The results indicate that the prepared suspensions were rheologically stable with minor rheological changes even after 60 days of natural aging.

Table 8. Herschel-Bulkley (HB) Model parameters fitted for the BF sample at 25°C after a) 1 day b) 30 days and c) 60 days.

<table>
<thead>
<tr>
<th>Aging (days)</th>
<th>$\tau_y$ (Pa)</th>
<th>$K$ (Pa·s$^n$)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$\sum Q^2$ (Pa)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.41</td>
<td>0.083</td>
<td>0.770</td>
<td>0.9992</td>
<td>0.74</td>
</tr>
<tr>
<td>30</td>
<td>3.69</td>
<td>0.095</td>
<td>0.754</td>
<td>0.9985</td>
<td>1.42</td>
</tr>
<tr>
<td>60</td>
<td>3.76</td>
<td>0.093</td>
<td>0.759</td>
<td>0.9983</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Figure 40. Rheograms of the BF (Na-bentonite) sample at 25°C for a) fresh conditions, b) after 30 days and c) after 60 days.

4.2.3 Na-bentonite suspension with addition of C Fe$_2$O$_3$ nanoparticles

Addition of commercial Fe$_2$O$_3$ nanoparticles (C Fe$_2$O$_3$ NP) at different concentrations affected the rheological properties of the BF at all tested temperatures (up to 60°C). The
rheograms for the BF as well as for the nano-based drilling fluids containing 0.5, 1.5 and 2.5 wt% Fe$_2$O$_3$ NP at 25°C are shown in Figure 41. Table 9 presents the rheological parameters as determined by fitting the raw viscometric data to the Herschel-Bulkley model for the different samples at 25°C, 40°C and 60°C. All samples exhibited a yield stress, followed by a shear thinning behavior. It can be clearly seen that addition of Fe$_2$O$_3$ nanoparticles increased the shear stress at all shear rates when compared to the base fluid by raising the rheogram and essentially affecting the yield stress. The most remarkable change was noticed upon addition of 2.5 wt% Fe$_2$O$_3$ NP, which almost doubled the shear stress values at all shear rates compared to the base fluid (BF), while smaller changes were observed for the samples containing 0.5 and 1.5 wt% Fe$_2$O$_3$ NP. Higher temperatures increased even further the yield stress values of all tested samples at all different concentrations, which can be attributed most probably to the gelation of bentonite particles as well as to the aggregation of the NP, which lead to higher yield stress values. More specifically, addition of 0.5 wt% Fe$_2$O$_3$ NP gave a yield stress value of 6.85 Pa at 25°C, 8.59 Pa at 40°C and 11 Pa at 60°C (Figure 42 and Table 9). The sample containing 1.5 wt% Fe$_2$O$_3$ NP showed a yield stress value of 9.44 Pa at 25°C, 12.19 Pa at 40°C and 16.41 Pa at 60°C. The highest concentration of NP (2.5 wt%) gave the highest yield stress values of 13 Pa, 16.47 Pa and 22.59 Pa, at 25, 40 and 60°C, respectively. The flow consistency index decreased at higher temperatures. The flow behavior index increased with increasing temperature. The HB model provides an excellent fit with $R^2>0.99$.

Figure 41. Rheograms of the sample containing 0.5, 1.5 and 2.5 wt% C Fe$_2$O$_3$ NP at 25°C.
Figure 42. Rheograms of the sample containing 0.5 wt% C Fe$_2$O$_3$ NP at 25°C, 40°C and 60°C.

Table 9. Herschel-Bulkley (HB) Model parameters fitted for the sample containing different concentrations of C Fe$_2$O$_3$ NP at 25°C, 40°C and 60°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Herschel-Bulkley Model</th>
<th>% NP</th>
<th>$\tau_y$ (Pa)</th>
<th>$K$ (Pa·s$^n$)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$\sum Q^2$ (Pa)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td></td>
<td>0.5</td>
<td>6.85</td>
<td>0.068</td>
<td>0.819</td>
<td>0.9996</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>9.44</td>
<td>0.070</td>
<td>0.818</td>
<td>0.9960</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>13.04</td>
<td>0.045</td>
<td>0.894</td>
<td>0.9936</td>
<td>1.38</td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td>0.5</td>
<td>8.59</td>
<td>0.056</td>
<td>0.852</td>
<td>0.9994</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>12.19</td>
<td>0.049</td>
<td>0.867</td>
<td>0.9984</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>16.47</td>
<td>0.046</td>
<td>0.898</td>
<td>0.9987</td>
<td>1.61</td>
</tr>
<tr>
<td>60°C</td>
<td></td>
<td>0.5</td>
<td>11.00</td>
<td>0.036</td>
<td>0.884</td>
<td>0.9986</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>16.41</td>
<td>0.020</td>
<td>0.966</td>
<td>0.9974</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>22.59</td>
<td>0.018</td>
<td>0.998</td>
<td>0.9941</td>
<td>5.17</td>
</tr>
</tbody>
</table>

The results obtained from this study agree with those reported from Jung et al. (2011), who examined the rheological properties of 5 wt% bentonite fluids (used as base fluid) containing different concentrations (0.5 and 5 wt%) of iron oxide (Fe$_2$O$_3$) NP (3 and 30 nm) as a function of temperature (20–200 °C) and pressure (1–100 atm). More specifically, they reported that an increase in concentration of Fe$_2$O$_3$ NP in the bentonite suspension resulted in increasing yield...
stress values (Table 10), and strength of particle interaction. Furthermore, they noticed that smaller sizes of NP resulted in higher yield stress values. They attributed this rheological enhancement to the fact that Fe$_2$O$_3$ NP embedded in randomly dispersed pore structure on the surface of clay particle and conferred links between bentonite particles, which in turn promoted gelation of the bentonite particles.

Table 10. Change of yield stress as a function of content of Fe$_2$O$_3$ NP in 5 wt % bentonite aqueous suspension (base fluid-BF) at 25 °C and atmospheric pressure (Jung et al. 2011).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Yield Stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>1.27</td>
</tr>
<tr>
<td>BF + 0.5 wt % Fe$_2$O$_3$ NP (30 nm)</td>
<td>1.80</td>
</tr>
<tr>
<td>BF + 5.0 wt % Fe$_2$O$_3$ NP (30 nm)</td>
<td>7.67</td>
</tr>
<tr>
<td>BF + 0.5 wt % Fe$_2$O$_3$ NP (3 nm)</td>
<td>3.33</td>
</tr>
<tr>
<td>BF + 5.0 wt % Fe$_2$O$_3$ NP (3 nm)</td>
<td>36.89</td>
</tr>
</tbody>
</table>

Mahmoud et al. (2016) evaluated the performance of drilling fluids containing commercial Fe$_2$O$_3$ at various concentrations (up to 2.5 wt %), for minimizing formation damage at HP/HT conditions. A 7 wt % Ca-bentonite aqueous suspension was used as base fluid. The results showed that higher temperatures generate higher yield stress for the base fluid, which is in agreement with the results reported in this study. They reported that adding Fe$_2$O$_3$ NP changed the rheology of bentonite-based drilling fluids at temperatures up to 93°C, by increasing the yield point by 50% on average at the different tested temperatures. Furthermore, addition of Fe$_2$O$_3$ NP resulted in a small increase in the plastic viscosity at different temperatures and concentrations. They concluded that all the drilling fluids tested in this work exhibited shear-thinning behavior (i.e. apparent viscosity decreases with increasing shear rate). An increase in the concentration of Fe$_2$O$_3$ NP resulted in a more stable viscosity at higher temperatures, which is an indication of the ability of FeO$_3$ NP to suppress viscosity reduction, thereby yielding similar rheological behavior for varying temperatures. The Herschel-Bulkley model was found to be the best fitted model. The authors performed aging tests at 176°C (350°F) for 16 h, and they observed that the rheology of bentonite-based drilling fluid containing Fe$_2$O$_3$ NP remained stable minor decreases in the yield point values at different temperatures, which indicates a minor loss of gel structure.

Therefore, it can be concluded that addition of Fe$_2$O$_3$ NP can affect the rheological characteristics of water-bentonite (Ca-based or Na-based) suspensions even at low concentrations (<1 wt%).
4.2.4 Na-bentonite suspension with addition of C Fe₃O₄ nanoparticles

The rheograms for the samples containing different concentrations of C Fe₃O₄ NP at 25°C are shown in Figure 43. It is evident that addition of C Fe₃O₄ NP at different concentrations shifted up the rheogram of the BF and that higher concentrations of NP led to higher shear stress values at all shear rates. The most notable change was observed upon addition of 2.5 wt% Fe₃O₄ NP, which almost quadrupled the yield stress value of the BF. Figure 44 shows the rheograms of the sample containing 0.5 wt% C Fe₃O₄ NP at the three tested temperatures. One can easily observe that higher temperatures led to higher yield stress values. Table 11 presents the rheological parameters as determined by fitting the raw viscometric data to the Herschel-Bulkley model for the different samples at 25°C, 40°C and 60°C. It can be clearly seen that higher temperatures result in higher yield stress values for the sample containing 0.5 wt% C Fe₃O₄ NP at all different concentrations, with 6.28 Pa at room temperature, while the maximum yield stress value of 11.0 Pa was achieved at 60°C. Addition of 1.5 wt% C Fe₃O₄ NP gave a yield stress of 9.44 Pa at 25°C, 12.19 Pa at 40°C and 16.41 Pa at 60°C. The sample containing 2.5 wt% Fe₃O₄ NP gave the highest yield stress value at all tested temperatures of 13 Pa, 16.47 Pa and 22.59 Pa at 25°C, 40°C and 60°C, respectively. The flow consistency index decreased at higher temperatures, while the flow behavior index increased with increasing temperature with a high value of 0.996 at 2.5 wt% of NP and at 60°C tending towards Bingham plastic behavior. Again, the HB model provides a very good fit with R²>0.99 at all tested temperatures and concentrations of NP.

![Graph showing rheograms of samples with different concentrations of C Fe₃O₄ nanoparticles at 25°C, 40°C, and 60°C.](image-url)
Figure 43. Rheograms of the sample containing 0.5, 1.5 and 2.5 wt% C Fe₃O₄ NP at 25°C.

Figure 44. Rheograms of the sample containing 0.5 wt% C Fe₃O₄ NP at 25°C, 40°C and 60°C.

Table 11. Herschel-Bulkley (HB) Model parameters fitted for the sample containing different concentrations of C Fe₃O₄ NP at 25°C, 40°C and 60°C.

|  | Herschel-Bulkley Model |  |
|---|---|---|---|---|---|---|
|  | % NP |  |  |  |  |  |
|  | τ_y (Pa) | K (Pa·s^n) | n | R^2 | ΣQ^2 (Pa) |
| 25°C | 0.5 | 6.28 | 0.098 | 0.791 | 0.9992 | 0.30 |
|  | 1.5 | 9.72 | 0.083 | 0.821 | 0.9960 | 0.72 |
|  | 2.5 | 13.37 | 0.111 | 0.792 | 0.9933 | 1.33 |
| 40°C | 0.5 | 8.59 | 0.053 | 0.881 | 0.9992 | 0.49 |
|  | 1.5 | 12.88 | 0.046 | 0.884 | 0.9991 | 0.97 |
|  | 2.5 | 17.42 | 0.098 | 0.912 | 0.9973 | 1.47 |
| 60°C | 0.5 | 11.0 | 0.041 | 0.891 | 0.9992 | 0.98 |
|  | 1.5 | 17.21 | 0.024 | 0.971 | 0.9982 | 1.67 |
|  | 2.5 | 21.91 | 0.022 | 0.996 | 0.9912 | 3.87 |
4.2.5 Na-bentonite suspension with addition of CM-B Fe₃O₄ nanoparticles

In the previous sections we determined that 0.5 wt% of C Fe₃O₄ NP caused moderate modifications in the rheological profile of the BF (which is desirable without excessive changes), and thus we tested further the fluids containing CM (bare and citric acid coated) Fe₃O₄ NP at 0.5 wt%.

Figure 45 shows the rheograms for the sample containing 0.5 wt% CM-B Fe₃O₄ NP at different temperatures (up to 70°C). For comparison purposes the rheograms of BF at 25°C and 70°C are also included. Table 12 presents the HB rheological parameters for the samples at the different tested temperatures. It can be seen that addition of the CM-B Fe₃O₄ NP caused a significant increase in the rheogram of the BF at all tested temperatures especially at low shear rates. The most remarkable increase was noticed at 70°C with an average increase of 200% at all shear rates compared to that of the BF. As it can be seen from Table 12 addition of 0.5 wt% CM-B Fe₃O₄ NP gave a yield stress of 8.73 Pa at 25°C, 9.68 Pa at 40°C, 11.18 Pa at 60°C and 17.2 Pa at 70°C, which represents an increase of +163%, +103%, +56% and 220%, respectively, compared to the base fluid values. The flow consistency index decreased at higher temperatures, while the flow behavior index increased at higher temperatures reaching a maximum value of 0.974 at 70°C tending towards Bingham plastic behavior. The high $R^2$ and low $\Sigma Q^2$ gives high confidence in the Herschel-Bulkley model.

![Figure 45](image_url)

Figure 45. Rheograms of the base fluid (BF) at 25°C and 70°C and of the sample containing 0.5 wt% CM-B Fe₃O₄ NP at 25°C, 40°C, 60°C and 70°C.
Table 12. Herschel-Bulkley (HB) Model parameters fitted at different temperatures for the sample containing 0.5 wt% CM-B Fe₃O₄ NP.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(\tau_y) (Pa)</th>
<th>(K) (Pa·sⁿ)</th>
<th>(n)</th>
<th>(R^2)</th>
<th>(\sum Q^2) (Pa)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8.73</td>
<td>0.054</td>
<td>0.749</td>
<td>0.9696</td>
<td>0.98</td>
</tr>
<tr>
<td>40</td>
<td>9.68</td>
<td>0.038</td>
<td>0.834</td>
<td>0.9757</td>
<td>1.61</td>
</tr>
<tr>
<td>60</td>
<td>11.10</td>
<td>0.029</td>
<td>0.853</td>
<td>0.9914</td>
<td>3.37</td>
</tr>
<tr>
<td>70</td>
<td>17.20</td>
<td>0.025</td>
<td>0.974</td>
<td>0.9901</td>
<td>4.26</td>
</tr>
</tbody>
</table>

4.2.6 Na-bentonite suspension with addition of CM-CA Fe₃O₄ nanoparticles

Figure 46 and Table 13 present the rheograms and HB rheological parameters of drilling fluids containing 0.5 wt% of CM-CA Fe₃O₄ NP at different temperatures. It can be observed from Table 13 that CM-CA NP at low temperatures give higher yield stress values compared to that of the base fluid, but give almost similar yield stress values to that of base fluid at the two tested higher temperatures. More specifically, at 60°C and 70°C the yield stress increased from 7.15 Pa in the base fluid to 7.55 Pa upon addition of 0.5wt% CM-CA NP and from 8.18 Pa to 8.69 Pa, respectively. This represents a change of less than 10% in yield stress values. It is worth noting that at the same concentration (0.5 wt%), C NP exhibited larger changes on the yield stress values with an average increase of 60% (see Figure 43 and Table 11). This can be possibly explained from the fact that CM-CA NP are better dispersed in the drilling fluid system as they are much smaller compared to the commercial C Fe₃O₄ NP and potentially they could be linked easier with the clay platelets. This will be analyzed in detail at a later section (HR-TEM analysis). The flow consistency index, \(K\), of CM-CA Fe₃O₄ NP decreased at higher temperatures and its values are smaller than their C-Fe₃O₄ NP counterparts and even smaller than the base fluid (BF) as can be seen in Table 13 (see also Table 7 for BF and Table 11 for C-NP). This could suggest possible means of interaction of NP with clay particles. The flow behavior index, \(n\), increased for higher temperatures and has similar values as for the base fluid. The statistical correlators, \(R^2\) and \(SQ^2\) show also the very good fit by the Herschel-Bulkley model.
Figure 46. Rheograms of the base fluid (BF) at 25°C and 70°C and of the sample containing 0.5 wt% CM-CA Fe₃O₄ NP at 25°C, 40°C, 60°C and 70°C.

Table 13. Herschel-Bulkley (HB) Model parameters fitted at different temperatures for the sample containing 0.5 wt% CM-CA Fe₃O₄ NP.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>τ_y (Pa)</th>
<th>K (Pa·s^n)</th>
<th>n</th>
<th>R²</th>
<th>ΣQ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5.39</td>
<td>0.045</td>
<td>0.799</td>
<td>0.9996</td>
<td>0.31</td>
</tr>
<tr>
<td>40</td>
<td>6.22</td>
<td>0.019</td>
<td>0.919</td>
<td>0.9989</td>
<td>1.26</td>
</tr>
<tr>
<td>60</td>
<td>7.55</td>
<td>0.012</td>
<td>0.946</td>
<td>0.9991</td>
<td>0.18</td>
</tr>
<tr>
<td>70</td>
<td>8.69</td>
<td>0.010</td>
<td>0.987</td>
<td>0.9921</td>
<td>1.89</td>
</tr>
</tbody>
</table>

4.2.7 Na-bentonite suspension with addition of C SiO₂ nanoparticles

Addition of different concentrations (0.5, 1.5 and 2.5 wt%) of C-SiO₂ NP resulted in a totally different behavior (Figure 47). The most remarkable point here is that addition of 2.5 wt% SiO₂ NP resulted in high shear rates while also at low shear rates the shear stress values
decreased significantly below the BF values. Figure 48 shows the rheograms for the sample containing 0.5 wt% SiO$_2$ NP at the three different tested temperatures. It can be seen that the shear stress values show a change of less than 15% at all shear rates and different temperatures. Table 14 presents the rheological parameters as determined by fitting the raw viscometric data to the Herschel-Bulkley model for the samples at the different tested concentrations and temperatures (up to 60°C). One can easily observe that addition of C SiO$_2$ NP showed decreased yield stress values compared to these of the Bent SPN for all tested temperatures and concentrations. More specifically, the sample containing 0.5 wt% SiO$_2$ NP gave a yield stress of 1.36 Pa at 25°C (-58.9% compared to that of the BF), 1.76 Pa at 40°C (-63%) and 2.72 Pa at 60°C (-61.8%). The highest yield stress value of 2.81 Pa obtained for the sample containing 2.5 wt% SiO$_2$ NP at 60°C. These results indicate the potential of nanosilica to be used as a thinner of water-bentonite dispersions. The flow consistency index increased at higher temperatures, while the flow behavior index decreased. The statistical correlators, R$^2$ and SQ$^2$ show also the very good fit by the Herschel-Bulkley model, with R$^2$ >0.99 for all samples and different temperatures.

Figure 47. Rheograms of the sample containing 0.5, 1.5 and 2.5 wt% C SiO$_2$ NP at 25°C.
Figure 48. Rheograms of the base fluid (BF) at 25°C and of the sample containing 0.5 wt% C SiO₂ NP at 25°C, 40°C and 60°C.

Table 14. Herschel-Bulkley (HB) Model parameters fitted for the sample containing different concentrations of C SiO₂ NP at 25°C, 40°C and 60°C.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Herschel-Bulkley Model</th>
<th>% NP</th>
<th>τ_y (Pa)</th>
<th>K (Pa·s^n)</th>
<th>n</th>
<th>R²</th>
<th>ΣQ² (Pa)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td></td>
<td>0.5</td>
<td>1.36</td>
<td>0.072</td>
<td>0.811</td>
<td>0.9998</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>1.67</td>
<td>0.258</td>
<td>0.704</td>
<td>0.9999</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>1.77</td>
<td>1.392</td>
<td>0.572</td>
<td>0.9998</td>
<td>3.97</td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td>0.5</td>
<td>1.76</td>
<td>0.081</td>
<td>0.773</td>
<td>0.9994</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>1.97</td>
<td>0.316</td>
<td>0.657</td>
<td>0.9996</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>2.14</td>
<td>1.493</td>
<td>0.545</td>
<td>0.9995</td>
<td>7.6</td>
</tr>
<tr>
<td>60°C</td>
<td></td>
<td>0.5</td>
<td>2.72</td>
<td>0.206</td>
<td>0.619</td>
<td>0.9987</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2.75</td>
<td>0.399</td>
<td>0.611</td>
<td>0.9972</td>
<td>6.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>2.81</td>
<td>2.191</td>
<td>0.487</td>
<td>0.9976</td>
<td>11.14</td>
</tr>
</tbody>
</table>

Belayneh et al. (2016) focused on the effect of nano-silica (SiO₂) on polymer (HV-CMC, LV-CMC, xanthan gum) and salt (KCl, NaCl) treated water-bentonite drilling fluid systems. They developed a base fluid containing 0.2 g low viscosity (LV)-carboxymethyl cellulose (CMC) and 0.3 g xanthan gum polymers in 25 g bentonite/500 g water with 2.5 g KCl. They
added different amounts of SiO$_2$ NP in the base fluid giving concentrations of up to 0.5 wt% and checked the rheological and the filtration properties. The results indicated that addition of SiO$_2$ NP caused an upward shift on the rheograms with respect to that of the base fluid and the fluids exhibited shear thinning behavior. A maximum yield stress of 10 Pa was measured upon addition of 0.25 g of SiO$_2$ NP compared to 5.5 Pa of the base fluid system. These results are not in agreement with these reported in this study, as addition of SiO$_2$ NP increased the rheological profile of the base fluid, while we showed that addition of SiO$_2$ NP resulted in decreased rheological values of the base fluid. The different formulation of the base fluid (xanthan gum and CMC) can possibly explain this behavior.

On the other hand, the reported results are in good agreement with these reported by Mahmoud et al. (2016) who tested drilling fluids containing different concentrations (up to 2.5 wt%) of SiO$_2$ NP in a 7 wt% Ca-bentonite suspension (used as base fluid). They showed that addition of SiO$_2$ NP decreased the yield stress of the base fluid at all different concentrations of NP by 40% on average at all tested temperatures (up to 90°C).

Afolabi et al. (2017) evaluated the rheological properties of bentonite mud at three different concentrations (6.3 wt %, 13 wt % and 15 wt %) containing different concentrations of SiO$_2$ NP (0 wt %–1.5 wt %). They developed a new hyperbolic model to evaluate the rheological properties of the bentonite mud with and without silica nanoparticles. In addition they compared its performance against various rheological models: Herschel Bulkley, Sisko, Casson (Figure 49a). They observed that the hyperbolic rheological model outperformed the other models and estimated the rheological behavior of the nano-modified mud with high accuracy. The reliability of the different models was investigated using the Root Mean Square Error (RMSE), residual plot analysis and the coefficient of determination ($R^2$) values. They noticed that the range of $R^2$ at all tested concentrations of bentonite and SiO$_2$ NP was ranging from 0.991–0.999, 0.999, 0.982–0.996, 0.674–0.964 for the Herschel-Bulkley, Hyperbolic, Casson and Sisko model, respectively. The residual plots for the Herschel-Bulkley model and the Hyperbolic model (Figure 49b) indicated that there was a random variation in the plot of the residuals with the fitted data points and these two models provided the best fit to the experimental data. For the Casson model, there was a systematic pattern of deviation in the plot of the residuals revealing its poor performance. The good fit of the HB model for nano-enhanced drilling fluids containing SiO$_2$ NP has also been confirmed in this study giving $R^2 >0.99$ at all tested concentrations and temperatures (Table 14).
4.2.8 Effect of dynamic thermal aging

Dynamic aging of the base fluid (Bent SPN) as well as of the sample containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP in a roller oven for 16 h at 177°C (350°F) was performed using a 500 ml aging cell in order to assess the capability of the developed fluids to maintain their rheological properties under dynamic conditions.

Figure 50 shows the photos of the aged samples in the aging cell. One can easily notice that both fluids look completely like gels and have lost their fluidity as per visual observations. However, by agitation for 5 minutes in the high speed mixer they return to their fluid form.
Figure 51 shows the rheograms before and after aging for both the base fluid (BF) and the nano-based fluid (NF) containing 0.5 wt% CM-CA Fe₃O₄ NP. Aging results in a significant decrease (-51%) of the yield stress for the BF (1.69 Pa) (Figure 51a) compared to the value before thermal aging (3.38 Pa). A noteworthy point here is that at higher shear rates the aged BF sample had higher stress values than the fresh sample, while there is a cross over point at a shear rate of 340.46 s⁻¹ (200 rpm). Moreover, the BF aged sample showed a decrease in the shear stress values at lower shear rates. This indicates that the thermal aging adversely affected the BF causing loss of its gel structure evident at low shear rates. At the same time it gives higher apparent viscosity at high shear rates meaning more discrete solids which cannot form gel structure but increase viscosity.

The sample containing 0.5 wt% CM-CA Fe₃O₄ NP maintained its rheological characteristics after thermal aging (Figure 51b), but exhibited higher shear stresses at all shear rates. An upward shift of the rheogram of the aged nano-based fluid for the entire shear rate range was observed, and a yield stress value of 6.22 Pa was obtained compared to 5.39 Pa of its fresh counterpart (at 25°C). This represents an increase of +15% in the yield stress, which shows the ability of the CM Fe₃O₄ NP to withstand such extreme conditions, however it gives higher yield stress values. More specifically, the increase in the shear stress obtained from the nanofluid when comparing before and after aging results is bigger at higher shear rates (approximately 120% higher stress values at 1021.38 s⁻¹). However, at low shear rates this difference becomes smaller (almost 30% higher stress values at 10.21 and 5.11 s⁻¹). This increase in yield stress is considered not to significantly affect fluid performance compared to the BF, which has lost completely its yield stress. The superior performance of the newly developed nano-enhanced drilling fluid can be attributed to the physico-chemical properties of the CM-CA Fe₃O₄ NP, which improve the gel-like structure of the water bentonite suspensions by creating a rigid microstructure network with the clay platelets.

In addition, the flow consistency index (K) values of the BF after aging, is smaller than this obtained for the nano-enhanced drilling fluid by approximately five times (Table 15). Furthermore, the flow behavior index (n) of the BF exhibited higher values compared to the nano-enhanced drilling fluid, which indicates less shear thinning characteristics. Another noteworthy issue is that one can easily be misled if using only shear stress values at higher shear rates of 1021.38 and 510.67 s⁻¹ (600 and 300 rpm). The dramatic decrease of shear stress values measured at low shear rates indicates that the BF sample after aging completely lost its structure, being unable to maintain a satisfactory yield stress value. Similar observations have been made in the past for bentonite based drilling fluids (Kelessidis et al., 2007a).
Figure 51. Rheograms at 25°C after thermal aging at 177°C (350°F) for 16 hrs: a) base fluid (7 wt% Na-bentonite), and b) nano-enhanced drilling fluid (BF+0.5 wt% CM-CA Fe₃O₄ NP).

Table 15. Herschel-Bulkley (HB) model parameters, from rheograms taken at 25°C, after thermal aging at 177°C (350°F) for 16 h, for the base and nano-enhanced drilling fluid (BF+0.5 wt% CM-CA Fe₃O₄ NP)

<table>
<thead>
<tr>
<th></th>
<th>Before Aging</th>
<th>After Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Herschel-Bulkley Model Parameters</td>
<td>Herschel-Bulkley Model Parameters</td>
</tr>
<tr>
<td></td>
<td>$\tau_y$ (Pa)</td>
<td>$K$ (Pa·s^n)</td>
</tr>
<tr>
<td>BF</td>
<td>3.38</td>
<td>0.097</td>
</tr>
<tr>
<td>0.5 wt% CM-CA Fe₃O₄ NP + BF</td>
<td>5.39</td>
<td>0.045</td>
</tr>
</tbody>
</table>

The sample containing 0.5 wt% CM-CA Fe₃O₄ NP exhibited also exceptional gel strength profiles, both before as well as after thermal aging. The 10 sec and 10 minute gel strength values are shown in Figure 52. The flat type gel strength profile of the nano-enhanced drilling fluid compared to the progressive type gel strength of the BF demonstrate its superior functional behavior while drilling. Before aging, The BF showed a 10 sec gel strength value of 5.74 Pa and 10 minute value of 14.84 Pa. After aging the 10 sec and 10 minute gel strength values were slightly decreased to be 4.79 Pa and 11.0 Pa, respectively. The nanofluid before aging showed values of 3.35 Pa and 4.31 Pa for the 10 sec and 10 minute gel strength, respectively, while after aging 2.87 Pa and 3.83 Pa. This superior flat type gel strength profile
reveals the ability of NP to improve the gel strength properties of the water-bentonite suspensions. This will prevent problems such as hole pack-off and mechanical pipe sticking by developing and maintaining adequate gel strength profile in the event of cessation of drilling operations at high temperature downhole environments (Amanullah et al. 2011). An interesting trend can be observed when comparing the 10 sec gel strength values with the yield stress values obtained from the tested samples. The gel strength values are significantly higher than the yield stress values for the BF, while the nanofluid showed the opposite behavior and showed decreased gel strength values compared to the yield stress. This complex behavior can be attributed to the ability of NP to reduce the progressive gel structure, which is mainly caused by the bentonite particles, thus promoting stability.

![Figure 52. Gel Strength of the base fluid (7 wt% bentonite) and nano-enhanced fluid (BF+0.5 wt% CM-CA Fe₃O₄ NP): a) With no thermal aging, and b) After dynamic thermal aging at 177°C (350°F) for 16 h.](image)

**4.2.9 Comparative rheological analysis**

Figures 53 and 54 present the rheograms of all samples containing 0.5 wt% (determined as optimal concentration as it caused moderated changes in the rheological profile of the base fluid) of the different nanoparticles at 25°C and 60°C, respectively. One can easily observe that at 25°C the sample containing C Fe₃O₄ NP exhibited the highest shear stress values at high shear rates, but at lower shear rates the sample containing CM-B Fe₃O₄ NP exhibited the highest shear stress values among all samples. The only sample that gave lower yield stress values compared to the base fluid is the sample containing SiO₂ NP. At 60°C (Figure 54), addition of C Fe₂O₃, C Fe₃O₄ and CM-B Fe₃O₄ NP caused the largest changes in the shear...
stress values compared to the ones obtained for the base fluid. The CM-CA Fe$_3$O$_4$ NP caused very small changes compared to the base fluid at low shear rates, but they are large at high shear rates, while SiO$_2$ NP led to smaller shear stress values at all shear rates.

![Graph](image1)

**Figure 53.** Rheograms of all tested suspensions at 0.5 wt% of NP and at 25°C.

![Graph](image2)

**Figure 54.** Rheograms of all tested suspensions at 0.5 wt% of NP and at 60°C.

In Figure 55, the variation of yield stress ($\tau_y$) with temperature is shown for all tested samples at the three tested temperatures. Data show an almost linear increase of yield stress with temperature for all samples at the tested temperatures albeit at different slopes. The Bent SPN (base fluid), Bent SPN with C Fe$_3$O$_4$ NP and Bent SPN with C Fe$_2$O$_3$ NP samples have
approximately the same slope, while the Bent SPN with CM-CA and CM-B Fe$_3$O$_4$ NP samples showed smaller slope with respect to the base fluid. Bent SPN with C SiO$_2$ NP gave a minimal slope with almost no changes, indicating potential use of C SiO$_2$ NP for development of flat rheology fluids.

Figure 55. Yield stress as a function of temperature for all tested samples.

Figure 56 presents the variation of the flow consistency and flow behavior index with temperature for all tested suspensions containing 0.5 wt% of the different nanoparticles. It can be seen that at higher temperatures the flow consistency index ($\kappa$) decreased and the flow behavior index ($n$) increased (tends towards the value 1.0) at higher temperatures for all the tested samples except of the Bent SPN with SiO$_2$ NP sample, for which the $\kappa$ and $n$ followed exactly the opposite trend. The Bent SPN with C Fe$_2$O$_3$ NP exhibited a $\kappa$ greater than of the Bent SPN at all temperatures by 20% on average. The Bent SPN with CM-CA Fe$_3$O$_4$ NP sample had the lowest $\kappa$ values compared to all other samples with an average decrease of 60% at 60°C compared to the Bent SPN. The sample with CM-B Fe$_3$O$_4$ NP showed slight increase of the $\kappa$ values compared to the Bent SPN with CM-CA Fe$_3$O$_4$ NP. The Bent SPN with C SiO$_2$ NP sample showed increased $\kappa$ values for high temperatures with the highest at 60°C with $\kappa = 0.207$ Pa s$^n$, much higher than that of the Bent SPN. All samples containing Fe$_3$O$_4$ NP (C, CM-B, CM-CA Fe$_3$O$_4$ NP) showed increased $n$ values at higher temperatures becoming more Newtonian, while the sample containing C-SiO$_2$ NP exhibited smaller $n$ values indicating more shear thinning behavior at higher temperatures.
The rheological measurements showed that addition of the different nanoparticles (C Fe$_2$O$_3$, C Fe$_3$O$_4$, CM-CA Fe$_3$O$_4$, CM-B Fe$_3$O$_4$, C SiO$_2$) at 0.5, 1.5 and 2.5 wt%, affected in different ways the rheological behavior of the Bent SPN (7 wt% bentonite-base fluid). Higher temperatures resulted in higher shear stress values over the entire shear rate range for the Bent SPN. This behavior is attributed to the fact that at high temperatures bentonite platelets form a continuous gel structure and large aggregates, mainly through FF associations, which lead to higher yield stress values. This is in agreement with the findings of Zhou et al. (2012) who suggested that, given the edge shape irregularity and its extremely small width, neither the EE nor FE attachment are highly probable in a suspension as clay platelets tumble and rotate rapidly due to the Brownian motion and this leaves the FF mode as the dominant attachment mode. Mouzon et al. (2016) showed that bentonite platelets associated in FF or EF
arrangements, creating associations of Y-type. As it has been postulated by Kelessidis (2017), the yield stress of charged particle suspensions arises due to the existence of interparticle forces between the particles which link them in various configurations. An increase in this net attractive force results in an increase of the yield stress.

The most significant rheological changes were noticed upon addition of custom-made bare (CM-B) magnetite nanoparticles Fe₃O₄ NP in the Bent SPN, which almost doubled the yield stress values of the Bent SPN at all tested temperatures (up to 60°C). This behavior is not only a result of the aggregation of the bentonite platelets but also of the aggregation of the bare Fe₃O₄ NP due to magnetic forces (long-range attractive interaction, compared with van der Waals and electrical double layer interactions) that prevail especially at 60°C, over the relatively weak clay-nanoparticle electrostatic forces and thus promote interconnected microstructures with aggregates, which in turn increase the yield stress. Phenrat et al. (2007), demonstrated that bare magnetite nanoparticles in aqueous solution (pH=7.4) rapidly aggregated due to magnetic attractive forces between the particles. Furthermore, they stated that the magnetic attraction dominated the interaction energy, and there was no energy barrier to resist aggregation.

Addition of different concentrations of citric acid coated (CM-CA) Fe₃O₄ NP showed a moderate increase of the yield stress values compared to that of the Bent SPN at low temperatures (especially at 0.5 wt%-determined as optimal concentration), and almost similar yield stress values at the highest tested temperature (60°C). This behavior can be attributed to the formation of clay/NP aggregates but to a lesser extent compared to those formed with the uncoated nanoparticles (C and CM-B Fe₃O₄ NP). The coating appears to significantly minimize the aggregation of Fe₃O₄ NP, which in turn affects the rheological behavior of such suspensions.

Addition of C SiO₂ NP (Bent SPN with SiO₂ NP) showed decreased yield stress values compared to these of the Bent SPN or to Bent SPN with C, CM-CA and CM-B Fe₃O₄ NP for all tested temperatures and concentrations as well as a very modest increase of yield stress with temperature. This behavior can be explained by the fact that C SiO₂ NP have negative charges which result in the domination of strong electrostatic repulsive forces. Thus, the C SiO₂ NP are fully dispersed within the clay platelet faces even at higher temperatures without forming aggregates and interconnected structures, leading to lower shear stress values at all shear rates. These results are in agreement with those reported by Elochukwu et al. (2017), who showed that the rheological characteristics of water-bentonite dispersions decreased upon addition of bare SiO₂ NP. These authors showed that with appropriate modification with a cationic
surfactant (alkylbenzyldimethylammonium chloride), addition of SiO$_2$ NP in water-bentonite dispersions can improve their rheological and filtration properties. They explained that addition of the surfactant causes an ionic attraction between the positive surface of the cationic surfactant and the negative surface of nanosilica and at this state, the steric repulsion between nanosilica and bentonite increases, leading to a stable mono-dispersed system.

4.3 Modeling of rheology

The modeling efforts are based on the rheological experimental data presented in this study for the base fluid (see section 4.2.2) and for the sample containing C Fe$_3$O$_4$ NP (see section 4.2.4) and were created by the team of Dr. Gerogiorgis (University of Edinburgh).

The development of first principle models for rheology of nanofluids, which can characterize the fluid behavior as a function of shear rate, nanoparticle volume fraction and temperature, is critical toward high-fidelity computational modelling, design and planning of cost-effective drilling campaigns (Reilly et al., 2016). When successfully validated against experimental data, such models ensure general applicability to a variety of similar nanoparticle-enhanced drilling fluids, eliminating the need for parameterized approximations of fluid rheology.

Reilly et al. (2016) proposed a first-principles approach to the rheology of smart drilling fluids containing Fe$_3$O$_4$ NP which have shown advantages to increasing drilling efficiency in a variety of reservoir environments. Their models were based on original experimental data. The model for shear stress was developed based on a force balance between the Van der Waals attractions of monodispersed Fe$_3$O$_4$ NP spheres. The model for viscosity was created by considering the force required to maintain the NP in suspension being equal to the drag force as calculated for Stokes flow approximation about a sphere. At first they developed bivariate (shear rate, NP concentration) viscosity and shear stress models at a range of temperatures (25 °C–60 °C) and they concluded that the produced results by the first–principle showed good agreement with the experimental data for the shear stress and viscosity. They observed a continuous increase in shear stress and apparent viscosity at higher NP concentrations as well as increased temperatures reduced the degree of shear thinning predicted by the model leading to discrepancies in shear stress predicted at high shear rates. They also incorporated the parameter of T in their bivariate models, this leading to the development of trivariate viscosity and shear stress models (Figure 57). They stated that heating effects and low NP concentrations
increased standard error and concluded that the newly developed models described the rheological effects of shear rate, nanoparticle concentration and temperature with high predictive potential with correlation coefficients ($R^2 > 0.983$).

Figure 57. Trivariate models plots for shear stress and viscosity at different temperatures (Reilly et al. 2016).

Gerogiorgis et al. (2017) started from microstructural arguments and force equilibria assumptions and developed physics-based (not data-driven) correlations. They developed first-principles rheological models of nano-enhanced drilling fluids containing Fe$_3$O$_4$ NP, which are considered to be explicit multivariate functions of temperature, NP volume fraction and shear rate. They concluded that all composed drilling fluids exhibited a yield stress behavior and are sensitive to both NP addition and temperature, which induced an upward shift on yield stress values as well as shear stress surfaces. They achieved a very good agreement and model consistency, with a slight discrepancy at the lowest temperature (Figure 58). They also stated that the variation of surface inclination as a function of temperature is more pronounced for high NP volume fraction, an observation corroborating the indication of strong microstructural effects (interconnected network formation leading to gelation). Finally, they examined the reliability of the developed models by calculating and comparing the $R^2$ values as well as the sum of squared errors ($\Sigma Q^2$) and found that the trivariate models showed high predictive potential, with $R^2 > 0.97$ for all subsets of shear stress.
From the above data it can be concluded that the produced models consistently capture the non-Newtonian fluid behavior, with only one parameter set computation needed for the entire dataset. The experimentally observed consistent increase of yield stress with temperature is also captured very well. Brownian motion as well as the evolution of complex microstructures within the nanofluid may explain this extraordinary rheological behavior; evidence suggests that a robust mesoscopic inter-particle network may form due to the interactions of NP with bentonite platelets and this will be examined in a later section (see section 4.5). Detailed analysis of the models and the techniques used for the rheological modeling can be found in Reilly et al. (2016) and Gerogiorgis et al. (2017).

### 4.4 High-Pressure High-temperature (HP/HT) Rheological Measurements

The base fluid (7 wt% water Na-bentonite suspension) and nano-enhanced drilling fluid containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP were tested at 69 bar (1000 psi) and up to 120°C (250°F) in order to examine their rheological behavior under HP/HT conditions (Chandler 7600 Ultra HP/HT viscometer/performed at TAMUQ). The readings were taken from high to low speeds, while rotation lasted for 60s at each rotational speed, with readings being recorded every 10s, thus giving six measurements for each rotational speed with a total duration of 8 min per cycle. These six values were averaged and recorded. Before recording any measurements the sample was agitated for 200s. Furthermore, the sample was stirred for 5 min using the high speed mixer (Hamilton Beach) prior to each measurement, in order to achieve the same shear history. The
Firstly, the BF was tested at continuous temperature ramping (25-40-60-80-100-120°C) at 69 bar. The desired temperature was achieved in approximately 1 min for the different steps. Then an identical sample (7 wt% water Na-bentonite suspension) was prepared and tested directly at 120°C without taking any other measurements at other temperatures (approximately 5 min to reach 120°C). This was done in order to examine the effect of temperature ramping history on the rheological profile of such fluids. The sample containing 0.5 wt% CM-CA Fe₃O₄ NP was tested only at continuous temperature ramping conditions (up to 120°C and 69 bar).

Figure 59 and Figure 60 present the rheograms for the two fluids. As can be seen from Figure 59 higher temperatures (up to 120°C) caused an upward shift of the rheogram for the BF with the most remarkable change observed at 120°C, which the shear stress values increased by 50% on average compared to the ones obtained at 25°C. In addition, one can observe that the BF shows a shear thickening profile for temperatures >60°C and especially at high shear rates. These phenomena can be possibly attributed to the fact that bentonite particles form a gel-like structure at higher temperatures, this causing significant changes in their rheological profile. Another noteworthy point here is that direct testing of the base fluid at 120°C gave almost identical results with the continuous ramping test, which shows that the effect of temperature ramping history did not affect significantly the rheological profile of water-bentonite suspensions for these tested samples.

Figure 60 shows the rheogram for the nano-enhanced drilling fluid and in this case an upward shift of the rheogram is observed which becomes larger under higher temperatures. Higher shear stresses are observed at higher temperatures. The nano-enhanced drilling fluid exhibits a shear thinning behavior up to 60°C, however for temperatures >80°C becomes shear thickening.

Figure 61 shows the increase of yield stress with temperature (up to 120°C) for the BF and it is really interesting the pattern that is followed from the BF which can be described very well with an exponential fit. However, up to 80°C it follows a linear trend, which is a similar trend to the one observed in previous sections for the effect of temperature at atmospheric pressure. However, the yield stress values obtained at atmospheric pressure are lower by 55% on average for both BF and sample containing 0.5 wt% CM-CA Fe₃O₄ NP than these obtained from the HP/HT measurements at all different temperatures (25°C, 40°C and 60°C). This difference can be possibly attributed to either the effect of pressure (69 bar) or to the measurement apparatus itself. However, taking into consideration that the pressure has minimal impact on the
rheological behavior of a fluid (Alderman 1988), it is considered that the experimental apparatus is the main reason for such differences.

**Figure 59.** HP/HT rheological measurements at 1000 psig and different temperatures, after continuous ramping up to 120°C and one direct at 120°C for the 7 wt% water Na-bentonite suspension (BF).

**Figure 60.** HP/HT rheological measurements at 1000 psig and continuous ramping up to 120°C for the nano-enhanced drilling fluid with 0.5 wt% CM-CA Fe₃O₄ NP.
4.5 Magnetorheological measurements

Engineering a drilling fluid tailored to meet specific downhole and environmental demands with tunable rheological properties can revolutionize the drilling industry. For this reason, 7 wt% water Na-bentonite suspensions containing two concentrations of superparamagnetic CM-CA Fe₃O₄ NP (0.5 wt% and 1.0 wt%) were examined for their potential to offer in-situ rheological controllability by exploring their rheological behavior under a range of applied magnetic fields (0 to 0.7 T). The rheological behavior of the produced drilling fluids was examined at room temperature of 25°C as a function of volume fraction of NP, shear rate and magnetic field strength.

The effect of various magnetic flux densities (0.0, 0.1, 0.5 and 0.7 T) on the rheological profile of the samples containing 0.5 wt% and 1 wt% CM-CA Fe₃O₄ NP can be seen in Figure 62 and Figure 63, respectively. Both fluids exhibited a significant increase in shear stress with increasing magnetic flux density at all shear rates. This suggests that particles progressively build clusters within the fluids under increasing magnetic fields giving rise to higher shear stress values. Furthermore, the apparent viscosity increases with increasing the strength of the magnetic field and the system shows shear thinning behavior.
Table 16 presents the HB rheological parameters of the tested samples. It can be observed that all samples exhibited higher yield stress values at higher magnetic flux densities. For the sample containing 0.5 wt% CM Fe₃O₄ NP, the flow consistency index, K, showed a steady increase, while the flow behavior index, n, exhibited small variations. The sample with the highest concentration of NP (1.0 wt%) displayed large fluctuations in K and n, tending to Newtonian behavior for higher magnetic flux densities. The rheological behavior of all samples at all tested magnetic flux densities was described fairly well by HB model, with $R^2 > 0.99$ but with higher values of $SQ^2$ at different conditions compared to the non-magnetorheological tests.

Figure 62. Shear stress vs shear rate of 7 wt% water Na-bentonite suspension (BF) + 0.5wt% CM Fe₃O₄ NP, at different magnetic flux densities at 25°C.
Figure 63. Shear stress vs shear rate of 7 wt% water Na-bentonite suspension (BF) + 1.0 wt% CM Fe₃O₄ NP, at different magnetic flux densities at 25°C.

Table 16. Herschel-Bulkley (HB) Model parameters at different magnetic flux densities for samples containing 0.5 wt% and 1 wt% CM-CA Fe₃O₄ NP, at 25°C with 7wt% water Na-bentonite suspension as base fluid (BF).

<table>
<thead>
<tr>
<th>Magnetic Flux Density (T)</th>
<th>BF+0.5 wt% CM Fe₃O₄ NP</th>
<th>BF+1.0 wt% CM Fe₃O₄ NP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τHB (Pa)</td>
<td>K (Pa sⁿ)</td>
</tr>
<tr>
<td>0</td>
<td>2.16</td>
<td>0.866</td>
</tr>
<tr>
<td>0.1</td>
<td>4.27</td>
<td>1.081</td>
</tr>
<tr>
<td>0.5</td>
<td>7.86</td>
<td>1.439</td>
</tr>
<tr>
<td>0.7</td>
<td>10.51</td>
<td>1.573</td>
</tr>
</tbody>
</table>

More specifically, the sample containing 0.5 wt% CM-CA Fe₃O₄ NP, showed a yield stress of 4.27 Pa upon application of 0.1 T compared to 2.16 Pa without magnetic field, which represents an increase of 97%. Increased yield stress values were obtained at higher magnetic flux densities up to 0.7 T (the highest tested magnetic flux density), achieving a final yield stress value of 10.51 Pa (Table 17). The fluid with 1.0 wt% of CM-CA Fe₃O₄ NP showed even larger differences upon the application of magnetic field. At 0.1 T achieved a yield stress of 9.78 Pa, at 0.3 T 22.55 Pa and at 0.7 T 39.74 Pa, which represent +75%, +302% and +609% increase, respectively, compared to the yield stress obtained without application of magnetic field (Table 17).

Table 17. Change in yield stress at various magnetic fields in fluids containing 0.5 wt% and 1 wt% CM-CA Fe₃O₄ NP, with 7wt% water Na-bentonite suspension as base fluid (BF).

<table>
<thead>
<tr>
<th>Magnetic Flux Density (T)</th>
<th>BF+0.5 wt% CM Fe₃O₄ NP</th>
<th></th>
<th>BF+1.0 wt% CM Fe₃O₄ NP</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield Stress (Pa)</td>
<td>% increase</td>
<td>Yield Stress (Pa)</td>
<td>% increase</td>
</tr>
<tr>
<td>0.0</td>
<td>2.16</td>
<td>-</td>
<td>5.60</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>4.27</td>
<td>97</td>
<td>9.78</td>
<td>74.6</td>
</tr>
<tr>
<td>0.5</td>
<td>7.86</td>
<td>263</td>
<td>22.55</td>
<td>302</td>
</tr>
<tr>
<td>0.7</td>
<td>10.51</td>
<td>386</td>
<td>39.74</td>
<td>609</td>
</tr>
</tbody>
</table>
The yield stress versus the magnetic flux density at the two concentrations of NP can be seen in Figure 64. The yield stress for both fluids increases with an increase of the applied magnetic flux density. This is possibly due to the stronger pull forces between nanoparticles upon the application of a magnetic field. As the magnetic field strength increases, a greater shear stress is required to break the chain-like structures and initiate the flow. This occurs due to the strong chain-like structures between CM-CA Fe₃O₄ NP that have been formed at high magnetic field strengths (inset in Figure 64). The interparticle interactions are an important aspect of magnetic fluids that cause the evolution of complex microstructures, which in turn affect the rheological profile of magnetic suspensions. Therefore, in addition to the arrangement of Fe₃O₄ NP in chain-like structures, there is certainly an attractive interaction between the bentonite platelets and iron oxide nanoparticles that allows the development of a continuous microstructural network and this is intended to be addressed in a future work.

It is interesting to notice also the different trends that are followed by the two samples. The sample containing 0.5 wt% CM-CA Fe₃O₄ NP showed a linear increase in the yield stress with respect to increased magnetic flux densities. The sample with higher concentration of NP (1.0 wt%) exhibited a linear increase up to 0.3 T and then increased sharply at higher magnetic flux densities, which can be described very well by an exponential fitting, as can be seen in Figure 64. This can be plausibly attributed to the fact that higher concentrations of magnetic nanoparticles have the ability to retain higher yield stress values under the presence of larger magnetic flux densities.

![Figure 64. Yield stress vs magnetic flux density for fluids containing 0.5 wt% and 1.0 wt% CM Fe₃O₄ NP with 7 wt% water Na-bentonite suspension as base fluid (BF). Inset: The formation of chains by magnetic particles upon the application of a magnetic field (Lo, 2011).]
The ability of magnetic nanofluids to recover their original state after the application of a magnetic field is a significant advantage of such fluids. However, a critical point is to examine if they can fully recover after the application of a magnetic field and if the other additives present in the fluid (bentonite) affect this response. Figure 65 and Figure 66 present the rheograms for the two tested samples before and after the application of magnetic flux densities up to 0.7 T. The sample containing 0.5 wt% CM-CA Fe₃O₄ NP showed almost a full recovery of its initial rheological properties with shear stress values increased by +5% on average at all shear rates compared to them obtained before the application of the magnetic field (Figure 65). The sample with 1.0 wt% CM-CA Fe₃O₄ NP exhibited a larger deviation of 15% on average at all shear rates (Figure 66). This suggests possibly that higher concentrations of NP can have a large impact on the reversibility of rheological behavior of magnetic nanofluids, and their interactions with the bentonite platelets that induce higher shear stress values by forming progressive microstructural networks cannot return to their initial state upon the removal of the magnetic field.

Figure 65. Shear stress vs shear rate before and after the application of magnetic field for the fluid containing 0.5 wt% CM-CA Fe₃O₄ NP.
Figure 66. Shear stress vs shear rate before and after the application of magnetic field for the fluid containing 1.0 wt% CM-CA Fe₃O₄ NP.

Both tested samples showed a spectacular increase in yield stress values upon the application of 0.7T with increase up to +386% and +609% for the 0.5 wt% and 1 wt% NP, respectively, while showed the ability to recover their original state upon removal of the magnetic field. Their unique ability to withstand a rapid increase in the viscosity and yield stress in the presence of an external magnetic field could enable drillers to formulate drilling fluid systems with instantaneous responses to continuously changing drilling environment, leading to enhanced well control and contributing to decreased non-productive time and costs. However, these are preliminary results and thus, further tests should be performed in order to take full advantage of such fluids and use them in the field.

4.6 HR-TEM analysis

Bentonite suspensions aggregate and flocculate at higher temperatures, mainly through FF associations (Mohtadi and Rao, 1973), causing significant changes in their rheological behavior. However, the microstructures which develop in systems containing both bentonite particles and nanoparticles are more complicated. These complex microstructures, which probably impact the flow behavior of such suspensions, were examined using HR-TEM images. Parameters such as surface charges possessed by the different nanoparticles and the effect of coating of nanoparticles were taken into consideration. In order to capture as accurately as possible the evolved microstructures at the different tested temperatures, an
effective drying process was adopted using freeze-granulation and freeze-drying (FG-FD) techniques, as described earlier.

Figure 67 presents the TEM images taken from the different suspensions at 25°C and 60°C after drying by FG-FD. Bent SPN forms tactoids even at 25°C, which consist of approximately 15 platelets (Figure 67a). This phenomenon is more pronounced at 60°C (Figure 67b), where larger stacks of approximately 40-50 platelets are formed, which are associated through FF associations.

Figures 67c and 67d, show the TEM images of the water bentonite suspensions containing commercial Fe₃O₄ NP (Bent SPN with C-NP), at 25° and 60°C, respectively, after FG-FD. At 25°C (Figure 67c), one can observe the tendency of the C Fe₃O₄ NP to attach to the edges of the clay platelets, while forming small aggregates. This behavior can be attributed to the fact that the isoelectric point (IEP) of the commercial Fe₃O₄ nanoparticles is at pH 6.5-7.0 (Mandel et al. 2015), which is close to the pH of the tested suspensions (8.0-8.2). Therefore their zeta potential (surface charge), although typically negative, has a relatively small value of the order of -10mV at pH=8 (Mandel et al. 2015), and could even change sign when the local conditions are appropriate, which could possibly explain their tendency to attach to the negative edges of the clay platelets. The aggregates formed by the C Fe₃O₄ NP are becoming more significant at 60°C. TEM images (Figure 67d) show that the C-NP are spread throughout the surface of the platelets, are detached from the edges of the clay platelets and form large clusters of clay/C Fe₃O₄ NP agglomerates, forming a voluminous network. This could be due to the strong magnetic forces that dominate the relatively weak clay-nanoparticle electrostatic forces. Generally, the aggregation occurs when attracting forces outweigh repulsive forces between the particles. In the case of both coated or uncoated Fe₃O₄ nanoparticles, magnetic forces between particles contribute to attractive forces, and the forces increase with particleaggregate radius to the sixth power (Phenrat et al. 2007), thereby leading to increased aggregation of nanoparticles. These aggregates act in conjunction with the existing bentonite particles rigid network at 60°C and this could be the reason for the significant increase of the rheological parameters at 60°C compared to the ones at 25°C, as was presented earlier.

Figures 67e and 67f, present the TEM images from the water-bentonite suspension containing citric-acid coated Fe₃O₄ NP (Bent SPN with CM-CA Fe₃O₄ NP), after FG-FD. The images at both temperatures are similar and it is evident that the CM-CA NP form aggregates at length scales up to about 120 nm, which are surrounded by the clay platelets. The clay platelets are mainly associated through FF contacts leading to thicker particles, while at the same time several fully dispersed clay platelets can be observed. Unlike the C Fe₃O₄ NP, the
IEP of citric acid coated Fe$_3$O$_4$ nanoparticles is close to pH=2 (de Sousa et al. 2013), significantly lower than pH=8.0-8.2 of the tested suspensions. Furthermore, the zeta potential of the CM-CA Fe$_3$O$_4$ NP suspensions is strongly negative, around $-36$ mV, for the entire range of pH 4-11 (de Sousa et al. 2013), therefore, they possess high negative surface charges. CM-CA Fe$_3$O$_4$ NP do not show an attaching preference to the bentonite platelet edges, instead they arrange to the face of clay platelets, showing distinct clustering between islands of clay platelets. This could be attributed to their tendency to aggregate (both at 25°C and 60°C) which is due to the strong attractive magnetic forces between them. These mixed particle flocs bridge between the clay platelets, form many interparticle bridges which lead to a significant increase of yield stress of such suspensions compared to pure bentonite suspensions.

By contrast, water-bentonite suspensions containing C SiO$_2$ NP (Bent SPN with C SiO$_2$ NP) (Figures 67g and 67h), show a completely different behavior. SiO$_2$ NP are finely dispersed on the face of the clay platelets with more evidence of isolated particles and smaller aggregates both at 25°C and 60°C. This can be attributed to the absence of strong attractive magnetic forces in these suspensions. The IEP of uncoated SiO$_2$ nanoparticles is close to pH=2.5 and, at pH=8, they possess strong negative zeta potential values, of the order of -40mV (Kim et al. 2014). It can be also observed that there is less tendency for clay particles to form stacks in such suspensions, which promotes a much looser structure than the Bent SPN (7 wt% bentonite), thus leading to decreased rheological values. Elochukwu et al. (2017) stated that due to the domination of strong electrostatic repulsive forces between negatively charged bentonite particles and SiO$_2$ nanoparticles, weaker gels are formed compared to pure bentonite suspensions, which in turn decrease the rheological properties of the mixed suspension.

For more HR-TEM images please see Appendix A.
Figure 67. TEM picture of (a) Bent SPN (7 wt% bentonite suspension) at 25°C, (b) Bent SPN at 60°C, (c) Bent SPN with C Fe\textsubscript{3}O\textsubscript{4} NP at 25°C, (d) Bent SPN with C Fe\textsubscript{3}O\textsubscript{4} NP at 60°C, (e) Bent SPN with CM-CA Fe\textsubscript{3}O\textsubscript{4} NP at 25°C, (f) Bent SPN with CM-CA Fe\textsubscript{3}O\textsubscript{4} NP at 60°C, (g) Bent SPN with C SiO\textsubscript{2} NP at 25°C, (h) Bent SPN with C SiO\textsubscript{2} NP at 60°C.
The coating appears to significantly minimize the aggregation of Fe$_3$O$_4$ NP, which in turn affect the rheological behavior of such suspensions. Citric acid coated (CM-CA) Fe$_3$O$_4$ nanoparticles have a lower tendency to aggregate compared to their uncoated counterparts. The effect of coating can be clearly seen in Figure 68, which presents a TEM picture from the Bent SPN containing 0.5 wt% custom-made bare (CM-B) Fe$_3$O$_4$ NP (Figure 68a) and from the Bent SPN containing 0.5 wt% custom-made citric acid coated (CM-CA) Fe$_3$O$_4$ NP (Figure 68b) at 25°C. It is evident that the CM-B NP form huge aggregates, which is attributed to the strong magnetic attractive forces between the NP, which is pronounced in the absence of the coating giving rise to increased yield stress values compared to the sample containing CM-CA Fe$_3$O$_4$ NP. Even with the large electrostatic energy barrier provided by the citric acid, agglomeration is unavoidable due to the strong magnetic attractive forces between NP, which are able to suppress the electrostatic repulsions. This has been also reported from Phenrat et al. (2009) for Poly(styrene sulfonate) modified reactive nanoscale iron particles, and was suggested that the surface coating did not significantly affect the magnetic properties of the nanoparticles.

![TEM picture](image_url)

**Figure 68.** TEM picture of: (a) Bent SPN with custom-made bare magnetite nanoparticles (CM-B Fe$_3$O$_4$ NP) at 25°C (scale bar at 50nm) and (b) Bent SPN with citric acid coated magnetite nanoparticles (CM-CA Fe$_3$O$_4$ NP) at 25°C (scale bar at 20nm).

From all the above analysis based on HR-TEM images, Figure 69 presents schematically what it may happen in terms of the various interactions in water bentonite suspensions containing different nanoparticles between clay particles and different nanoparticles used in this study at 25°C and 60°C, which directly impacts their flow behavior.
Figure 69. Proposed model of the interactions evolving in a) water Na⁺-bentonite suspensions b) water-bentonite suspension with addition of C Fe₃O₄ NP c) water-bentonite suspension with addition of CM-CA Fe₃O₄ NP and d) water-bentonite suspension with addition of C SiO₂ NP at 25°C and 60°C in alkaline pH.

The proposed model (Figure 69) based on the observations from the HR-TEM images shows that bentonite platelets in aqueous suspensions partly exfoliate and aggregate at higher temperatures, mainly through FF associations. The presence of different nanoparticles affects in different ways the produced microstructures. More specifically, addition of commercial Fe₃O₄ NP promotes the creation of a voluminous network through the creation of large clusters of clay/C Fe₃O₄ NP agglomerates giving rise to increased rheological values. The C Fe₃O₄ NP attach to the edges of the clay platelets at 25°C, while tend to spread at the face of clay platelets at 60°C by forming of large aggregates. The CM-CA Fe₃O₄ NP tend to arrange to the face of clay platelets by forming large aggregates (both at 25°C and 60°C). Their tendency to aggregate is due to the strong attractive magnetic forces acting between them. These mixed particle flocs bridge between the clay platelets, form many interparticle bridges which lead to a significant
increase of yield stress of such suspensions compared to pure aqueous bentonite suspensions. On the other hand, SiO$_2$ NP are finely dispersed on the face of the clay platelets with more evidence of isolated particles and smaller aggregates both at 25°C and 60°C, while there is less tendency for clay particles to form stacks in such suspensions, which promotes a much looser structure than the base fluid (7 wt% bentonite), thus leading to decreased rheological values. This was attributed to the domination of strong electrostatic repulsive forces in such suspensions leading to weaker structures.

From the above observations, it can be deduced that for like charged clay-nanoparticle binary mixtures, like the ones in this study, the situation is complicated; in some cases (e.g. addition of C, CM-CA and CM-B Fe$_3$O$_4$ NP) the microstructures result in a strengthened clay gel, where the electrostatic repulsions between particles are suppressed and face–face aggregation is promoted, while in others the opposite occurs with weaker microstructure networks (e.g. addition of C SiO$_2$ NP). It is well known that at basic pH, the clay platelets are above the point of zero charge (PZC) for the edge sites, and the electrical double layer arising from the (negative) face charge is sufficiently extended to screen any edge effects; thus, electrostatic interactions are purely repulsive. The clay platelets therefore remain at or above the PZC of the edge sites, and their electrostatic interactions with each other and the iron or silica nanoparticles are dominated by the negative face charges. The most important factor that determines these microstructure networks in water-bentonite suspensions containing NP is the surface charge and the nature (e.g. magnetic) of the added particles as well as the use of NP coating, which in turn determines the formation of smaller or larger clay platelets or nanoparticle aggregates as it has been evidenced from HR-TEM images.

4.7 Fluid loss measurements and filter cake characterization

The filtration characteristics of drilling fluids are dictated by the amount and physical state of the colloidal materials used in the mud system. If there are adequate colloidal materials in the mud, then the fluid loss can be reduced. Furthermore, if the drilling fluid system has high particle flocculation, this may cause the formation of thicker mudcake which in turn leads to other problems such as differential sticking.

The effect on fluid loss control of drilling fluids by adding various nanoparticles at different concentrations to 7 wt% Na-bentonite suspension was determined using static LP/LT and
HP/HT filter presses. The results showed that addition of different nanoparticles affected to different extent the filtration capabilities of the water-bentonite suspension.

4.7.1 LP/LT filtration measurements

Figure 70 shows the cumulative filtrate volume after 30 min for the sample containing 0.5, 1.5 and 2.5 wt% C Fe₂O₃ compared to that of the base fluid from a standard LP/LT API filter press. The results indicate a significant improvement in the filtration capability of the drilling fluid with addition of C Fe₂O₃ NP giving a final filtrate volume of 9.8 ml at 0.5 wt%, 9.1 ml at 1.5 wt% and 8.7 ml at 2.5 wt% compared to 10.9 ml of that of the base fluid (which is <15 ml and considered as acceptable by API). This represents 10%, 16.5% and 20% reduction in the fluid loss, respectively, which can be attributed to the rubbery and more compact filter cake (as per visual observations) formed upon addition of the C Fe₂O₃ NP. It should be also noted that the fluid loss pattern can be very well described by a power law fit with an exponent (b) value of 0.4944 (Figure 70), which agrees with the theory (b=0.5). Table 18 presents the filter cake thicknesses of the filter cakes produced just after the LP/LT filtration test. It can be seen that higher concentrations of C Fe₂O₃ NP caused increased filter cake thicknesses with the highest thickness shown at 2.5 wt% of C Fe₂O₃ NP with 23.5% increase compared to that obtained for the base fluid.

Another noteworthy point is the significant decrease in the spurt loss when the C Fe₂O₃ nanoparticles are added to the drilling fluid. By definition, spurt loss is the instantaneous volume (spurt) of sample that passes through the filter medium measured at the first minute of the filtration process. Spurt loss is one of the major challenges that needs to be alleviated by drilling fluids. Spurt losses decreased by half when compared to that of the base fluid which is possibly due to the ability of the C Fe₂O₃ NP to form an instantaneous layer that prevents fluid losses stemming from their extremely small size and high surface area to volume ratio. Spurt loss was reduced by a maximum of 43% upon addition of 2.5 wt% C Fe₂O₃ nanoparticles at LP/LT conditions, giving spurt loss values of 1.2 ml and 2.1 ml for the C Fe₂O₃ NP and for the base fluid, respectively (Figure 70).
Figure 70. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of C Fe$_2$O$_3$ NP at LP/LT conditions (6.9 bar/100 psi differential pressure and 25°C).

Table 18. Filtration characteristics of base fluid and nano-enhanced drilling fluids with different concentrations of C Fe$_2$O$_3$ NP at LP/LT conditions (6.9 bar/100 psi and 25°C).

<table>
<thead>
<tr>
<th>C Fe$_2$O$_3$ NP (wt%)</th>
<th>Filter Cake Thickness (mm)</th>
<th>Change in Thickness (%)</th>
<th>Filtrate Volume (ml)</th>
<th>Change in Filtrate Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.1</td>
<td>-</td>
<td>10.9</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>5.4</td>
<td>+5.8</td>
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</tr>
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<td>-16.5</td>
</tr>
<tr>
<td>2.5</td>
<td>6.3</td>
<td>+23.5</td>
<td>8.7</td>
<td>-20.2</td>
</tr>
</tbody>
</table>

Jung et al. (2011) examined the LP/LT filtration properties of 5 wt % bentonite fluids (used as base fluid) containing different concentrations (0.5 and 5 wt %) of Fe$_2$O$_3$ NP (3 and 30 nm). They found maximum reduction in the fluid loss (-45%) achieved upon addition of 0.5 wt % 30 nm of Fe$_2$O$_3$ NP. Higher concentrations of NP (5 wt %) led to a decreased fluid loss control capacity. They suggested that near this critical concentration, the net repulsive and attractive forces were in a ratio such that the clay platelets aligned more in face-to-face (FF) than face-to-edge (FE) configurations, thus decreasing the penetrable surface area of the filter cake formation.

Barry et al. (2015) investigated the fluid loss properties of 5 wt% aqueous bentonite suspensions, containing 0.5 wt% Fe$_2$O$_3$ NP (3 and 30 nm) additives under both LP/LT (25 °C, 6.9 bar) and HP/HT (200 °C, 70 bar) conditions. The authors reported that addition of 0.5 wt
% of 3 nm and 0.5 wt % of 30 nm Fe$_2$O$_3$ NP unexpectedly increased the filtration volume at LP/LT conditions compared to the base fluid by 11.5% and 2.1%, respectively. However, at HP/HT conditions the samples containing 0.5 wt % 3 and 30 nm Fe$_2$O$_3$ NP reduced the fluid loss compared to the base fluid by 27.6% and 23.4%, respectively. The authors suggested that at HP/HT conditions the Fe$_2$O$_3$ NP replaced dissociated Na$^+$ cations, deflocculating the solution which yielded a low permeability filter cake.

Figure 71 shows the cumulative filtrate volume after 30 min for the sample containing 0.5, 1.5 and 2.5 wt% C Fe$_3$O$_4$ compared to that of the base fluid at LP/LT conditions. Addition of C Fe$_3$O$_4$ NP decreased significantly the fluid loss by 20.2%, 21.1% and 18.4% compared to the base fluid, at 0.5, 1.5 and 2.5 wt% nanoparticle concentration, respectively (Table 19). The superior filtration characteristics can be attributed to the ability of NP to form a rigid and compact filter cake. Table 19 presents the filter cake thicknesses of the filter cakes produced just after the LP/LT filtration test. As it was observed for the C Fe$_2$O$_3$ NP, higher concentrations of NP caused increased filter cake thicknesses with the highest thickness at 2.5 wt% of C Fe$_3$O$_4$ NP with 27.5% increase compared to that obtained for the base fluid. Furthermore, the spurt loss was reduced by a maximum percentage of 47.6% upon addition of 1.5 wt% C Fe$_3$O$_4$ NP.

![Figure 71. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of C Fe$_3$O$_4$ NP at LP/LT conditions (6.9 bar/100 psi differential pressure and 25°C).](image-url)
Table 19. Filtration characteristics of base fluid and nano-enhanced drilling fluids with different concentrations of C Fe$_3$O$_4$ NP at LP/LT conditions (6.9 bar/100 psi and 25°C).

<table>
<thead>
<tr>
<th>C Fe$_3$O$_4$ NP (wt%)</th>
<th>Filter Cake Thickness (mm)</th>
<th>Change in Thickness (%)</th>
<th>Filtrate Volume (ml)</th>
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<tr>
<td>2.5</td>
<td>6.5</td>
<td>+27.5</td>
<td>8.9</td>
<td>-18.4</td>
</tr>
</tbody>
</table>

Figure 72 presents the cumulative filtrate volume after 30 min for the sample containing 0.5, 1.5 and 2.5 wt% C SiO$_2$ NP compared to that of the base fluid at LP/LT conditions. In contrast with the samples containing iron oxide nanoparticles, addition of nanosilica caused a significant increase in the filtration volume with the largest occurring upon addition of 2.5 wt% SiO$_2$ NP (57.8% increase compared to that of the base fluid). Addition of 0.5% and 1.5% wt% of nanosilica resulted in an increase by 54.1% and 46.8%, respectively (Table 20).

Figure 72. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of C SiO$_2$ NP at LP/LT conditions (6.9 bar/100 psi differential pressure and 25°C).
Table 20. Filtration characteristics of base fluid and nano-enhanced drilling fluids with different concentrations of C SiO$_2$ NP at LP/LT conditions (6.9 bar/100 psi and 25°C).

<table>
<thead>
<tr>
<th>C Fe$_3$O$_4$ NP (wt%)</th>
<th>Filter Cake Thickness (mm)</th>
<th>Change in Thickness (%)</th>
<th>Filtrate Volume (ml)</th>
<th>Change in Filtrate Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.9</td>
<td>-</td>
<td>10.9</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
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<td>16.8</td>
<td>+54.1</td>
</tr>
<tr>
<td>1.5</td>
<td>6.9</td>
<td>+17.0</td>
<td>16.0</td>
<td>+46.8</td>
</tr>
<tr>
<td>2.5</td>
<td>7.9</td>
<td>+33.9</td>
<td>17.2</td>
<td>+57.8</td>
</tr>
</tbody>
</table>

4.7.2 HP/HT filtration measurements

The base fluid as well as the nano-enhanced drilling fluids containing different concentrations (up to 2.5 wt%) of C Fe$_3$O$_4$, CM-B Fe$_3$O$_4$, CM-CA Fe$_3$O$_4$ and C SiO$_2$ nanoparticles were further tested in a static HP/HT filter press (20.7 bar/300 psi differential pressure and 121°C). Figures 73, 74, 75 and 76 present the cumulative filtrate volume after 30 min for the base fluid as well as for the samples containing 0.5, 1.5 and 2.5 wt% C Fe$_3$O$_4$, CM-B Fe$_3$O$_4$, CM-CA Fe$_3$O$_4$ and C SiO$_2$ NP, respectively, compared to that of the base fluid at HP/HT conditions. One can easily observe that addition of all different types of Fe$_3$O$_4$ NP at 0.5 wt% gave maximum fluid loss reduction compared to that of the base fluid. Higher concentrations gave higher fluid loss values compared to these obtained at 0.5 wt%. However, this is not the case for the SiO$_2$ NP as addition of these NP gave higher fluid loss values compared to the base fluid in a similar fashion to LP/LT filtration measurements.

Figure 77 presents a comparative diagram for the samples containing 0.5 wt%, 1.5 wt% and 2.5 wt% CM-CA Fe$_3$O$_4$ NP compared to that of the base fluid. It can be clearly seen from Figure 77 that maximum fluid loss reduction was achieved at 0.5 wt% of CM-CA Fe$_3$O$_4$ NP of the three concentrations tested, while higher concentrations gave higher fluid loss values. Having determined that the optimal concentration of NP is 0.5 wt%, Figure 78 presents a comparative diagram for the samples containing only 0.5 wt% of the different nanoparticles compared to that of the base fluid along with the measured filter cake thicknesses. Table 21 presents filtration and filter cake characteristics of the drilling fluids that have different nanoparticle types and concentrations at 20.7 bar/300 psi differential pressure and 121°C, while Figure 79 shows pictures of the filter cakes formed from HP/HT filtration for the base fluid as well as for the nano-enhanced drilling fluids containing 0.5 wt% C and CM-CA Fe$_3$O$_4$ NP.
The maximum reduction in fluid loss (~40%) was achieved upon addition of 0.5 wt% CM-CA Fe$_3$O$_4$ NP compared to that obtained for the base fluid (Figure 77 and Table 21). Addition of 0.5 wt% C Fe$_3$O$_4$ NP led to 34.3% reduction, while addition of 0.5 wt% of CM-B decreased the fluid loss by 16%. Higher concentrations of all nanoparticles gave higher fluid loss values than these obtained at 0.5 wt%, which means that we should carefully determine their optimal concentration for optimal results. More specifically, addition of 2.5 wt% of C Fe$_3$O$_4$ NP, CM-B Fe$_3$O$_4$ NP and CM-CA Fe$_3$O$_4$ NP led to a fluid loss reduction of 11.4%, 14.3%, and 20%, respectively. On the contrary, addition of 2.5 wt% of SiO$_2$ NP increased the fluid loss by 28.6% compared to that of the base fluid. A noteworthy point here is the increase in the filter cake thickness for all different concentrations and types of nanoparticles. Higher concentrations of nanoparticles led to higher filter cake thicknesses. However, especially for the CM-CA Fe$_3$O$_4$ NP this increase in filter cake thickness is relatively small (+28.6% at 0.5 wt%) which is expected not to cause any significant problems in the drilling process (i.e. differential sticking). The smallest spurt loss was achieved from the sample containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP, with a 50% decrease compared to the spurt loss value of the base fluid.

![Graph](image)

*Figure 73. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of C Fe$_3$O$_4$ NP at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).*
Figure 74. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of CM-B Fe$_3$O$_4$ NP at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).

Figure 75. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of CM-CA Fe$_3$O$_4$ NP at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).
Figure 76. Cumulative filtrate volume versus time for base fluid and nano-enhanced drilling fluids with different concentrations of C SiO₂ NP at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).

Figure 77. Cumulative filtrate volume (30 minutes) and filter cake thickness for drilling fluids having 0.5 wt%, 1.5 wt% and 2.5 wt% of CM-CA Fe₃O₄ nanoparticles compared to the base fluid at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).
Figure 78. Cumulative filtrate volume (30 minutes) and filter cake thickness for drilling fluids having 0.5 wt% of different nanoparticles compared to the base fluid at HP/HT conditions (20.7 bar/300 psi differential pressure and 121°C).

Table 21. Filtration and filter cake characteristics of the drilling fluids that have different nanoparticle types and concentrations at 20.7 bar/300 psi differential pressure and 121°C.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Filter</th>
<th>Percentage</th>
<th>Cumulative</th>
<th>Percentage</th>
<th>Spurt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cake</td>
<td>Change In</td>
<td>Filtrate</td>
<td>Change in</td>
<td>Loss</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>Thickness</td>
<td>Volume</td>
<td>Filtrate Volume</td>
<td>Volume</td>
</tr>
<tr>
<td>C FeO₄ NP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(wt%)</td>
<td>(mm)</td>
<td>(%)</td>
<td>(ml)</td>
<td>(%)</td>
<td>(ml)</td>
</tr>
<tr>
<td>0.0</td>
<td>7.0</td>
<td>—</td>
<td>17.5</td>
<td>—</td>
<td>5.0</td>
</tr>
<tr>
<td>0.5</td>
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<td>11.5</td>
<td>-34.3</td>
<td>3.5</td>
</tr>
<tr>
<td>1.5</td>
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<td>+64.3</td>
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<td>-17.1</td>
<td>4.5</td>
</tr>
<tr>
<td>2.5</td>
<td>15.0</td>
<td>+114.3</td>
<td>15.5</td>
<td>-11.4</td>
<td>5.0</td>
</tr>
<tr>
<td>CM-B FeO₄ NP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(wt%)</td>
<td>(mm)</td>
<td>(%)</td>
<td>(ml)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
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<td>+71.4</td>
<td>14.7</td>
<td>-16.0</td>
<td>6.0</td>
</tr>
<tr>
<td>1.5</td>
<td>15.0</td>
<td>+114.3</td>
<td>15.5</td>
<td>-11.4</td>
<td>6.5</td>
</tr>
<tr>
<td>2.5</td>
<td>17.0</td>
<td>+142.3</td>
<td>15.0</td>
<td>-14.3</td>
<td>6.0</td>
</tr>
<tr>
<td>CM-CA FeO₄ NP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(wt%)</td>
<td>(mm)</td>
<td>(%)</td>
<td>(ml)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>9.0</td>
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<td>10.5</td>
<td>-40</td>
<td>2.5</td>
</tr>
<tr>
<td>1.5</td>
<td>11.0</td>
<td>+57.1</td>
<td>12.5</td>
<td>-28.6</td>
<td>3.5</td>
</tr>
<tr>
<td>2.5</td>
<td>14.0</td>
<td>+100</td>
<td>14.0</td>
<td>-20</td>
<td>4.0</td>
</tr>
<tr>
<td>C SiO₂ NP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(wt%)</td>
<td>(mm)</td>
<td>(%)</td>
<td>(ml)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>8.0</td>
<td>+14.3</td>
<td>20.5</td>
<td>+17.1</td>
<td>8.0</td>
</tr>
<tr>
<td>1.5</td>
<td>10.0</td>
<td>+42.9</td>
<td>21.5</td>
<td>+22.9</td>
<td>9.0</td>
</tr>
<tr>
<td>2.5</td>
<td>13.0</td>
<td>+85.7</td>
<td>22.5</td>
<td>+28.6</td>
<td>9.5</td>
</tr>
</tbody>
</table>
The sample containing 0.5 wt% CM-CA Fe₃O₄ NP (which gave the maximum reduction in fluid loss) was further tested for its fluid loss characteristics after dynamic thermal aging at 177°C (350°F) for 16 h (i.e. placed in a pressure cell in a rolling oven at 177°C and then tested in the HP/HT filter press as per normal procedures). Figure 80 shows its cumulative filtrate volume at HP/HT conditions before and after thermal aging along with results of the BF. Table 22 shows the filtration data together with the data of filter cake thicknesses. Addition of CM-CA Fe₃O₄ NP at 0.5 wt% results in a significant reduction of the cumulative filtrate volume compared to that of the base fluid (BF) even after thermal aging. Moreover, this reduction in the filtrate volume is greater in the case of thermally aged sample, which shows the ability of the synthesized NP (CM-CA) to withstand higher temperatures without losing their superior properties, thus leading to superior filtration control.
BF gives a cumulative filtration volume of 17.5 ml for the samples with not aging, while after aging it gives a filtrate volume of 19.3 ml. The higher filtration volume of the BF can be attributed to the fact that bentonite forms a weaker structure under HP/HT conditions leading to a less compacted and more permeable filter cake that allows more fluid to escape from the filter medium. On the other hand, the uniquely engineered nano-enhanced drilling fluid gives a filtrate volume of 10.5 ml (without aging) and a filtrate volume of 11.0 ml after aging, which represents a change of only 5% under HP/HT conditions compared to 10% of the BF. The excellent results obtained by using CM-CA Fe₃O₄ NP as drilling fluid additives can be plausibly attributed to their superior physico-chemical properties, which help to form a more rigid network with the bentonite particles.

Figure 80. 30 minute HP/HT cumulative filtrate volume of the base fluid (BF) and BF+0.5 wt% CM-CA Fe₃O₄ NP a) With no thermal aging, and b) After dynamic thermal aging at 177°C (350°F) for 16 h.
Table 22. Filtration characteristics at HP/HT conditions of 24.1 bar (300 psi) and 121°C (250°F) of base fluid (BF) and BF+0.5 wt% CM-CA Fe₃O₄ NP, a) before thermal aging and b) after thermal aging at 177°C (350°F) for 16 h.

<table>
<thead>
<tr>
<th>CM-CA Fe₃O₄ NP (wt%)</th>
<th>Filter Cake Thickness (mm)</th>
<th>Change in Thickness (%)</th>
<th>Filtrate Volume (ml)</th>
<th>Change in Filtrate Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.0</td>
<td>-</td>
<td>17.5</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>9.0</td>
<td>+22.2</td>
<td>10.5</td>
<td>-40.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CM-CA Fe₃O₄ NP (wt%)</th>
<th>Filter Cake Thickness (mm)</th>
<th>Change in Thickness (%)</th>
<th>Filtrate Volume (ml)</th>
<th>Change in Filtrate Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>6.0</td>
<td>-</td>
<td>19.3</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>-20.0</td>
<td>11.0</td>
<td>-43.0</td>
</tr>
</tbody>
</table>

The very good filtration performance of iron oxide nanoparticles at HP/HT conditions has also been reported in other studies. Mahmoud et al. (2016) carried out filtration experiments at HP/HT conditions (20.7 bar-300 psi differential pressure and 121°C-250 °F) both at static and dynamic conditions in 7 wt% Ca-bentonite suspension (used as base fluid) containing various concentrations (up to 2.5 wt%) of Fe₂O₃ and SiO₂ NP. The results showed that 0.5 wt % of Fe₂O₃ NP was the optimum NP concentration, as it has also determined in this study, giving a reduction in the filtrate volume by −42.7%, compared to that of the base fluid, with a corresponding increase in the filter cake thickness by 17.32% (Table 23). At the concentration of 0.5 wt %, a smoother filter cake morphology with less agglomeration was observed from SEM images. However, addition of SiO₂ NP adversely affected the filtration characteristics of the base fluid by increasing the fluid loss values by 13% and 57% at 0.5 wt% and 1.5 wt% of SiO₂ NP, respectively. The filter cakes were further examined with Computed-Tomography (CT) scans and SEM analysis. The authors concluded that addition of Fe₂O₃ NP to the drilling fluids improved the filter cake characteristics under both static and dynamic filtration conditions. The best filter cake characteristics were obtained at 0.3–0.5 wt % Fe₂O₃ NP. The filter cake produced after addition of Fe₂O₃ NP consisted of two layers, as indicated by the CT scan (Figure 81). The layer close to the rock surface was the main layer, in which the NP played a key role in building a good microstructure. Moreover, at high NP concentrations a new layer was formed, consisted mainly of the agglomerated NP, which adversely affected the filter cake efficiency.
Figure 81. CT scan image of the filter cakes generated by the drilling fluids that have 0.5 wt% ferric oxide (Fe$_2$O$_3$) nanoparticle under static condition at a differential pressure of 20.6 bar/300 psi and a temperature of 121°C (Mahmoud et al. 2016).

Table 23. Filtration characteristics of the drilling fluids that have different NP types and concentrations at 20.6 bar/300 psi differential pressure and 121°C (Mahmoud et al. 2016).

<table>
<thead>
<tr>
<th>Iron Oxide Nanoparticles</th>
<th>Concentration (wt %)</th>
<th>Mode</th>
<th>Filter Cake Thickness (in.)</th>
<th>Percentage Change In Thickness (%)</th>
<th>Cumulative Filtrate Volume (cm$^3$)</th>
<th>Percentage Change In Filtrate Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>Static</td>
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<td>—</td>
<td>12.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.3</td>
<td>Static</td>
<td>0.3123</td>
<td>1.25</td>
<td>10.0</td>
<td>—16.67</td>
<td>—</td>
</tr>
<tr>
<td>0.5</td>
<td>Static</td>
<td>0.3618</td>
<td>17.32</td>
<td>6.9</td>
<td>—42.50</td>
<td>—</td>
</tr>
<tr>
<td>1.5</td>
<td>Static</td>
<td>0.4330</td>
<td>40.40</td>
<td>9.0</td>
<td>—25.00</td>
<td>—</td>
</tr>
<tr>
<td>2.5</td>
<td>Static</td>
<td>0.4760</td>
<td>54.35</td>
<td>11.9</td>
<td>—0.83</td>
<td>—</td>
</tr>
</tbody>
</table>

| Silica Nanoparticles     | 0.5 Static           | 0.3462 | 12.26                       | 13.6                              | 13.33                               |                                      |
|                          | 1.5 Static           | 0.4280 | 38.78                       | 18.9                              | 57.50                               |                                      |

4.7.3 HP/HT filter cake morphology

Filter cake surface morphology for the base fluid and the sample containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP after HP/HT filtration was evaluated using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). SEM analysis allows getting better insights of surface morphologies of the produced filter cakes. The EDS micro-analysis provides information on the local elemental composition of the filter cakes.

Figures 82a and 83a show the SEM images of the filter cakes obtained for the BF and the nano-enhanced drilling fluid, respectively. Addition of 0.5 wt% CM Fe$_3$O$_4$ NP leads to the formation of different microstructure compared to the filter cake produced with BF. The surface of the filter cake obtained with the BF appears to be very smooth without significant anomalies, the surface of the nanofluid filter cake is substantially rougher. Chain-like structures of width of 0.5-1.0 μm and length of 5.0-15.0 μm are clearly obvious in the image shown in
Figure 83a. The presence of these structures increases the surface area of the filter cake and furthermore it may enhance its ability to interact more efficiently and finally to attach firmly on the surface of the filter media. The CM-CA Fe₃O₄ NP cannot be detected (Figure 83a), which indicates that the magnetite nanoparticles are not aggregated but they are finely dispersed among the bentonite plate-like particles. This is most probably the reason for their exceptionally good performance, described in the previous paragraphs. For more SEM images of the filter cakes see Appendix B.

The EDS analysis spectra of both filter cake surfaces are shown in Figures 82b and 83b. Figure 82b shows that the filter cake of the BF contains the prevailing Si and Al, and it contains also Ca, K, Na, Mg, Ti and Fe at significant concentrations. The filter cake obtained from the nano-enhanced drilling fluid (Figure 83b) has the same elemental composition, however the relative concentration of Fe is increased, due to the addition of the CM-CA Fe₃O₄ NP.

Figure 82. a) SEM image of the filter cake formed from the base fluid (BF) after HP/HT filtration test at 24.1 bar (300 psi) and 121°C (250°F) (magnification of x5000), and b) EDS elemental analysis of the surface of the filter cake produced from the BF.

Figure 83. a) SEM image of the filter cake formed from the sample containing 0.5 wt% CM-CA Fe₃O₄ NP after HP/HT filtration test at 24.1 bar (300 psi) and 121°C (250°F)
(magnification of x5000), and b) EDS elemental analysis of the surface of the filter cake produced from the same sample.

4.7.4 Formation damage potential of new drilling fluids

We tried to develop for the first time a technique to provide in depth information regarding the assessment of formation damage potential of drilling fluids. We will provide preliminary results of this approach, which was presented in SPE Conference/ADIPEC 2017 (Vryzas et al. 2017a) with details of the technique used.

The characterization of the formation damage potential of water-bentonite suspensions with and without nanoparticles (0.5 wt% CM-CA Fe₃O₄ NP) was attempted by using an integrated characterization approach which combined a modern and non-destructive analysis of the filter media (ceramic discs) and of the produced filter cakes using NMR and MRI. The NMR technique is well known in the oil and gas industry. In this study it has revealed the pore size distribution of the filter media. The MRI technique is a rather new entry in the oil and gas industry, particularly when applied to drilling operations. Of course it is widely known for its use in medical applications as well as in reservoir characterization (Ersland et al. 2010; Matenoglou et al. 2016).

Two samples were prepared and analyzed with the NMR. The fluid containing only deionized water (DW) and the nano-enhanced fluid (BF+0.5 wt% CM-CA Fe₃O₄ NP). Only the sample containing 0.5 wt% CM-CA Fe₃O₄ NP was selected to be tested in NMR as first approach. The examined filter discs were tested directly after the HP/HT filtration experiments and upon removal of the produced filter cake.

Figure 84 shows the spin-spin T₂ relaxation time, which provides the pore size distribution, of the filter medium (ceramic disc) produced from pure deionized water (blue line) and the nano-enhanced drilling fluid containing 0.5 wt% CM-CA Fe₃O₄ NP (orange line). It can be clearly seen that the nano-enhanced drilling fluid had substantially different pore size distribution than that of the deionized water. More specifically, the sample containing only deionized water shows a large peak T₂ between 440-1400ms, which is indicative that the water occupies the largest pores in the ceramic disc (larger T₂ values indicate larger pores), while the T₂ values of the nano-enhanced drilling fluid have been shifted to the left (two distinct peaks; one at 7ms and the other at 126ms) showing the ability of the nano-enhanced drilling fluids to seal effectively the filter medium. It is important to state here that more samples of different fluids should be used to have more information and such studies can be performed in the future.
MRI can provide direct visualization of the produced filter cake and filtrate penetration depth, given the appropriate methodology. MRI methodologies utilize NMR principals in order to acquire and reconstruct a 3-D image of the characterized sample. Thus they are capable of quantitative demarcation of various fluids inside the rock samples and also provide spatial information of the petrophysical properties.

Figure 84. Spin-spin $T_2$ relaxation time of the filter discs produced from deionized water (blue line) and bentonite with 0.5%wt custom-made citric acid coated magnetite nanoparticles (CM-CA Fe$_3$O$_4$ NP-orange line) at HP/HT conditions (34.5 bar/500 psi differential pressure and 49.5°C/121°F).

MRI measurements revealed the saturation profiles of the tested drilling fluids (filtrate) inside the ceramic discs, in 3-D space. This allowed the visual representation of the penetration depth of the filtrate produced in the ceramic discs of the different drilling fluids allowing the evaluation of their formation damage mitigation potential. Table 24 shows the experimental MRI parameters used for all samples.

Table 24. MRI experimental parameters.

<table>
<thead>
<tr>
<th>Slices (in each dimension)</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution (pixels x pixels)</td>
<td>256 x 256</td>
</tr>
<tr>
<td>Repetition Time (ms)</td>
<td>200</td>
</tr>
<tr>
<td>Averages</td>
<td>16</td>
</tr>
</tbody>
</table>
Three samples were prepared and analyzed with the MRI (Figure 85). The fluid containing only deionized water (DW), the base fluid (BF-7 wt% water bentonite suspension) and the nano-enhanced fluid (BF+0.5 wt% CM-CA Fe₃O₄ NP). The yellow arrows in Figure 85 show the direction of filtrate flow during the filtration experiments. In Figure 85a (f, t, s) (our reference stage) one can easily observe water, the white layers at both faces of the disc, to be still there, as only water flushed through the disc and either it left intact or flushed already the water present in the pores from the wetting preparation phase. Upon using the BF (Figure 85 f, t, s) one observes the white layer to be apparent only at the front face of the filtering medium (the ceramic disc) being also a bit more intensive color in the middle of the disc, while it disappeared from the bottom face of the disc. Further observation of the disc after using the CM-CA Fe₃O₄ NP with BF (Figure 85c) shows an even more different picture than the ones depicted in Figure 85b or in Figure 85a, with the white layer completely disappearing and only observing one white spot at the front face top corner of the disc.

It is not possible to fully explain these preliminary results and thus assess the full impact of these measurements and observations. However, one can easily observe that we have a significant differentiation of the response to MRI measurements of the disc after pressure filtration with three different fluids. Upon further development of the technique, which could incorporate also image analysis of the surfaces of the disc by using for e.g. SEM (Scanning Electron Microscopy) measurements, these responses could well be converted to more quantitative measurements of the impact of using different nanofluids on the filtration characteristics, by monitoring the effects of any potential filtrate flow through the disc and thus being able to assess the penetration depth of the filtrate onto the disc with MRI. This approach could then allow to fully assess the formation damage potential of any newly developed drilling fluid.
Figure 85. MRI images at three dimensions of the filter medium (ceramic disc) of a) deionized water (DW), b) base fluid (BF) and c) sample containing 0.5 wt% CM-CA Fe₃O₄ NP at: f) front view t) top view, and s) side view.
Chapter 6. Conclusions

This thesis investigated the effect of the addition of commercial iron oxide nanoparticles (C Fe₂O₃ and C Fe₃O₄ NP), custom-made bare (CM-B) and citric acid coated (CM-CA) magnetite nanoparticles and commercial nanosilica (C SiO₂) on the rheological and filtration behavior of aqueous Na⁺ bentonite suspensions. An attempt was made to understand their rheological properties with the evolved microstructures which happen in such suspensions. The prepared samples were examined for their rheological characteristics over a Newtonian shear-rate range from 5 to 1021 s⁻¹ and at four temperatures, 25°C, 40°C, 60°C and 70°C in Couette geometry. All samples exhibited a yield stress followed by a shear thinning behavior. Selected samples were tested for their rheological characteristics at HP/HT conditions (up to 120°C and 69 bar/1000 psig). LP/LT and static HP/HT filter presses were used to assess the fluid loss control capabilities of the drilling fluids containing different nanoparticles. This was also done on selected samples after thermal aging. Scanning Electron Microscopy (SEM) was used to analyze the morphology of the filter cake of selected samples as well as to give deep insights for their microstructure, the interfacial phenomena and the interaction between bentonite particles and the nanoparticles. The development of magnetically controllable drilling fluids containing custom-made citric acid coated (CM-CA) iron oxide (Fe₃O₄) magnetic NP, which could potentially offer in-situ control of the drilling fluid viscosity and yield stress, under the application of an external magnetic field was also investigated.

A freeze granulation - freeze drying (FG-FD) technique of bentonite suspensions containing different nanoparticles was implemented in order to capture effectively the associated microstructures at the different temperatures prior to physicochemical characterization. XRD and FTIR analysis revealed that the FG-FD drying process did not cause any structural alterations to the bentonite suspensions. Nitrogen adsorption – desorption isotherms indicated that introduction of the commercial C Fe₃O₄ NP did not alter the sorption characteristics of bentonite, but addition of CM-CA Fe₃O₄ NP induced the emergence of mesopores with diameters 1-6 nm, possibly due to the partial dissociation of the clay platelets, induced by the addition of the CM-CA nanoparticles. Commercial SiO₂-NP interacted strongly with the clay platelets, thus increasing their separation. Fourier Transform Infrared (FTIR) spectra of the bentonite samples with C Fe₃O₄ and C SiO₂ NP are just superposition of the spectra of neat bentonite and the corresponding spectra of the nanoparticles. However, new peaks appear in the FTIR spectrum of bentonite suspension containing citric acid coated Fe₃O₄.
NP (Bent SPN with CM-CA NP), located at 1434, 1598 and 1665 cm$^{-1}$. They were interpreted as denoting the partial weakening of the covalent bond between the magnetite NP and the citric acid, which led to increased particle aggregation as revealed also by the HR-TEM images. HR-TEM images revealed that the association of the nanoparticles with the bentonite platelets in different configurations plays a critical role in the rheological characteristics of aqueous bentonite suspensions. The charge and nature (e.g. magnetic, coated or not) of the added nanoparticles are also important factors in determining the magnitude of the effects observed.

The three parameter Herschel-Bulkley model provided excellent fit of the experimental data of all samples. Yield stress of the Bent SPN increased upon addition of all types of NP and at all concentrations (up to 2.5 wt%) of Fe$_3$O$_4$ NP (commercial and custom-made) at all tested temperatures, while the opposite happens when C SiO$_2$ NP were added. This rheological behavior is attributed to the flocculation of bentonite particles and to the formation of large NP aggregates due to the absence of coating for the case of bare C and CM-B Fe$_3$O$_4$ NP and smaller NP aggregates for the CM-CA Fe$_3$O$_4$ NP due to the citric acid coating, which probably induces steric stabilization. It is suggested that attractive magnetic forces between the magnetite nanoparticles suppress the electrostatic repulsions and play a key role in promoting their aggregation which in turns affects the rheological profile of such suspensions. Citric acid coating helped to reduce NP aggregation and did not affect significantly the magnetic properties of nanoparticles. Addition of C SiO$_2$ NP caused the formation of weaker structures giving decreased shear stress values over the entire shear rate range compared to the base fluid.

Elevated temperatures affected significantly the yield stress and apparent viscosity of all tested fluids containing iron oxide nanoparticles except of those containing SiO$_2$ NP. Yield stress increases linearly with temperature up to 60°C (140°F). Apparent viscosity also increased at higher temperatures over the entire shear rates used. The sample containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP exhibited flat type gel strength profile compared to the progressive type gel strength of the base fluid. Dynamic thermal aging of the fluids at 177°C (350°F) for 16 h adversely affected the rheological properties of the base fluid. On the other hand, the nano-enhanced drilling fluid containing 0.5 wt% CM-CA Fe$_3$O$_4$ NP maintained its good rheological properties. The flow consistency index ($K$) tended to decrease for higher temperatures, while the flow behavior index ($n$) increased with values tend to 1 showing Newtonian behavior. Addition of SiO$_2$ NP showed decreased rheological values compared to the base fluid, however they remained stable at the different tested temperatures indicating potential use of C SiO$_2$ NP for development of flat rheology fluids.
LP/LT filtration results indicated maximum reduction in fluid loss by 21.1% when C Fe₃O₄ NP was used at 1.5wt% as drilling fluid additives with an increase in the filter cake thickness by 13.7% compared to that of the base fluid. The filtration behavior at HP/HT conditions showed reduction in the fluid loss, when compared to that of the base fluid, for all types of Fe₃O₄ NP (C Fe₃O₄ NP, CM-B NP and CM-CA NP). 0.5 wt% was determined as the optimal concentration of nanoparticles at HP/HT conditions. C Fe₃O₄ NP at 0.5 wt% decreased the fluid loss by 34.3% and CM-CA Fe₃O₄ NP yielded even greater reduction by 40% compared to that of the base fluid. The fluid containing 0.5wt% CM-CA Fe₃O₄ NP showed even greater reduction of -43% in fluid loss after dynamic thermal aging (a very significant parameter in the drilling process) and this was the maximum reduction in fluid loss among all samples. The spurt losses decreased by 50% upon addition of CM-CA Fe₃O₄ NP, while lower reduction (40% on average at the different tested concentrations) was observed for the sample containing C Fe₃O₄ NP and for the sample containing CM-B Fe₃O₄ NP with 25% reduction on average. Filter cake thicknesses increased upon addition of NP before aging, while it decreased after thermal aging. Filter cakes formed under HP/HT conditions for the sample containing 0.5wt% CM-CA Fe₃O₄ NP were characterized as very compact and less permeable compared to the filter cakes of the base fluid, which contributed to the great fluid loss reduction. SEM images revealed the complex morphology of the filter cakes produced upon addition of CM-CA Fe₃O₄ NP, giving rise to such superior filtration characteristics and showed that the CM-CA Fe₃O₄ NP are finely dispersed among the bentonite plate-like particles. Using the CM-CA Fe₃O₄ NP increases the ability of bentonite-based fluids to control filtration losses at HP/HT conditions, and shows the ability of the nano-based fluids to build a thin and impermeable filter cake, resulting in improved and cost-effective drilling operations.

The fluids containing 0.5 wt% and 1.0 wt% CM-CA Fe₃O₄ NP were tested and evaluated for their potential to offer in-situ rheological controllability under the application of an external magnetic field (0.0 to 0.7T). All fluids exhibited a typical monotonic increase in shear stress and apparent viscosity with increasing magnetic field strength. The yield stress for all samples increased with increase of the applied magnetic field strength. This occurs possibly due to the strong chain-like structures between CM-CA Fe₃O₄ NP that may have formed at high magnetic flux densities. The sample containing 0.5 wt% CM-CA Fe₃O₄ NP exhibited a linear increase in yield stress in respect to the increased magnetic field strength, while the sample with 1.0 wt% CM-CA Fe₃O₄ NP showed a linear increase up to 0.3 T and after that a sharp increase (0.5 T and 0.7 T), which can be described very well by an exponential fitting. Both samples showed maximum yield stress values upon the application of the maximum tested magnetic flux density.
of 0.7 T with increase up to +386% and +609% for the 0.5 wt% and 1.0 wt% NP, respectively. The developed magnetic nanofluids have the ability to recover most of their original state upon removal of the magnetic field, reflecting the disintegration of particles chains because of random movements due to Brownian forces.

The ability to synthesize custom-made nanoparticles by changing their surface properties or by optimizing their terminal units in order to accomplish different functional tasks promises to substantially influence the landscape of drilling fluid industry by developing smarter drilling fluids that can aid significantly the drilling industry. Clay nanoparticle suspensions offer exciting opportunities to produce advanced materials with enhanced properties and at the same time present numerous scientific challenges. Once we fully understand their microcosmos, we can better exploit such systems for numerous applications.
Chapter 7. Contribution to Knowledge

The results of this thesis can benefit oil and gas professionals and companies giving access to the developed methodologies on fluid preparation, which led to very good repeatability of the measurements and on data analysis. The newly developed nano-based drilling fluids using custom-made nanoparticles at relatively low concentrations of NP (<1 wt%) can provide the basis and open new avenues for oil and gas companies to develop improved drilling fluids, relatively inexpensive, that can lead to less formation damage and support the drillers’ efforts to achieve the reservoirs’ highest potential by eliminating the use of aggressive and potential damaging chemicals. Furthermore, our attempts to understand the interactions between different nanoparticles and clay platelets, utilizing HR-TEM, SEM, NMR and MRI techniques, may allow better understanding of the particle-to-particle interactions that govern the properties of such suspensions as it provides a useful background for researchers to further examine and develop improved and greener drilling fluids.
Chapter 8. Suggestions for Future Research

Researchers so far have mainly focused on drilling fluids containing only one nanoparticle type while few studies have been carried out using complete drilling fluid formulations. Hence, further studies should be attempted focusing on the use of different nanoparticles in combination with commonly used polymers (for e.g., CMC or PAC). Furthermore, the quantification of side effects by using nano-based drilling fluids should be fully carried out, e.g., any issues with filter cake removal after the drilling process to allow for optimum production.

Extensive rheological analysis, especially at HP/HT conditions, should be carried out in different nano-based drilling fluids in order to assess the effectiveness of nano-enhanced drilling fluids to maintain their properties at demanding downhole conditions.

Measurement integration and methodology development for the full assessment of formation damage by any drilling fluids should be carried out as formation damage can cause well integrity problems which may lead to enormous costs. Future studies should focus on the interfacial phenomena taking place and the modes of interaction between various types of nanoparticles with different size, shape and charge and other drilling fluid particles and especially bentonite particles aided by macroscopic measurements, so that we can better understand the causes behind the good performance of nano-enhanced drilling fluids, particularly at HP/HT applications.

In-depth characterization of the produced filter cakes using sophisticated quantitative techniques such as Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI), which can assess the formation damage minimization potential of any novel drilling fluids along with comparisons against conventional experimental filtration data at HP/HT conditions needs to be developed in order to formulate nano-based drilling fluids with tailor-made properties that can minimize formation damage risks leading to costless and more efficient drilling activities.

Drilling fluids containing custom-made magnetic nanoparticles, tailored to meet specific downhole and environmental demands with tunable rheological properties that could potentially offer in-situ control of the drilling fluid viscosity and yield stress can be investigated by researchers in the future. Such fluids have the unique ability to rapidly increase the viscosity and the yield stress in the presence of an external magnetic field and thus, offer the potential for drillers to formulate and use drilling fluid systems with instantaneous responses to
continuously changing drilling environment, leading to enhanced well control and contributing to decreased non-productive time and costs.

Several works reported in this review use what we may call, 'minimal exposure testing' of the developed nanofluids, i.e., reporting only high shear rate rheological measurements (PV and YP) and not the full rheogram, as well as only LP/LT API filtration tests. The main aim to develop and incorporate appropriate nanoparticles into drilling fluid formulations is to combat the harsh conditions of high temperatures and high pressures, hence fluid loss tests should only be carried out for HP/HT conditions. Furthermore, the full rheograms should be tested, because the extreme danger with respect to pressure loss evaluation is in the annulus region where the fluids encounter low shear rates, where PV and YP have little meaning. Furthermore, the 'true' yield stress of the fluids should be determined which gives the good information regarding the cuttings carrying capacity of the drilling fluids.
Bibliography


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Appendix A

HR-TEM images

Bent SPN with CM CA \( \text{Fe}_3\text{O}_4 \) NP

Bent SPN

25°C

60°C

(a)

(b)

(c)

(d)

(e)

(f)
Figure B-1. TEM picture of (a) Bent SPN (7 wt% bentonite suspension) at 25°C, (b) Bent SPN at 60°C, (c) Bent SPN with C Fe₃O₄ NP at 25°C, (d) Bent SPN with C Fe₃O₄ NP at 60°C, (e) Bent SPN with CM-CA Fe₃O₄ NP at 25°C, (f) Bent SPN with CM-CA Fe₃O₄ NP at 60°C, (g) Bent SPN with C SiO₂ NP at 25°C, and (h) Bent SPN with C SiO₂ NP at 60°C.
Appendix B

SEM images of filter cakes

Figure C-1. SEM image of the filter cake of base fluid at 20μm.

Figure C-2. SEM image of the filter cake of base fluid at 2μm.
Figure C-3. SEM image of the filter cake of the sample containing 0.5 wt% C Fe₃O₄ NP at 50µm.

Figure C-4. SEM image of the filter cake of the sample containing 0.5 wt% C Fe₃O₄ NP at 1µm.
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<table>
<thead>
<tr>
<th>Name</th>
<th>Zisis Vryzas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>School of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece, 54124</td>
</tr>
<tr>
<td>Email</td>
<td><a href="mailto:vryzas.z@gmail.com">vryzas.z@gmail.com</a></td>
</tr>
<tr>
<td>Education</td>
<td>BSc/MSc, Environmental Engineering, Technical University of Crete, 2010</td>
</tr>
<tr>
<td></td>
<td>MSc, Petroleum Engineering, Heriot-Watt University, 2012</td>
</tr>
<tr>
<td></td>
<td>DBA, Business Administration, Paris School of Business, 2015</td>
</tr>
</tbody>
</table>