



Pickering Stabilized Drilling Fluids for deep and ultra-deep Drilling Operations

Ramy Ghosn

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Ramy Ghosn. Pickering Stabilized Drilling Fluids for deep and ultra-deep Drilling Operations. Chemical engineering. Université Paris Saclay (COMUE), 2016. English. NNT : 2016SACL022 . tel-01573468

HAL Id: tel-01573468

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NNT : 2016SACLY022

THESE DE DOCTORAT
DE
L'UNIVERSITE PARIS-SACLAY
PREPAREE A
“ECOLE NATIONALE SUPERIEURE DE TECHNIQUES AVANCEES”

ECOLE DOCTORALE N°579
Sciences Mécaniques et Energétiques, Matériaux et Géosciences

Spécialité de doctorat : Génie Des Procédés

Par

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Pickering-Stabilized Drilling Fluids for Deep and Ultra-Deep Drilling Operations

Thèse présentée et soutenue à « Palaiseau », le « 20 Décembre 2016 »

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REMERCIEMENTS

A l'issue de la rédaction de cette thèse, je suis convaincu que ce travail est loin d'être un travail solitaire. En effet, je n'aurais jamais pu le réaliser sans le soutien d'un grand nombre de personnes dont la générosité, la bonne humeur et l'intérêt manifesté à l'égard de ma recherche, m'ont permis de progresser et de l'achever.

En premier lieu, je remercie mon directeur de thèse, Monsieur Didier DALMAZZONE, pour la confiance qu'il m'a accordé dès le début de la thèse pour diriger mon travail en me donnant une grande autonomie, ainsi que pour sa patience et le temps qu'il m'a consacré surtout dans la dernière partie de la thèse.

Je remercie également mon co-directeur de thèse, Monsieur Jean-François HOCHEPIED, pour sa contribution dans les expériences, son soutien et son dynamisme personnel et professionnel.

Un grand merci pour mon encadrant, Monsieur François MIHELIC, qui a toujours été prêt à m'aider et à m'encourager, par sa perspective jeune et dynamique du monde industriel en général, et pétrolier en particulier, qui m'a permis de beaucoup m'enrichir de son expérience dans ce domaine.

Ce travail n'aurait pu être mené à bien non plus sans l'aide de toute l'équipe d'Oil Recovery Services (ORS Group), à commencer par Monsieur Zahi KATTAR, le gérant de l'entreprise. Cette PME n'a pas seulement financé ma thèse et contribué au soutien matériel, mais elle m'a aussi accueilli chaleureusement pour faire partie de son équipe à Paris. Je n'oublie pas non plus de remercier Madame Florence JOURNET pour sa patience et sa contribution indispensable dans la partie administrative de cette thèse.

J'exprime encore tous mes remerciements à l'ensemble des membres de mon jury: Monsieur Philippe BARBOUX, Madame Isabelle PEZRON et Monsieur Yves CHEVALIER.

Je remercie toute l'équipe de l'ENSTA ParisTech en général et, plus particulièrement, l'équipe de l'Unité de Chimie et Procédés (UCP) présidée par Monsieur Laurent CATOIRE qui m'ont permis de réaliser ma thèse dans leur laboratoire.

J'exprime ma gratitude à l'Association Nationale de Recherche et Technologie (ANRT) qui a contribué au financement d'une partie de cette thèse CIFRE.

Je remercie particulièrement mes ami(e)s et collègues que j'ai rencontrés par le biais de l'UCP durant ces trois ans, en commençant par Luiz-Paulo SALES SILVA, Adeline TROUVÉ, Aurélie DOS SANTOS et Amokrane BOUFARES, pour les moments inoubliables qu'on a passés ensemble, pour leur soutien, pour leur aide, pour leur humour et leur amitié qui nous réunit aujourd'hui.

Enfin, les mots les plus simples étant les plus forts, j'adresse toute mon affection à ma famille et en particulier à mes parents et à ma chère sœur. Vous m'avez donné beaucoup de votre intelligence, votre confiance, votre tendresse et votre amour qui me guident tous les jours. Merci pour m'avoir aidé à être ce que je suis aujourd'hui. Je vous aime.

Merci à la personne qui a pris mon cœur et mon esprit depuis 5 mois. La personne qui m'a supporté pendant les 5 mois les plus difficiles de la thèse. Tu m'as permis de me lever chaque matin, motivé, le cœur léger et l'esprit tranquille. Tes mots de confiance et de fierté que tu m'as répétés chaque jour sont la source de ma réussite aujourd'hui. Je t'aime pour toujours!

Une pensée en terminant ces remerciements pour mon père, qui n'a pas vu l'aboutissement de mon travail, mais je sais que tu aurais été fier de ton fils!

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Nomenclature

Symbol	Definition
EOR	Enhanced Oil Recovery
ES	Electrical Stability
HT/HP	High Temperature/High Pressure
K	Consistency Index
N	Flow Index
OBM	Oil-Based Muds
PV	Plastic Viscosity
RPM	Rotations per minute
WBM	Water-Based Muds
YP	Yield Point
γ	Shear Rate
μ	Viscosity
ρ	Density
θ	Dial Indicator
τ	Shear Stress

INTRODUCTION

This enduring situation of volatile oil prices has been seen as a decline and a challenge at the same time for the oil and gas industry. While the availability of oil fields and the associated equipment is always paramount for the oil and gas companies. It is during this slump that they own the opportunity to focus on cost-effective production solutions, which very often means bringing new-technologies and further improving processes.

Adequate understanding of the impact of drilling fluids properties and rheology, so as to selectively design fluids that could address the wide range of difficulties encountered in oilfield drilling operations, is a key portfolio that has gathered considerable attention. Nonetheless, the inherent concern on how they could be substantially modified for success becomes very critical to justifying project economics.

Oil Recovery Services (ORS) is one of the fastest growing international Oil servicing companies providing the world's leading energy companies with truly innovative systems and best quality services. Since 1993, *ORS* was shaped with high values of costumer first, integrity, trust, protection of people and the environment, etc. With a clear vision of developing and supplying quality innovative products coupled with a determined mission of being and remaining the highest value partner. *ORS* and *ENSTA ParisTech* grabbed the opportunity of the invasion of nanotechnology in numerous scientific industries (electronic circuitry, material composites, medical, cosmetics, etc ...) to invest in the future of drilling and completion fluids.

Drilling engineering increasing problems from stuck pipes, differential sticking, formation damage, fluid loss, destabilization of the fluids, hydrate formation in the pipes, acid gas invasion and so on, are all related in a way or another to the drilling fluids composition and functioning. The drilling industry is facing a paramount challenge as easily drilled reservoirs are depleted. Therefore, the tendency today is searching for new tools and technologies that can help the drilling industry to drill in hostile environments

such as deep and ultra-deep wells where temperatures and pressures are high enough to cause hysteresis to the already existing drilling systems.

Pickering emulsions or particles-stabilized emulsions were widely investigated since decades [1-2]. The fact that solid particles can act as emulsifiers/surfactants attracted wildly many industrial fields especially those of pharmaceutical and food industries [3-4]. However, the possibility of using such systems in the oil and gas industry, especially for deep and ultra-deep reservoirs, was shyly introduced via few works that have been published.

From a fluids' perspective, chemical solutions take center stage over engineering design, with a focus on either functionality, mode of introduction, or the combination of both. Thus when one considers the application of nanotechnology to the area of drilling or completion fluids, a center question must be asked: what does nanotechnology accomplish that cannot be addressed with existing chemistries?

Hence, this work presents the synthesis of a novel generation of surfactant-free drilling fluids of both types, Oil-Based-Mud (OBM) and Water-Based-Mud (WBM), based on the principle of Pickering emulsions using various types of silica nanoparticles. These systems were characterized for their potential to be used for deep and ultra-deep drilling operations where HTHP stability is required.

This thesis is composed of four main chapters:

The first chapter presents an introduction to the drilling engineering field in all its generalities and details. The drilling fluids compositions and functions are presented with the main problems that are facing the drilling world today giving an opening to the new solutions that nanotechnology can bring to the field.

The second chapter consists of the experimental methods and techniques used in this work to prepare and characterize the emulsions as well as the drilling fluids prepared

using silica nanoparticles. The stability, morphology as well as the rheology of the drilling fluids testing equipments and protocols are described in details.

The third chapter presents the results obtained of the W/O Pickering emulsions prepared using hydrophobic silica nanoparticles and their characteristics at High-temperature and High-pressure (HTHP) conditions.

Finally, **the fourth and final chapter** presents the results of the preparation of O/W emulsions using hydrophilic silica nanoparticles and their potential to be used in various drilling and completion operations especially those of Enhanced-Oil-Recovery (EOR).

At the end conclusions and perspectives summarizing the main results and potential of further works to be done on this subject are stated.

Chapter 1

Bibliographic Report

Introduction

The recent interest of nanotechnology in the oil and gas sector has garnered the attention of many drilling companies for its ability to solve many of the current exploration and production problems. With very limited handful of papers published concerning the use of nanoparticles in the upstream oil and gas sector for many reasons of confidentiality, the application of nanotechnology has given real optimistic horizons as the future of the oil and gas exploration sector.

This chapter represents a bibliographic study of the work done so far on the application of nanotechnology in the oil and gas sector. It is composed of three main sections.

The first section of this chapter presents an introduction to the upstream sector of oil and gas focusing essentially on the drilling phase and more precisely on the drilling fluids. Nonetheless, the functions and the main properties of drilling fluids are presented.

The second section shows a detailed review of emulsions. The composition of emulsions as well as the main parameters influencing their stability is presented.

The third and final section presents a wide study on Pickering emulsions and the potential of using them in the preparation of drilling fluids. Therefore, the protocols adapted for the characterization of such emulsions and the measurements of their properties as well as the works done so far to apply such new systems in the upstream sector are presented.

1.1. Introduction to Drilling Fluids: Functions, Types and Properties

1.1.a. Introduction

Since the first exploration of oil and gas, the petroleum industry has flourished as one of the greatest energy sources of all time. However, the dramatic increase of population, advanced technologies and thus the need for more energy, have forced the industries to search for revolutionary and new developed solutions. Hence, renewable, nuclear and hydro energies were invented and developed as an optimistic plan to help the world recovering their lack of energy.

Nevertheless, according to the Institute of Energy Research [IER] in the United States, the most realistic scenarios of renewable energy projects (wind, solar, geothermal ...) will only make up 15 to 20% of the total energy by 2040 (**Fig. 1.1.1**).

Thus, the role of these new energies will be to complement not to replace the petroleum industry, and our world will remain a ‘fossil-fuelled’ world for decades coming.

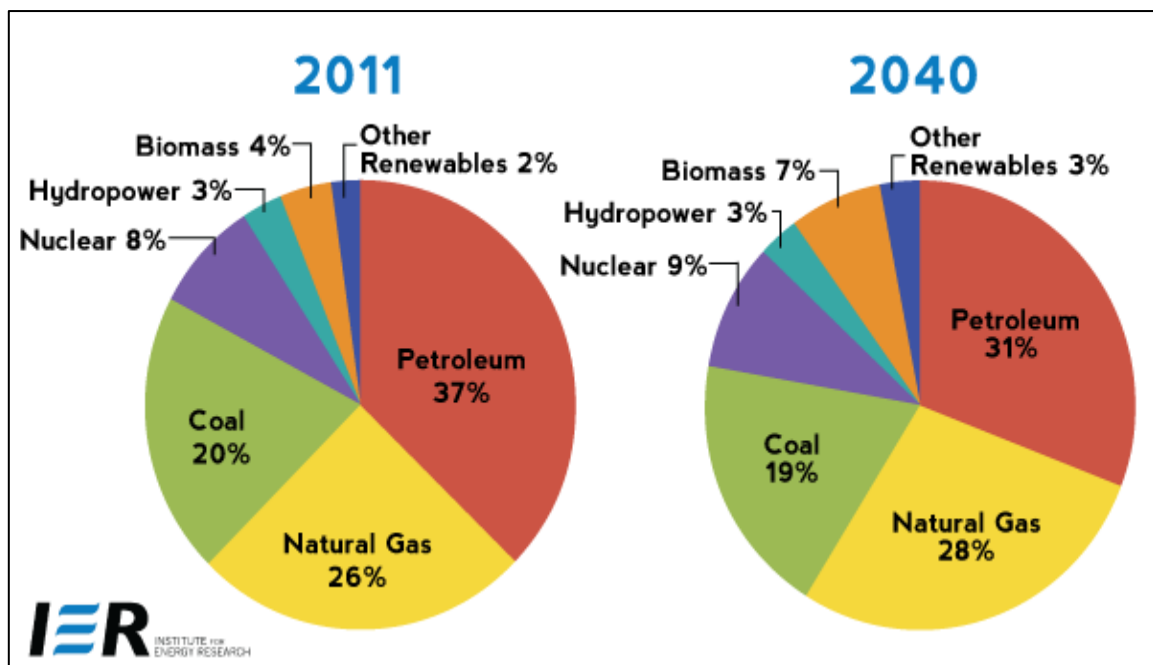


Figure 1.1.1: Various Sources of Energy Consumption Statistical Review [5]

Petroleum is known as a complex mixture of hydrocarbons of various molecular weight and other organic compounds, oxidized from underground sedimentary rocks to form layers of gas and oil followed by a layer of water buried under the earth surface (**Fig. 1.1.2.a**).

The fundamental drilling processes for Oil & Gas are still the same, but the development of technologies and engineering have helped improving performance and safety.

The extraction and production of petroleum is done through four main stages:

- *Exploration*: It consists of identifying the geological structure by applying magnetic, gravimetric or seismic methods
- *Exploitation*: It is the drilling phase, where a hole is drilled in the ground allowing oil and gas to be extracted. During this stage, a drilling mud is

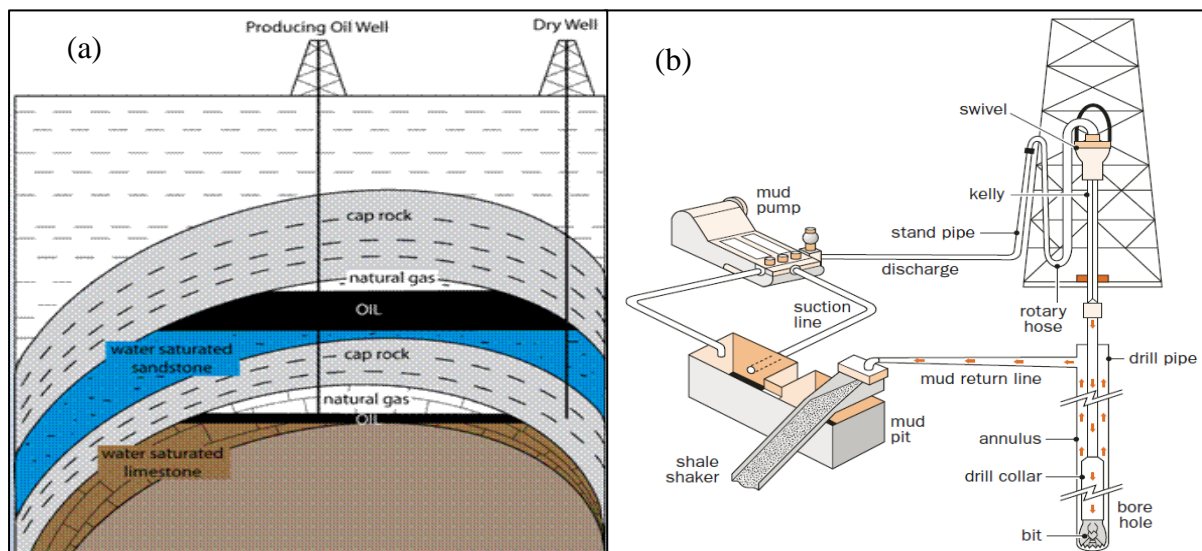


Figure 1.1.2: (a) Example of a petroleum reservoir (b) The drilling Mud Cycle

continuously circulated inside the pipes. Therefore, this phase is usually accompanied by casing and cementing to assure the stability of the formation drilled. Note that the drilling process comprises 80% of the total well costs [6].

- *Development and Production*: It is the extraction phase of oil and gas. Normally

wells are free flowing but sometimes additional aid is needed to maintain reservoir pressure and this is called Enhanced Oil Recovery.

- *Decommissioning and Rehabilitation*: It is the final stage which involves removal of the equipments and restoration of the site to environmental-sound conditions.

Petroleum reservoirs vary from shallow to deep and ultra-deep reservoirs. Nevertheless, the formations drilled can sometimes have extremely different characteristics (water sensitive shale, different rock types, different tectonic properties...). Therefore, petroleum and drilling engineers ought to find economical tools (optimized drilling bits, new chemicals, etc ...) that can be modified to go with every formation drilled for an efficient as well as economical drilling operation. Hence, one of these tools is the *drilling fluid* or what is called *drilling mud*.

As shown in **Fig. 1.1.2.b**, to drill a reservoir, the drilling fluid has to accomplish what is called a mud cycle. The best place to start with, is the mud pumps. Mud pumps represent the ‘heart’ of the mud cycle, and the drilling fluid is the lifeblood of the drilling operation. When the mud exits the pumps at high pressure (sometimes up to 5000 psi [344.7 bars]) into the discharge line, it reaches the standpipe, rotary hose, swivel and then down the kelly till it gets to the drill string and then the bit. Each drilling bit is accompanied by two or more nozzles (little openings in the bit also called jets) which accelerate the mud at the bottom hole to keep it clean while drilling. After the drill bit, the mud starts its way back to the surface through the annulus carrying all the cuttings back into the return line to the shale shakers. The shakers are mesh screens that work on separating the drilled cuttings (solid particles) from the liquid phase which drops into the mud pit. The mud pit is a mud reservoir split into two sections. The first part called a ‘settling pit’. It is a static reservoir allowing any more large cuttings present in the mud to settle before it moves to the second section of the pit, the ‘stirring pit’. In this latter, mud is treated -if needed-, as well as gas, silt and sand are removed from the mud before it goes into the suction line and back into the mud pumps.

1.1.b. Functions of Drilling Fluids

The main objective of a drilling operation is the extraction of oil and gas efficiently. To do so, drilling fluids are designed and formulated to perform many functions that are tasks, a drilling fluid should be able to perform, and they vary from a well to another.

The four main functions of a drilling mud are going to be discussed in this section:

- Removal of cuttings and suspension of solids when drilling is halted
- Controlling subsurface pressure to prevent formation damage and blowout
- Sealing permeable formations
- Lubricating and cooling the drill bit

Removal and suspension of cuttings

The drilling mud injected at the bit nozzles, exerts a jetting action to remove cuttings and debris formed by the drilling bit, and carry them up the surface allowing fresh and new rocks to be drilled. In some situations where the drilling operation should be interrupted (e.g. logging or displacement...) the mud should show a high carrying capacity of the cuttings to avoid any settling, causing differential sticking of the drill string as well as formation damage.

Many factors influence the cuttings transport and suspension ability of the mud such as: cuttings size, shape and density as well as annular velocity, density and viscosity of the mud, and borehole angle.

Controlling Subsurface Pressures

Formation stability results in equilibrium of mechanical stresses and physico-chemical interactions and pressures. However, after drilling a well, the drilling fluid must overcome the tendency of the borehole to collapse from mechanical failure and/or from chemical interaction of the formation with the mud. That is done by adjusting the mud density and mud properties (solid concentration, chemicals...). Therefore, in practice, the mud weight should be limited to the minimum necessary for well control and wellbore stability.

Sealing Permeable Formations

Most permeable formations have pore openings too small to allow the passage of the whole mud into the formation. However, while drilling, cuttings and solid particles contained in the drilling fluid will help plugging the formation pores by forming a thin, low permeable layer called *filter cake*. This layer helps sealing the formation and prevents the invasion of any more fluid.

Drilling fluids which produce low quality or thick filter cakes cause problems such as stuck pipe, difficulty in running casing and poor cement jobs. In this case, the drilling mud can be treated with bentonite, polymers and organic deflocculating additives to improve mud cake quality.

Lubricating and Cooling the Drill Bit

During drilling operations, heat and friction are generated at the bit and between the drill string and the formation due to physical interactions. This contact creates a considerable torque and drag during rotation and trips. Therefore, drilling fluids should transport this heat away from the frictional sites and lubricate the bit. Hence, reducing torque and drag, resulting in a smoother and efficient drilling operation as well as a higher Rate of Penetration (ROP).

1.1.c. Types/Classification of Drilling Fluids

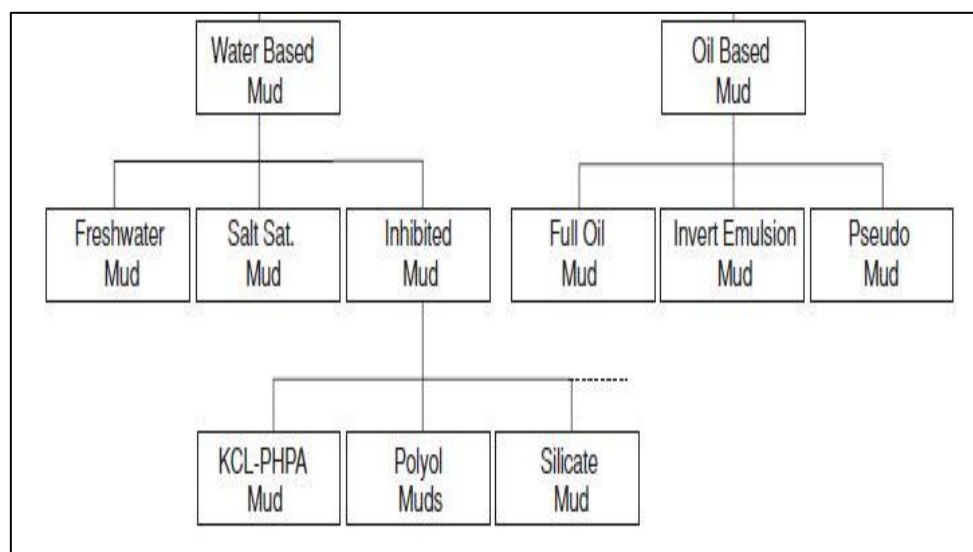


Figure 1.1.3: Classification of Drilling Fluids [7]

Reservoir formations are formed of rock layers and sands where oil and gas are trapped inside. The properties and composition of these rocks differ from one site to another.

While drilling, the mud interacts with the formation. This interaction can lead to leakage of mud into the cracks and voids (pores), resulting in formation damage, fluid loss, sticking, blowout and many other drastic problems.

Hence, each formation requires the use of an appropriate drilling fluid that suits its properties. Therefore, drilling fluids can be classified into two main categories: Oil-Based Muds (OBM) [or Synthetic-Based Mud (SBM)], Water-Based Muds (WBM)

- Oil-Based Mud (OBM) [or Synthetic-Based Mud (SBM)]

They are Water-in-Oil (W/O) emulsions where diesel, mineral oil, or low-toxicity linear olefins and paraffins can be used as a continuous phase. Brine is mostly used as the dispersed phase.

OBMs are used for High-Temperature High-Pressure (HTHP) reservoirs and their compositions are more complicated and more expensive than those of the WBMs. On the other hand, OBMs show many advantages against WBMs such as fluid loss control, no shale swelling, adequate lubrication to drill bits, good cuttings carrying ability etc.

However, contamination of formations drilled with OBMs and the incapability of WBMs to withstand severe reservoir conditions have forced the drilling industries to invent a new category of drilling fluids called Synthetic-Based Mud (SBM), offering the same drilling performance of OBMs but with more environmentally-friendly fluids using synthetic oils.

The advantages and drawbacks of OBM/SBM are summarized in the following table.

Table 1.1.1: Advantages and Drawbacks of OBM/SBM

Advantages of OBM/SBM	Drawbacks of OBM/SBM
High penetration rates	Pollution Control Required
Lubricity and temperature stability	High Cost of Lost Circulation
Reduced tendency for differential sticking	Hazardous Vapors
Shale stability and inhibition	Special Logging Tools Required
Resistance to chemical contamination	Gas Stripping
Reduce Corrosion	Aqueous Contamination

- Water-Based Mud (WBM)

They are Oil-in-Water (O/W) emulsions where the main base fluid may be fresh water, seawater, or brine. These systems incorporate natural clays in the course of the drilling operation. Bentonite is added to aid fluid-loss control and to enhance hole-cleaning effectiveness.

Non-Inhibitive, Inhibitive and Polymer muds are three different types of Water-Based fluids used in the drilling industry. The former comprises native clays or bentonite and do not significantly suppress shale swelling. On the other hand, inhibitive WBMs appreciably retard clay and shale swelling with the use of cations such as Sodium (Na^+), Calcium (Ca^{++}) and Potassium (K^+). And finally polymers are sometimes used with WBMs as rheology modifiers.

1.1.d. Rheology of Drilling Fluids

Rheology is the part of physics that deals with deformation and flow of matter subjected to different sort of shear stresses. Thus, under flow the behavior of drilling muds is governed by their flow regime which reflects the ability of a fluid to perform its basic functions.

A flow regime is a relation between the flow rate and the flow pressure. Hence, a fluid can exhibit either '*Laminar Flow*' (low flow rates) or '*Turbulent Flow*' (high flow rates).

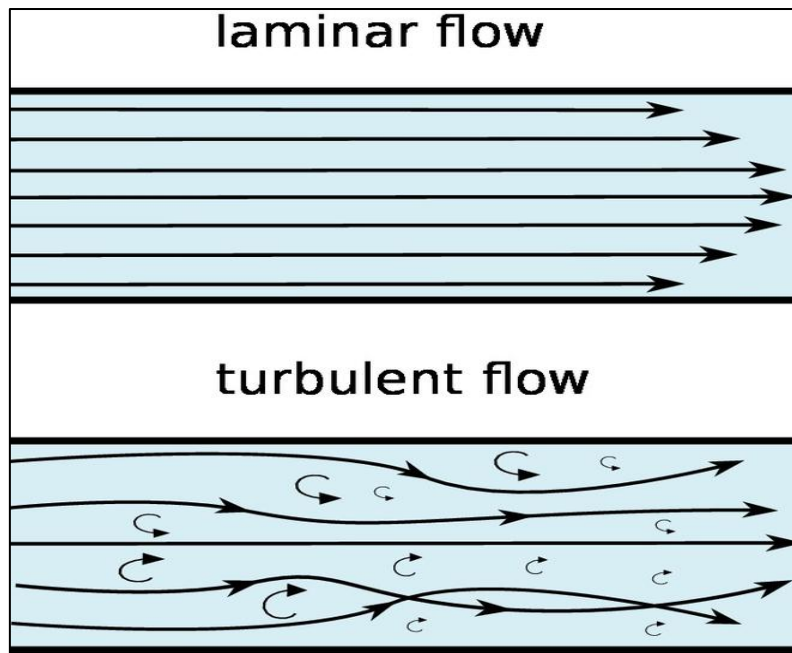


Figure 1.1.4: Sketch showing the difference between laminar and turbulent flows inside a pipe

On the other hand, flow behavior can be expressed by a relation between the shear stress (flow pressure) and the shear rate (flow rate). Hence, depending on this relation, fluids can be classified into two other categories:

- *Newtonian fluids*: for this type of fluids, the shear stress is proportional to the shear rate (under laminar flow and constant temperature). This proportionality can be graphically illustrated by a straight line passing by the origin. The slope of this line is the viscosity of the fluid.
- *Non-Newtonian fluids*: For this kind of fluids the viscosity is no longer constant but it may be shear rate or time dependent. Hence, the shear stress-shear rate relation is no longer linear.

Most -if not all- of the drilling fluids are non-Newtonian fluids, and great efforts were put to analyze and describe precisely the behavior of these fluids.

However, the effective viscosity of drilling fluids should be relatively high at low shear rates (in the drill pipe and bit nozzle) and relatively low at high shear rates (in the annulus which helps in borehole cleaning). In other words, the effective viscosity decreases when the shear rate increases. This is called '*shear thinning*' behavior and it is a very desirable characterization of drilling fluids.

Several mathematical flow models, which relate the flow behavior to flow characteristics while fluid is in a laminar flow, have been developed [7-10]. The utilization of these models coupled with shear stress-shear rate data measured by suitable instruments, allows an accurate determination of fluid behavior under different flow conditions. Thus, the evaluation of important aspects related to drilling fluid's performance, such as:

- Calculation of pressure losses
- Bit and jet nozzle hydraulics
- Relative hole cleaning efficiency
- Equivalent circulation density

There is no single rheological model which can exactly fit the shear stress-shear rate data for all fluids over a range of shear rates investigated. Hence, the models of great interest to the Drilling Fluid Engineering (DFE) are the following:

- Newton's Model

$$\tau = \mu \cdot \gamma \quad (\text{I.1.1})$$

τ	Shear Stress (Pa)
μ	Dynamic Viscosity (Pa.s)
γ	Shear Rate (s^{-1})

It is the simplest linear model where the shear stress, shear rate and the viscosity have a constant relationship leading to a linear curve as illustrated in **Fig. 1.1.5** [11].

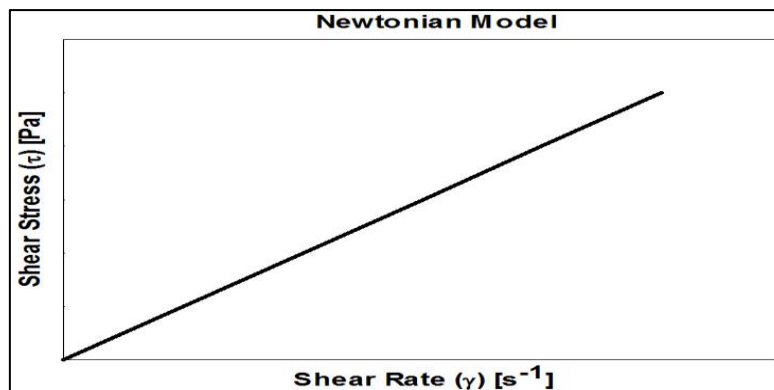


Figure 1.1.5: Shear Stress - Shear Rate plot for a Newtonian Fluid

Note that the majority of drilling fluids do not conform to this law. Hence, the Newtonian model has no value in predicting the behavior of a drilling fluid.

- Bingham Plastic Model

$$\tau = YP + PV \cdot \dot{\gamma} \quad (\text{I.1.2})$$

PV Plastic Viscosity (Pa.s)

YP Yield Point (Pa)

This model shows a dynamic yield stress that can be obtained by extrapolation to zero shear rate. The PV represents the slope of the curve; however, at and below the YP, PV tends to be infinite. As seen in **Eq. I.1.2**, the BP Model describes the shear stress/shear rate behavior of many shear thinning materials at low shear rates, although unfortunately, the value of the YP obtained depends on the shear rate ranges used for the extrapolation procedure (**Fig. 1.1.6**). The YP values obtained using this model, are always higher than the real yield stress values of the fluids.

On the other hand, it is important to know that the Plastic Viscosity is described as the portion of the viscosity that is caused by the interparticle friction and is affected by three main parameters:

- Solids concentration
- Size and shape of solids
- Viscosity of the liquid phase

Nonetheless, the Yield Point is another portion of the viscosity that is related to the electrical attractive forces. In other terms, it is the stress threshold needed to start the flow.

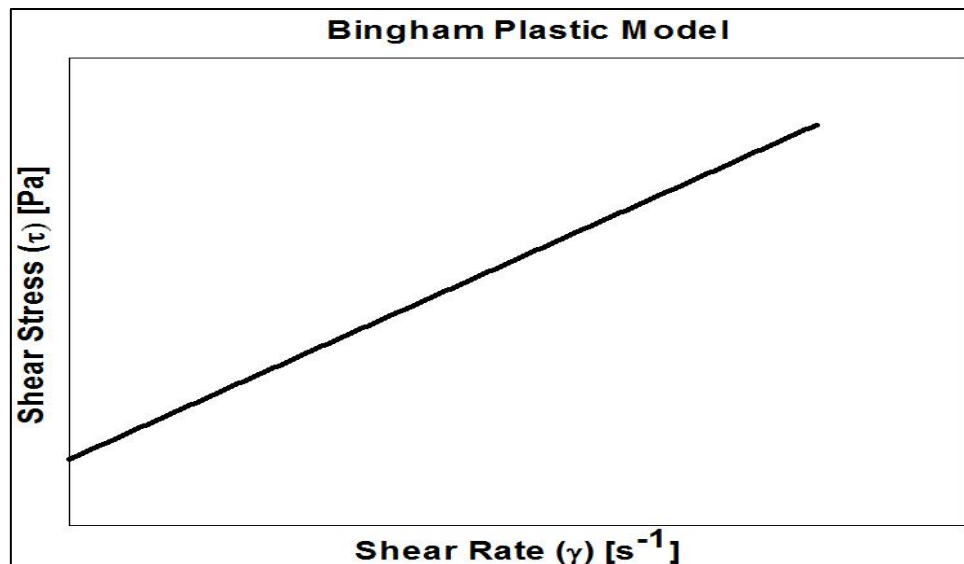


Figure 1.1.6: Flow curve for a Bingham-Plastic fluid

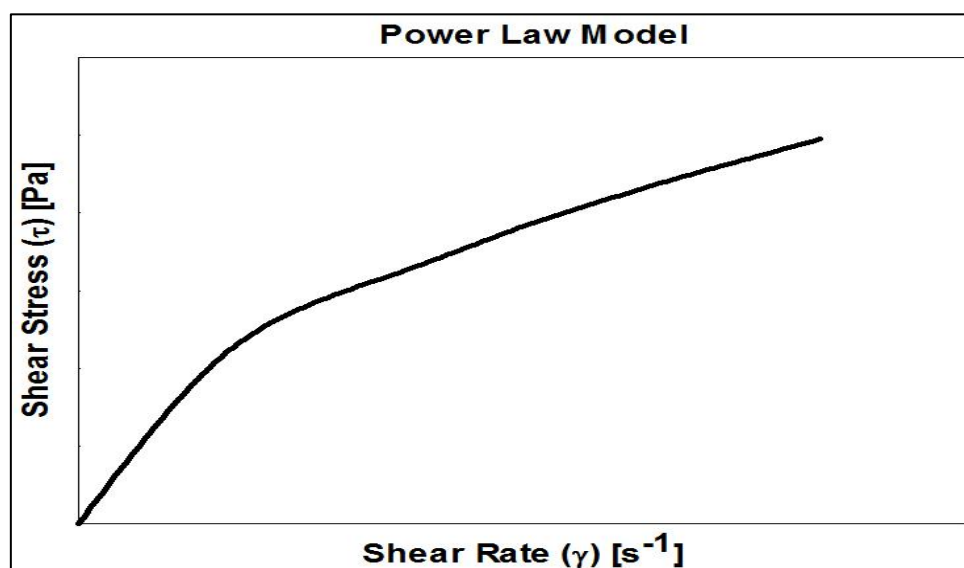
○ Power Law

Most drilling fluids exhibit a behavior that falls between the Newtonian and the Bingham-Plastic models. They are called “*pseudo-plastic*” fluids and their rheological equation can be written as:

$$\tau = K \cdot \gamma^N \quad (\text{I.1.3})$$

K Consistency Index

N Flow Index

Figure 1.1.7: Flow curve for a Power Law fluid exhibiting $N < 1$

Based on the 'N' value, the power law describes three different types of fluids:

Table 1.1.2: Correspondent fluids types depending
on the 'N' value of the Power Law

Value of N	Correspondent type of fluid
<1	Non-Newtonian fluid
=1	Newtonian fluid
>1	Dilatant fluid

In this case, the system does not show a yield value, but rather shows a limiting viscosity at low shear rates (called residual or 'zero shear' viscosity). By fitting experimental data to **Eq. I.1.3**, it is possible to obtain values of both K and N. The viscosity at a given shear rate can be calculated as:

$$\mu = \sigma/\gamma = k\gamma^N/\gamma = k\gamma^{N-1} \quad (\text{I.1.4})$$

○ Herschel-Bulkley Model (H-B Model)

The H-B model is a modified Power law model where the shear stress is presented in function of the yield point, the consistency and flow index (K, N) respectively. It is clearly seen from **Eq. I.1.5** that this model does not predict explicitly the plastic viscosity of the fluids.

The H-B Model is the most used rheological model for shear thinning fluids, and it is given as:

$$\tau = YP + K \cdot \gamma^N \quad (\text{I.1.5})$$

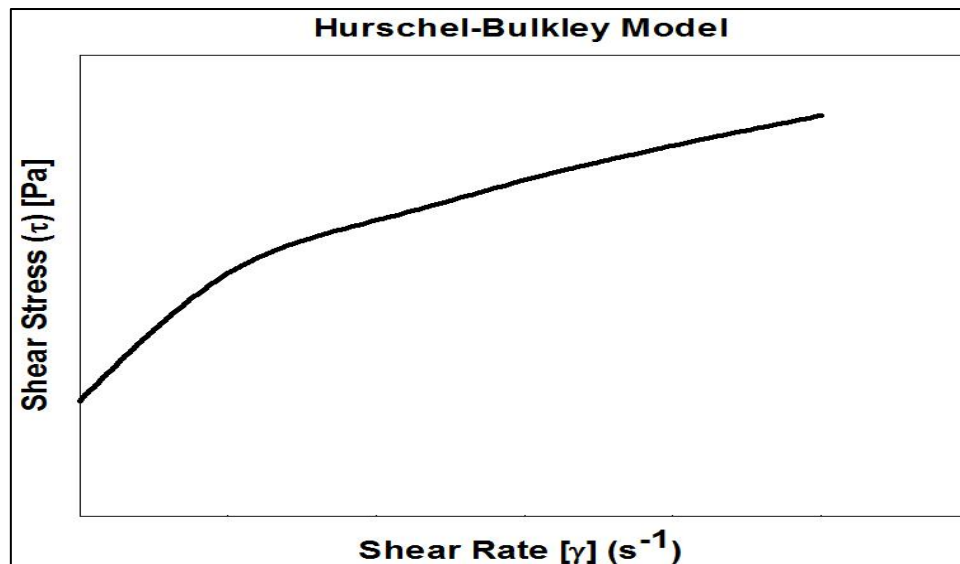


Figure 1.1.8: Herschel-Bulkley Rheological Model for $N < 1$

One should know that K tends to have the same properties as the plastic viscosity. Hence, the H-B converges to a Bingham Model for $N=1$ and to the Power Law when the $Y_P=0$. The H-B Model is widely used nowadays for its ability to describe accurately most fluids behaviors better than simple Power Law and Bingham models.

- Casson Model

It is a two-parameter model used in different industries but rarely used in the oil and gas industry. The rheological equation of this model is:

$$\tau = [Y_P^{0.5} + (PV \cdot \dot{\gamma})^{0.5}]^2 \quad (I.1.6)$$

Drilling fluids exhibits a dual behavior depending on the shear-rate range applied. At low shear-rate, the fluids should have high viscosity values allowing a better hole cleaning. However, increasing the shear rate should result in a decrease of the viscosity of the fluids giving rise to a 'shear thinning' behavior. This phenomenon results from the viscoelastic properties of the mud showing at the same time, a time-dependency property that is very essential for an efficient drilling operation.

Viscoelastic systems sheared in their linear region show time-dependency because the microstructure takes time to respond to the flow/stress. At short times (high frequencies), the structures cannot respond quickly, and an elastic response is obtained, while given time (low frequencies), the system can adjust itself continuously.

Thus, when observed over all time (and frequency) scales, the system is viscoelastic. For non-linear viscoelastic -or simply inelastic but shear-thinning systems- not only does the microstructure take time to respond to the flow, but it is also changed by the flow and this change will itself take time. This is the essential difference between linear viscoelasticity and thixotropy that while both are time effects, the former is in the linear region, where the structure responds but remains unchanged and the latter takes place in the non-linear region where the structure is broken down by deformation as well as responding to it. Shear thinning can occur for many reasons:

- Alignment of rod-like particles in the flow direction
- Loss of junctions in polymer solutions
- Rearrangement of microstructure in suspension and emulsion flow
- Breakdown of flocs

On the drilling rig, the thixotropic properties of drilling fluids are quite simply measured using a VG meter. These rheometers are simply used to estimate the plastic viscosity of fluids at specific rotational speeds (3, 6, 100, 200, 300 and 600 rpm). These rates are supposed to estimate the behavior of the drilling fluids at different stages of the drilling operation. However, the results obtained do not give a detailed description of the time-dependency of these fluids. Therefore, many new sophisticated and accurate methods were established on this purpose using the ‘Oscillatory Rheology’ technique. This technique is based on the measurement of the complex shear, loss and storage moduli over a range of strain/deformation applied at a constant frequency (or angular velocity) [12-13].

Mathematically speaking, the viscoelastic behavior of fluids can be expressed using the shear, loss and storage modulus as shown in **Eq. I.1.7**.

$$\mathbf{G} = \mathbf{G}' + i\mathbf{G}'' \quad (\text{I.1.7})$$

\mathbf{G}	Complex Shear modulus
\mathbf{G}'	Storage modulus
\mathbf{G}''	Loss modulus

The loss and storage moduli respectively characterize the solid-like and liquid-like contributions to the measured stress response. These characteristics are used to measure the strength of the microstructure existing in the fluids. These microstructures are forces resulting from the interaction of the molecules or particles in the system. If the applied forces are lower than the inter-particle forces, then G' is larger than G'' . Thus, the material shows a capacity to store energy which means that it possesses a solid-like structure and vice-versa.

Fig. 1.1.9 shows a simple amplitude-sweep [14-15] of a drilling fluid sample [16]. It is clear that for stress amplitudes smaller than 10 Pa, the loss and storage moduli are parallel with G' higher than G'' . This means that the fluid reacts more like a solid than a liquid. On the other hand, a threshold of stress amplitude exists which breaks down the structure of the fluid and make it more fluid like. This threshold is considered as the real yield stress of the fluid in oscillatory rheology.

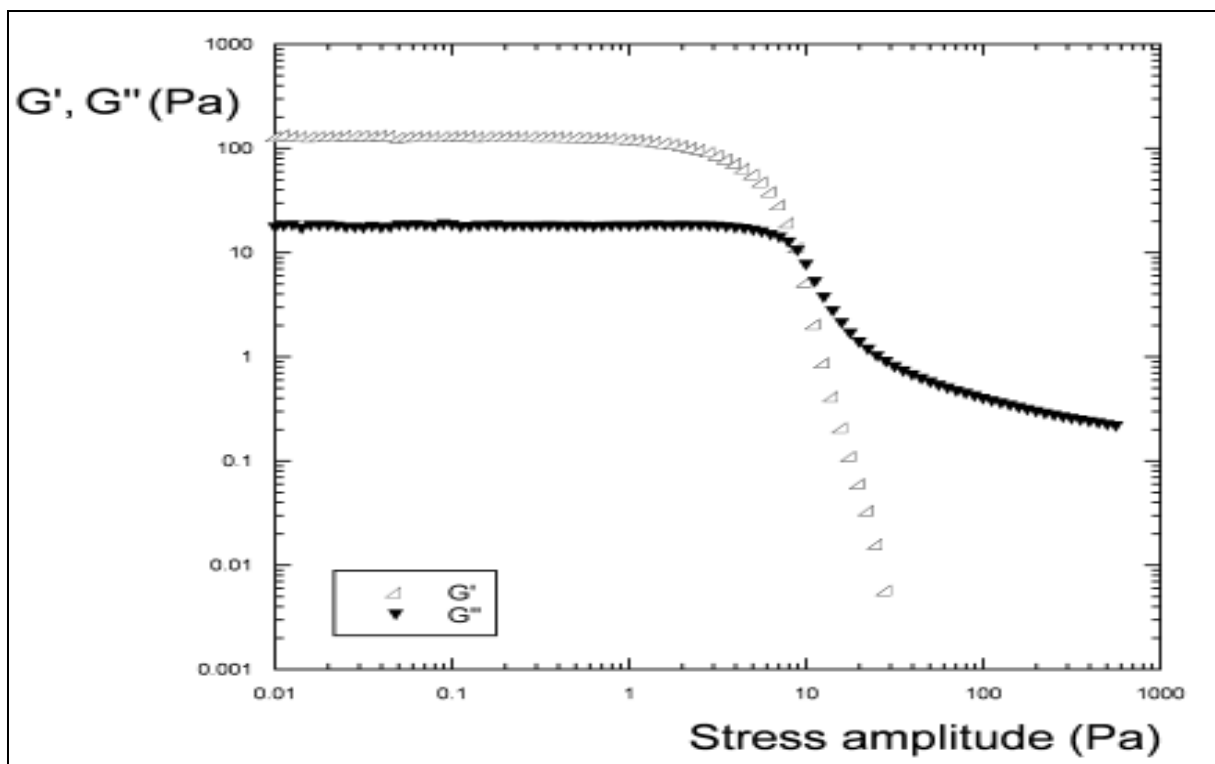


Figure 1.1.9: Amplitude Sweep of a Drilling Fluid Sample [16]

Under static conditions in relationship to time, some electrically charged molecules and clay particles aggregate to form a firm matrix. The measurements of these attractive forces are called “gel strength”. It is a very important characteristic for

drilling fluids and is related to the yield point in a way that when this latter decreases the gel strength will typically decrease.

Two types of gel strengths exist: progressive and fragile gel strengths. Where the former increases strongly with time, the latter has a slight increase and requires more time to built its gel structure [17-18].

1.2. Emulsions: Composition, Stability and Characterization

A colloidal dispersion is a two-phase system where one phase (called dispersed phase) is dispersed in the other (called continuous phase). If the continuous phase is a liquid, three main types of dispersions can be distinguished:

- Suspensions: where the colloidal particles are solid
- Foams: Where the colloidal particles are gas
- Emulsions: where the colloidal particles are liquid

When oil and water are placed together in a container, a layer of oil is formed over a layer of water (due to the density difference between both). This represents their thermodynamically most stable state. This is due to the fact that the system works on minimizing the contact area between the two phases and thus minimizing the free energy in the whole system. The layer formed between the two phases is called *interface*. The work required to change the shape of that interface is known as *interfacial tension* giving in **Eq. 1.2.1**.

$$\xi = (\partial G^\sigma / \partial A) \quad (\text{I.2.1})$$

Where ξ the interface tension, A the surface area and dG^σ is the surface free energy given by the Gibbs-Deuhem equation:

$$dG^\sigma = -S^\sigma dT + A d\xi + \sum n_i d\mu_i \quad (\text{I.2.2})$$

dG^σ is made of three main components: an entropy term $S^\sigma dT$, an interfacial energy term $A d\xi$ and a composition term $\sum n_i d\mu_i$ (n_i is the number of moles of the component i with chemical potential μ_i) [19]. Thermodynamics teaches that for phase separation to occur, the attraction between an oil molecule and a water molecule at the interface, must be less than the average of that between two oil molecules and two water molecules. Thus, the

amount of work that can be extracted, called ‘*free energy*’ (**Eq. 1.2.2**), per molecule must be higher in the interfacial area than in the bulk liquids.

Therefore, in order to form an emulsion, it is required to change the layer position between the two phases by bringing energy to the system overcoming the aforementioned free energy (i.e. agitation, homogenization). Under agitation, droplets (of oil or water) are formed. These droplets are constantly moving due to Brownian movement and/or gravity. Thus, they collide and may coalesce leading to the formation of larger droplets which, due to gravity, merge together and re-form the oil and water separate layers.

To form an emulsion two phenomena are required. At first, homogenization of the liquids leading to the formation of dispersed droplets inside a continuous phase by bringing energy to the system overcoming the total free energy. And then, maintaining the dispersed droplets from coalescence to avoid phase separation.

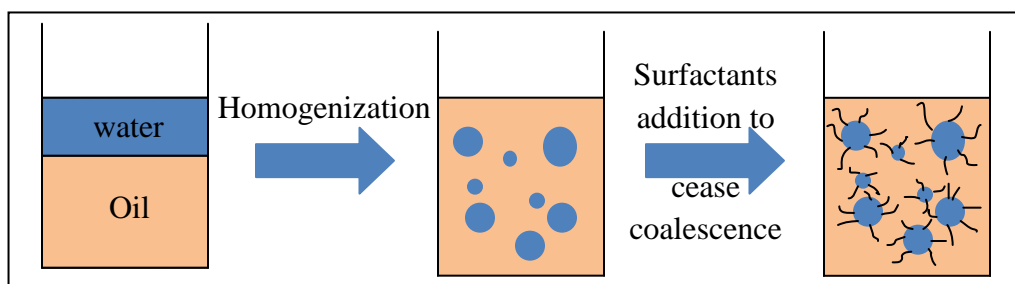


Figure I.1.10: Principle of emulsion formation and stabilization using surfactants

Homogenization or also called emulsification is the process of making an emulsion by mixing two immiscible liquids using high speed mixers. Many types of mixers are used today depending on the field of application (i.e. Hamilton Beach, IKA UltraTurrax, Ultrasonic homogenizers). During emulsification, dispersed droplets are formed. Many parameters affect the size of the droplets formed, such as:

- The flow regime: It is the movement of fluids (oil and water) during homogenization. It depends on the homogenizers used. Thus, different flow

regimes, responsible of the droplet break-up, can be distinguished: Laminar or Turbulent.

- Interfacial Tension: The interfacial forces, that keep oil droplets spherical, are characterised by the Laplace pressure (ΔP), which is the pressure difference between the inside and the outside of the droplet. It is expressed as follows:

$$\Delta P = 2\xi/r \quad (1.2.3)$$

Where ξ is the interfacial tension between oil and water and r the droplet radius. Thus, it is clear that the droplet diameter depends on the interfacial tension; droplets tend to be bigger if the interfacial tension is higher.

- Droplet coalescence: After homogenization, droplets are constantly moving and the frequency of collision is very high due to agitation. These collisions may lead to coalescence, increasing then the droplet size. Thus, the presence of emulsifiers in the system is mandatory to prevent droplets coalescence.

Emulsifiers tend to minimize the interfacial tension leading to the phase separation of the emulsion. Broadly speaking, an interface is a surface that forms the common boundary between the two phases. Note that the term surface tension is used when one of the interfaces is gaseous. The time taken by the emulsifier to adsorb at the interface is also important. Emulsifiers have two main functions:

- To decrease the oil-water interfacial tension to facilitate droplet disruption
- To form a protective skin around the dispersed droplets to prevent coalescence

Surfactants accumulate at interfaces in a process defined as ‘adsorption’ altering significantly the interfacial free energy of the interface. In aqueous media, surfactants have a characteristic molecular structure known as ‘amphiphilic’. It consists of two parts: the ‘head’ which is hydrophilic and has high affinity to water and little or no affinity to oil and the tail which is hydrophobic (has high affinity to oil and little or no affinity to water) [Fig. 1.2.1.a].

Various structures of surfactants exist depending on the nature of the head and tail groups [17]. The surfactants' solubility in aqueous media is determined by the affinity of the hydrophilic head with the media.

A surfactant dissolved in liquid can either adsorb at the interface or self-assemble to form micelles [Figs. 1.2.1.b and 1.2.1.c]. However, the micelles formation depends on the surfactants concentration. This concentration is well known as the 'critical micelle concentration' (CMC).

Fig. 1.2.2 shows clearly the effect of the surfactants concentration ('C') on the interfacial tension (' ξ '). It is seen that above the CMC concentration, no alteration of the interfacial tension occur. This is explained by the fact that surfactants molecules above the CMC must result in association to form micelles that have low activity.

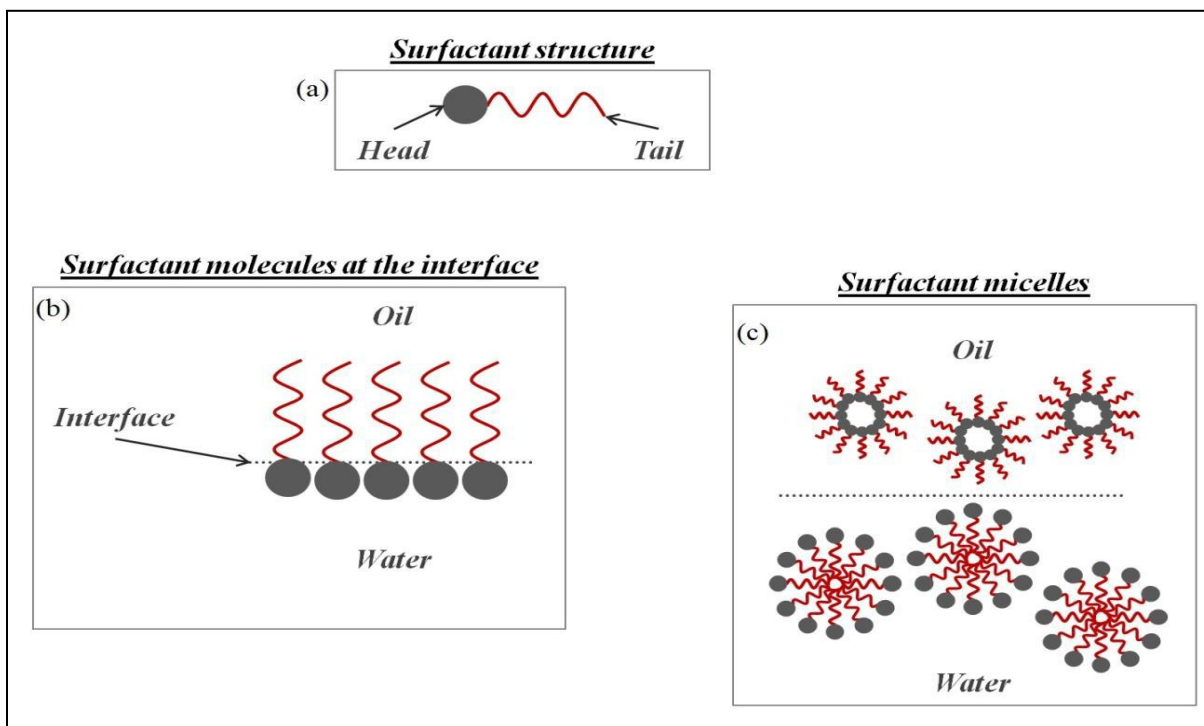


Figure 1.2.1: Schematic representation of (a) Surfactant structure
(b) Surfactant molecules at the interface, and (c) Surfactant micelles

The surfactant has two main roles to play: it lowers the interfacial tension, facilitating droplet break-up and it prevents re-coalescence. Surfactants are usually distinguished by

their Hydrophilic-Lipophilic Balance number (HLB). This can be explained by the difference in the geometry of the molecules which might exhibit longer hydrophilic chains over those hydrophobic which induces the formation of O/W emulsions and vice-versa. Thus, oil soluble surfactants tend to stabilize W/O emulsions, while water soluble surfactants tend to stabilize O/W emulsions. **Table 1.2.1** shows the classification of surfactants according to their HLB values and ability to stabilize emulsions.

Table 1.2.1: Surfactants characterization according to their HLB numbers' range

Type of emulsifiers	HLB range
W/O emulsifier	3-6
Wetting agent	7-9
O/W emulsifier	8-18+

Emulsions have invaded various domains from pharmaceutical to the food industry and even the oil and gas sector. The main issue which represents at the same time the main objective for all these industries is to understand and enhance the stability of such systems. Knowing that emulsions are thermodynamically unstable and they tend to always separate, industries have developed a lot of new strategies to enhance the kinetic stability of emulsions.

The term ‘emulsion stability’ refers to the ability of an emulsion to keep its properties unchanged over a certain period of time. However, as emulsions are thermodynamically unstable, changes of emulsion properties will occur; the more slowly the properties change, the more stable the emulsion is. Many phenomena can alter the stability of an emulsion: coalescence, flocculation, creaming, sedimentation, etc [**Fig. 1.2.2**]. Two or more of these instability phenomena may occur at the same time. Thus, it is important to understand the cause(s) of instability to select suitable components to form stable emulsions.

As aforementioned, dispersed droplets are constantly moving due to Brownian motion, gravity or mechanical agitation. Thus, they frequently collide with each other. Then, they can either move apart or aggregate. There are two main types of aggregation: Flocculation and Coalescence.

Flocculation is the aggregation of droplets that keep their physical properties. It can be reversible (weak flocculation) or irreversible (strong flocculation). On the other hand, coalescence is the aggregation of droplets that merge together (irreversible).

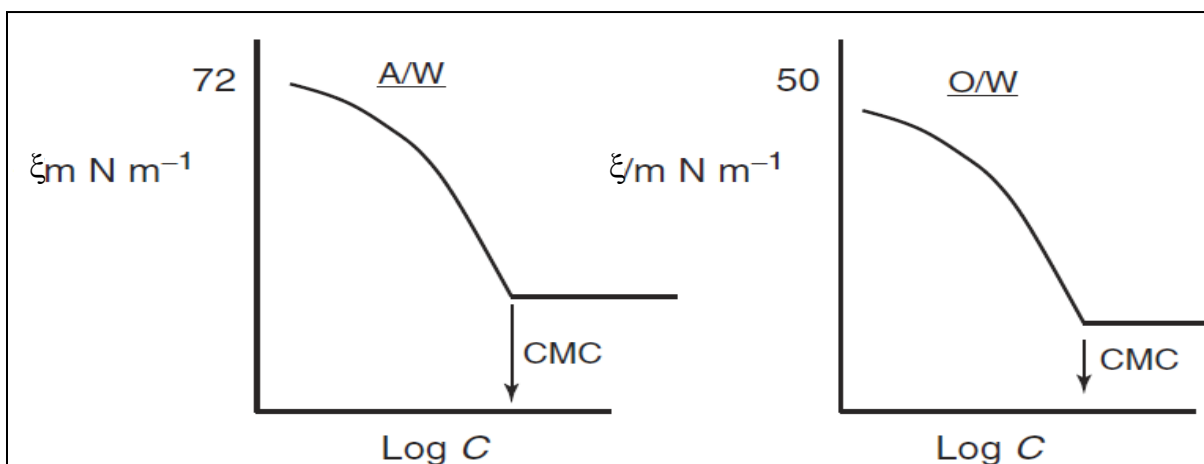


Figure 1.2.2: Interfacial Tension vs. Surfactants concentration [17]

To better understand the difference between flocculation and coalescence and their impact on the stability of emulsions one should know that every emulsion droplet is surrounded by the continuous phase in which the droplets are formed and dispersed. As droplets move closer to each other, a thin film of the continuous phase is formed between the droplets.

As long as this film exists, there is no droplets contact. Droplets aggregation occurs only when the liquid is squeezed out of the thin layer. The thin film forms a barrier between the droplets. The rupture of the film requires a certain level of energy which determines the nature of the collisions.

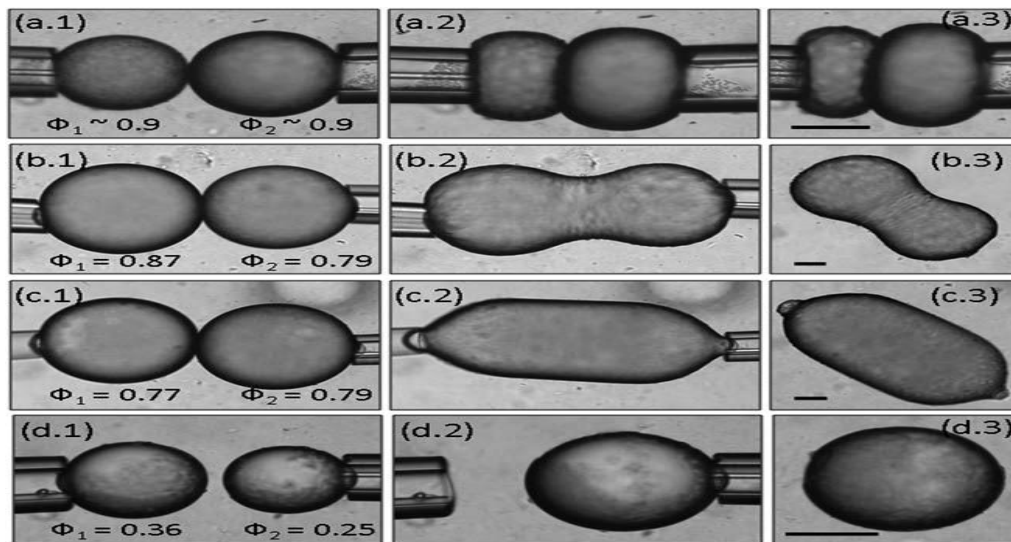


Figure 1.2.3: Coalescence phenomena of an emulsion dispersed droplets due to the thin film disruption [18]

Fig. 1.2.3 shows clearly the effect of the continuous phase thin film properties at the interface of two droplets stabilized by solid particles. At high energy barrier (rigid thin film), there is no aggregation and the droplets remain stable (**Fig 1.2.3.a**). At low energy barriers the droplets will start to show a weak coalescence (**Figs. 1.2.3.b** and **1.2.3.c**) until a complete merge of the two droplets occurs at a certain energy level (**Fig. 1.2.3.d**).

- Flocculation: Formation of flocs is a sign of emulsion instability. Flocculation has an influence on the creaming rate. Moreover, the presence of flocs increases the emulsion viscosity which in some cases is undesirable. On the other hand, creating a network between the dispersed droplets is sometimes an advantage (i.e. food emulsions). There are several methods to control flocculation. The most efficient way is to regulate the colloidal interactions between droplets (steric, electrostatic, etc.).
- Coalescence: Preventing droplet coalescence is a major issue in emulsion stabilization. A few methods have been developed to control or prevent coalescence as it depends on both the colloidal and hydrodynamic interactions between droplets, and the physico-chemical properties of the components used in the emulsion (primarily the continuous phase and the emulsifiers). Hence,

coalescence is mainly ceased by the presence of emulsifiers adsorbed at the oil-water interface. For example, the presence of charged emulsifiers at the droplet interface induces electrostatic repulsion between the droplets, which tends to prevent droplet contact. Fine divided solid particles also provide very good stability against coalescence as they form a solid layer that ceases the droplets to coalesce (Pickering Emulsions, discussed later).

- Ostwald ripening: It is the process of gradual growth of the larger droplets at the expense of smaller ones due to mass transport of soluble dispersed phase through the continuous phase. The solubility of liquids increases with decreasing the droplet radius.

All aforementioned instability phenomena can occur at the same time in an emulsion which makes it so hard for one to identify them individually. However, there are some common effects that should be recognized while studying the stability of emulsions, and there are some of them.

- Droplet size measurement: The instability phenomena of an emulsion either affect or are affected by the evolution of the droplet size with time. An emulsion is considered as stable if there is no evolution of the droplets sizes with time. In other words, if the droplets are fully covered and protected by the emulsifiers/surfactants so that they do not coalesce. Therefore, the measurement of the droplet size distribution (DSD) of an emulsion is of great importance for one to assess its stability.

Many techniques have been developed to measure droplet size distribution; the most used techniques are microscopy, light scattering, ultrasonic methods and more recently NMR [19-20].

- Creaming/sedimentation characterisation: These two phenomena are easily assessed by optical observations. As clearly seen in **Fig. 1.2.4**, in most cases, creaming is characterised by a whitish/yellowish layer on top of the emulsion, while a layer appears at the bottom if sedimentation occurs.

Creaming and sedimentation rates can be determined by a simple bottle test. It consists of measuring the volume of cream/sediment in the emulsion in function of time. This can be done easily by placing the emulsion in a calibrated beaker or tube and measuring the height of the cream/sediment with time. More sophisticated techniques are used sometimes to measure the creaming/sedimentation rate using the light scattering or ultrasonic imaging [21-25].

- Flocculation characterisation: The use of a microscope is the easiest method for one to observe the flocculation of droplets. Even though, special care should be taken not to break the flocs when preparing microscope slides. Particle sizing instruments as well as image analysis can be used to determine the size of droplets or flocs. The flocculation rate can be determined by measuring the flocs' size as function of time.
- Emulsions Conductivity: The electric conductivity of an emulsion is a very important parameter that can give a lot of information about the stability of emulsions. W/O emulsions tend to have a very low conductivity due to the insulating characteristic of the oil continuous phase. However, if the conductivity of the emulsion increases with time, this can be related to the coalescence phenomenon that is occurring inside the emulsions giving rise to larger droplets of water [26-27]. Nonetheless, conductivity measurement is a very important candidate for the assessment of the phase inversion of emulsions.



Figure 1.2.4: The main instability phenomena that can occur during emulsification

- Rheology of emulsions: Rheology is considered as a very effective tool for the measurement of emulsion stability. However, it might be complicated to assess separately the effect of each instability parameter. Tadros [28] has explained in detail how to measure the stability to creaming/sedimentation using rheological measurements. It is clear that low shear rheology is strictly related to the stability of the emulsion. At low shear rates (shear stresses), measurement of the yield stress reveals if any syneresis effects occurred (flocculation or appearance of a clear phase on top or bottom of the emulsion). Nonetheless, oscillatory rheology tests are used in some applications for the assessment of the stability of emulsions. These phenomena are going to be explained in the upcoming sections.

1.3. Pickering Emulsions in the Oil and Gas Industry

1.3.a. Introduction to Pickering Emulsions

The majority of reports describing the preparation, stability and characterization of macro-emulsions involve the use of low molar mass surfactants and surface-active polymers. Much less appreciated, are the solid particles that have attracted considerable attention recently for their ability to function as surfactants for stabilizing emulsions.

Therefore, this sub-section is dedicated for the solid particles-stabilized emulsions or Pickering emulsions: their stability, properties and characterization are going to be discussed in details. Nevertheless, the impact of such new technologies and the possibility of applying them in the oil field are going to be discussed as well.

In 1903, Ramsden had reported the stabilization of emulsions with solid particles for the first time [1]. However, Pickering stabilization derived its name from a paper by Pickering in 1907 who published the first extensive experimental study on particle-stabilized emulsions for plant spray applications [2]. Finkle et al. [29] established a direct relationship between the type of solids and emulsion type (O/W or W/O). They have stated that in an emulsion containing solid particles, one of the liquids will probably wet the solid more than the other where the more poorly wetting liquid tend to form the dispersed phase.

Solids-stabilized emulsions are commonly encountered during the production of crude oil and synthetic fuels. Consequently, a fundamental understanding of the mechanisms governing the stability of these emulsions is essential. Depending on the exact system, there are at least two mechanisms by which colloidal particles stabilize emulsions. In the first, the particles are required to adsorb at the oil-water interface and remain there

forming a dense film around the dispersed droplets impeding coalescence. In the second, additional stabilization arises when the particle-particle interactions are such that a three-dimensional network of particles develops in the continuous phase surrounding the drops.

Emulsions stabilized solely by solid particles or Pickering Emulsions are based on the principle of strong adsorption of solid particles at the oil/water interface resulting in rigid and insoluble solid skin around each dispersed droplet. The mechanism of this type of emulsions was first quantified by Levine *et al.* [30]. Assuming that the particles are small enough that the effect of gravity can be neglected (applicable in case of nanoparticles used in this work), the energy ‘E’ required to remove a spherical particle from the water-oil interface is given by:

$$E = \pi \cdot r^2 \cdot \xi_{ow} \cdot (1 \pm \cos\theta)^2 \quad (\text{I.3.1})$$

r	Particle radius
ξ_{ow}	Water-oil interfacial tension
θ	Contact angle

The sign inside the brackets is negative if the particle is removed into the water phase and positive if it is removed into the oil phase (**Fig. 1.3.1**).

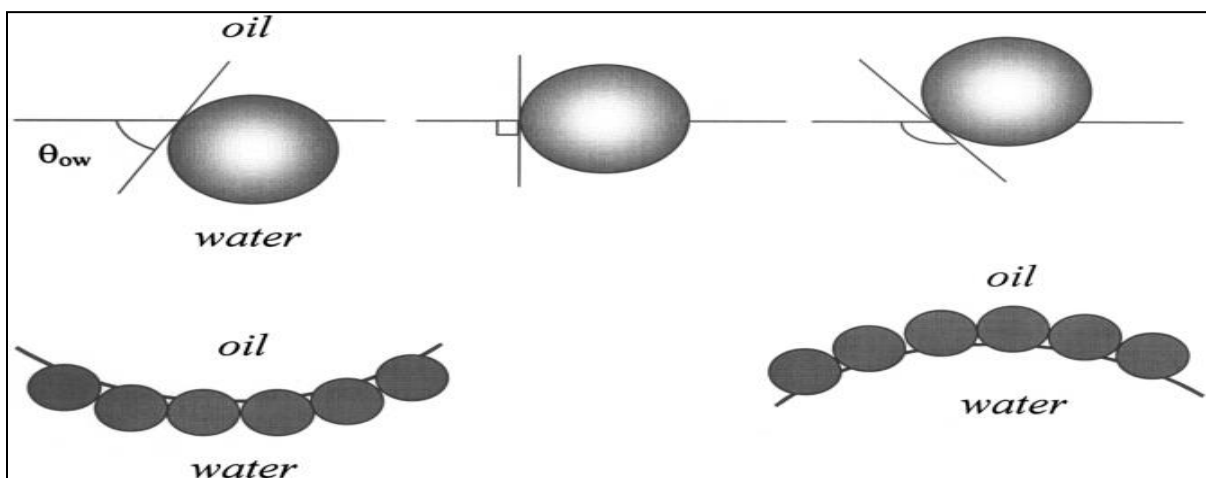


Figure 1.3.1: (Upper) Various contact angles of a small particle at a planar oil-water interface; (Lower) Position of solid particles at a curved interface – $\theta < 90^\circ$ (left) O/W emulsion can be formed, for $\theta > 90^\circ$ (right) W/O emulsion can be formed [31]

Strong adsorption of the particles at the oil-water interface is governed by the surface quality of the particles or their hydrophobicity. The positioning of a spherical particle at the interface can be best quantified by the contact angle θ . **Eq. I.3.1** shows that the maximum energy required to remove the particle from the interface is reached for $\theta = 90^\circ$.

In many ways like the surfactants' HLB, the contact angle determines the type of emulsion that the particle can stabilize [32]. Particles of contact angle (measured through the water phase) $\theta < 90^\circ$ tend to stabilize O/W emulsions and particles of $\theta > 90^\circ$ tend to stabilize W/O emulsions. However, too hydrophilic particles or too hydrophobic particles are more likely to stay dispersed in the water or the oil phase respectively.

One of the main roles of surfactants is to decrease the interfacial tension between the two phases allowing smaller droplets formation. Despite the fact that particles sit at the interface, their effects on the interfacial tension remain not well-understood. Some authors like Vignati *et al.* [33] demonstrated that interfacial tension was not affected by the presence of silica particles. They proved that changing the colloidal concentration and hydrophobicity did not affect the interfacial tension. However, Levine *et al.* [30] developed a theoretical model to calculate the interfacial tension of oil-water-particles

system in which particles are closely packed at a planar interface. They proved that the interfacial tension depends on the particles' hydrophobicity which was supported by Kim *et al.* [34] who investigated the amphiphilic character of graphite oxide.

Pickering [2] was the first to mention that emulsion stabilization should not depend on a decrease of the interfacial tension but on the size of the colloidal particles. When they are adsorbed at the interface, solid particles form a solid layer around the droplets which prevents the droplets to coalesce.

Thus, the ability of particles to stabilize emulsion depends on the magnitude of the steric hindrance to droplet coalescence. Tambe and Sharma [35] considered that a spherical particle could be displaced from the interface by three different mechanisms:

- Pushed into the dispersed phase (due to droplet collision)
- Pulled into the continuous phase by gravity
- Displaced laterally at the interface

Coalescence is unlikely to be due to the displacement of the particles into the droplet and it is only possible when particles are laterally displaced at the interface, making the uncovered droplet surface large enough for the droplets to merge. Thus, the effectiveness of solid particles in stabilizing emulsions seems to be due to the formation of closely packed layer of particles at the oil-water interface.

The examples given above show the contradictory effect of particles adsorbed at the oil-water interface. However, these particles were proven to provide, under certain conditions, long-term stable emulsions (O/W or W/O). As this stability cannot be directly linked to the lowering of the interfacial tension, it is worth wondering how solid particles stabilize emulsions.

The explanation as to how solid particles impart stability to emulsions is fundamentally different to stabilization by molecular surfactants, due to the relative large size of the stabilizing units and the presence of three-phases, resulting in a three-phase contact angle.

Despite the large number of experimental studies conducted on the role of colloidal particles in emulsion stability [36-40], the mechanism by which these particles stabilize emulsions is not yet fully understood. However, three main conditions can be stated so that solid particles can stabilize emulsions:

- Particles should exist at the interface before any stabilization can take place. Therefore, the ability of the solid particles to adsorb at the interface and remain there in a state of mechanical equilibrium depends largely on the size, wettability and the state of dispersion of the solids. Note that it is necessary that the size of the particles be much smaller than the size of the emulsion droplets for the particles to be properly located around the droplets
- Solid particles should form a rigid and protective interfacial film, possessing certain interfacial rheological properties
- The necessity of some degree of particle interaction, especially between particles at the interface, for effective stabilization to take place

In this work, silica nano-particles were used of different sizes and different wettabilities. One might question the choice of silica particles among other solid particles that were used in the food and pharmaceutical industries such as iron oxide, hydroxides or carbons [41-44] for the preparation of Pickering emulsions.

Many properties of silica particles have gathered the attention of various industries to use them as main stabilizers for the preparation of Pickering emulsions. At first, they are widely available in the market, easy to synthesize with a nice size control and cheap compared to other nanoparticles used; Nonetheless, the surface properties of these particles are very well known in the literature and have been studied for many years; and finally for the ability of easily changing their wettability from hydrophilic, amphiphilic to hydrophobic depending on the silylation process **Fig. 1.3.2**. These characteristics combined with the industry needs of new materials able offering a lightweight, ultrahigh strength, high electrical and heat conductivity and an increased surface area have all attracted the oil and gas industry into silica nanoparticles.

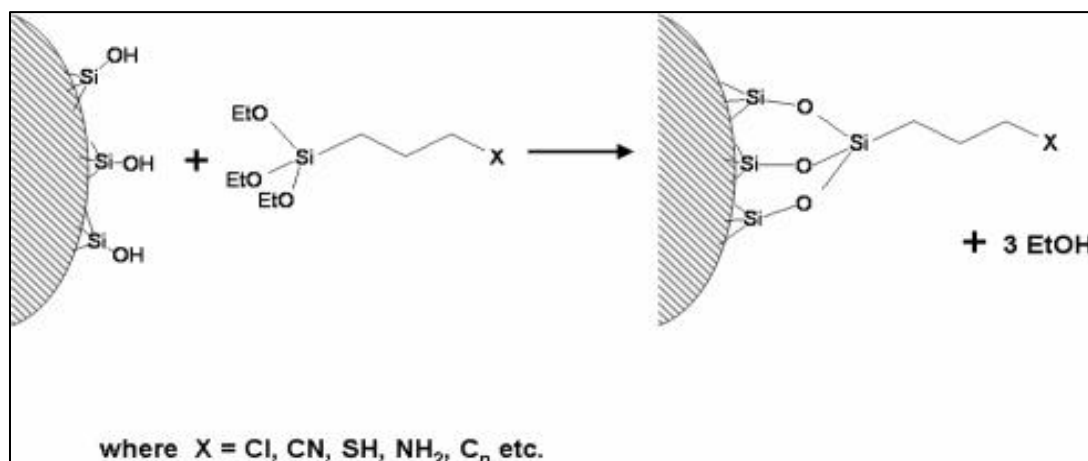


Figure 1.3.2: example of silylation of a silica surface using triethoxysilane [45]

Interactions of fumed silica particles are dominated by the surface siloxane bonds of the oxide backbone and the surface silanol groups. Approximately every second silicon atom on the fumed silica surface bears a silanol group ($4 \text{ SiOH molecules/nm}^2$) [42]. A large number of these silanols are not hydrogen bonded but are isolated and statistically distributed over the surface [45-47]. Owing to its surface silanol groups and its oxide nature, fumed silica is hydrophilic and exhibits a high surface energy. Deactivation of the surface silanol groups by silylation [48] strongly decreases the surface energy, and its surface becomes hydrophobic **Fig 1.3.2**.

Binks and Lumsdon [49] have shown the effect of changing the wettability of silica particles on the stability as well as the type of emulsions prepared. They have shown that particles with 100% Si-OH (very hydrophilic) groups and particles with 20% Si-OH (very hydrophobic) form stable emulsions as the particles tend to stay dispersed in the emulsions continuous phase. However, they have showed that particles with intermediate wettability (from 79% to 50% Si-OH) tend to be wetted by both phases and thus they can be used as stabilizers for the preparation of Pickering emulsions. Nonetheless, these particles tend to stabilize both O/W and W/O emulsions depending on the OWR used. At a certain OWR, a phase inversion occurs which depends strongly on the particles

wettabilities which include big droplet size changes. Nonetheless, they have shown that contact angle measurement can be replaced by an immersion test that measures the time needed for a floating particle to be completely immersed in the liquid phase which they have considered predictive of the particles wettability by the liquid phase. They have studied as well the effect of particles concentration on the stability to coalescence/sedimentation of different types of emulsions [50] and concluded that the particles concentration needed for the stability of any emulsion is strongly related to the wettability of the particles.

Levine and Sanford [37] have also claimed that to form stable emulsions, all particles should adsorb at the oil-water interface. One possibility is that unless the particles are extremely small ($\cong 0.001 \mu\text{m}$) thermodynamic equilibrium with respect to adsorption of particles is not achieved. On the other hand, many studies have been done on the possibility of using mixed systems for the stabilization of emulsions. Therefore, a mixture of surfactants and solid nanoparticles is used as an emulsifying system for the preparation of stable emulsions. It was shown that non-ionic surfactants when used with hydrophobic silica particles can trigger the stability of the emulsion due to the interaction between them both. Nonetheless, for such systems, the CMC value will significantly increase compared to surfactants alone [51-52].

1.3.b. Pickering Emulsions for Oil & Gas

Nano-products used as an additive in the drilling fluids have been investigated for several years with mixed success [53]. The desire to either solve problems or develop products that perform more efficiently has motivated fluids researchers to look towards nanotechnology and see what benefits it may bring in the area of rheology, fluid loss, system enhancement or shale stability of drilling fluids. As this work consists of improving the drilling phase through the optimization of drilling fluids performances, it is necessary to state the main drilling problems that serve as an introduction to where nanotechnology can contribute in the upstream industry. Therefore this sub-section is

going to present the main drilling problems, the introduction of nanoparticles in the drilling section as well as the main projects realized until today in the application of Pickering emulsions and nanotechnology in general in drilling fluids engineering.

At first it is very important to state that in the petroleum sector and more precisely in the drilling engineering section, colloidal particles have been used for ages. However, the definition of nano- or micro-particles might change from a domain to another. Drilling fluids engineers consider that colloidal particles are those having an average diameter less than 2 microns [54]. In respect to this, one could consider nanoparticles as small colloidal particles that have been used for decades in the oil and gas sector.

- Unconsolidated Formation and Loss Circulation: the potential economic impact of fluid loss into the formation as well as the hysteresis caused by the interaction of the drilling fluid with sensitive formations is a huge problem costing hundreds of millions of dollar to the drilling companies every day. Unconsolidated sand formation problems is very frequent while drilling due to inability of the conventional drilling fluids and chemicals (bentonite, polymers or a combination of them) to prevent sanding, hole collapse, washout, fracturing etc [55-56] This is due to their inability to generate inter-particle cohesion and cementation to strengthen near wellbore formation and widen the mud weight window. Shallow Water Flow (SWF) is another important problem faced during drilling especially in deep water drilling (North sea, Atlantic Frontier, Norwegian Sea, Southern Caspian Sea and Gulf of Mexico) [57]. This is related as well to the high permeability of such zones as well as the high pore diameters that is the source of geo-hazards [58]. Nonetheless, many Loss Circulation Materials (LCM) are used in the drilling industry today. However, the high solid content inside the drilling mud caused a huge decrease in the Rate of Penetration (ROP) which reduces the effectiveness of the drilling operation. Likewise, poorly consolidated formation with bad quality filter-cakes are very common problems encountered everyday in the drilling operation [59]. Therefore, nano-sized materials with their high surface to volume

ratio give them the ability to replace LCMs but with very low concentrations. Nano-particles can access the pores and inter-granular contact surfaces to form bonded networks within the formation matrix as well as fracturing of the formation. They can as well reduce the porosity and permeability of the near wellbore formation building structural barriers that provide effective sealing of the porous and permeable zones. Hence, nanoparticles can enhance the mechanical as well as the physical properties of the formation and improve hydraulic barriers within the formation matrix.

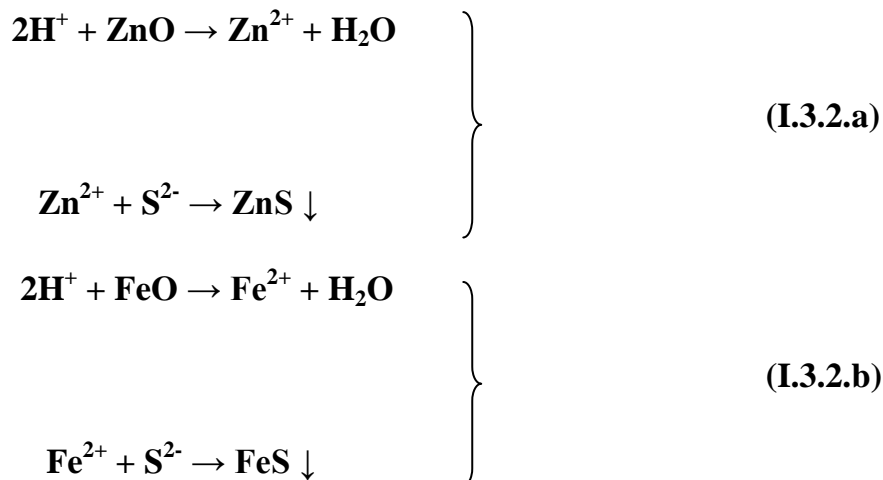
- Borehole instability: reactive shales are very sensitive shale formation that requires great carefulness especially when formulating appropriate drilling fluids. When water comes in contact with such formations, shale swelling can take place leading to formation collapse, loss circulation, differential sticking, etc. These problems come from a combined result of mechanical and chemical actions. Nanoparticles formulated fluids exhibits high interest because of the incorporation of sufficient number of functional groups on their surfaces providing a powerful inhibiting tool to prevent the chemical interaction between the drilling fluid and the formation [60]. Nonetheless, they inhibit the internal and external surfaces of clays to minimize the damage of shale formation with their high encapsulating capacity of the water droplets.
- High-Temperature High-Pressure (HTHP) hysteresis: After the reduction of tapped conventional wells, drilling fluids companies are looking forward for deep and ultra-deep wells where hostile environmental conditions exist. Temperatures and pressures in such environments can reach 200°C and 20 000 psi and can go as deep as 20 000 ft. Thermal degradation of conventional fluid loss additives, viscosifiers (polymer chains, emulsifiers, etc) occur at temperatures above 125-130 °C [61-66]. Therefore, chemicals used to stabilize drilling fluids and maintain their properties under thermal stresses can exhibit a drastic reduction in viscous and gelling properties of the fluids [67]. Nanoparticles having the ability to be used as surfactants in the formulation of drilling fluids with irreversible adsorption at the

oil-water interface, slightly dependent on temperature give them the advantage to formulate very stable emulsions that can withstand such conditions. These Pickering emulsions fluids are supposed to be the future candidates for untapping unconventional oil and gas wells.

- Gas Hydrate Formation: Under high pressure and low temperature (which is the case of deep sea water level) entrapment of natural gas by water is formed. This ice-like compound exhibits a real drilling challenge that makes drilling operations really difficult. Many works have showed that [68-69] the presence of gases whether as a solid, vapor or dissolved is hazardous due to their high impact on the drilling tools. However, hydrate bearing formation are of very high risk especially if the hydrates dissociate while drilling as they can bear a huge amount of gas which can cause a blowout situation [70]. Nonetheless, the dissociation of hydrates can cause a great change in the mud density, rheology and pressure leading to drastic inconveniences. Nanoparticles can prevent the dissociation of gas hydrates helping in providing effective means of degradation and borehole instability as well as preventing mud quality and rheology changes [67].
- H₂S and Acid Gases: Acid gases such as CO₂ and H₂S are very often encountered while drilling. These gases are very dangerous even at small concentrations. H₂S for example can become seriously dreadful at a concentration of 50 ppm in the surrounding environment. Therefore, a serious and rapid treatment of such gases should be conducted at the rig. Conventional treatments of such gases are done by conserving a high pH (> 11) of the drilling mud. This technique remains dangerous as these reactions are reversible and any decrease in the pH of the mud leads to the reformation of the acid gases. As the first pK_a of H₂S gas is known to be at neutral pH, thus once in the acid region, reformation of the gas into its molecular form occurs.

The drilling companies have proposed other solutions consisting of using solid particles especially metal oxides (zinc oxide and iron oxide) which interact with

the acid gases and lead to the dissociation and precipitation of the sulfur in an irreversible reaction. **Eq. I.3.2.a** and **I.3.2.b** shows two examples of the reactions taking place between H_2S gas and ZnO and FeO .



Nano-metal oxides used in drilling fluids as acid gas scavengers are extremely optimistic candidates for their high surface to volume ratio which enhanced the capture of the gases at low concentration at a very efficient dissociation rate [71].

Nonetheless, Kosynkin et al. have demonstrated an optimistic work concerning the use of Graphene Oxide (GO) nanoparticles as fluid loss control material. However, they stated that these GO nanoparticles were not able to stabilize the emulsions and were thermally unstable too. Likewise, Carbon Nanotubes (CNTs) were tested for their ability to withstand high temperatures and high pressures; however they were unsuccessful as emulsion stabilizers although they showed promising results as HTHP fluid loss controllers. Especially for their sheet-like shape which helps in plugging the formation pores giving a high quality filter cake.

Conclusion

This section presented the bibliographic review necessary for one to understand how the oil and gas industry can adopt the nanotechnology in its field of application. It was shown that the upstream sector of the oil and gas industry is in need of new technologies able to open new horizons to explore new hostile environments that have not been explored before. This imposes the search for new economical tools that can substitute the current tools used to drill the wells.

Therefore, solid nanoparticles in general and Pickering emulsions in particular, have shown high potential and very optimistic horizons for the oil and gas industry. However, this sector is still in its infancy and the lack of practical as well as experimental work done on the capability of replacing conventional drilling fluids with Pickering-stabilized ones, have pushed ORS and ENSTA ParisTech to collaborate into this project for the aim of synthesizing a new and novel technology that can be used as a new generation of drilling fluids for deep and ultra-deep drilling operation allowing the drilling companies to go further in the extraction of petroleum.

Chapter 2: Experimental Techniques

Introduction

This chapter describes the experimental techniques used in this work for a full characterization of the novel Pickering-based drilling fluids prepared in this work compared with the conventional surfactant-stabilized drilling mud. All the conventional petroleum and chemical used for the preparation of drilling mud (surfactant, emulsifiers, wetting agents, clay particles, weighting materials) were provided by Oil-Recovery-Services (ORS). The nanoparticles used were purchased from either Wacker-Chemie or Evonik-Degussa. *It should be noted that all the tests and materials done/used in this work comply with the American Petroleum Institute (API) recommendations for testing OBM and WBM.*

This chapter consists of six sub-sections:

The first describes in details the preparation procedure of the samples either prepared with surfactants or silica nanoparticles. Details of the products used as well as the characteristics and the properties of the silica particles were given. How to recognize the water-in-oil (W/O) or oil-in-water (O/W) emulsions was described, as well as how the composition of the aqueous phase was changed in pH and salt concentration.

The second sub-section describes the electrical stability test used on the petroleum rig to measure the stability of the drilling fluids.

The third part consists of describing the measurement of the morphology of the emulsions prepared. This involves the use of the BHS optical microscope as well as image treating software allowing one to estimate the droplet size distribution of the emulsions.

The fourth sub-section describes the rheological measurements measured in this work using the Anton Paar MCR302 rheometer with two different measuring systems (Double

Gap and Cylindrical Measuring System under pressure). Used in both rotational and oscillatory mode, these measurements allowed one to measure the plastic viscosity, yield stress, true yield stress as well as the thixotropic properties (gel strength) of the fluids prepared.

The fifth sub-section presents the static aging experiment of the fluids. This is a very important characterization of the stability of the drilling fluids at high-temperature and high-pressure. The fluids were characterized before and after aging as well as after re-homogenization of the samples compared with conventional surfactant-stabilized mud.

Finally, estimating the behavior of the fluids under reservoir conditions of various temperatures and pressures was done. This consists of measuring the flow behavior of the fluids at various temperatures from 20 °C (43 °F) to 180 °C (356 °F).

2.1. Composition of Drilling Fluids

This work consists of formulation drilling fluids based on the principle of Pickering emulsions. Therefore, two types of fluids were prepared: Oil-Based-Mud (OBM) and Water-Based-Mud (WBM). At first, an OBM, consisting of a W/O emulsion was prepared using AMODRILL 1100 mineral oil as continuous phase. This oil was purchased from INEOS Oligomers and its properties are presented in **Table 2.1**.

Table 2.1: Properties of the AMODRILL 1100 Mineral Oil	
Apparent Viscosity	2.38 mPa.s at 20 °C
Density	0.8 kg/m ³ at 20 °C
Boiling Point	279 °C (534 °F)

AMODRILL 1100 is an alpha olefin oil, water-white in color, 99.9% olefinic, more specifically Methylpropadiene. It is an environmentally friendly oil which is much recommended in European zones and zero discharge zones. Its structural properties are presented in **Table 2.2**.

Table 2.2: Structural Properties of AMODRILL 1100 Mineral Oil

Component	Amount
C12	1.5 wt.%
C14	65.7 wt.%
C16	32.3 wt.%
C18	0.6 wt.%
Mono-Olefin	99.4 wt.%
Paraffin	0.6 wt.%
Olefin isomers – linear internal	6.7 mole %

2.1.a. Surfactant-stabilized OBM sample preparation

Surfactant-stabilized drilling fluids were prepared using this same mineral oil as continuous phase with the addition of various other chemicals and solid particles. An example of the composition used for the preparation of a pilot test sample of a surfactant-stabilized OBM with an OWR of 80:20 is presented in **Table 2.3**.

Table 2.3: Composition of the components used for Pilot Test the preparation of surfactant-stabilized OBM (350 ml)

Component	Weight (g)
AMODRILL 1100	224.0 g
Water	70.0 g
CaCl ₂	17.5 g
Lime	16.0 g
ORS MUL I	4.5 g
ORS MUL II	4.5 g
ORS VIS	4.5 g

All the percentages are calculated based on the oil phase, apart from the brine phase, where the only dissolved salt used was CaCl₂, which percentage was calculated based on

the water phase. Note that through all this work, deionized water was used, which was passed through an osmosis unit and then a Milli-Q reagent water system.



Figure 2.1: High-intensity ultrasonic processor (Sonics & Materials, tip diameter 13 mm) [72]

The preparation of the samples requires the use of a homogenizer/mixer. In this work, and for the preparation of all samples, a high-intensity ultrasonic processor (Sonics & Materials, tip diameter 13 mm), operating at 20 kHz and 35% of the maximum ultrasonic power of 750 W was used (**Fig. 2.1**). During sonification, samples tend to heat up; therefore, all samples prepared were immersed in an ice bath to avoid any overheating of the emulsions.

ORS MUL I and ORS MUL II are respectively the primary and secondary emulsifiers used in this formulation. The first is formulated to give emulsifications and is most effective in the presence of small amounts of lime. It is based on fatty acids and when used with a secondary emulsifier then good fluid loss control and predictable rheology are imparted to the drilling fluid. ORS MUL II is used in conjunction with ORS MUL I to enhance the stability of the OBM and further reduce HTHP filtrate losses. It is a secondary emulsifier and wetting agent. It is developed for use in oil-based drilling

operations to provide high emulsifications and oil wetting. Both are ORS products and are provided by the company funding this work.

On the other hand, ORS VIS is an organophilic rheological clay additive, designed to offer cost effective performance and to produce high yield viscosity in moderate and high temperature drilling mud applications. It is a quaternized Montmorillonite clay developed to be used with mineral oils, low toxicity oils, diesel oil and crude oil as a viscosifier and anti-settling additive in applications including oil-based drilling mud, invert emulsion mud, packer fluids, completion fluids and work over fluids. As a result of its surface modification, ORS VIS disperses easily in diesel and mineral oil based systems and swells in the presence of the polar constituents of the system. It is used to offer a moderate to high yield value with good dispersion at ambient temperatures and is used to provide oil based drilling fluids with the required suspending and carrying properties. Cloisite Ca^{++} is a natural bentonite clay used for the preparation of WBMs and was purchased from BYK.

The addition of the above components should be strictly respected for the preparation of such fluids; therefore, the emulsifiers are firstly added to the mineral oil followed by the addition of lime which are mixed together and mixed for 20 seconds. ORS VIS is then added followed by the addition of the brine phase which is prepared aside by mixing the CaCl_2 salt with water and left to homogenize for 2 minutes.

2.1.b. Pickering W/O emulsions preparation

Three types of Pickering based W/O emulsions were prepared in this work using three different types of silica nanoparticles. The properties of those nanoparticles are presented in **Table 2.4**.

Table 2.4: Characteristics and Properties of commercial hydrophobic silica particles used in this work

Samples Name	BET surface area S (m²/g)	Average Spherical Diameter (nm) d = 6/ρ.S	MET particles Mean Diameter (nm)	Carbon content (% wt)	% Silanol Groups
AEROSIL R104	140 ± 20	20 ± 1	22 ± 1	0.9-1.8	50 %
HDK H20	200 ± 30	14 ± 1	15 ± 1	1.0-1.8	50 %
HDK H17	140 ± 20	20 ± 1	24 ± 1	4.0-5.2	20 %

For the preparation of OBM, hydrophobic silica particles were used for their ability to form W/O emulsions under certain circumstances. AEROSIL R104 (Evonik Industries) are fumed silica nanoparticles treated with octamethylcyclotetrasiloxane. However, HDK H20 and HDK H17 (Wacker Chemie) are treated with dimethyldichlorosilane reagent. All nanoparticles are treated to different extents, which are reported in **Table 2.4** by their carbon content as given by the purchasing companies. TEM images were measured and reported in **Fig. 2.2** which scale was set at 30 nm for all three pictures shown.

The preparation of Pickering W/O emulsions is different than that of the surfactant-stabilized OBM. For all three types of hydrophobic silica nanoparticles, a calculated amount of particles is added at first to the oil continuous phase and homogenized for 20 seconds. The particles were left for 24 hours to assure a good wetting of the solids. After that, the water/brine phase is added ‘slowly’ to assure a good homogenization of the whole amount of water used.

Note that for samples prepared with clay particles, those were added before adding the water phase and were left 24 hours to oil wet after adding the nanoparticles.

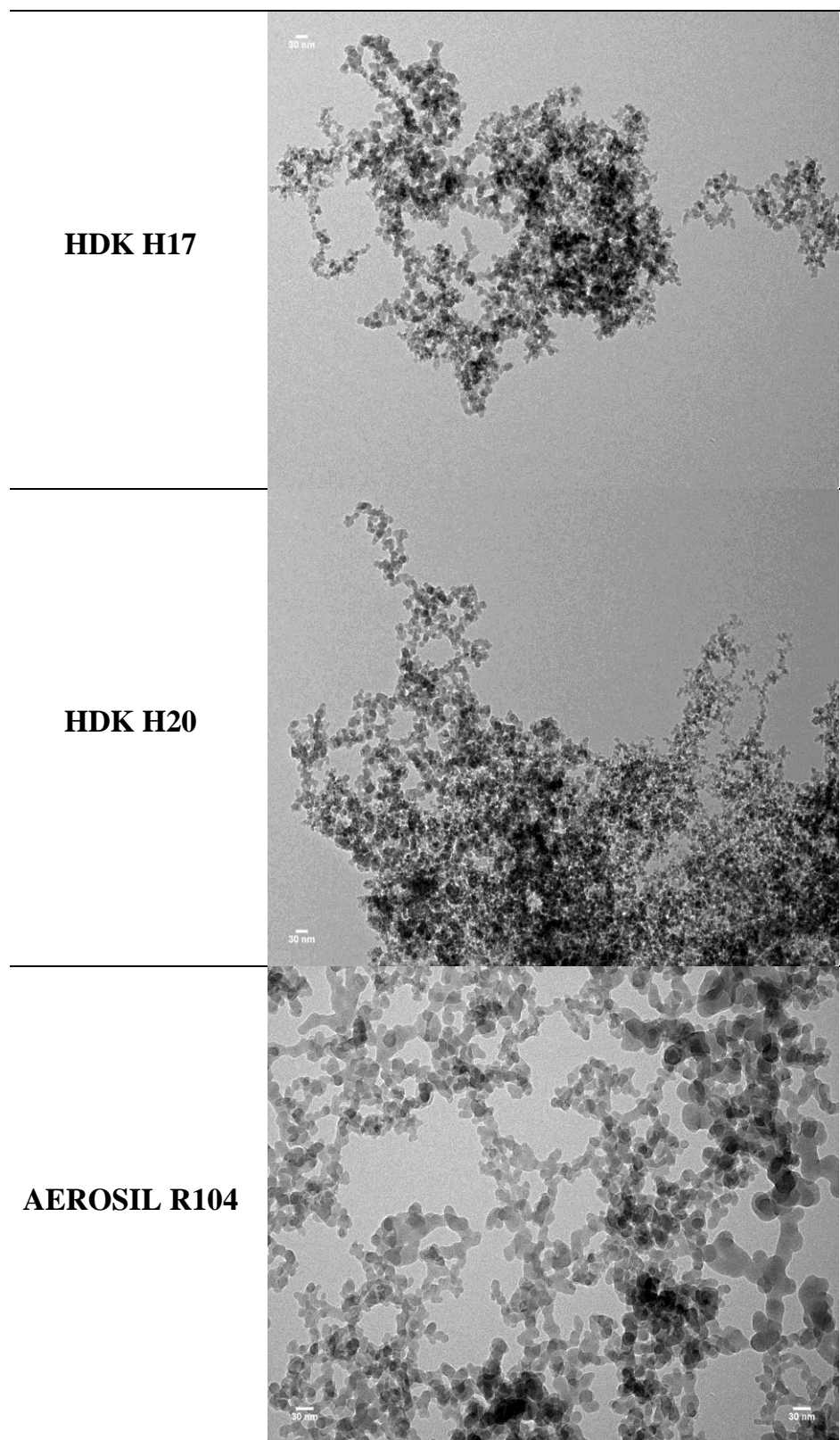


Figure 2.2: TEM images of the hydrophobic silica nanoparticles used in this work. All scale bars are of 30 nm

2.1.c Pickering O/W emulsions preparation

The preparation of the O/W Pickering drilling fluids consisted of using 3 different types of hydrophilic silica nanoparticles. The TEM images of these particles are given in **Fig. 2.3** where their characteristics are given in **Table 2.5**.

Table 2.5: Properties and Characteristics of Hydrophilic Silica nanoparticles used for the preparation of O/W Pickering drilling fluids

Samples Name	BET surface area S (m²/g)	Average Spherical Diameter (nm) d = 6/ρ.S	MET particles Mean Diameter (nm)	Carbon content (% wt)
AEROSIL R816	190 ± 20	14 ± 1	17 ± 1	0.9 - 1.8
AEROSIL 130	200 ± 25	14 ± 1	20 ± 1	0
AEROSIL OX50	50 ± 15	55 ± 1	61 ± 1	0

HDK N20 and AEROSIL OX50 are both bare silica nanoparticles (very hydrophobic), where AEROSIL R816 were treated with hexadecysilane. Both R816 and AEROSIL 130 have almost the same size where AEROSIL 130 and OX50 have the same hydrophilicity with different particle sizes as seen in **Fig. 2.3**.

The preparation of O/W Pickering-based drilling fluids or what called Water-Based Mud (WBM) consisted of the same procedure described in the previous section for the preparation of OBM. However, particles were dispersed in the water phase at first before adding the oil dispersed phase.

2.1.d. Type of emulsions

The types of the emulsions (water-in-oil or oil-in-water) were obtained by observing what happened when a drop of each emulsion was added to a volume of either pure oil (AMODRILL 1100 in this case) or pure water [49].

W/O emulsions dispersed in oil and remained as drops in water. However, O/W emulsions dispersed in water and remained as droplets in oil.

2.1.e. Composition of the aqueous phase

The pH of the water phase was adjusted using NaOH and HCl and varied from 3.5 to 12. The dilution and pH adjustment were achieved at NaOH and HCl concentrations such that the final volume of the dispersion was at the required pH.

CaCl₂ salt with 99.9% purity purchased from Sigma-Aldrich was used for the preparation of the brine phase. The salt concentration was varied between 0, 5, 15 and 25 wt.% calculated based on the amount of the water phase used.

2.2. Electrical Stability

The conductivity of the emulsions has been widely studied for the estimation of the stability of this latter. However, in the oil & gas field and more precisely in the characterization of drilling fluids, the electrical stability consists of an important parameter to be addressed for its significance to the stability of the fluids.

It is manifested by the breakdown voltage at which the emulsion becomes conductive, which is an indication of the stability of a water-in-oil emulsion. The electrical stability measurement consists of applying a voltage to the emulsion, under which an alignment of the water droplets will occur between the electrodes of the meter, allowing a passage of a current at which the electrical stability measurement is registered. Therefore, an Electrical Stability (ES) tester purchased from OFITE was used to measure the stability of the emulsions prepared (**Fig. 2.4**).

The measurement is done by heating a sample of 50 cm³ at 120 ± 5 °F (49 °C). The measuring probe was then immersed inside the sample without touching the sides or bottom of the cup. The test was run until the appearance of the measured voltage.

The measurement was repeated twice and considered acceptable if the error range was within $\pm 5\%$ of the measured ES and was reported in Volts (V).

It should be noted that the electrical stability meter was calibrated for both low (610 V) and high (1952 V) voltages using special input batteries delivering the mentioned voltages. Repeated three times each, errors of $\pm 2\%$ of the given voltages were obtained which is very acceptable according to the company's usage instructions.



Figure 2.4: Electrical Stability Meter

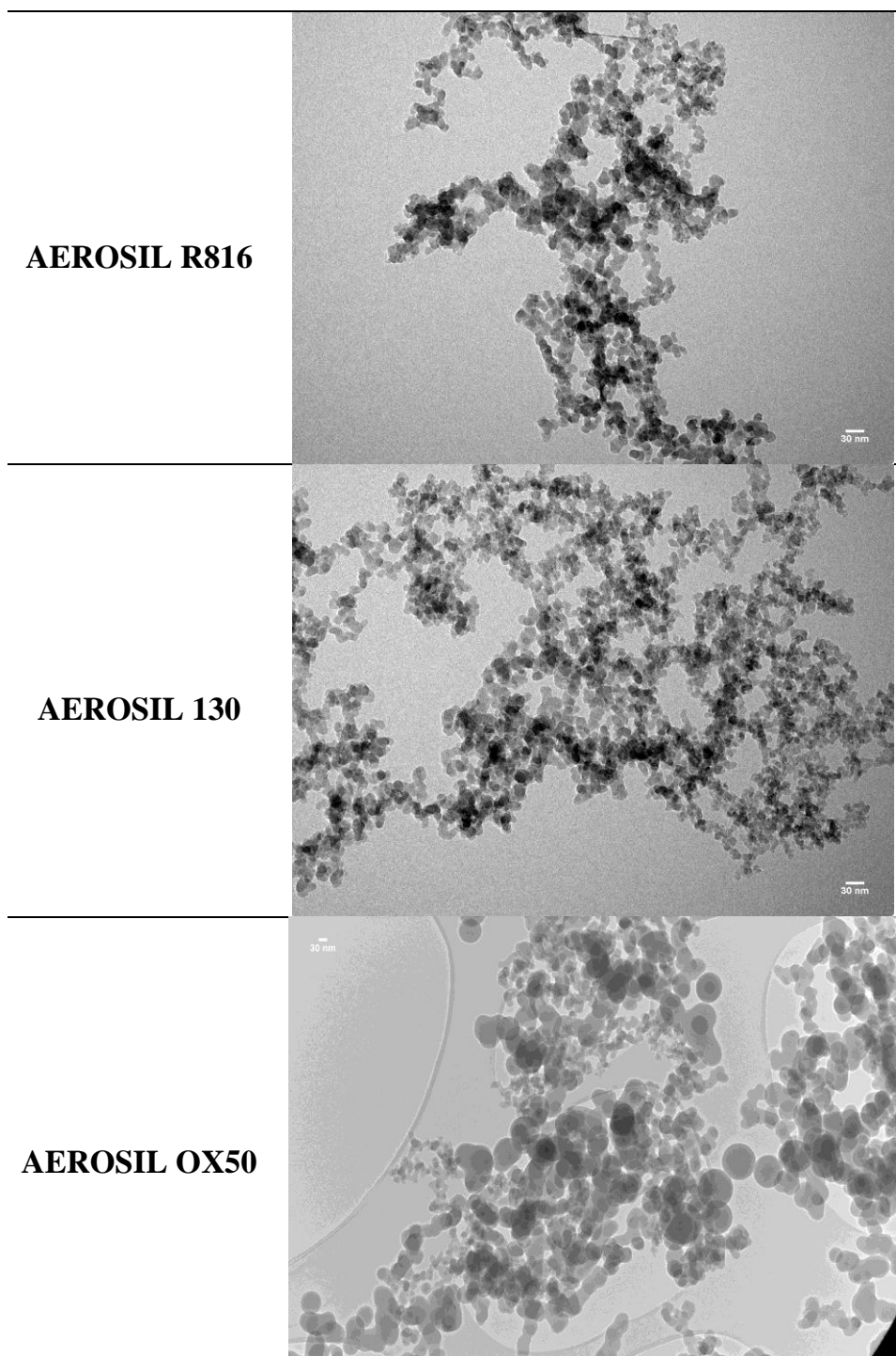


Figure 2.3: TEM Images of Hydrophilic Silica nanoparticles used for the preparation of O/W Pickering drilling fluids. All scale bars are of 30 nm

2.3. Microscopy and Droplet Size Distribution

Microscopy images of the emulsions prepared in this work were obtained using the BHS Olympus microscope coupled with a long barrel (LB) objective lens series (1x - 100x oil) with a focal length of 45 mm and a mechanical tube length of 160 mm that could be used for everything from regular bright field observations to polarization, fluorescence and phase contrast microscopy (**Fig. 2.5**). Image was taken using an E-M5II Olympus digital camera. Care was taken while putting the samples between the microscope glass slides so that no deformation of the emulsions droplets would occur.



Figure 2.5: Olympus BHS Microscope

Images were treated and proceeded using ImageJ software and the droplet size distribution was given after treating at least 1000 droplets. A mean particles diameter was calculated at the end using Excel.

It should be noted that the aim of estimating the droplet size distribution in this work was more to compare the effect of the different variations in the drilling fluids composition (pH and salt concentration, addition of clay, effect of aging, etc ...).

2.4. Rotational and Oscillatory Rheology

The rheological properties of drilling fluids prepared in this work were tested and measured using the Anton Paar MCR 302 (**Fig. 2.6**). It is an advanced rotational

rheometer providing torques down to 10 nNm for rotation and 2 nNm for oscillation with a torque resolution of 0.1 nNm. The temperature and pressure can vary between - 20 °C and 350 °C and up to 150 bars. This rheometer was used to do a more in depth analysis of fluids than the conventional viscometers used on the rig.

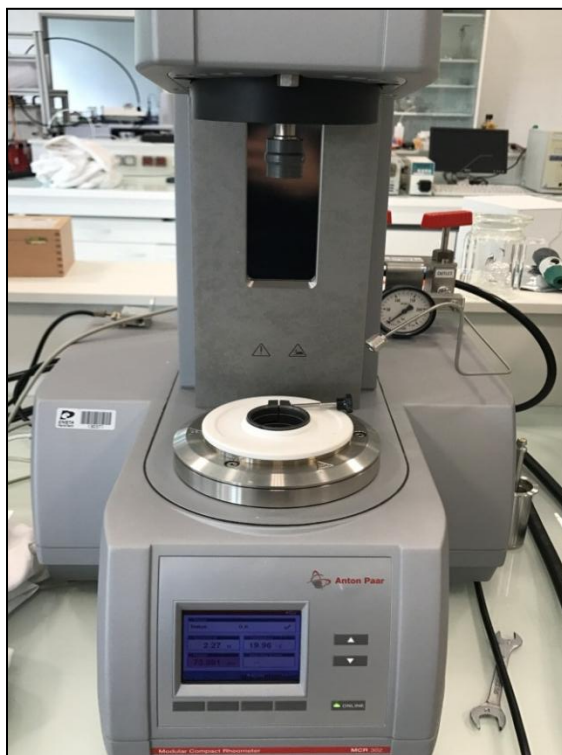


Figure 2.6: Anton Paar MCR 302 Rheometer

The rheological properties tested at atmospheric pressure were measured using a double gap cylinder measuring system (**Fig. 2.7**) which characteristics are listed in **Table 2.6**.

Table 2.6: Characteristics of the double gap measuring system DG 26.7

Double Gap Measuring System DG 26.7	
Outer Radius 1	13.80 mm
Outer Radius 2	12.33 mm
Maximum Shear Rate	3000.00 s ⁻¹
Maximum Shear Stress	1600.00 s ⁻¹
Gap 1	0.47 mm
Gap 2	0.42 mm

It consisted of double cylinders (outer and inner) where the outer cylinder is fixed and the inner one tend to rotate and the measure fluid is put between both. A volume of 5 ml of each sample was used to perform rheological measurements.

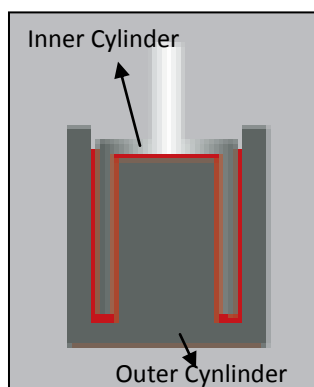


Figure 2.7: Double Gap Measuring System Illustration

Three types of measurements were done: Flow curve measurements, Amplitude Sweep measurements and Thixotropic measurements. The first consists of a rotational test where the last two were oscillatory. In both cases, all tests done at atmospheric pressure were done at an ambient temperature of 20 °C (68 °F).

The rheometer was calibrated using two different oils purchased from Anton Paar the APS3 and the APN14 covering the whole range of viscosities needed for drilling fluids

testing (from 0.84 mPa.s to 25.40 mPa.s). Note that the measurement errors normally occur at low viscosities; however, at high viscosities the exactness is much larger.

2.4.a. Flow Curve Measurements

It consists of measuring the variation of the shear stress ' τ ' [Pa] in function of an applied shear rate ' $\dot{\gamma}$ ' [s^{-1}]. Therefore, the shear rate was varied between $10 s^{-1}$ to $1022 s^{-1}$, while the rheometer software automatically calculated the viscosity at the given shear rates. **Fig. 2.8** shows an example of a flow curve measured on the samples used in this work. For the assessment of the rheological properties (plastic viscosity [PV], yield point [YP], etc ...) mathematical rheological models were used.

Herschel-Bulkley model (**Eq. II.1**) was used for offering the best fit to the experimental data obtained. However, it does not give a simple prediction of the plastic viscosity. Therefore, the Bingham-Plastic model (**Eq. II.2**) was as well used.

Herschel-Bulkley Model

$$\tau = \tau_0 + K.\dot{\gamma}^n \quad (\text{II.1})$$

Bingham Plastic Model

$$\tau = YS + PV.\dot{\gamma} \quad (\text{II.2})$$

Where τ is the shear stress (Pa), τ_0 is the Herschel-Bulkley yield stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), K the consistency index, n the flow index, YS is the Bingham-Plastic yield stress (Pa) and PV is the Bingham- Plastic plastic viscosity (mPa.s).

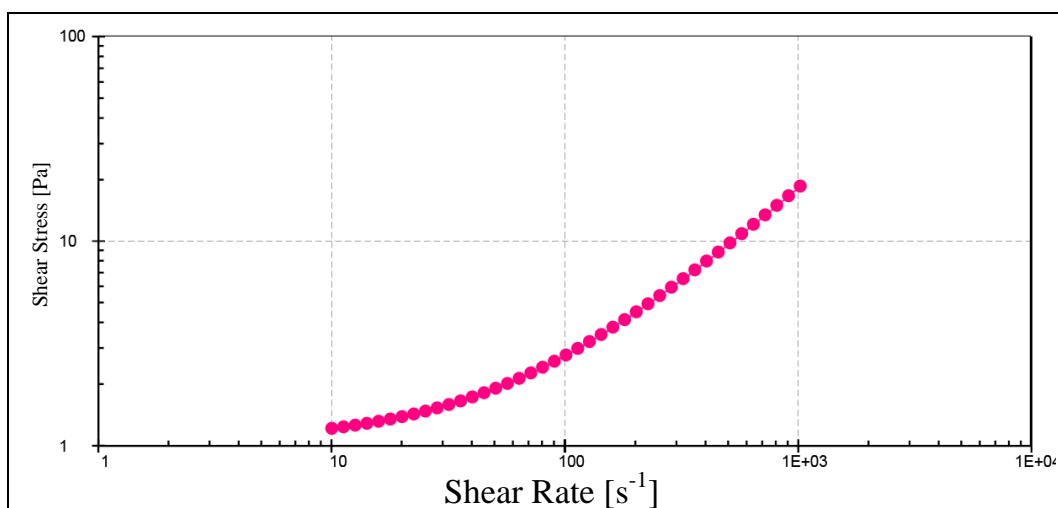


Figure 2.8: Flow Curve measurement showing the variation of the shear stress in function of the shear rate of a drilling fluid sample

2.4.b. Amplitude Sweep Measurements

Amplitude sweeps are tests done in oscillation, with increasing amplitude for a constant frequency. Amplitude sweeps are done in order to find the linear viscoelastic (LVE) range. Within the LVE range, fluids will act according to Hooke's law, meaning they will generally act as elastic [73]. The amplitude sweep measures the storage and loss moduli, G' and G'' respectively. If the storage modulus is greater than the loss modulus, the fluid has characteristics like a solid or gel. When the elastic part dominates the viscous one, the fluid displays certain rigidity. Some matters, such as lotions and coatings, exhibit flow behavior at medium and high shear rates, but $G' > G''$ within the LVE range. They have a gel-like consistency at low shear rates, and even if they only have a weak gel structure, stability and firmness are expected [73]. Stable dispersions, such as drilling fluids, are examples of this behavior. If the loss modulus G'' is greater than the storage modulus G' , viscous behavior dominates the elastic part. When the values of storage and loss moduli cross, the material starts to flow. Rheologically speaking, $G' = G''$ is known as the flow point of the fluid (**Fig. 2.9**). In the drilling industry the value is named yield point. Yield point in a rheological sense, is the point when the LVE plateau begins to deviate. The rheological yield point is hence the limit of the LVE range. For the rest of this work flow

point will be referred to as true yield stress, since this definition is the drilling industry standard.

In this work, an angular velocity was set at 10 rad/s and the strain was varied from 0.01% to 100% in oscillating modus. Both the G' and G'' moduli were reported in function of the strain and the intersection between both curves was measured. This test verifies the viscoelastic behavior of all samples used in this work which is a very important property for drilling fluids.

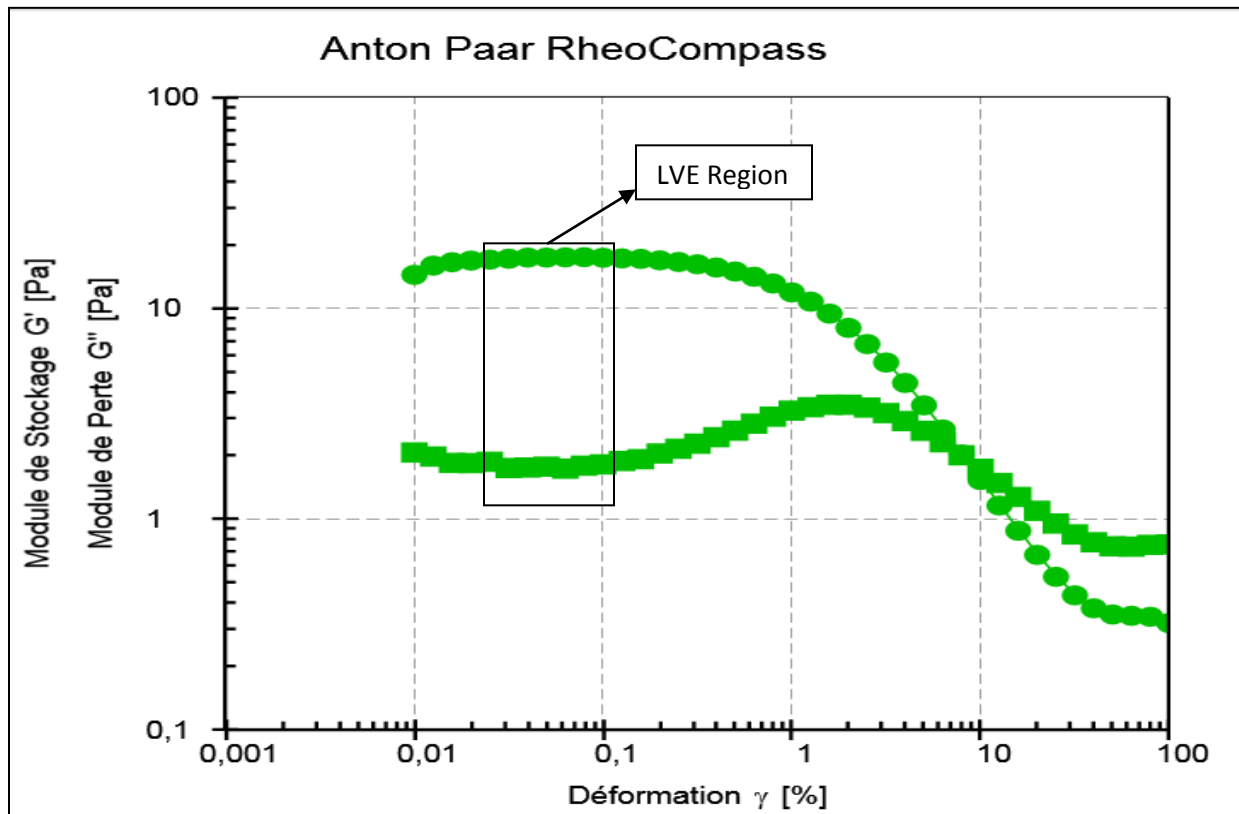


Figure 2.9: Amplitude Sweep of a drilling fluid sample showing the LVE region as well as the true yield stress. Filled Circles represents G' and Filled Squares G''

2.4.c. Thixotropic /Gel Strength Measurements

Thixotropy is the time dependent property of fluids. In other words, it measures the variations of the inter-structure of the fluids, especially that responsible of generating gel structures, such as clay and solid particles. Some fluids have a viscosity behavior

depending on time or what kind of shear stress they have previously been exposed to, sometimes called the shear history. Thixotropic fluids are showing signs that the viscosity is reduced when the shear force is constant for some time, i.e. the fluid flows easier with time under static shear stress. They develop a solid state structure when at rest or with decreasing shear rate, like a gel. The gel structure strength depends on the time at rest and when sheared. The gel will begin to break as shear is initiated, and will ultimately break completely when exposed to higher and prolonged shear [74-75].

In this work, the gel strength was measured by applying an oscillatory-rotational-oscillatory measurement. This consists of applying a constant and pre-defined strain which was chosen in the LVE region pre-measured via an amplitude sweep as described before. The fluids were left for at least an hour for structure regeneration and to allow a minimum of shear history effect on the measurements. This step allows one to measure the gel structure (viscoelasticity) of the sample. Thereafter, a rotational measurement at a constant shear rate of 1022 s^{-1} was applied to break the gel structure of the fluids. Finally, the same oscillatory step taken at the beginning of this test is re-applied, with the same strain, allowing the measurement of the re-generation of the gel strength of the fluids (**Fig. 2.10**).

In the drilling fluids field, the gel strength of the drilling mud is measured at 10 sec and 10 min intervals. Sometimes a 30 min measurement is done as well given a wider analysis range of the fluids. In this work, the gel strength was given by the recuperation percentage of the initial gel structure of the fluid at 10 sec and 10 min.

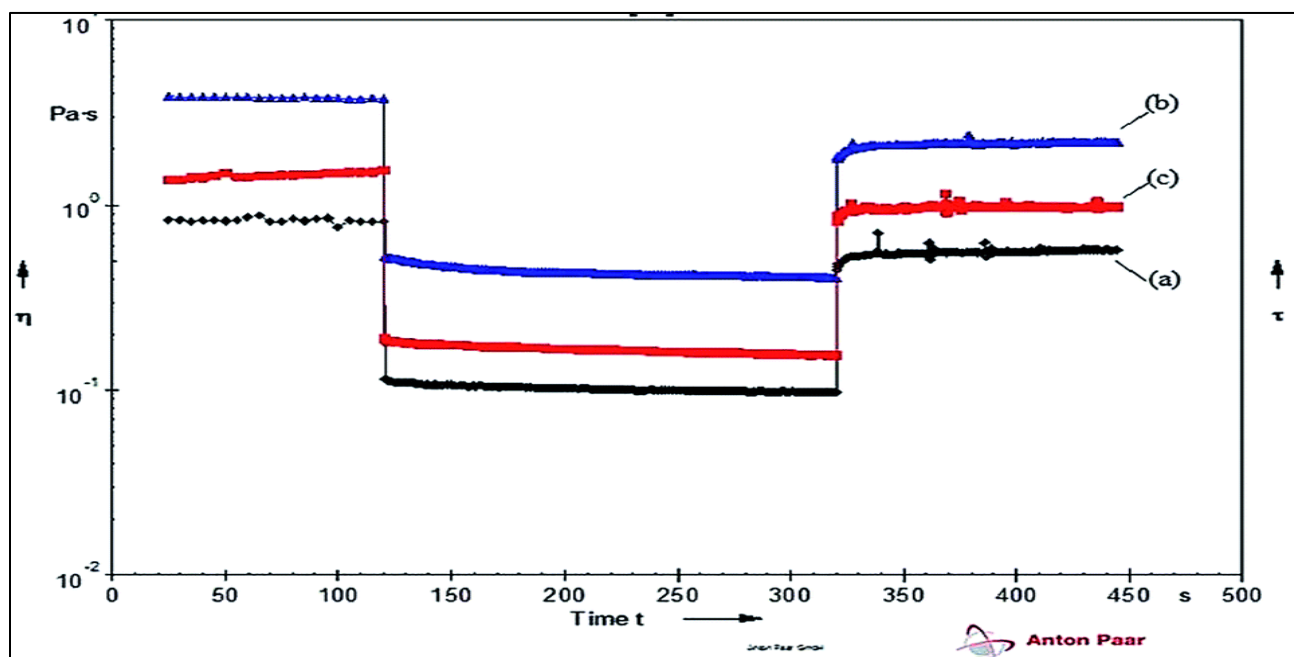


Figure 2.10: Gel Strength Measurement showing the variation of the viscosity with time of three different samples

2.5. Aging

Pilot test consisting of the preparation of 350 cm³ of drilling fluids was done for the static aging experiment. This consisted of heating up the drilling muds at 177 °C (350 °F) under 35 bars (500 psi) pressure for 16 hours according to the API normalized aging tests [76-78].

The aim of this test is not to simulate the behavior of the fluids under HTHP, but to test the stability of such fluids under HTHP conditions. The 'static' aging is one of two aging tests normally done for drilling fluids ('rotary' aging is the second test) and is called 'static' because no homogenization of the fluids was applied.

The test was done by placing 200 cm³ of the drilling fluid sample inside the aging cell, which was firmly closed and sealed. The heating was done using a heating jacket put around the cell and the temperature variation was measured via a thermocouple placed inside the aging cell at the fluids level. Nitrogen gas was used to pressurize the cell and this was used to avoid any phase change of the fluids components (more precisely the water dispersed phase) while heating.

The cell was depressurized once it has cooled down to ambient temperature. The fluids were then tested for rheology, morphology as well as electrical stability before being re-homogenized using the ultra-sonic horn and re-tested as aforementioned allowing the comparison of the fluids properties before/after aging and after re-homogenization.

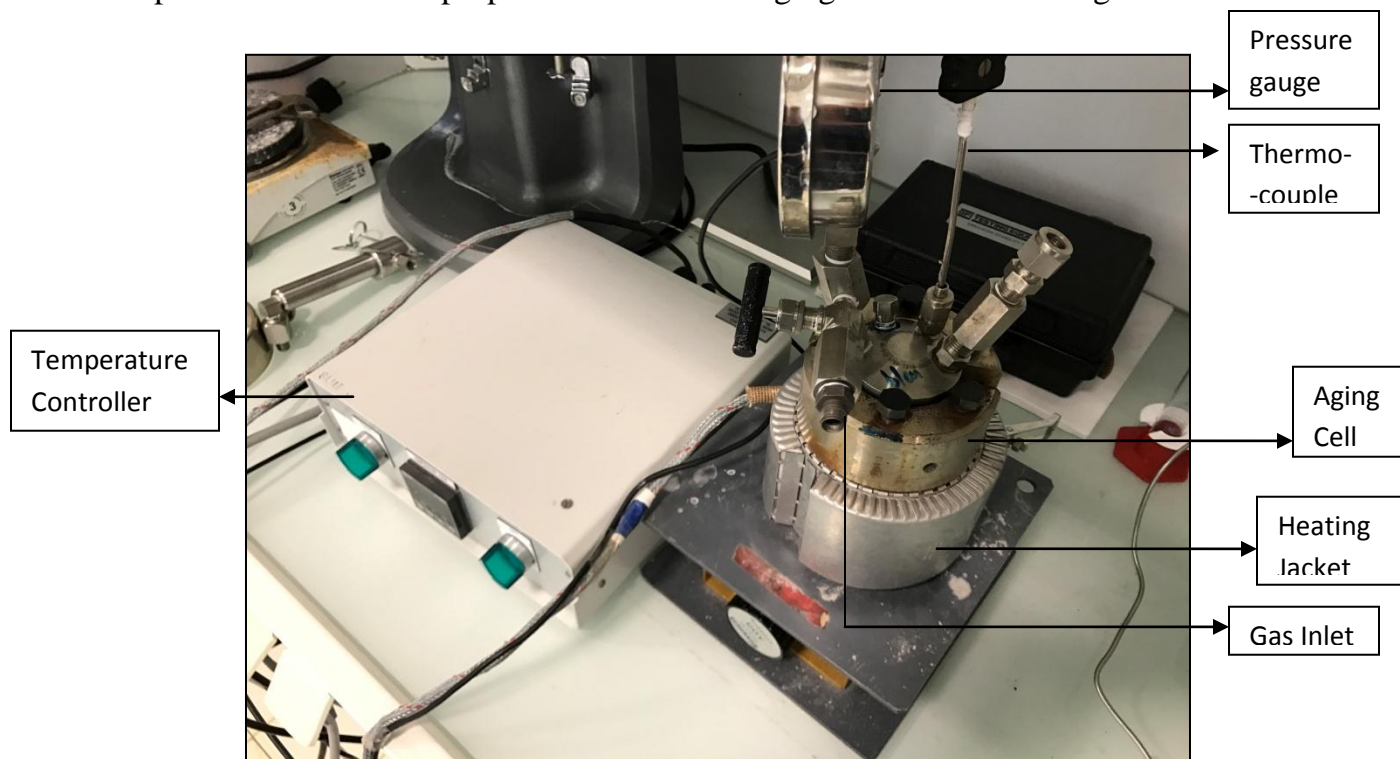


Figure 2.11: Aging cell equipment

2.6. HTHP Rheology

The behavior of the drilling fluids under reservoir conditions consist of testing their rheological properties (which are used to anticipate the borehole cleaning efficiency, debris transport capacity, hydrostatic and fracturing pressures of the mud) under such hostile conditions. It should be noted that temperature control of the rheometer was done via a Peltier system coupled with a cooling bath allowing the measurement of the temperature with a variation of ± 0.2 °C.

This test was done using the Anton Paar MCR 302 rheometer coupled with the C-PTD200 cell and the CC25 cylindrical measuring system (**Figs. 2.12.a and 2.12.b**).

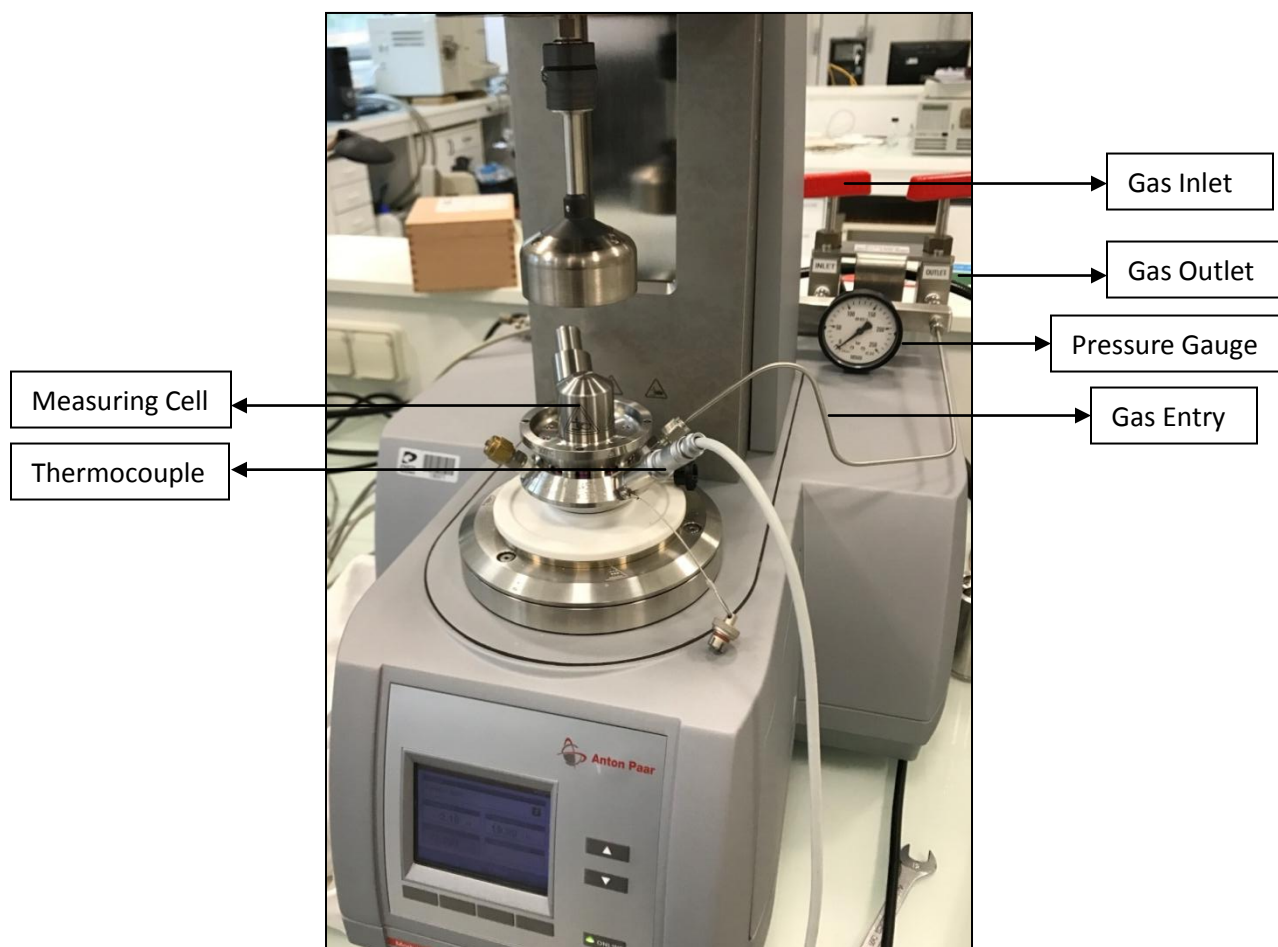


Figure 2.12.a: HTHP Pressure Cell



Figure 2.12.b: CC25 Cylindrical Measuring System

Since the effect of the variation of the pressure on the rheological properties of the samples is almost negligible, contrary to that of the temperature (see chapter 3 - section 3.7), the pressure was fixed at 75 bars (1021 psi) and for that Nitrogen gas was used. The temperature of the samples was then varied from 20 °C (68 °F) to 180 °C (356 °F) and flow curve measurements (as described in section 2.4.a) were done. Both the Bingham-Plastic (BP) and Herschel-Bulkley (HB) models were used to analyze the results. The variations of the viscosity of the fluids with temperature were then reported in comparison with surfactant-stabilized OBM.

Chapter 3 **Pickering Oil-Based Drilling Fluids**

Introduction

For decades, the drilling companies have invested millions of dollars into inventing new chemicals (surfactants, polymers, rheology modifiers, etc ...) and new products helping in solving all the drilling problems faced. Providing adequate supply is driving the industry to explore areas previously unexplored, or minimally explored. This demands new drilling techniques and new tools that can be adapted to the new drilling environments.

Therefore this chapter presents the work done in the aim of synthesizing a novel generation of drilling fluids based on the principal of Pickering emulsions. This new system, adopts the idea of generating oil-based drilling fluids stabilized by silica nanoparticles. The stability of these emulsions from coalescence/sedimentation to electrical stability, morphology manifested by the droplet size distribution as well as the rheology of the emulsions were all measured and reported.

HTHP drilling is a new subset of activity for today drilling. Developing HTHP prospects can require overcoming many drilling difficulties encountered in unconventional formation drilling nowadays. Rigs capable of HTHP drilling are larger due to the requirements such as hook load, mud pumps, drill pipe and surface mud capacity to name a few. Hence, more expensive drilling is attained requiring a higher density fluid which typically requires high solids loading. This contributes in higher pressure demands combined with the competency of rock depth leading to low penetration rates and therefore added drilling costs. In extreme cases, pressure, temperature and acid gas levels can limit the selection and function of down-hole tools and fluid selection.

Thus, a need for an innovative solution is highly required to overcome all these obstacles. The fluids prepared in this work were tested for their ability to withstand HTHP conditions through aging as well as HTHP rheology measurements. They are

compared with surfactant stabilized OBM and the ability to use these fluids with and without clay particles.

3.1. Stability to Coalescence/Sedimentation

Wettability of solid particles is usually assessed by their contact angle with the liquid phase. However, adequate contact angle measurements are very difficult if possible at all [79]. Therefore, it was essential for one to find a new and representative method for the measurement of the wettability of solid particles. Binks and Lumsdon [49] have shown that measuring the time necessary for the particles to be fully wetted by the liquid phase is an effective and representative measurement of the wettability of the particles. This method measures the time taken by the liquid to penetrate into the voids and replace the air phase contained between the particles aggregates [49]. On the other hand, they showed as well that the percentage of the silanol groups present on the surface of the grafted silica particles is proportional to the wettability of these particles and can be used as a tool to describe particles wettability.

Table 2.4 showed the characteristics and the properties of the commercial silica particles used in this work. All of the three samples are hydrophobic particles treated to different extents with various silanol groups. The percentage of carbon content measured represents the length of the silanol hydrophobic chain adsorbed at the surface of the silica particles after grafting. The longer the chain, the higher the carbon content and therefore the more hydrophobic the particles are. Nonetheless, this latter as well as the percentage of the silanol groups were given by the synthesizing company (Evonik Degussa and Wacker Chemie). This percentage gives the amount of the grafted silica surface compared to its bare initial state (where 100% represents the bare silica surface). **Fig. 3.1** shows an example of the grafting (silylation) procedure of AEROSIL particles given by Evonik Degussa.

The BET surface area which can, under certain geometric considerations, predict the size of the particles was measured in the laboratory. To complete the characterization of the particles, MET spectroscopy images were done and presented in **Fig. 2.2**.

The effect of nanoparticles concentration on the stability of Pickering emulsions is manifested by the formation of a good protective skin around each dispersed droplet, preventing any possibility of re-coalescence. Hence, by increasing the nanoparticles concentration, the particles adsorption rate at the oil-water interface increases, limiting re-coalescence and preserving stable and smaller droplets sizes.

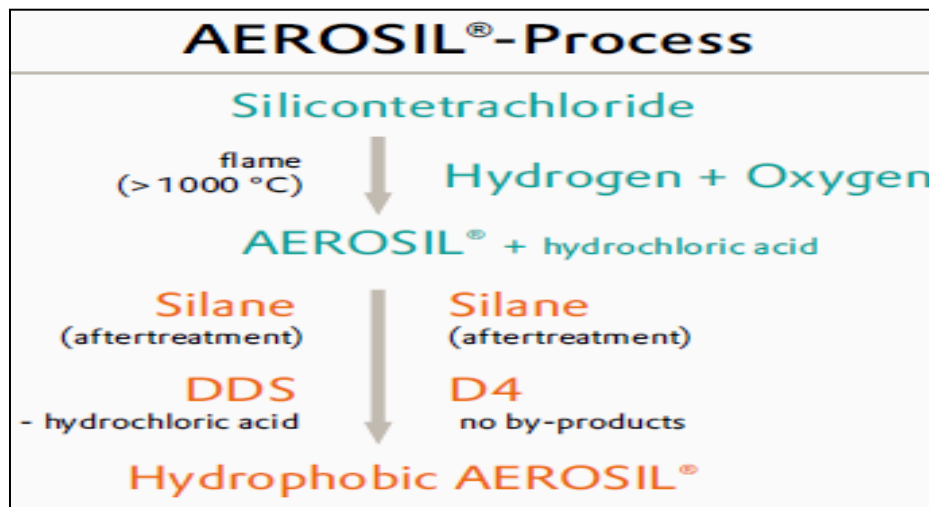


Figure 3.1: Silylation procedure of AEROSIL silica nanoparticles

Fig. 3.2 shows the effect of nanoparticles concentration on the stability to coalescence/sedimentation of the emulsions prepared using the three types of silica nanoparticles described in **Table 2.4**. The stability of the emulsions was assessed by measuring the amount of oil separating on top of each sample [49]. This definition of the stability of coalescence/sedimentation given by Binks is independent of the internal phase volume fraction (which in this case is the water phase volume fraction). Therefore, for all

samples prepared in this test, the Oil-Water-Ratio (OWR) was fixed and chosen arbitrarily as 80:20.

For HDK H20, a nanoparticles concentration of 2 wt.% was sufficient to generate well covered water droplets that did not show any sign of re-coalescence after homogenization. However, for both AEORSIL R104 and HDK H17, at least 5 wt.% were necessary to stabilize the same amount of water. This difference in nanoparticles concentrations between the various types of silica particles is due to the difference in wettability and particle size.

This was due to the fact that different Silane agents have different effects on the wettability of the particles. Thus, H20 which was treated with dimethyldichlorosilane showed a higher affinity to water than R104 which were treated with octamethylcyclotetrasiloxane.

Nonetheless, the relation between particles sizes and the stability of emulsions is not very well understood. Binks [49-50-80] have showed that smaller particles tend to adsorb less (having less adsorption energy) than larger particles, and therefore tend to form less stable emulsions. However, this comparison should be made on particles having different sizes but same shape and hydrophobicity. This complexity makes it difficult for one to assess the role of the surface quality of the particles as well as their sizes independently. Binks and Whitsby [80] have figured out that, via microscopy images, the range of droplets sizes observed in the emulsions does not appear to change with the particles diameters. Likewise, they stated that particles wettability does not change with the particles size for moderately large particles (>100nm).

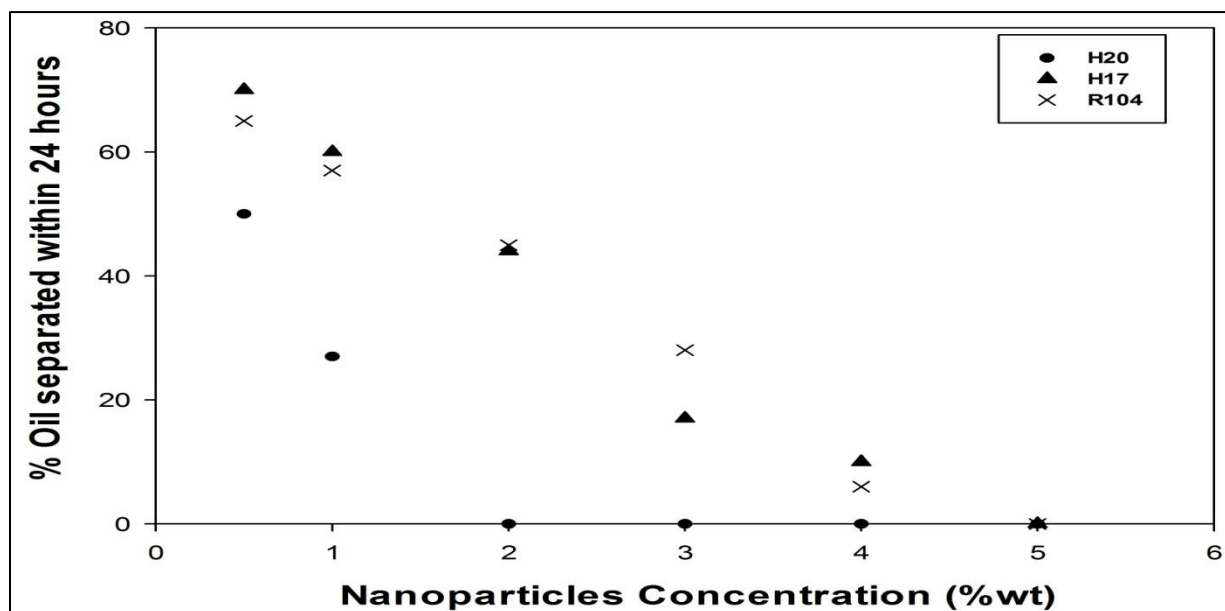


Figure 3.2: Effect of nanoparticles concentration on the stability to coalescence/sedimentation of the emulsions

On the other hand, since sedimentation velocity depends on both the emulsion drop size and the continuous phase (oil in this case) viscosity, it was clear that the systems showing no coalescence showed no droplet size evolution with time and were stable to coalescence for more than 12 months.

Thereafter, three emulsion systems were established and used for the rest of this work. For all emulsions prepared with HDK H20, 2 wt.% of colloidal particles were used. However, for both R104 and H17, a concentration of 5 wt.% was used instead.

Finally, all three established systems allowed the preparation of samples that showed very good emulsion stability to coalescence/sedimentation for more than 12 months.

3.2. Effect of Oil-Water-Ratio (OWR)

At different stages of the drilling operation and according to the drilled formation properties, a convenient drilling mud should be prepared. The OWR of the mud can significantly change the properties of the fluid especially when connate water invades the mud and get mixed with the fluid. Thus, the fluid should be prepared in a way as its

external composition is always able to withstand any excess of the internal phase.

Otherwise, some operations impose the dilution of the mud to change its density or its rheological properties. Such problems should be estimated at the beginning to avoid any destabilization of the mud and therefore a successful drilling operation.

Hence, a full characterization of the possibility of using Pickering emulsions for the preparation of drilling fluids imposes the study of the effect of varying the water phase volume fraction (ϕ_w).

The effect of the aqueous phase volume fraction variation was assessed by measuring the arithmetic mean particle diameter assuring a good packing of the particles at the oil/water interface ceasing any particles coalescence. As well as the electrical stability (conductivity) of the emulsions prepared, used to help determining the conductivity of the emulsions which is a tool for one to compare the effect of varying the water phase volume fraction on the properties of the emulsions [80]. The type of the emulsions was assessed by dispersing a droplet of each in either pure oil or pure water [49]. The emulsion is meant to be W/O (oil continuous) if the droplet disperses in oil and remains as a drop in water and vice-versa.

Fig. 3.3, showed that, for all systems, increasing ϕ_w lead to an increase in droplet sizes. That can be explained by the fact that decreasing the OWR (increasing ϕ_w), at a constant nanoparticles concentration (constant nanoparticles surface density) and a constant total interfacial area, will lead to an increase in the droplets sizes. This induces a lesser amount of nanoparticles at the oil-water interface which in return enhances the possibility of re-coalescence. However, not all systems have undergone the same changes. For R104, it was seen that the mean droplet diameter has increased from 1.83 μm to 3.95 μm at OWRs of 90:10 to 50:50 respectively, maintaining a W/O emulsion type even at an OWR of 50:50. Nonetheless, H17 particles followed the same trend with a higher increase in the droplet size especially at $0.4 \leq \phi_w \leq 0.5$, and the emulsions remained W/O. For HDK H20, at $0.1 \leq \phi_w \leq 0.2$, the droplet size did not change significantly. However, a

remarkable increase in the droplet mean diameter from 2.41 μm to 7.14 μm at $0.2 \leq \phi_w \leq 0.3$ was obtained. A further increase in the arithmetic mean droplets diameter was obtained for OWRs of 60:40 and 50:50. That was due to a catastrophic inversion that started around the OWR 70:30. Thus, emulsions prepared with HDK H20, at $\phi_w \geq 0.4$, were definitely O/W.

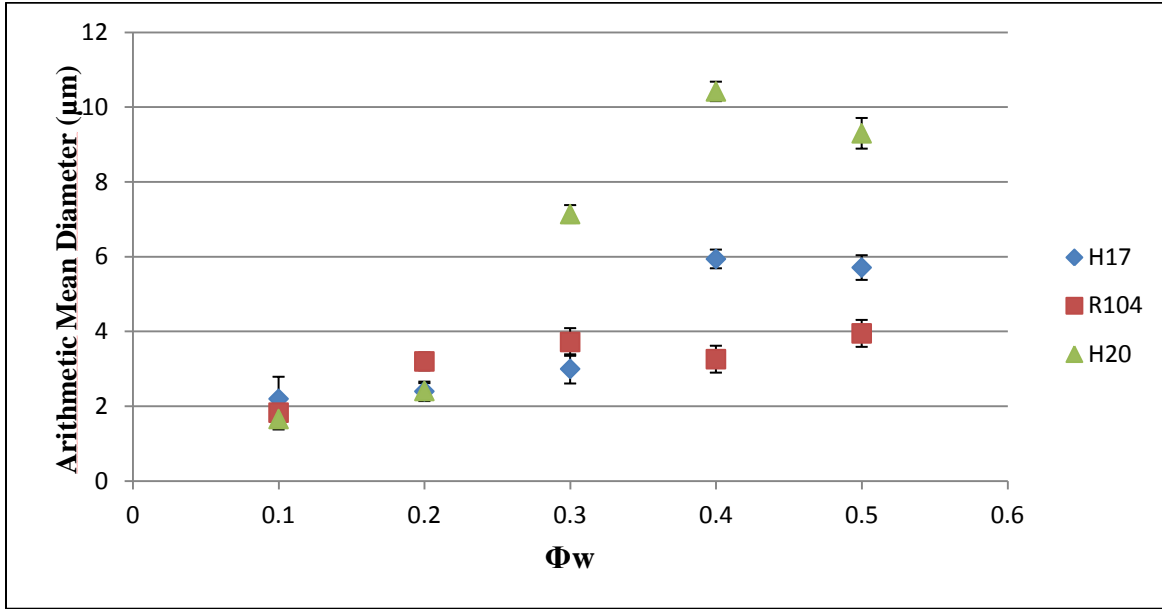


Figure 3.3: Variation of the arithmetic mean particle diameter with the water phase volume fraction for all three nanoparticles types.

However, at $0.3 \leq \phi_w \leq 0.4$, the emulsion was most likely to be oil-in-water-in-oil. Phase inversion occurs when the dispersed phase reaches the close-packed condition for sphere droplets which in our case occurred around an internal phase volume fraction of 0.3. This was in accordance with the results obtained by Binks and Lumsdon [50] that showed phase inversion occurring for nanoparticles of intermediate wettability upon increasing the water phase volume fraction.

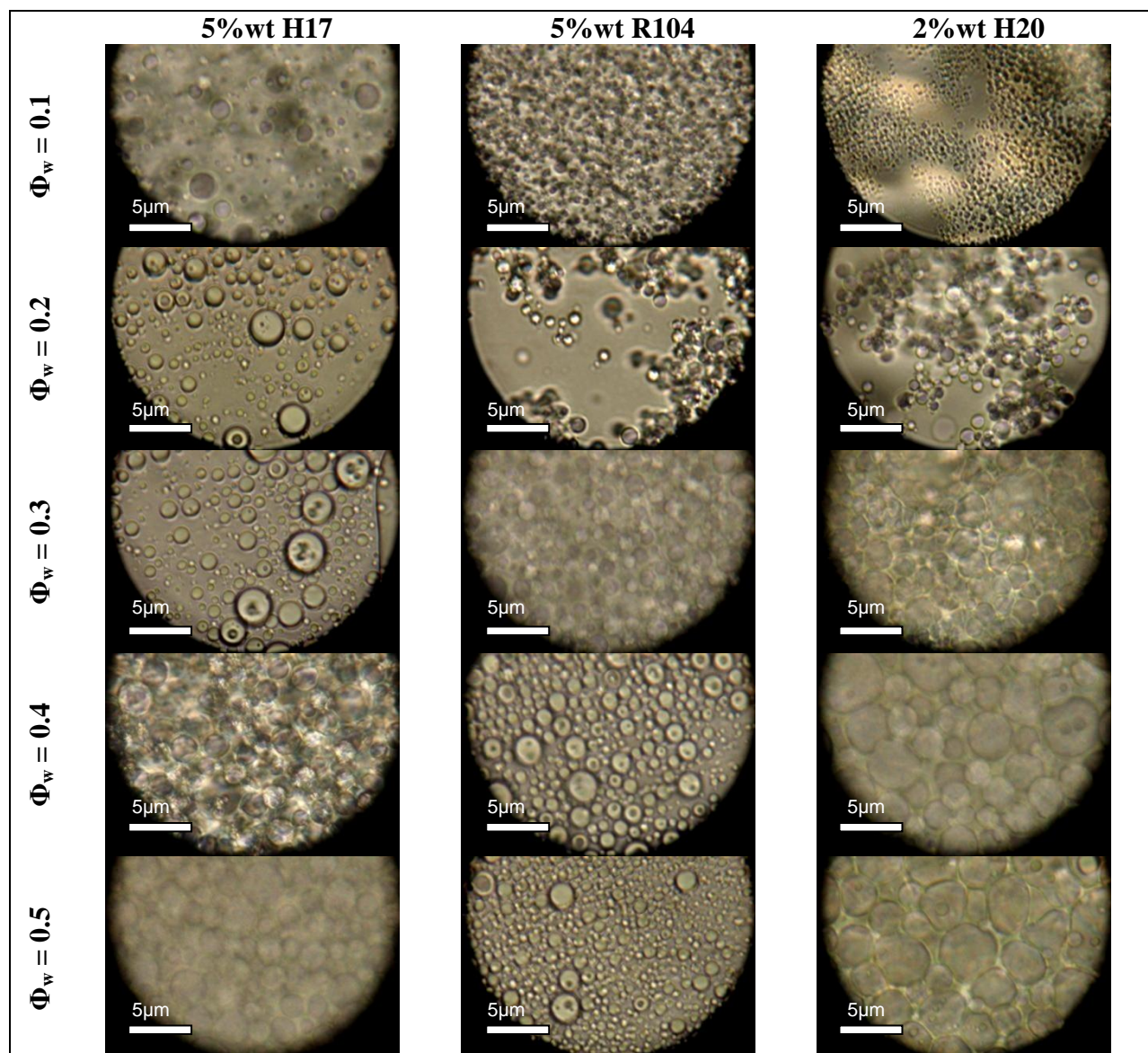


Figure 3.4: Effect of the OWR on the morphology of the emulsions

On the other hand, **Fig. 3.4** shows the microscopy images of the emulsions prepared at different OWRs. It is remarkable that an increase in the droplet sizes was obtained upon increasing the water volume fraction. Nonetheless, the particles are more compact which enhances the possibility of re-coalescence. However, it is clear that for the H20 particles, a significant increase in the droplets sizes was obtained at the ‘critical’ water volume fraction [50] at the limit of the catastrophic inversion ($\phi_w = 0.4$).

Another way for one to measure the stability of a W/O emulsion, is by measuring its conductivity. Generally, W/O emulsions are non-conductive emulsions for their oil continuous/external phase. The Electrical Stability (ES) measurements (**Fig. 3.5**) were in accordance with the results obtained in **Fig. 3.3**. A decrease in the ES stability was obtained while increasing ϕ_w . That was due to the formation of larger droplets allowing to easily forming bridges between the two electrodes giving lower electrical stability values. Hence, for both R104 and H17 particles, the stability of the emulsion decreased significantly while increasing the water fraction from 0.1 to 0.3.

However, for H17, the ES stability decreased from 1022 V at $\phi_w = 0.1$ to almost stabilize at 503.5 V at an OWR of 70:30.

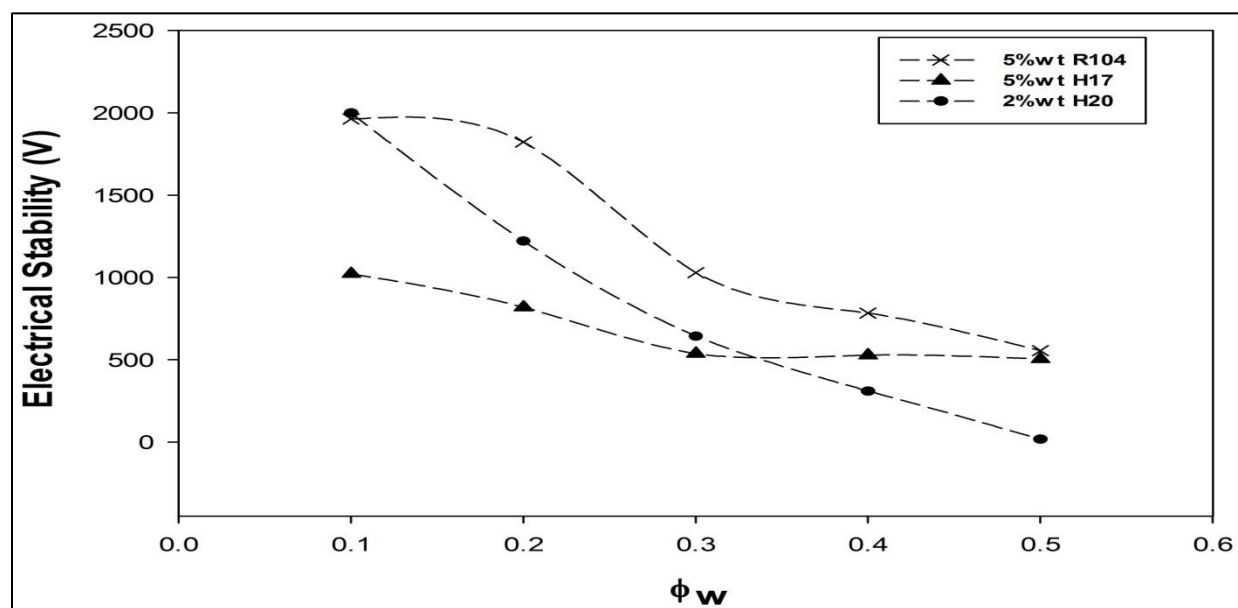


Figure 3.5: Effect of the water phase volume fraction on the electrical stability measurements

Nonetheless, for the HDK H20, it was seen that the ES values deteriorated rapidly from a value of 1999 V (maximum) at $\phi_w = 0.1$ to 8V at $\phi_w = 0.5$, assuring that a catastrophic inversion took place to form an oil-in-water (O/W) emulsion.

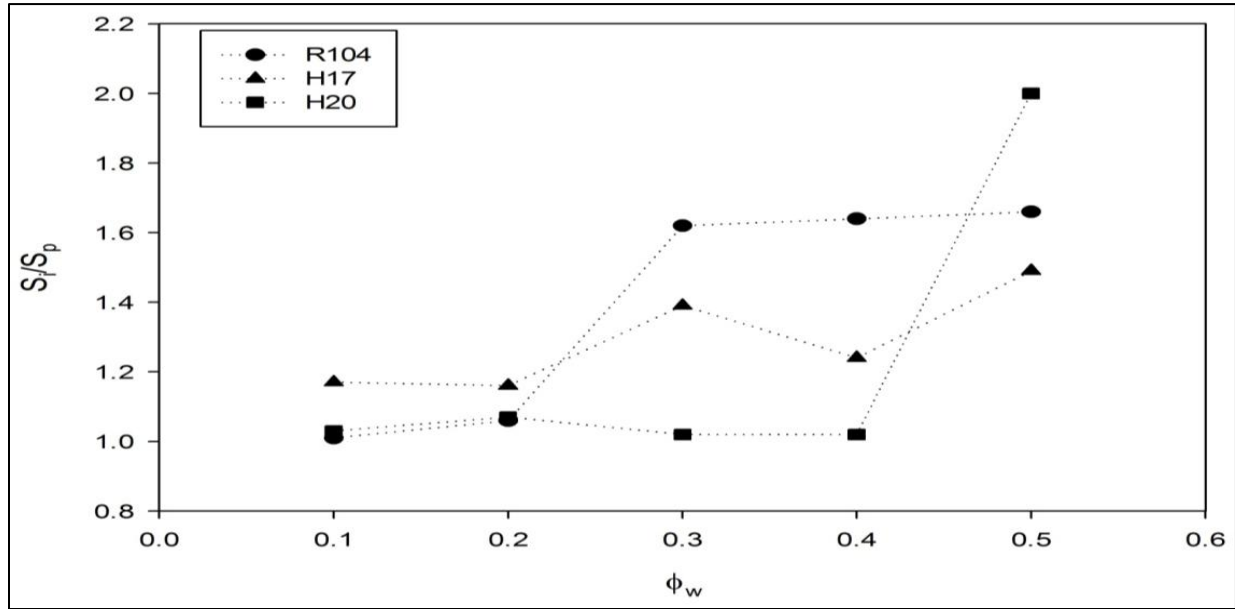


Figure 3.6: Emulsifying Properties of Silica nanoparticles

A simple technique allowing the estimation of the coverage rate of the droplets surfaces by the nanoparticles in function of the water phase volume fraction is based on the calculation of the ratio between the droplets surface area developed per unit volume of fluid (S_i) and the projected particle area (S_p). This technique will permit to evaluate the emulsifying properties of the nanoparticles compared to surfactants. In other words, if the S_i/S_p approaches unity, then good emulsifying properties are obtained and the nanoparticles can be considered to achieve almost the same functions as surfactants/emulsifiers used to stabilize the emulsions. If $S_i/S_p \gg 1$ there are not enough particles to play a significant role at the interface, and if $S_i/S_p \ll 1$ there is an excess of particles which means their main part is not located at the interface.

It should be noted that (S_i) was calculated based on the microscopy image treatment done using ImageJ software. However, S_p was calculated based on the TEM microscopy images of the nanoparticles and a mean particle diameter was estimated. **Fig. 3.6**,

presents the ratio S_i/S_p in function of the water phase volume fraction (ϕ_w). As clearly shown, H20 particles showed very good emulsifying properties with a ratio very close to unity for $\phi_w < 0.4$. However, it is clear that a sudden increase was obtained for $\phi_w > 0.4$ when a phase inversion of the emulsions occurred. For both H17 and R104 particles, it was seen that the ratio approached unity for water volume fraction less than 0.2. However, they did not have the same behavior as H20 particles where the ratio increased while increasing ϕ_w . Nonetheless, both types of particles still stabilized the emulsions prepared at all water volume fractions tested.

3.3. Effect of the Aqueous Phase Composition

3.3.a. Effect of pH of Water

Aside with the particles wettability and surface chemistry, the composition of the aqueous phase plays a very important role in the stabilization process of Pickering emulsions. Knowing that W/O and O/W emulsions react differently to the change in the water phase composition as in the former the water phase is dispersed inside the oil phase where the particles were initially dispersed. However, in the latter, the water phase constitutes the continuous main phase where the particles are more likely to get affected by any changes of the water phase composition. Therefore, this sub-section presents the results obtained for changing the pH of the water phase between 3.5, 5, 7, 10.5 and 12 before adding it to the oil continuous phase.

These results were interpreted in terms of electrical stability or conductivity of the emulsions for the possible effect of particles wettability changes and phase inversion as well as the morphology of these emulsions.

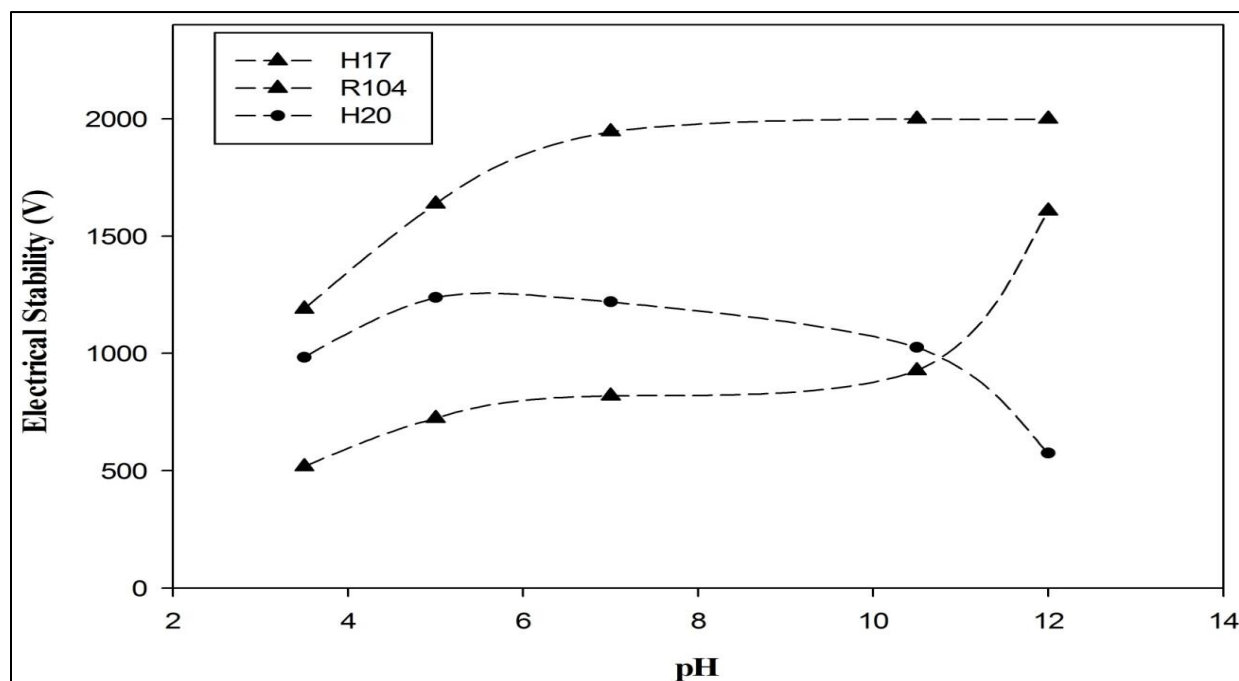


Figure 3.7: Effect of pH of the aqueous phase on the stability of the emulsions prepared

Firstly, the particles size distribution was presented through microscopic images taken for the emulsions prepared at different pH values. It should be noted that all emulsions in this sub-section were prepared with a constant OWR of 80:20.

Starting with HDK H20, increasing the pH from 3 to 7 enhanced the electrical stability of the emulsions prepared (**Fig. 3.7**). However, upon increasing the pH from neutral to 12, a decrease of the electrical stability of the emulsions with this type of nanoparticles was seen. That can be due to the increase in hydrophilicity of the particles which may cause the particles to be forced into the water phase at high pH. Nonetheless, this drastic change in the electrical stability measurement obtained with this system can be referred to irreversible surface reactions that took place at high pH values inducing their hydrophobicity. It should be noted that the charging behavior of the particles at the oil-water interface is still unclear and not very well understood [81-82].

On the other hand, HDK H17 and AEROSIL R104 did not have such behavior. For these types of nanoparticles, the electrical stability of the emulsions was enhanced while increasing the pH of water. This can be due to the decrease in the hydrophobicity of the particles, thus particles have a higher affinity to water, being responsible for an increasing of the adsorption rate at the oil-water interface. This was confirmed by the microscopy images presented in **Fig. 3.8** and was in accordance with the results obtained by Binks *et al.* [83] using fumed silica nanoparticles for particle-stabilized foams where they demonstrated the decrease of the contact angle of the silica particles with increased pH. This means that the particles are getting more hydrophilic while increasing the pH of the water phase.

Nonetheless, for very hydrophobic particles (such as H17), the hydroxyl groups of the silica surface may not be accessible due to shielding by the larger silane agent coating the particles [84]. For HDK H20 particles, for $3.5 \leq \text{pH} \leq 7$, the droplets sizes seem not to change. However, for $\text{pH} > 7$, particles tend to coalesce leading to the formation of larger droplets especially at $\text{pH} = 12$. For both AEROSIL R104 and HDK H17, an increase in the pH of the aqueous phase lead to a decrease in the particles size of the droplets enhancing at the same time the stability of the emulsions. It should be noted that coated hydrophobic silica particles are not dissolved even at high pH, although bare silica particles can dissolve at high pH.

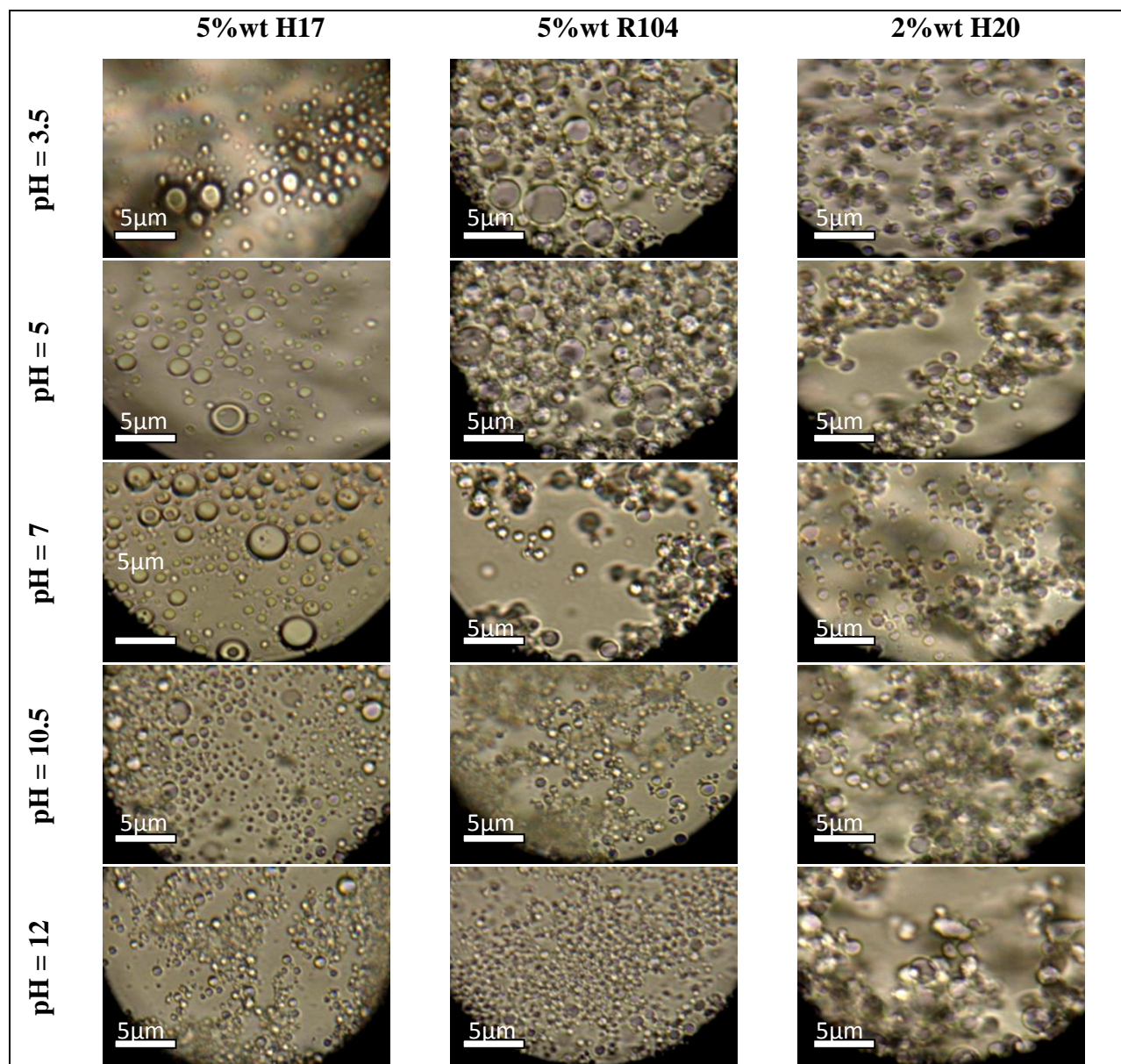


Figure 3.8: Effect of changing the pH of the aqueous phase

3.3.b. Effect of salt concentration

The importance of controlling the effects of the salinity of the water phase lies within the control of water activity when it gets in contact with shale or clay formations. Thus, salts reduce the ability of the active shale or clays to hydrate and swell. As described in the previous section, the effect of the salt concentration in W/O emulsions is very different than that in O/W emulsions for the difference in the continuous phase composition.

In this work the salt concentration was varied between 0, 5, 15 and 25 wt.% and the salt used was CaCl_2 as it is known for the preparation of the brine phase of Oil-Based-Mud (OBM). **Fig. 3.9** shows the effect of salt concentration on the conductivity of emulsions. This is related to the possibility that the added salt can change the charging of the particles and thus alter their wettability. All emulsions prepared at different salinities did not show any signs of destabilization. However, the decreasing conductivity obtained for all samples while increasing salt concentration, could be due to flocculation of the droplets which induces the formation of the bridge between the electrodes giving lower conductivity values.

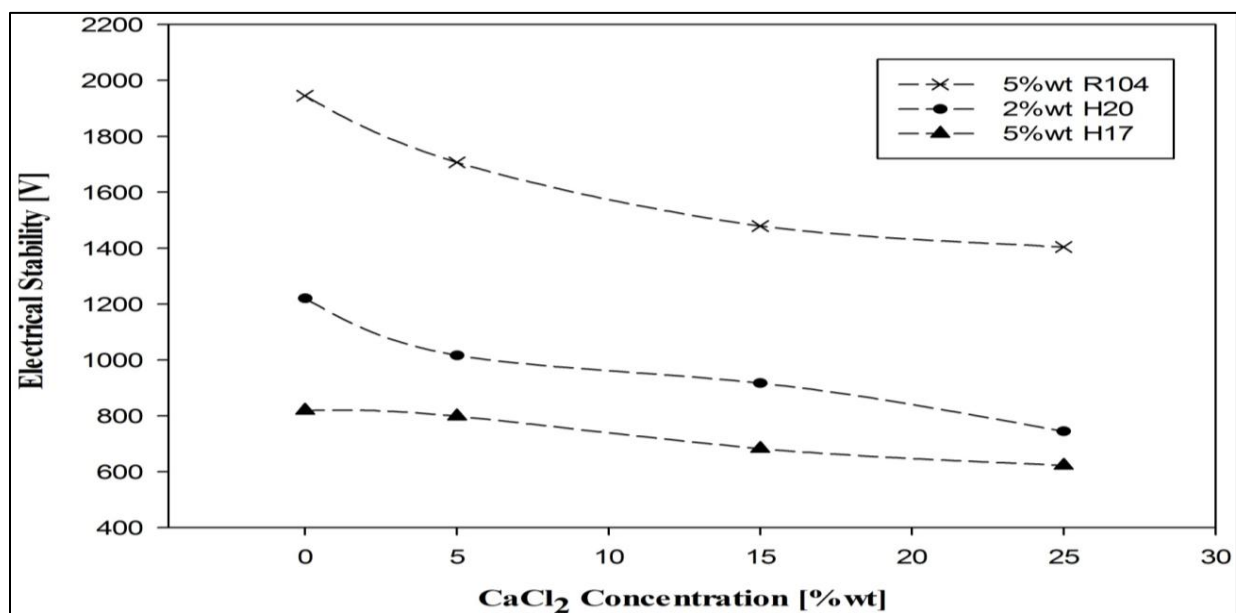


Figure 3.9: Effect of the salt concentration on the stability of the emulsions

Since silica particles are dispersed in the oil phase, therefore the effect of changing the salinity of the water phase is not significant to alter the properties of the emulsions. This is not the case for particles used to prepare WBM, where silica particles are dispersed in the water phase (see chapter 4).

Finally it is important to note that the time given for the interaction between the particles and the brine phase is an important factor that should be taken into consideration [85-86]. Therefore, the conductivity of all samples prepared with different salt concentrations were tested straight after preparation as well as after 48 hours and the conductivities of the emulsions remained the same with an error reaching a maximum of 3% (which lies in the acceptable error interval of electrical stability measurements of 5%). Finally, microscopy images have shown no effect on the droplets size distributions for all emulsions prepared at different salinity concentrations even after 48 hours.

3.4. Effect of the Oil Continuous Phase Composition

The composition of the oil continuous phase in OBMs is as important as that of the internal water phase. Many restrictions have been set by governments around the world for using some oils such as Diesel in some regions for environmental conditions. Therefore, the drilling companies have started to use different kinds of oils that are more environmentally friendly.

However, this change in oil composition can alter the stability and the properties of Pickering emulsions for its ability to affect the properties of the particles. Hence, three different oils (Diesel, Toluene and Amodrill 1100) were used to test the effect of changing the oil phase composition on the stability, morphology as well as rheology of Pickering emulsions. The choice of the oil phase was not based on the application of these oils in the drilling operation but on the effects that they can bring to the water-oil interface properties and thus the affinity of the particles at the interface which can alter the emulsions stability.

Table 3.1: Effect of the oil phase composition on the rheological properties of the samples prepared with the three types of silica particles

Samples	Amodrill-Based Mud [+ 2 wt.% H20]			Diesel-Based Mud [+ 2 wt.% H20]			Toluene-Based Mud [+ 2 wt.% H20]		
Rheological Properties	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]
	12.0	3.3	3.0	11.3	2.8	2.5	12.6	3.0	2.9
Samples	Amodrill-Based Mud [+ 5 wt.% H17]			Diesel-Based Mud [+ 5 wt.% H17]			Toluene-Based Mud [+ 5 wt.% H17]		
Rheological Properties	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]
	17.1	1.6	1.2	16.5	4.2	4.0	19.6	1.4	1.0
Samples	Amodrill-Based Mud [+ 5 wt.% R104]			Diesel-Based Mud [+ 5 wt.% R104]			Toluene-Based Mud [+ 5 wt.% R104]		
Rheological Properties	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]	PV [mPa.s]	YS [Pa]	τ_0 [Pa]
	18.5	3.3	2.7	17.5	3.6	2.8	13.4	2.5	2.1

All samples were prepared as described before. For a full characterization of the samples, the nanoparticles concentrations were varied for each of Diesel and Toluene as described in **Fig. 3.2** in a goal to test if changing the oil phase could change the nanoparticles concentration threshold necessary to stabilize the emulsions.

The primary results showed that for the three types of nanoparticles, no changes in the nanoparticles thresholds responsible for the stabilization of the emulsions prepared with different oil phases was obtained. Therefore, the oil phase did not have an effect on the adsorption of the nanoparticles at the oil-water interface.

On the other hand, many studies have been done on the effect of oil polarity on solid particles surfaces [50]. Binks et al. [80] have shown that addition of polar oils may affect the interaction between the polar species and the surface silanol groups of the particles. This property is of high importance for drilling operations, especially in the Enhanced Oil Recovery (EOR), as it represents the wettability of reservoir rocks changes by the adsorption of polar compounds present in polar oil phases. This is as well related to the particles wettability as demonstrated by Binks et al. [50-80] showing that particles of

intermediate wettability tend to form W/O emulsions with polar oils and O/W emulsions with non-polar oils.

Therefore, **Table 3.1** shows the rheological properties of the samples measured using both the Bingham (PV and YP) and Herschel-Bulkley (τ_0) models. It is clear that the results obtained were in accordance with the microscopic images shown in **Fig. 3.10**. For H20 particles, no significant changes in the rheological properties or the morphology were obtained after changing the oil phase. A slight decrease in the droplet size was seen with Diesel oil which did not affect the rheology. However, toluene gave the highest flow index of these particles of 0.9 indicating that the fluid approaches the Newtonian behavior, which is not recommended for drilling fluids.

On the other hand, for H17 particles, a great increase in the YP with Diesel was manifested with a large increase in the flow index as well to reach 0.9. The highly compacted emulsions obtained and seen in Fig. 3.10, gave these emulsions stability to coalescence up to 3 months before a slight oil phase appeared on top of the samples.

Finally, no coalescence was seen for R104 particles up to 6 months. However, toluene affected the droplet size distribution giving larger droplets decreasing by that the plastic viscosity of the fluids.

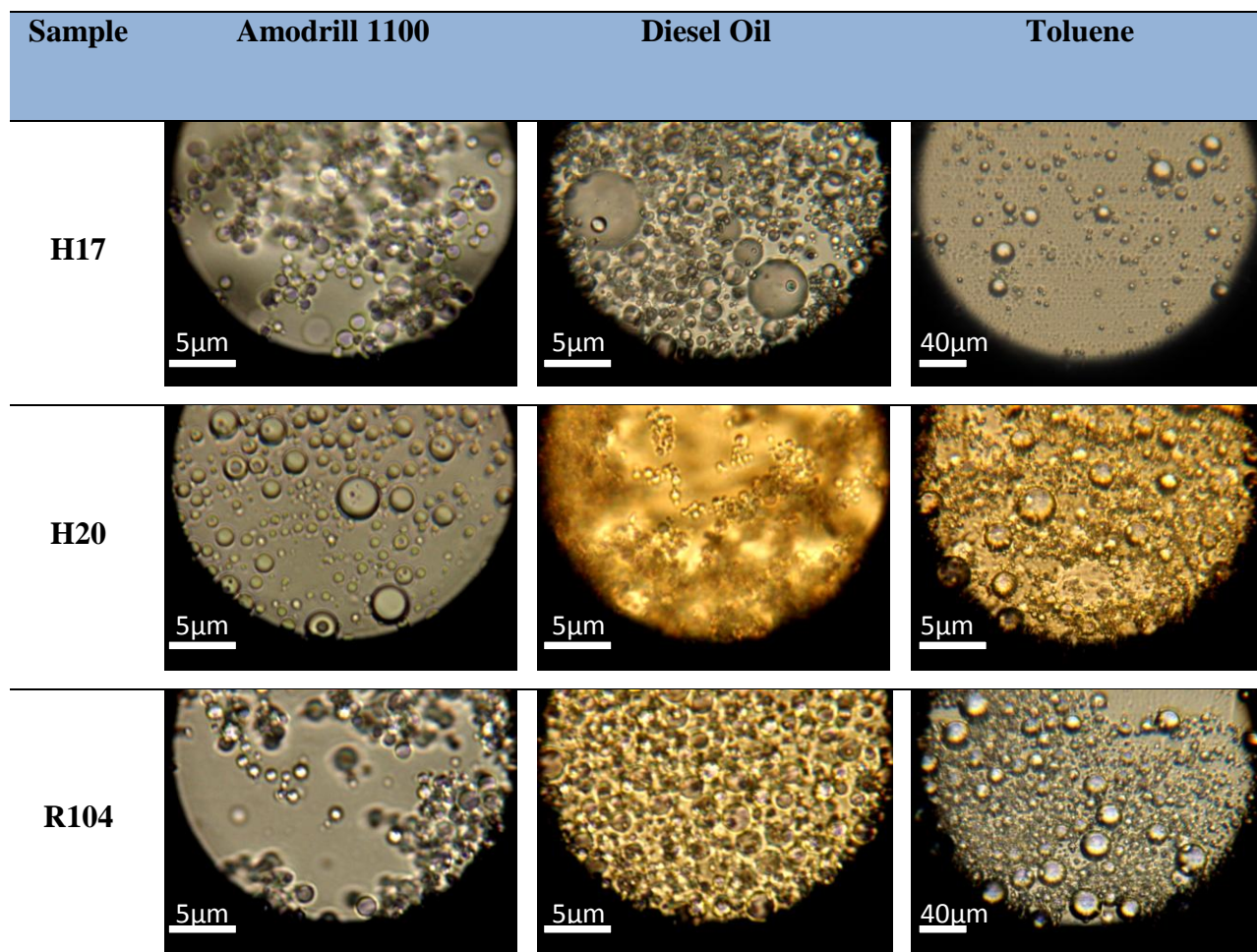


Figure 3.10: Effect of Oil phase composition on the morphology of the emulsions

Hence, the effect of changing the oil phase composition is of great importance as the type of oil used can alter the silanol groups present at the surface of the silica particles. This interaction gave rise to many rheological changes and affected at the same time the droplet size distribution of the fluids as well as their visco-elastic behavior. A clear vision of how the oil composition can alter the stability of the emulsions is not very well seen [80], however, it can be concluded that if the oil phase composition has to be changed, its effect on the particles wettability should be firstly tested.

3.5. Effect of Adding Clay Particles

Clay particles are usually added to drilling fluids for their ability to generate high gel-structures as well as thixotropic properties contributing into a better drilling operation (Rate-Of-Penetration [ROP], hole cleaning ...). This is due to their Cation-Exchange-Capacity (CEC), which allows them to hydrate (swell) when getting in contact with water. The hydration of clay particles is controlled by the type and amount of cations associated with them.

In this work, surface modified clay particles (ORS VIS), were added to each of the three systems already described before. Nonetheless, these systems were compared with surfactant-stabilized OBM and reported in terms of electrical stability as well as rheological properties.

Table 3.2 presents the electrical stability measurements showing the contribution of clay particles on the stability of the Pickering emulsions. It is clear that for all samples, a wide increase in the stability of the emulsions was obtained after addition of clay particles except for R104 that showed a slight decrease upon adding clay. Many works have been done on the use of clay particles for the stabilization of Pickering emulsions for their affinity to both phases (oil and water) with varying success [87-88]. This was due to the high interaction between clay particles and water on one side, and the uncontrollability of the accumulation of more clay particles from the formation which increases largely the yield stress causing flowability and pumping problems.

The enhancement of the stability of the prepared emulsions due to clay addition is related to two factors. The first is the increase of the oil continuous phase viscosity which decreases the sedimentation rate. The second is the ability of the clay particles to form a three-dimensional network enhancing the coating of the dispersed droplets, increasing by that the emulsions stability.

Therefore, measurement of the viscosity of the oil phase after addition of clay particles was mandatory. **Table 3.3** shows the variation of the viscosity for oil prepared with a mixture of the silica particles and the ORS VIS. For that, a fixed amount of nanoparticles (2 wt. %) was used for the three types of silica particles for one to assess the effect of the interaction between silica particles and the clay ones. The results obtained are very interesting as they show the effect of the interaction between nanoparticles and clay particles. This interaction is strongly related to the enhancement in the stability of the emulsions.

Table 3.2: Effect of addition of clay particles
on the electrical stability of the emulsions

Samples	ES (V)
2% wt H20	1120
5% wt R104	1945
5% wt H17	818
2% wt H20 + 2% wt ORS VIS	1626
5% wt R104 + 2% wt ORS VIS	1740
5% wt H17 + 2% wt ORS VIS	1494
Surfactant-Stabilized OBM + 2% wt ORS VIS	806

As aforementioned, two rheological models were used to measure the rheological properties of the fluids, the Bingham-Plastic (BP Model) and the Herschel-Bulkley (HB Model). The latter was more adapted and fitted better the flow curves obtained. However, it does not provide a simple measurement of the plastic viscosity, thus justifying the usage of the BP model.

On the other hand, this increase in the stability of the emulsions is reflected on the enhancement of the rheological properties of the samples. Hence, **Fig. 3.11** shows the flow curves (shear stress in function of shear rate) of all the samples prepared (with and

without clay particles).

Table 3.3: Effect of silica and clay particles interactions on rheology

Samples	PV [mPa.s]	YP [Pa]	τ_0 [Pa]	K	n
Oil + 2 wt.% H17 + 2 wt.% ORS VIS	9.80	2.70	2.30	0.06	0.73
Oil + 2 wt.% H20 + 2 wt.% ORS VIS	17.00	6.40	3.20	0.75	0.44
Oil + 2 wt.% R104 + 2 wt.% ORS VIS	8.50	2.10	1.60	0.06	0.70

To compare these results, the consistency and flow indices (k and n respectively) were given by the Herschel-Bulkley model. They can assess the degree of visco-elasticity of the fluids. It is clear, that H20, due to their intermediate wettability, gave the lowest flow index 'n' of 0.44, thus the highest visco-elastic behavior. This can be explained by the fact that if these particles were used, they have the tendency to give high rate-of-penetrations (ROPs) as well as high borehole cleaning and debris transport.

As it can be seen, all samples showed a good shear-thinning behavior as the viscosity decreased while increasing the shear rate. This behavior was complementary with the thixotropic properties measured. It was clear that the addition of clay particles highly increased the plastic viscosity and the thixotropic properties (yield point and gel strengths) of the samples. Note that for the preparation of the surfactant-stabilized OBM, the same amount of clay particles was used (2 wt.% ORS VIS).

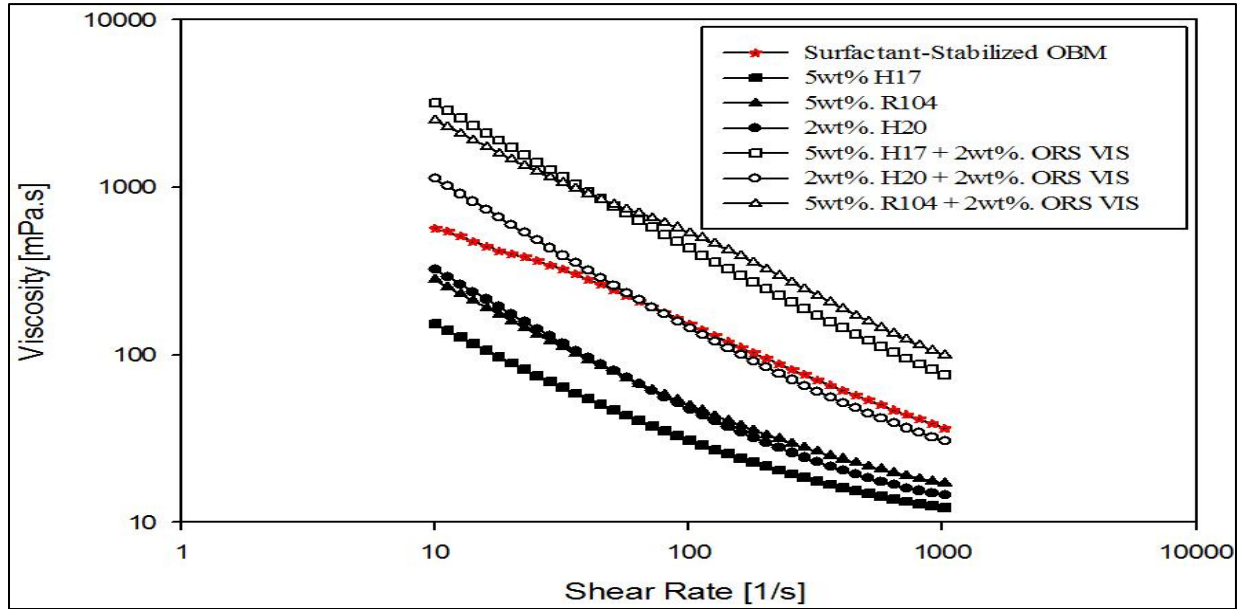


Figure 3.11: Flow curves of various samples prepared

Fig. 3.12 shows the visco-elastic properties of the samples before and after addition of clay particles. The crossover point of the G' and G'' curves gives the true yield point of each sample after the addition of 2 wt.% of ORS VIS clay particles.

This jump is very essential for the drilling operation as it improves the cleaning efficiency of the mud as well as the carrying capacity to hold the debris from the borehole to the surface.

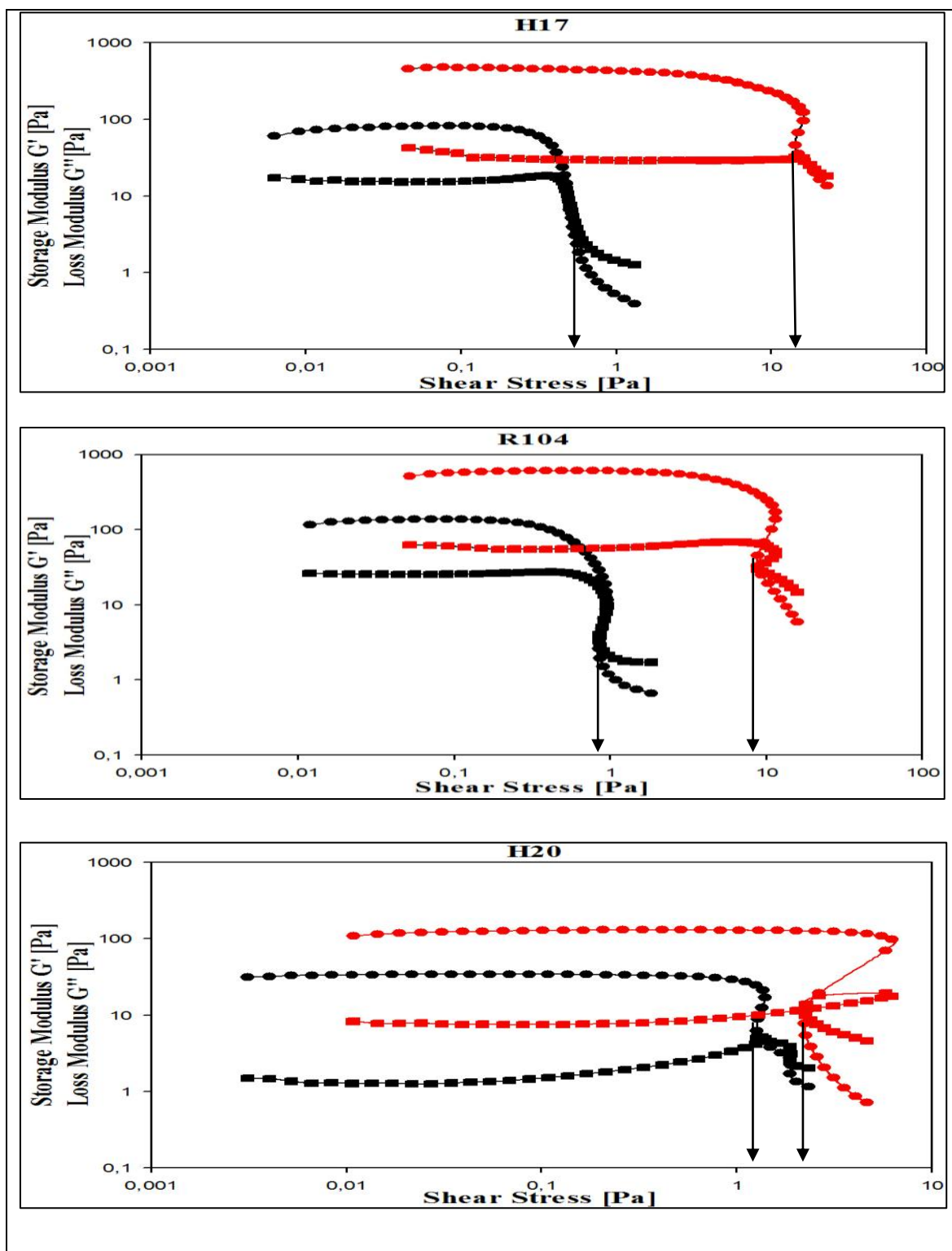


Figure 3.12: Effect of clay particles on the thixotropic properties of Pickering emulsions.
 a) H17 b) R104 and c) H20. Black plots are before clay addition and red ones are for after clay addition. Symbols are as follows: \bullet - G' and \blacksquare - G''

3.6. Effect of Aging

The challenge of synthesizing new drilling fluids lies in what these fluids can address as solutions to the actual existing market. Therefore, the focus was on searching to know what Pickering emulsions can offer to the drilling industry that current technologies cannot. Degradation of surfactants and polymer components used for the stabilization of drilling fluids is a big problematic that have prevented the exploration of deeper reservoirs or those that show hostile environmental conditions of high temperatures and pressures. Hence, the afore-prepared stable Pickering emulsions were passed through a static aging test at 350 °F (177 °C) and 500 psi (35 bars) for 16 hours. The electrical stability, morphology as well as the rheological properties of the samples were presented for tests done before/after aging and after re-homogenization. The results were presented in two sections (with and without clay particles), allowing one to compare the effect of clay on the aging process of the samples.

3.6.a. Without Clay Particles

Static aging of the samples is mandatory for the characterization of the muds. It doesn't consist in simulating the downhole conditions as much as it simulates the ability of the fluids to withstand severe environmental conditions during trapping/connections where no flow occurs.

Figs. 3.13 (a, b and c) show the flow curves (shear stress vs. shear rate) of the samples prepared without clay particles. The corresponding rheological properties were reported in **Table 3.4**. It should be noted that PV and YP are calculated using the BP-Model where τ_0 is calculated based on the HB-Model.

Table 3.4: Effect of aging on the rheological properties of samples prepared without clay particles.

Samples	2 wt.% H20			5 wt.% R104			5 wt.% H17		
	PV	YS	τ_0	PV	YS	τ_0	PV	YS	τ_0
Properties	[mPa.s]	[Pa]	[Pa]	[mPa.s]	[Pa]	[Pa]	[mPa.s]	[Pa]	[Pa]
Before Aging	12.0	3.3	3.0	18.5	3.3	2.7	17.1	1.6	1.2
After Aging	7.9	0.3	0.3	14.5	2.3	1.7	12.1	1.0	0.7
After ReMixing	10.3	1.0	0.7	16.2	3.0	2.4	12.2	1.1	0.7

For all samples tested, the plastic viscosity and the yield stress decreased after aging. However, emulsions prepared with H20 presented a big loss of their yield stress that could not be recovered even after re-homogenization.

This is supposed to be due to the effect of the high temperature applied on the hydrophobic silanol groups present at the surface of these particles deteriorating their ability to re-form their gel structure after aging. However, the other samples seemed to recover most of their properties after re-mixing of the emulsions.

Table 3.5: Effect of aging on the gel strength of the samples prepared without clay particles.

Samples	Before Aging		After Aging		After Re-Homogenization	
	Gel 10s	Gel 10min	Gel 10s	Gel 10min	Gel 10s	Gel 10min
2%wt H20	81.1	100.0	35.7	79.1	40.6	100.0
5%wt H17	69.1	100.0	48.5	98.9	64.2	100.0
5%wt R104	90.7	100.0	82.2	100.0	91.9	100.0

Regarding the gel structure of the fluids, **Table 3.5** presents the gel strength at 10 s and 10 min of all three samples. The aim of these measurements is to characterize the ability of the fluids to generate a strong gel strength that recuperates once the flow is ceased and breaks easily once a shear stress is applied. It is remarkable that the gel strength of the

samples prepared with H₂O deteriorated after aging from 81.1 % to 35.7 % (for the gel 10 s) and did not recover completely to reach 40.6 % after re-homogenization.

These are in accordance with the yield stress measurements described in **Table 3.4**, which shows additional reasoning of the effect of temperature on the inter-particle interactions after aging. However, all samples completely recovered their gel structure after 10 minutes after re-homogenization of the emulsions.

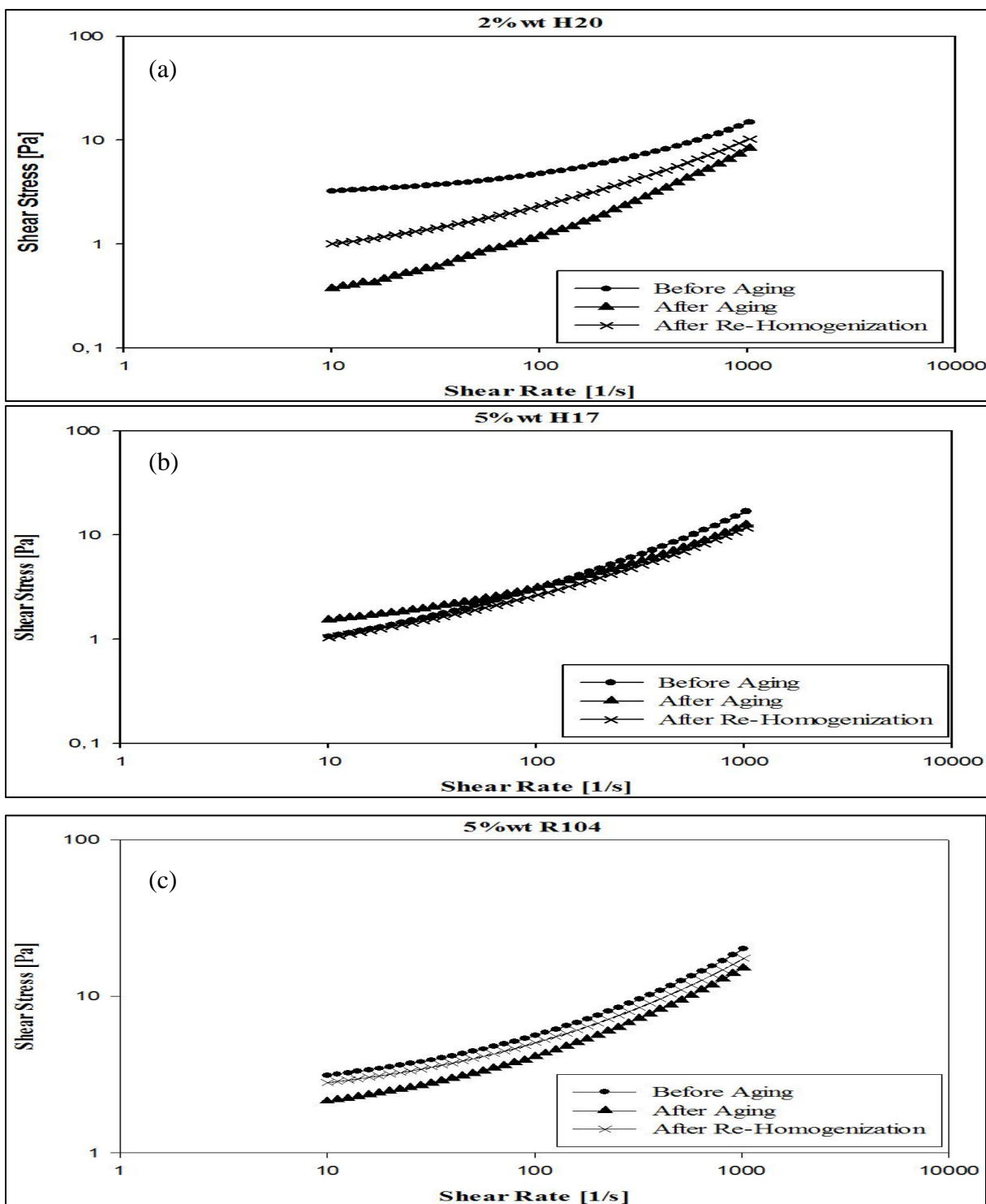


Figure 3.13: Flow curves of all samples prepared without clay particles showing the effect of aging and remixing on the rheological properties.
 (a) 2 wt.% H2O (b) 5 wt.% H17 and (c) 5 wt.% R104.

3.6.b. With Clay Particles

The effect of adding clay particles on the rheological properties of the emulsions was already seen in **Fig. 3.10**. Hence, the effect of aging on rheology as well as the electrical stability and the morphology of these emulsions were reported.

Table 3.6 shows the effect of aging on the rheological properties of samples prepared with clay particles. The existence of clay particles enhanced the recovery of the structures of the emulsions especially that of the gel strength measured and reported in **Table 3.7**.

Table 3.6: Rheology of samples prepared with clay particles before/after aging and after re-homogenization.

Samples	2 wt.% H20			5 wt.% R104			5 wt.% H17		
	+ ORS VIS			+ ORS VIS			+ ORS VIS		
Rheological Properties	PV	YS	τ_0	PV	YS	τ_0	PV	YS	τ_0
	[mPa.s]	[Pa]	[Pa]	[mPa.s]	[Pa]	[Pa]	[mPa.s]	[Pa]	[Pa]
Before Aging	24.7	11.8	10.7	69.7	47.0	37.3	60.2	35.3	25.7
After Aging	15.9	6.5	5.7	47.8	23.3	13.1	45.9	15.6	8.5
After Re-Mixing	21.2	9.2	9.0	67.4	30.9	19.9	50.8	19.1	8.8

On the other hand, the surfactant-stabilized OBM separated completely after aging and did not re-emulsify even after mixing. This is related to the degradation of the surfactants at high temperatures which could not recover their emulsifying properties even after re-homogenization.

Nevertheless, the electrical stability of these emulsions was measured and compared before/after aging and after re-homogenization (**Table 3.8**). It can be clearly seen that a decrease in the electrical stability is obtained after aging for all samples.

Table 3.7: Effect of adding clay on the rheological properties of the samples before/after aging and after re-homogenization.

Samples	Before Aging		After Aging		After Re-Homogenization	
Gel Strength (%)	Gel 10s	Gel 10min	Gel 10s	Gel 10min	Gel 10s	Gel 10min
2 wt.% H2O + 2 wt.% ORS VIS	100.0	100.0	81.9	100.0	97.3	100.0
5 wt.% H17 + 2 wt.% ORS VIS	100.0	100.0	90.0	100.0	98.5	100.0
5 wt.% R104 + 2 wt.% ORS VIS	100.0	100.0	89.1	100.0	100.0	100.0

However, after re-homogenization, most of the samples recovered most of their initial stability where the surfactant-stabilized OBM failed completely after aging.

The variations in the rheological properties are related as well to the variation in the morphology of the emulsions due to the aging process. Therefore, microscopy images (**Fig. 3.14**) showed clearly the effect of aging on the droplet size distribution of samples prepared without clay particles. Nevertheless, **Table 3.9** shows the effect temperature aging on the mean droplet diameter. It should be noted that those prepared with clay particles could not be analyzed through microscopy because of the high compacted dense emulsions obtained.

Aging lead to an increase in the droplet size distribution of the emulsions, which manifested in the loss in rheological properties as well as electrical stability. Nonetheless, emulsions did not show any sign of instability or phase separation after aging and a simple re-homogenization of the samples was sufficient to recover the initial droplets sizes.

This recovering ability of these fluids is very important while drilling, as it offers many advantages such as less fluid treatments which means less chemicals used. These fluids can be used to drill many wells for their ability to conserve their properties with time and even after aging, etc ...

Table 3.8: Effect of Aging on the electrical stability of samples prepared with and without clay particles compared to surfactant stabilized OBM.

Samples	Before Aging	After Aging	After Re-Homogenization
2 wt.% H20	1120	943	1065
5 wt.% R104	1945	1231	1606
5 wt.% H17	818	372	687
2 wt.% H20	1626	841	1158
+ 2 wt.% ORS VIS			
5 wt.% R104	1740	1146	1432
+ 2 wt.% ORS VIS			
5 wt.% H17	1494	1019	1237
+ 2 wt.% ORS VIS			
Surfactant-Stabilized OBM	806	Emulsions Phase Separation	Emulsions Phase Separation

A complete characterization of the fluids requires one to show how these fluids will perform while circulating into a hostile environment. In other words, the flow behavior of these fluids at high temperatures and high pressures was mandatory for a complementary characterization of their ability to replace surfactant-stabilized muds.

Table 3.9: Effect of Aging on the Mean Particle Diameter [μm] of the samples prepared

Samples	Before Aging	After Aging	After Re-Homogenization
AEROSIL R104	3.2 ± 1	4.2 ± 1	3.7 ± 1
HDK H17	2.4 ± 1	9.2 ± 1	3.0 ± 1
HDK H20	2.4 ± 1	3.2 ± 1	2.8 ± 1

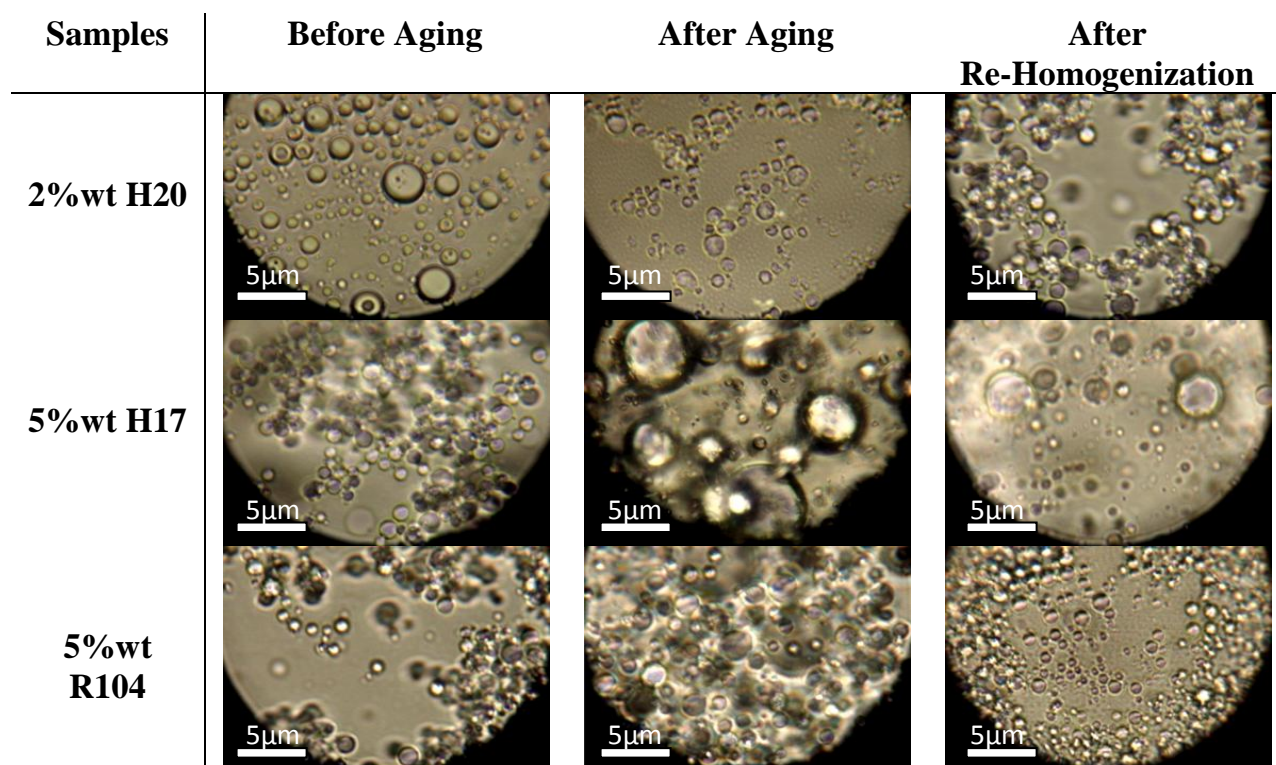


Figure 3.14: Morphology of the emulsions of all samples (without clay particles) before and after aging as well as after re-homogenization.

3.7. High-Temperature/High-Pressure Rheology

E&P activity increasingly involves operations in high-pressure, high-temperature downhole conditions. This environment introduces difficult technical concerns throughout the life of a well. Scientists and engineers are developing advanced tools, materials and chemical products to address these challenges [89].

Although HPHT wells are fundamentally constructed, stimulated, produced and monitored in a manner similar to wells with less-demanding conditions, the HPHT environment limits the range of available materials and technologies to exploit these reservoirs. However, there are no industry-wide standards that define HPHT conditions and the associated interrelationship between temperature and pressure. Schlumberger uses guidelines that organize HPHT wells into three categories chosen according to technology thresholds (**Fig. 3.15**).

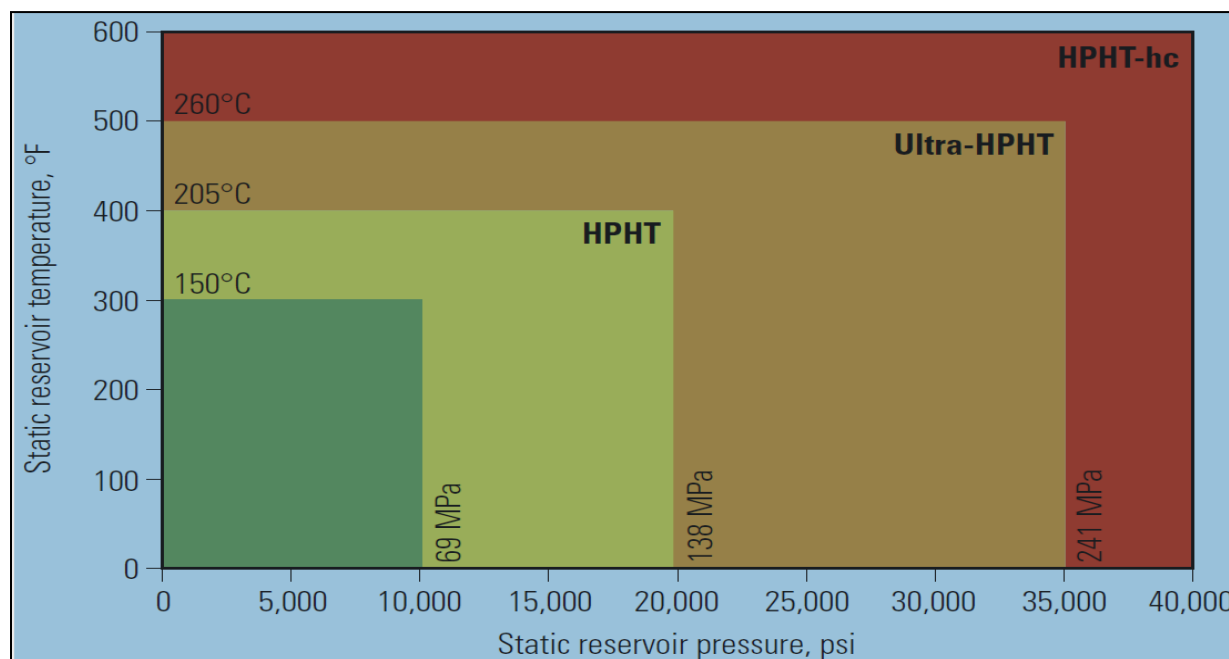


Figure 3.15: HPHT Classification System limits for well-service-tool components devices

However, these thresholds are not unique and are not equally applied to all oil wells, therefore many oil drilling companies have defined HPHT wells as if either temperature or pressure meets the HPHT condition the project counts as a HPHT [90].

Hence, this sub-section presents the rheological properties of the aforementioned drilling fluids measured at various temperatures and pressures covering a wide range of reservoir depths. At first, many works have been done for the characterization of the behavior of drilling fluids at HPHT conditions [91-98]. However, no works were published showing the effect of these hostile environmental conditions on drilling fluids stabilized with solid particles.

Likewise, the effect of temperature and pressure on the rheological properties of the fluids is not the same. An example shown in **Fig. 3.16**, shows the variation of the viscosity of the fluid prepared with H2O particles with temperature and pressure. It is seen that upon increasing the pressure by a factor of 60 (from 1 bar to 60 bars) the viscosity of the fluid decreased from 17 cP to 14.5 cP. This loss of 15% of the viscosity due to this great increase of the pressure can be neglected in the drilling operation as this

can happen due to dilution or fluid loss. However, increasing the temperature from 20 °C to 100 °C, lead to a loss of almost 60% of the initial measured viscosity which, if happened during drilling, can cause production inhibition.

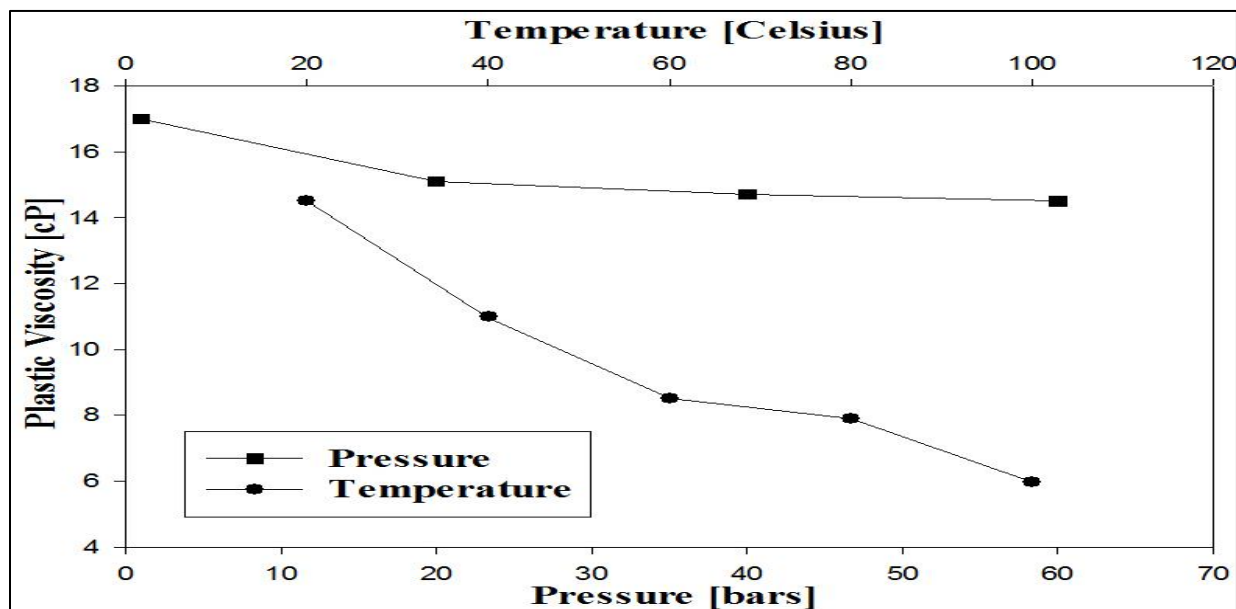


Figure 3.16: Comparison of the effect of the temperature and pressure on the plastic viscosity of samples prepared with H2O

Therefore, for the characterization of the samples at different HPHT conditions, a protocol had to be set respecting the limitations of the equipments used. Regarding the fact that the effect of pressure is so much less than that of the temperature, the pressure in the rheometer cell was fixed at 75 bars (1071 psi) and the temperature of the samples was varied between 20 °C (68 °F) and 180 °C (350 °F). The pressure was chosen in order to respect the phase diagram of water to avoid any phase changes of the internal phase of the emulsions. On the other hand, according to the Schlumberger diagram shown in **Fig. 3.15**, the measurements done in this work lie at the limit of the HPHT and ultra-HPHT zones.

The effect of temperature and pressure on the properties of drilling fluids does not summarize in the stability of the fluids under these conditions but exceeds to reach the ability of these fluids to address their main functions. The muds getting in contact with the formation, should address an ability to transfer cuttings up to the surface, maintain formation stability, avoid non-productive time (NPT), increase the Rate-of-Penetration (ROP), avoid barite sag especially in deviated wells, etc ...

Pressure and pressure variation have only a slight effect on rheological properties of fluids. Emphasis is placed on the influence of temperature on the rheological properties of drilling fluids. Thus, **Fig. 3.17** shows the effect of temperature on the plastic viscosity and the yield stress measured with the Bingham Plastic model at a constant pressure of 75 bars.

It is clear that for all samples the viscosity of the fluids decreased with increasing temperature. However, it should be noted that all Pickering emulsions prepared with silica nanoparticles were prepared without clay particles where the surfactant-stabilized samples had clay particles in their structures. That explains why the surfactant-stabilized fluids had higher plastic viscosity and yield stress than those prepared with H17 and H20.

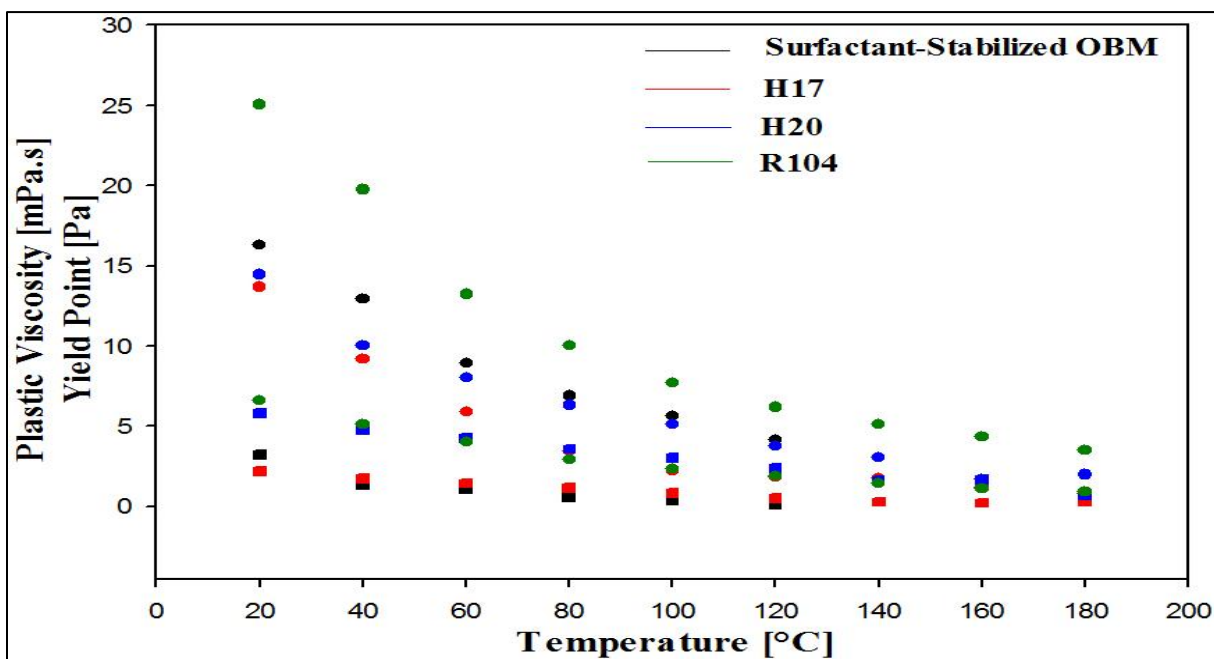


Figure 3.17: Effect of temperature on the rheology of drilling fluids
 -●- Plastic Viscosity and -■- Yield Stress

On the other hand, at temperature as high as 140 °C (284 °F), the surfactant tend to degrade and a phase separation occurred in the fluids (**Fig. 3.18**) that gave rise to hysteresis in the rheological profile of these fluids. However, all samples prepared with silica nanoparticles remained stable and their properties were reported as shown in **Fig. 3.17**. It is important to note that R104 gave the highest rheological properties among all samples where the yield stress of the H20 sample showed a slight increase at 180 °C (356 °F). This can be due to the affection of the particles surfaces at this temperature, giving higher particles interactions and thus a higher yield point.



Figure 3.18: Surfactant-Stabilized drilling fluid after rheology measurement at 140 °C (284 °F) (samples prepared with an OWR 80:20, 2 wt.% primary emulsifier, 2 wt.% secondary emulsifier, lime, and 2 wt.% ORS VIS clay particles)

However, **Fig. 3.19** shows the rheology of samples prepared with clay particles at various temperatures compared with the surfactant-stabilized OBM.

A simple comparison between the samples prepared with and without clay particles show clearly the effect of the visco-elasticity created by the clay particles. It is clear that these particles can highly alter the rheological properties at high-temperature and high-pressure of the samples. However, if one compares the behavior of the surfactant stabilized OBM with both samples (with and without clay), a simple remark can be made considering the effect of the interaction between the silica and the clay particles. As seen in **Fig. 3.17**, Pickering emulsions prepared without clay particles showed twice the losses of those prepared with clay particles.

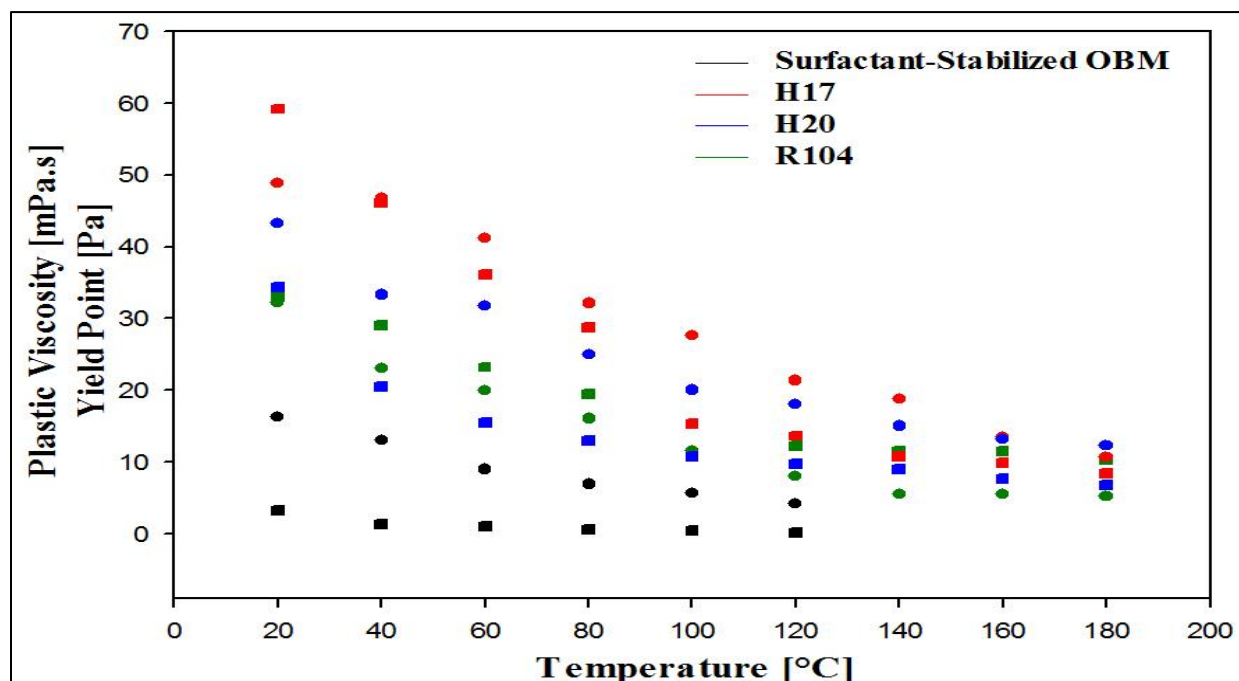


Figure 3.19: Effect of temperature on samples prepared with clay particles

-●- Plastic Viscosity and -■- Yield Stress

Samples shown in **Fig. 3.19** are of high importance for the drilling operation as the fluids (apart from the R104) conserved a plastic viscosity higher than 10 mPa.s even at temperatures as high as 180 °C (356 °F). However, with the R104 particles, they exhibited yield points as high as 10 Pa at 180 °C (356 °F). This reflects a high tendency of borehole cleaning and debris transport, two main problems faced with the surfactant-stabilized muds which impose the use of high solid contents. On the other hand, all samples prepared with the three types of silica nanoparticles showed a high stability to coalescence sedimentation even after being exposed to high temperature and pressure. Contrary to the surfactant stabilized mud that wasn't reliable at temperatures above 140 °C (284 °F).

Conclusion

This chapter presented the results obtained for the preparation of a new generation of drilling fluids based on the principle of Pickering emulsions. Thus, many fluids were prepared using three types of silica nanoparticles of various sizes and hydrophobicity. It was seen that 2 wt.% of HDK H20 were enough to stabilize W/O emulsions however 5 wt.% for each of HDK H17 and AEROSIL R104 were necessary to give such stability.

Firstly, fluids prepared with three different types of silica nanoparticles were able to remain stable for more than 12 months. Thus, HDK H20 conserved an mean droplet diameter of 2.4 μm where H17 generated a droplets of 2.4 μm diameter and R104 generated slightly larger droplets of 3.2 μm in diameter.

Depending on the particles wettability (HDK H20 and AEROSIL R104 were 50% grafted with Polymethylsiloxo and octamethylcyclotetrasiloxane respectively, where HDK H17 were 20% grafted with dimethyldichlorosilane), the fluids showed high reliability to be used in various environments via changing their water phase volume fraction (ϕ_w) or what is called their OWR. The fluids showed high affinity to changing their internal structure, however, samples prepared with HDK H20 showed a catastrophic inversion at OWRs around 60:40. This property confirms the fact that these fluids are able to be used in different drilling environments where the dilution of the fluids is necessary to adapt to the drilling conditions.

The composition of the internal water phase (pH and salt) was modified in order to assess the effect on the particles wettability and thus the stability of the fluids. It was seen that changing the pH of the emulsions did affect the particles wettability by creating flocculation inside the emulsions. However, the fluids remained stable and no phase separation occurred. On the other hand the salt concentration of the brine phase was changed by adding CaCl_2 salt. The addition of salt did not affect the stability of the

OBMs and that could be due to the fact that nanoparticles are dispersed in the continuous oil phase and their contact with water is limited to by their degree of wettability.

The oil phase composition showed an important property to be tested as well for the possibility of changing the oil phase while drilling for mechanical or environmental conditions. Therefore, three different oils were tested (Amodrill 1100, Diesel and Toluene), and their effect on the stability as well as the droplet size distribution and the rheology of the fluids were examined. It was seen that particles wettability and the inter-particles interactions can be altered by the oil phase composition (especially for H20 and H17) due to its effect on the silanol groups present at the surface of the silica particles.

The aforementioned prepared fluids were thereafter statically aged at 350 °F (177 °C) and 500 psi (35 bars) for 16 hours. They showed great stability after aging and they were able to regenerate their rheological properties after a simple re-homogenization. All three types of silica nanoparticles were able to recuperate 100% of their gel structure after 10 minutes. However, the H20 particles showed the least recuperation at 10 seconds.

Finally, an estimation of the performance of these fluids under deep and ultra-deep reservoir conditions was made through HTHP rheology measurements. Compared with the surfactant-stabilized OBM, these fluids showed a significant improvement of drilling mud performance under such hostile conditions thanks to their high plastic viscosity and yield stress measured at high temperatures. Adding clay particles to the drilling fluids had a great impact on their ability to conserve high rheological properties (especially high yield stresses at various temperatures), which is extremely important for borehole cleaning as well as formation stability (debris carrying capacity and filtration loss control) under such extreme downhole conditions.

Chapter 4 Pickering Water-Based Drilling Fluids

Introduction

Environmental considerations have led to increasing interest in the use of water-based drilling fluids in applications where oil-based fluids have previously been preferred. In Europe, for example, where environmental regulations prohibit the use of oil-based mud, wells are drilled with water-based fluids.

Thus, this chapter presents the results obtained for the preparation of O/W Pickering emulsions that are used afterwards for the preparation of Water-Based-Mud (WBM). It is divided into three main sub-sections:

The first presents the stabilization procedure of these emulsions using three different types of hydrophilic silica nanoparticles. Then the Oil-Water-Ratio (OWR) of the emulsions was changed from 10:90 to 50:50 (vol:vol) and the stability to coalescence/creaming was tested. Microscopy images as well as the means droplets size diameters were reported as well.

The second sub-section presents the effect of the water phase composition (pH and salt type and concentration) on the stability as well as the rheology of the emulsions for one to assess the possibility of using such fluids in the Enhanced-Oil-Recovery (EOR) field.

Finally, the effect of adding clay/bentonite to the fluids was investigated and reported in terms of rheology. Thereafter, the possibility of using such fluids in hostile environments of temperature and pressure was reported where the rheology of the emulsions was assessed in function of the temperature variation (from 20 °C [68 °F] to 180 °C [356 °F]).

4.1. Stability of Pickering WBM

As described in the previous chapter, the stability of Pickering emulsions is simply tested via the capacity of the nanoparticles used to adsorb at the water-oil interface to form a protective skin around each dispersed droplet. This definition imposes the characterization of the effect of changing the nanoparticles concentration so that a threshold of particles is detected capable of stabilizing the emulsions against creaming/sedimentation and/or coalescence.

In this chapter, oil-in-water (O/W) emulsions were prepared using hydrophilic silica nanoparticles of different types. The properties of these particles were already presented in **Table 2.5**.

4.1.a. Effect of particle size and wettability

Hydrophilic silica nanoparticles tend to stabilize O/W emulsions for their high affinity to the water phase and little affinity to oil [31]. Considering the difference in density between water and oil, creaming is much more probable to occur in such emulsions. This phenomenon is manifested by the appearance of a clear/whitish water phase at the bottom of the vessel and a cream layer on top of it representing the oil droplets accumulating on top of the emulsion (**Fig. 4.1**). This is of course an undesirable property showing the instability of the emulsions. This is affected by many properties, mainly the wettability of the particles responsible of stabilizing the emulsions. Bare silica nanoparticles are known

to be very hydrophilic and thus they do not disperse in the oil phase. Therefore, while preparing the emulsions, the silica nanoparticles in this section, were dispersed at first in the water phase before adding oil to it. The amount/concentration of nanoparticles was calculated based on the water phase fraction used. For this sub-section, the Oil-Water-Ratio (OWR) was chosen arbitrarily as 20:80 and the nanoparticles concentrations were varied between 0.5 wt.% to 15 wt.%.

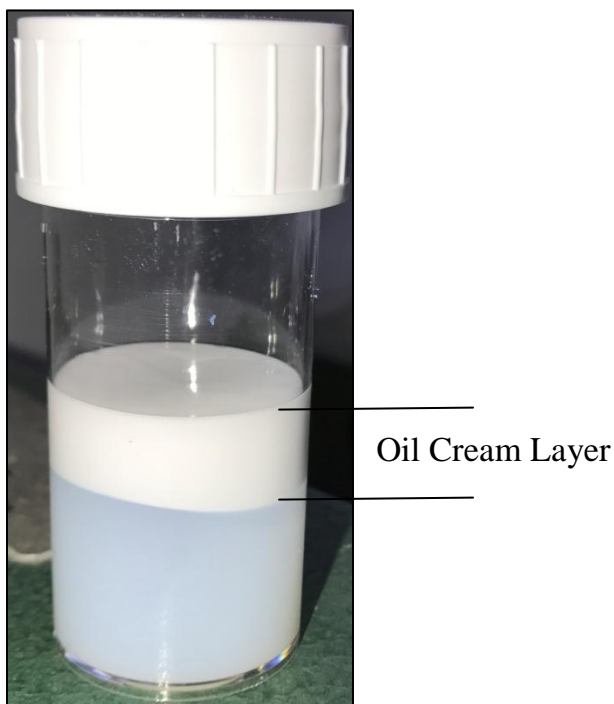


Figure 4.1: Creaming phenomenon of oil on top of an O/W emulsion (sample prepared with 15 wt.% AEROSIL 130)

Fig. 4.2 shows the effect of changing the nanoparticles concentration on the stability to creaming/sedimentation of the oil-in-water emulsions prepared in this work. This was manifested by the measurement of the water volume fraction separating on the bottom of the vessels within 24 hours. As mentioned in the previous chapter, samples not able to stabilize the emulsions for at least 24 hours, are not considered good candidates to be used in the preparation of drilling fluids.

It is seen that for AEROSIL OX50, we were not able to stabilize the emulsions. The nanoparticles seemed to stay dispersed in the water phase with a layer of oil on top of the

emulsions even at concentrations as high as 15 wt.%. That could be related to the high hydrophilicity of the particles as well as their very low surface area that forced them to stay dispersed in the water phase and not adsorb at the oil-water interface [99]. **Fig. 4.3** shows the oil phase separating on top of the emulsion with the particles dispersed in the water phase.

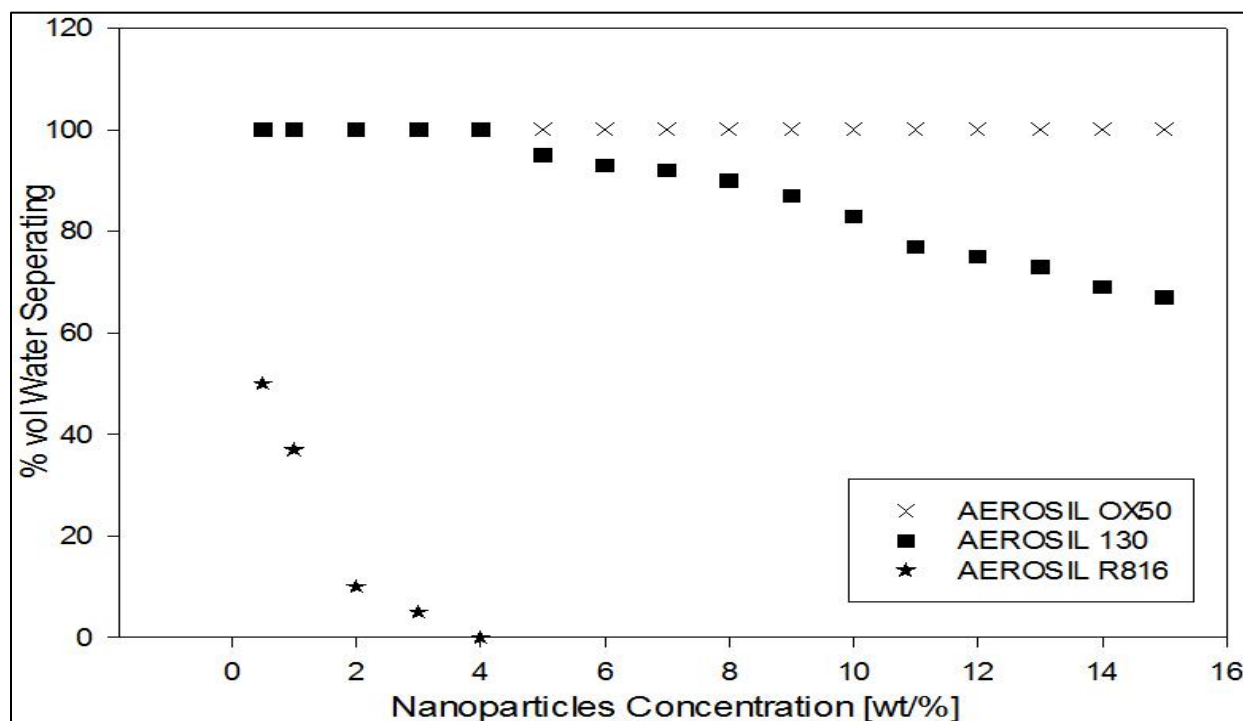


Figure 4.2: Effect of nanoparticles concentration on the stability of O/W emulsions prepared after 24 hours

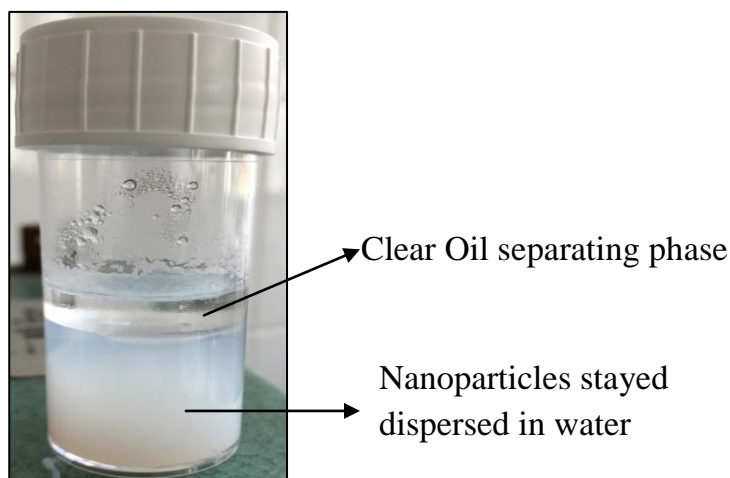


Figure 4.3: Destabilization of an emulsions prepared with 15 wt.% of AEROSIL OX 50 with an OWR of 20:80.

However, AEROSIL 130 particles were able to emulsify the oil volume fraction (0.2 in this case) but were not stable to creaming. Therefore, a layer of cream was formed on top of the emulsions even at 15 wt.% particles concentrations (**Fig 4.1**). This phenomenon has to be avoided in the drilling industry as the fluids cannot address their whole functions as they tend to lose their properties (viscosity change, loss in yield stresses and gel structure, etc ...). These results obtained with very hydrophilic nanoparticles, were in accordance with those from Binks and Lumsdon [49] for bare silica nanoparticles. It should be noted that using this types of particles (AEROSIL 130) showed a very good stability to coalescence (no signs of coalescence occurred in the cream layer for more than 18 months). **Figs. 4.4** shows the microscopy images of the oil droplets in the cream layer of the emulsions prepared with 15 wt.% of AEROSIL 130 at an OWR of 20:80, straight after preparation (**Fig. 4.4.a**) and after 18 months (**Fig. 4.4.b**). Therefore the particles were able to tightly cover the oil surfaces however not able to prevent creaming.

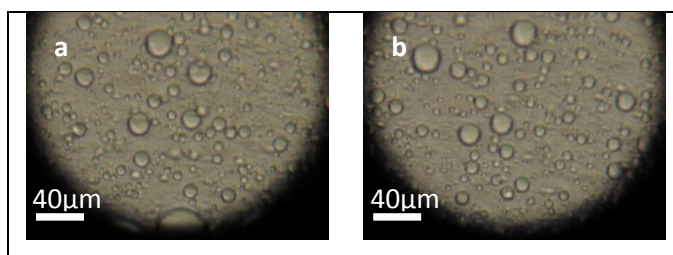


Figure 4.4: Morphology of O/W emulsions prepared with 15 wt.% AEROSIL 130
(a) 24 hours after preparation (b) after 18 months

On the other hand, AEROSIL R816 treated silica particles showed very promising results compared with the other nanoparticles. R816 were able to fully stabilize the emulsions at concentrations of 4 wt.% (**Fig.4.2**) against creaming and coalescence. These particles were able to stabilize the emulsions for more than 18 months.

Fig. 4.5, shows the effect of the variation of the nanoparticles concentration between 0.5 wt.% and 4 wt.% on the morphology of the emulsions prepared with AEROSIL R816. It is seen that with increasing the nanoparticles concentration the droplet sizes decreases.

This is due to the higher adsorption of the nanoparticles at the oil-water interface which decreases the possibility of coalescence. At a concentration of 4 wt.%, stable emulsions (up to 18 months) were formed showing no sign of coalescence or creaming/sedimentation.

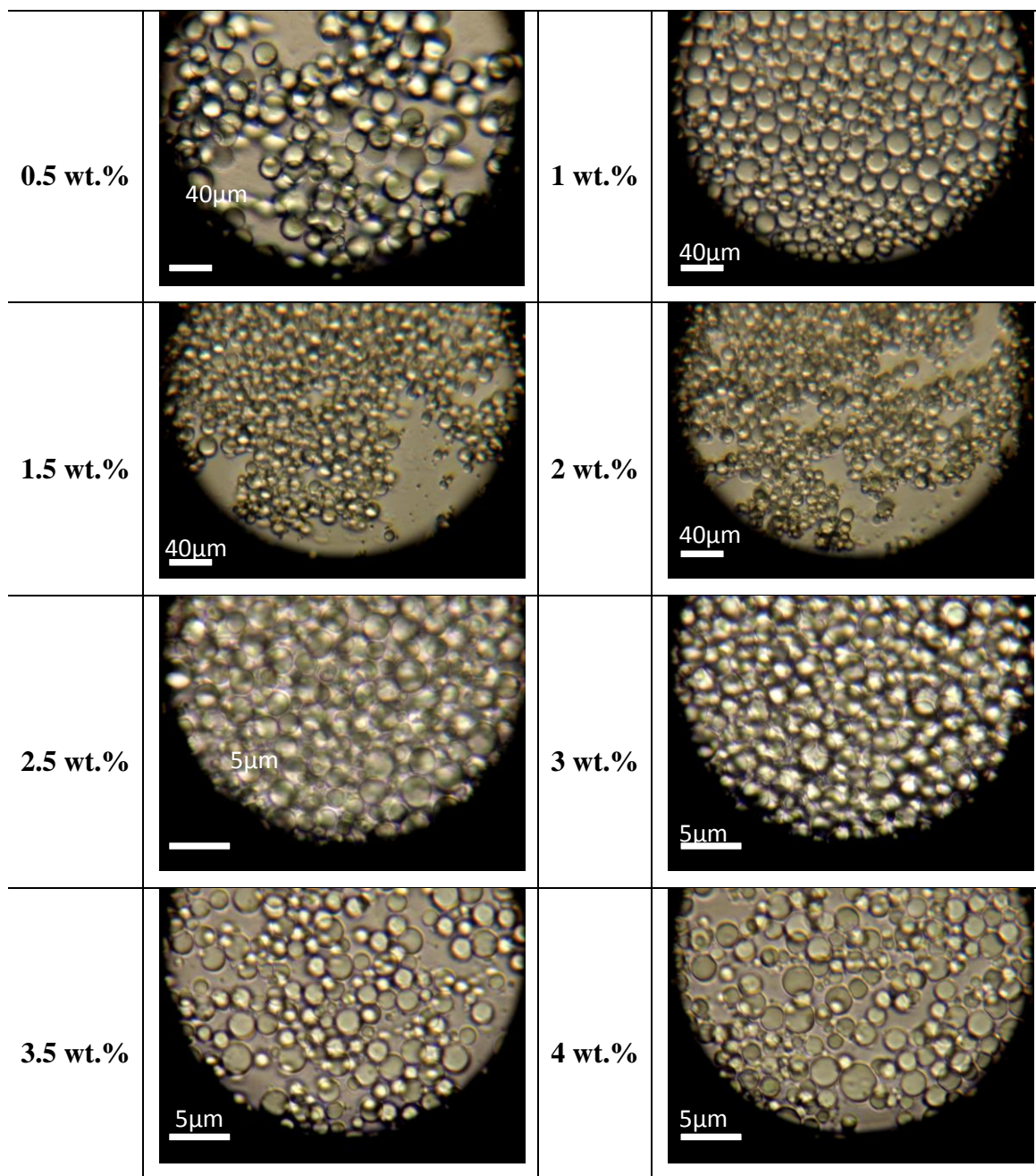


Figure 4.5: Variation of the droplet size distribution of the emulsions in function of the nanoparticles concentration of AEROSIL R816

Thereafter, for the rest of this chapter, all Pickering O/W drilling fluids tested, were prepared with 4 wt.% AEROSIL R816 silica nanoparticles.

4.1.b. Effect of OWR

In this section, for the R816 sample, the OWR was varied between 10:90 to 50:50 conserving a constant nanoparticles concentration of 4 wt.%. The stability of the emulsions was once again assessed by the volume of water sediment on the bottom of the samples. **Fig. 4.6** shows the morphology of the emulsions prepared at various oil fractions. These were accompanied with images treatment (**Fig. 4.7**) giving the variation of the mean droplets diameter in function of the oil volume fraction used.

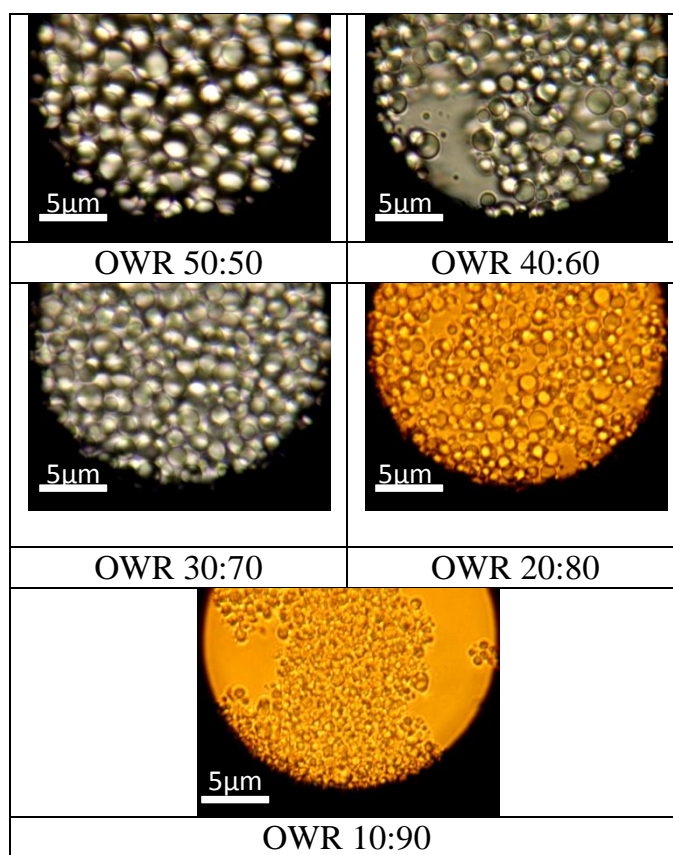


Figure 4.6: Effect of OWR on the morphology of O/W Pickering WBM

An increase in the droplets size distribution was obtained while increasing the oil volume fraction which may be related to the distribution of the R816 particles at the droplets surface (interface). Since the silica nanoparticles concentration is fixed at 4 wt.%, larger

droplets have to be formed to keep the same value of the total interface area (i.e. to keep the interfacial energy at a supposed minimum), as long as there are enough nanoparticles to cover the interface. If we suppose a constant surface density of the nanoparticles at the oil/water droplet interface, the total oil volume writes

$$V_o = \text{OWR} \times V_{\text{total}} = n V_{\text{drop}} \quad (\text{IV.1})$$

Whereas the interface area writes

$$S_i = n \cdot S_{\text{drop}} \quad (\text{IV.2})$$

Therefore

$$S_i/V_{\text{total}} = \text{OWR} \times (S_{\text{drop}}/V_{\text{drop}}) = \text{OWR} \times 6/d \quad (\text{IV.3})$$

In other words, there is an equivalence between a constant interface area and a proportionality law between OWR and droplet size. This law is clearly verified in our case over the whole oil fraction range considered as seen in **Fig 4.7**.

From the slope we can deduce the interface area per unit volume: $S_i/V_{\text{total}} = 420 \text{ m}^2/\text{L}$.

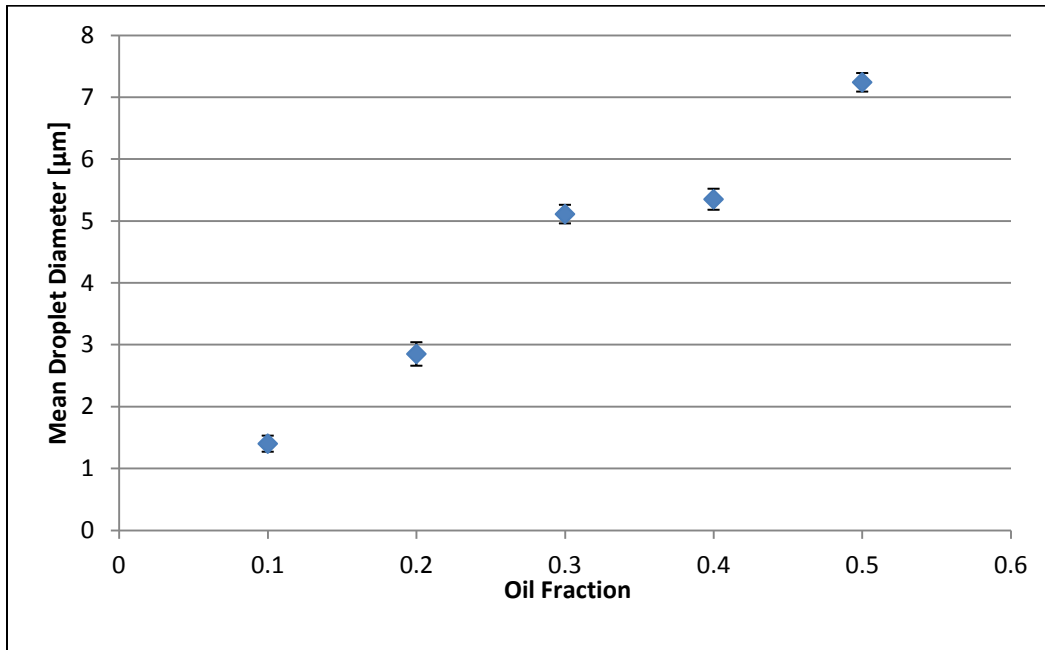


Figure 4.7: Effect of the OWR on the mean droplets diameter

Water-based drilling fluids constitute the future of the drilling industry. At first, they are environmentally friendly, which is a big advantage allowing them to be used in various drilling environments. Nonetheless, they are cheap and easily recycled, therefore, very attractive products for the oil and gas companies. On the other hand, these fluids have suffered with many difficulties including high contact with clay and shale formations, fragility to changes in temperature and pressure conditions and so on [100-107]. Nevertheless, it is very well known that the productivity of a petroleum reservoir is a big problematic for the drilling companies. 67% of the petroleum discovered remains in place for the lack of advanced technologies that can permit the extraction of higher amount of oil and gas. Enhanced-oil recovery represents a major field of development nowadays for the increase in energy demand. Many techniques have been involved for the extraction of high amount of petroleum (CO₂ injection, steam injection, reservoir heating, etc ...) [108-110]. The aim of all these techniques is to changing the interactions between the rock surfaces and the petroleum phase, thus, to be able to carry a higher amount of petroleum to the surface.

Nanoparticles have been very good candidates for EOR [111-122]. However, this field has not been fairly explored. Therefore, the ability of the already prepared O/W emulsions with AEROSIL R816 to hold oil concentrations up to 50% of their total volume fraction give them the advantage to be considered as very good candidates for EOR operations.

However, many other characterizations must be done as typical oil reservoir conditions with various pHs, electrolytes concentration and high temperature modifies the way that nanoparticles interact with the solution. Therefore, the effect of changing the properties of the water continuous phase was mandatory.

4.2. Water Phase composition

4.2.a. Effect of pH of water

Since hydrophilic silica nanoparticles responsible of the stabilization of O/W emulsions are dispersed in the water phase, thus, the effect of changing the aqueous phase composition is of a huge importance as it might affect directly the behavior of the particles at the interface.

Many works have been done to study the effect of pH and salt on the stability of emulsions [123-127]. Depending on the nanoparticles types and surface configuration as well as the type of ions used, a change in the nanoparticles behavior at the oil-water interface (change in hydrophobicity, phase inversion, etc ...) was observed.

Therefore, the pH of the water phase was changed from 1 to 13, for emulsions prepared with all four hydrophilic silica nanoparticles. The effect of changing the pH was reported in terms of the percentage of the water sediments at the bottom of the emulsions as well as the droplets size distribution.

WBMs are sensitive fluids that alter a big interaction between the continuous water phase and the formation. Shale formations are sometimes drilled with WBMs where the control of pH is of a high importance to inhibit any shale swelling or further fracturing of the formation. Nonetheless, WBMs getting in contact with acid gases might highly contribute in the destabilization of these fluids leading to big changes in their rheological properties (viscosity, flowability, gel structure, etc ...), hence, destabilization of the whole drilling operation.

Hence, starting with AEROSIL R816, **Fig. 4.8** shows the variation of the volume fraction of water sediment in function of the pH of the emulsions prepared. It is clear that once the water phase is in the alkaline zone, a destabilization of the emulsions occurs. This is due to the high charge of the silica surfaces at high pH values which increases the

hydrophilicity of the particles to force them to stay in the water phase and not adsorb at the oil-water interface.

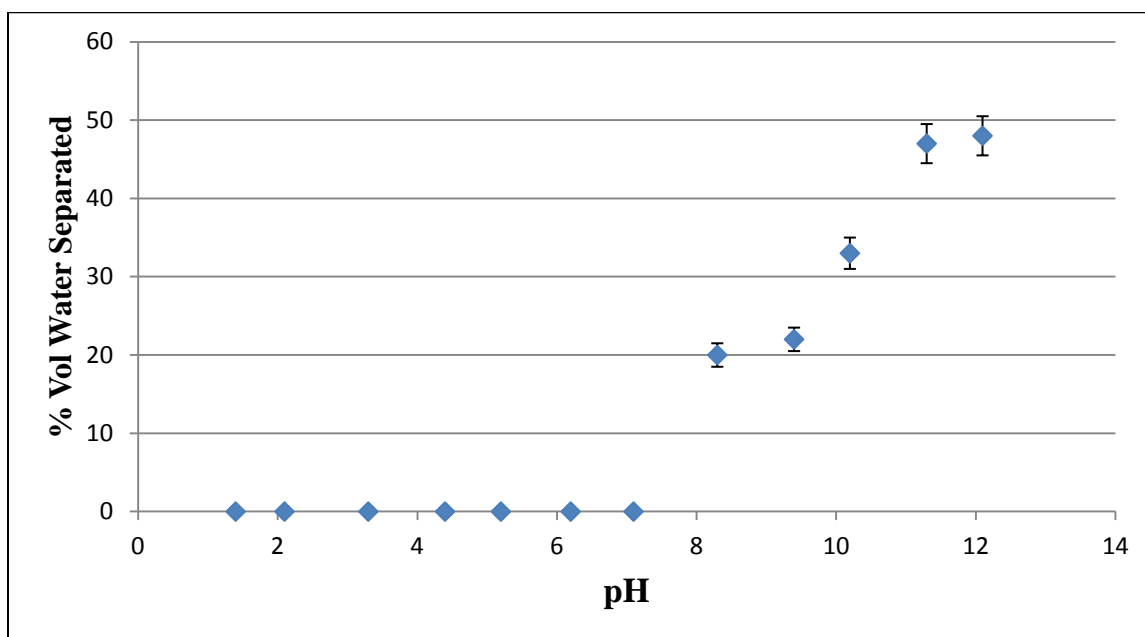


Figure 4.8: Effect of pH on the stability of O/W Pickering WBM prepared using the AEROSIL R816 silica nanoparticles

Fig. 4.9, shows the samples prepared with AEROSIL R816 at different pH of the water phase accompanied with microscopy images presented in **Fig 4.10**. What can be clearly stated is that once getting farther from the neutral pH zone ($\text{pH} = 7.1$), the droplets sizes largely increase to reach a plateau at a certain value.

For $\text{pH} < 7$, it can be seen that the droplets sizes slightly change for pH values going from 1.4 to 5.2. At $\text{pH} = 6.2$, an increase of the droplets size was obtained to reach almost $30 \mu\text{m}$. Nonetheless, for $\text{pH} > 7.1$, the particles tend to have an average droplet size of approximately $35 \mu\text{m}$. What is very remarkable is that emulsions prepared with R816 at $\text{pH} = 7.1$, gave a mean droplet diameter of approximately $5 \mu\text{m}$. This variation of the droplet size with a minimum at pH neutral, gives rise to the effect of the pH of the water phase on the wettability of silica nanoparticles.

As seen in **Fig. 4.8**, the more alkaline the water phase, the less stable the emulsions are. This explains the higher droplets size obtained at $\text{pH} > 7.1$. On the other hand, changing the pH of the water phase can alter the surface charges of the particles and thus their affinity to adsorb at the oil-water interface. These results are in accordance with the results obtained by Binks et Duncumb [83] which confirms the large effect of the pH of the water phase on the charging of the silica particles and thus on the stability of the emulsions.



Figure 4.9: Effect of pH of the water phase on the stability of the Pickering O/W emulsions

Table 4.1, showing the mean droplets diameters of the emulsions prepared at various pHs, mostly verified the observations in the microscopy images (**Fig. 4.10**) regarding the nanoparticles behavior at the oil-water interface due to changing the pH of the water continuous phase.

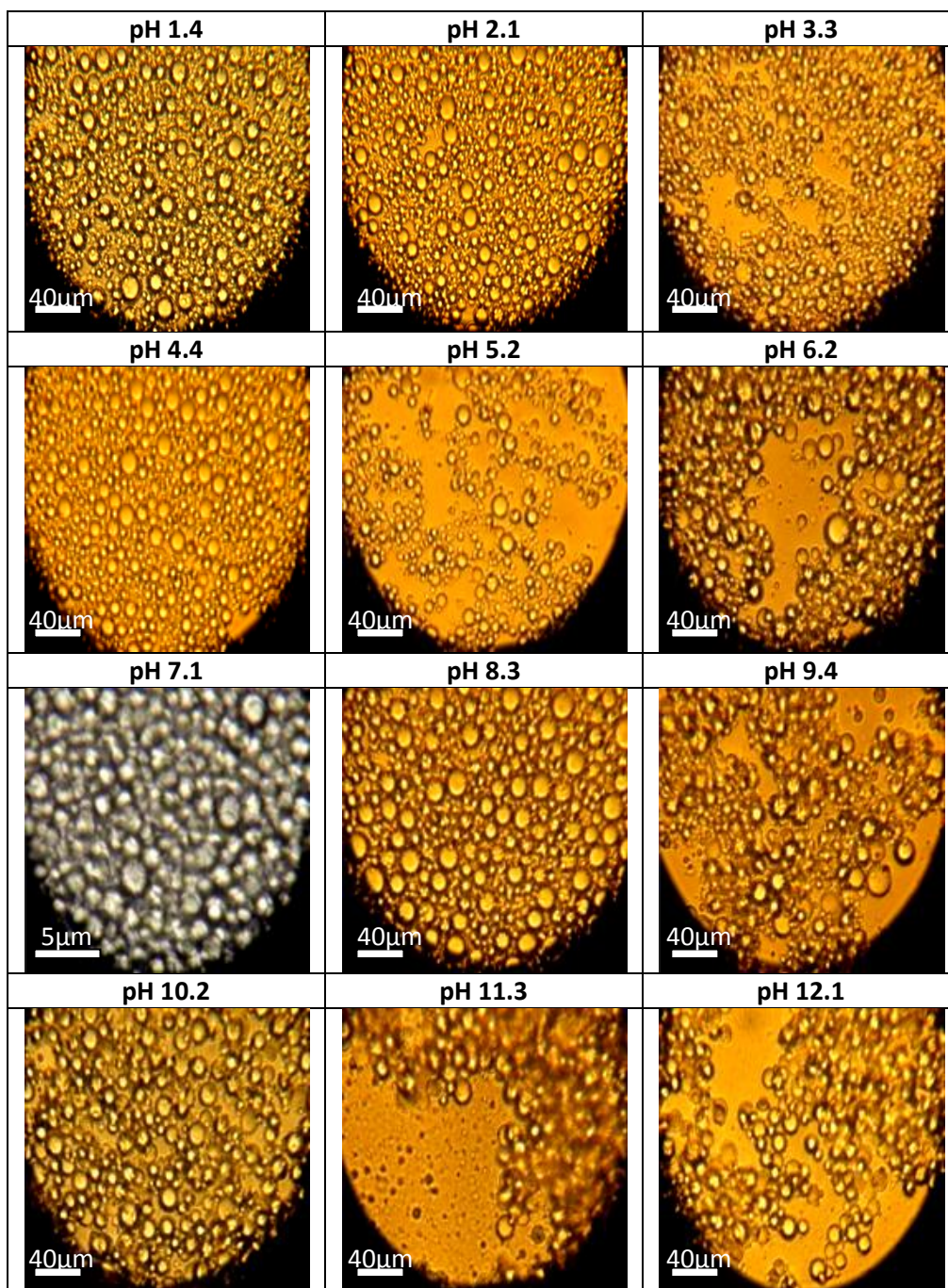


Figure 4.10: Effect of pH on the morphology of the WBM prepared with AEROSIL R816

Table 4.1: Droplet Mean Diameter of the WBM prepared with R816 in function of the pH of water

pH of the water phase	Droplets Mean Diameter (μm)
1.4	25 ± 1
2.1	21 ± 1
3.3	20 ± 1
4.5	27 ± 1
5.2	22 ± 1
6.2	30 ± 1
7.1	4 ± 1
8.3	33 ± 1
9.4	31 ± 1
10.2	35 ± 1
11.3	36 ± 1
12.1	39 ± 1

That was in accordance with the zeta potential measurements done on dispersion of AEROSIL R816 particles in water. **Fig. 4.11** shows the variation of the zeta potential in function of the pH of water.

It is seen that for the acid range ($\text{pH} < 7.1$), the nanoparticles are positively charged and thus altering a higher inter-particle repulsion giving higher stability to coalescence. However, increasing the pH, the particles became more negatively charged from $\text{pH} = 8.2$, where the stability of the emulsions started to decreased as the particles tend to solubilize in water.

It is seen that for these particles, the iso-electric point was at $5.2 < \text{pH} < 6.2$. It should be noted that since AEROSIL R816 particles are surface modified, thus the silane agents present at their surface might affect the interaction and the charging of the particles when changing the pH of water.

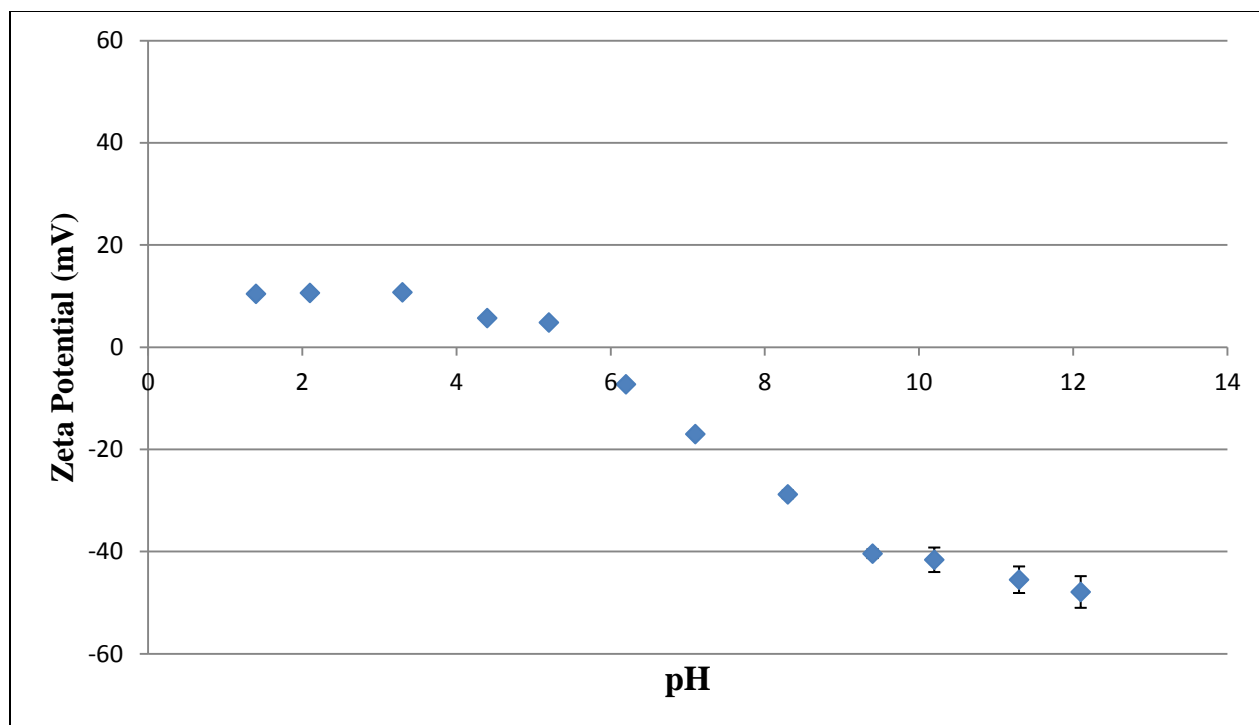


Figure 4.11: Effect of pH on the zeta potential of dispersions of AEROSIL R816 in water

On the other hand, for emulsions prepared with AEROSIL 130 (15 wt.%), **Fig. 4.12** shows the samples prepared at different pH of the water phase. It is clear that even with changing the pH of the water phase, AEROSIL 130 particles could not form stable emulsions to creaming and sedimentation. However, it was clear that the effect of pH on the behavior of the particles at the oil-water interface and thus on the wettability of the silica nanoparticles. For $1.4 \leq \text{pH} \leq 2.1$, an oil phase was seen on top of the emulsion. Which means that the particles hydrophilicity has increased so that the nanoparticles stayed dispersed in the water phase. Getting closer to pH neutral ($3.3 \leq \text{pH} \leq 6.2$), AEROSIL 130 particles tend to form a layer of creaming oil on top of a bluish/white water phase indicating that excess silica nanoparticles exist in the water phase.

For $7.1 \leq \text{pH} \leq 10.2$, the emulsions stayed creamed with no change in the volume of the oil cream on top of the samples. For $\text{pH} > 10.2$, a clear water phase starts to appear, indicating the destabilization of the samples. Which is confirmed at $\text{pH} = 13.4$, where two clear oil and water phases were obtained with no silica particles existing. It is remarkable

as well that at $\text{pH} = 12.1$, the silica nanoparticles tend to accumulate at the oil-water interface, where an oil layer started to appear on the top of the emulsion.

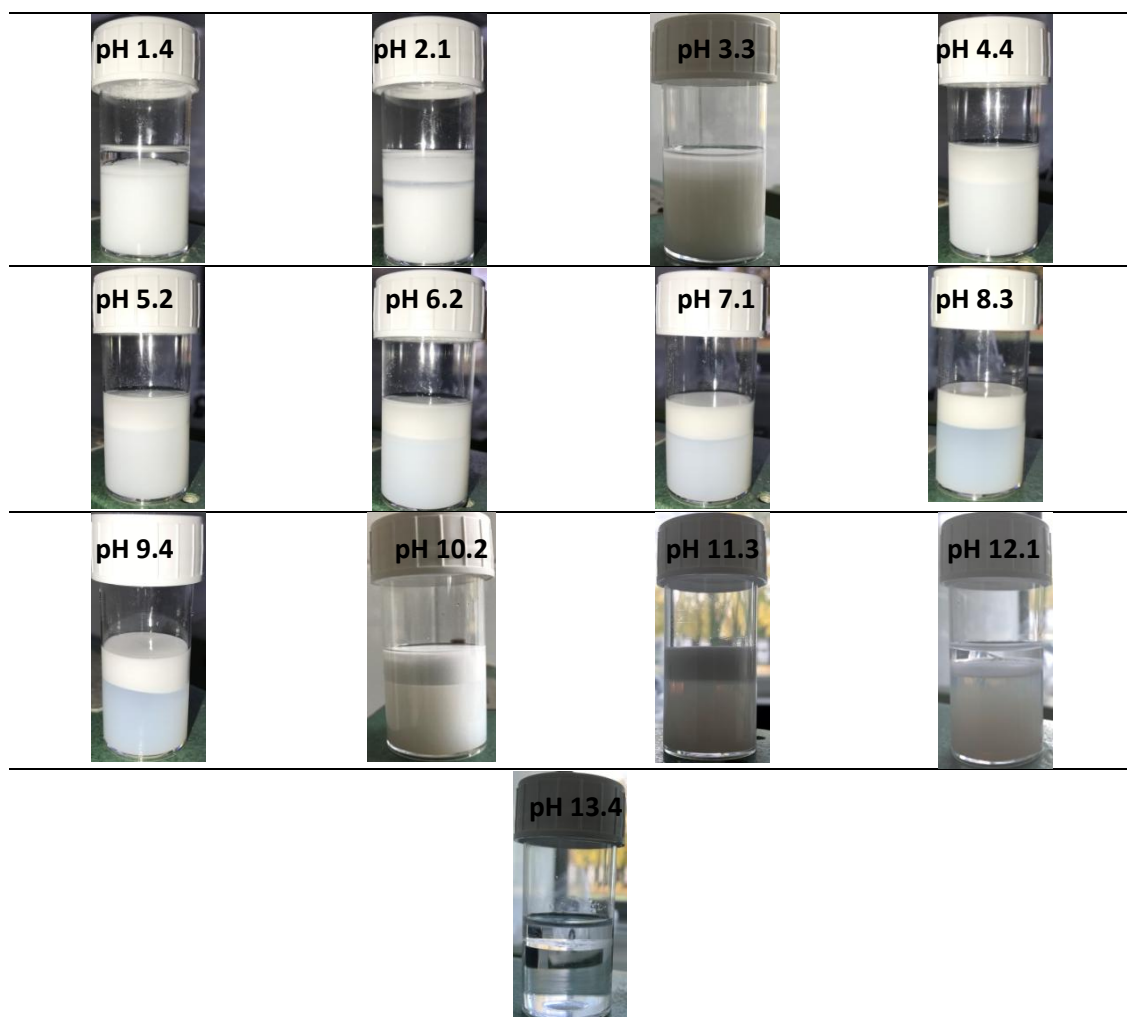


Figure 4.12: Stability of Pickering O/W emulsions prepared using 15 wt.% of AEROSIL 130 in function of the pH of the water phase

4.2.b. Effect of salt concentration

In the core of the formulation of WBM and completion fluids, lies the usage of various salts which play a fundamental role in the success of a drilling operation. Salts are used for the inhibition of clay and shale swelling which might be encountered while drilling. Nonetheless, salts are used to increase the density of the water phase and thus that of the drilling fluid which might be necessary for a minimum of hydraulic pressure needed to maintain the stability of the formation.

Many works have been done on the influence of salt ions on the charges of the solid particles used for the stabilization of Pickering emulsions [128-129]. Therefore, it was mandatory for us to study the effect that might result upon varying the salt concentration in the water phase from 0 wt.% to 10 wt.%, the eligible concentration used for the preparation of WBM. For that, three types of salts were used in this work for the preparation of the fluids (NaCl, KCl and CaCl_2). For each, the salt concentration was tested at 0, 0.1, 1 and 10 wt.%. Thereafter, the effect of the variation of the salt concentration was seen on the rheology, morphology (microscopy images) as well as on the stability of the emulsions against creaming or sedimentation.

Firstly, all samples prepared with 4 wt.% AEROSIL R816 were indefinitely stable to creaming even at salt concentrations as high as 10 wt.% and for the three types of salts used. No water phase appeared in the bottom of the samples and no creaming occurred. However, the added salt had an effect on the flocculation of the particles which was manifested by a slight change in the droplets size distribution of the emulsions. **Fig. 4.13**, shows the comparison between samples prepared without salt and with 10 wt.% of KCl, NaCl and CaCl_2 . A slight decrease in the droplet size was seen upon adding salt, which could be related to the change in the wettability of the particles affected by the ionization of the silanol groups present at their surfaces by the salt molecules.

It should be noted that no changes were seen on samples prepared with 0.1 and 1 wt.% of any of the three salts used. Therefore, a comparison of the effect of adding salt on the samples has been done between samples prepared without salt and those prepared with 10 wt.% of salt.

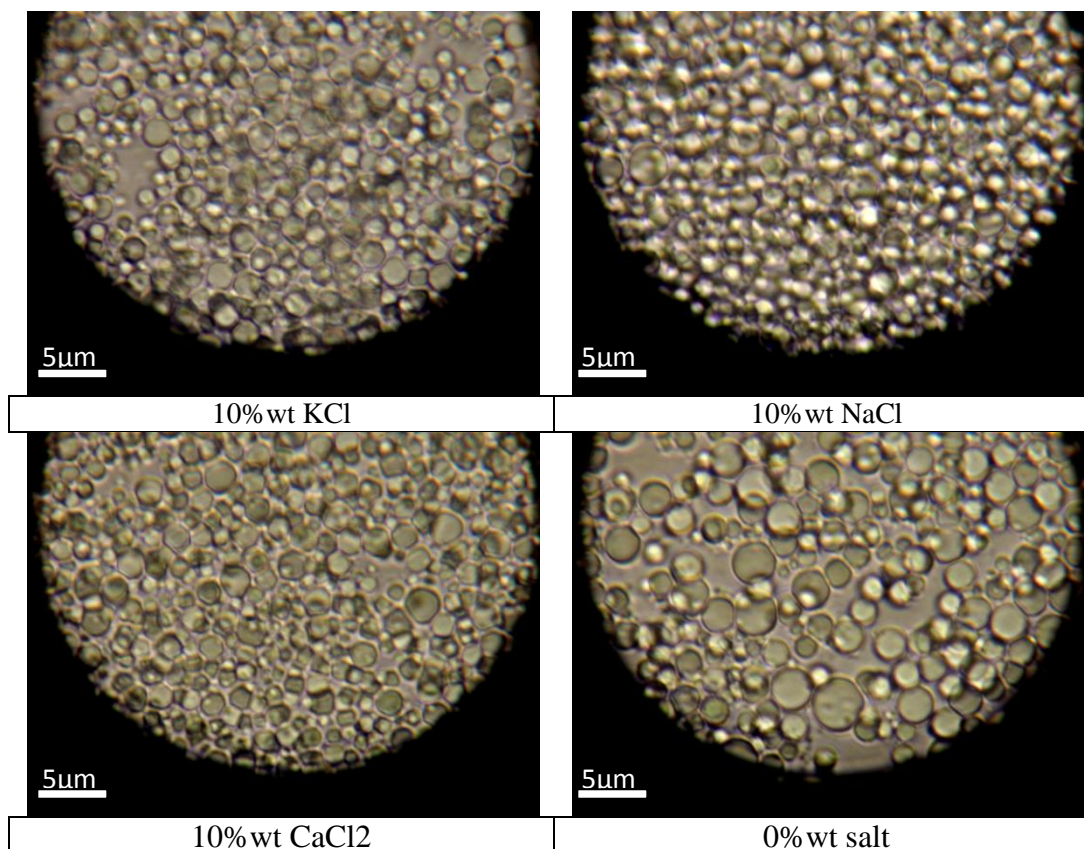


Figure 4.13: Effect of salt concentration on the droplet size distribution of the emulsions

On the other hand, this change was seen as well on the rheological properties of the samples which describe widely the behavior of the fluids. Therefore, **Table 4.2** presents the rheological properties of the fluids after addition of 10 wt.% of salt. As described before, both the Bingham-Plastic (BP) and the Herschel-Bulkley (HB) models were used.

Table 4.2: Effect of salt on the rheological properties of WBM

	0 wt.% Salt	10 wt.% NaCl	10 wt.% CaCl ₂	10 wt.% KCl
PV [mPa.s]	6.1	4.6	8.0	6.9
YP [Pa]	4.4	38.6	15.1	19.4
τ_0 [Pa]	3.4	35.6	13.7	17.1

Where PV and YP are the plastic viscosity and the yield point calculated based on the BP Model and τ_0 is the yield stress calculated based on the HB model.

Nonetheless, amplitude sweep were done for one to assess the effect of salt on the inter-particles interaction manifested by the change in the true yield stress measured through oscillatory rheology.

It is seen that samples prepared without salt exhibited the lowest yield stresses. This could be related to the fact that salt acts on decreasing the repulsive forces between the particles and this enhancing flocculation. Samples prepared with NaCl exhibited a low plastic viscosity with a wide increase in yield point. This could be related to the high flocculation phenomenon that occurred inside the emulsions due to lowering of the particles repulsive forces affected by the presence of salt. These results are in accordance with those obtained with Rodriguez and Binks [99] which showed that adding 2 mM of NaCl to the emulsions leads to flocculation.

On the other hand, **Table 4.3**, shows the true yield point measured using oscillatory rheology of the samples prepared without salt and those prepared with 10 wt.% of salt. It is clear that the presence of salt increased the yield stress of the fluids. On the other hand, NaCl showed the highest yield stress between samples prepared with salt, followed by CaCl_2 and finally KCl which showed the lowest values. These results were in accordance with those of Zhang et al. [128] that showed the effect of salt at different concentrations on solid particles behavior. Horosov and Binks [129] reported as well that a critical value of the loss and storage moduli at limit of the LVE region of 2 Pa is mandatory for a significant stabilization of the samples.

The high yield stresses obtained after adding salt can be considered as an advantage and a deficit at the same time. High yield stresses imposes higher pumping which is sometimes limited to a certain capacity at the rig. However, it provides a very good cleaning efficiency as well as carrying capacity of the fluids to inhibit settling of rocks debris when the drilling has to be halted.

Table 4.3: Effect of salt concentration on the true yield stress

Samples	True Yield Stress [Pa]	Storage and Loss Modulus [Pa] ($G' = G''$ at the true yield stress)
Without Salt	3.1	8.7
10 wt.% KCl	11.0	11.8
10 wt.% CaCl_2	11.6	14.9
10 wt.% NaCl	22.5	23.9

4.3. HTHP Rheology

Many works has been done for the characterization of drilling fluids and more specifically water-based mud. However, in this work the aim of synthesizing water-based drilling fluids based on the principle of Pickering emulsions lies in the potential of substituting OBM with those newly generated and environmentally friendly fluids. Therefore, these fluids have to be tested for their eligibility to be used under various reservoir conditions to test their behavior as well as to see if they can address their main functions under such circumstances.

The behavior of drilling fluids is highly affected by the change in temperature and pressure of the formation drilled. Temperature mainly has a very high effect on the rheological properties of drilling fluids. The effect of temperature was related to degradation of additives, dehydration of solid particle surfaces which influence the internal structure of the fluids and thus their flowability [130]. Therefore, fluids under certain elevated temperatures can exhibit a thinning behavior. This is explained by a decrease in the plastic and apparent viscosity of the fluids with temperature. Nonetheless, temperature can thicken the fluids, and this is manifested by an increase in their plastic viscosity. Finally, solidification of fluids can be attained with increasing temperature which is a very undesirable property for drilling fluids [131].

Bentonite is a main additive that is used to enhance the shear thinning (visco-elasticity) behavior of WBM. Therefore, Cloisite Ca^{++} hydrophilic clay particles were added to the water-based fluids prepared.

Brine and clay are usually used hand to hand in the formulation of WBM that is related to the fact that salt ions inhibits the swelling of the clay particles and thus limit the high increase in the yield stresses of the samples.

Fig. 4.14 shows the swelling behavior of the clay platelets when they get in contact with fresh water. According to their Cation-Exchange-Capacity (CEC), clay particles tend to swell more or less than others. Ca^{2+} clay particles swell up to 17 Å while Na^{+} clay particles swell up to 40 Å [132]. This is related to the fact that divalent cations increase the attractive forces between the platelets and thus a lesser amount of water is absorbed. The larger the water layer absorbed, the more swelled the clay particles are and thus the higher the visco-elasticity of the samples.

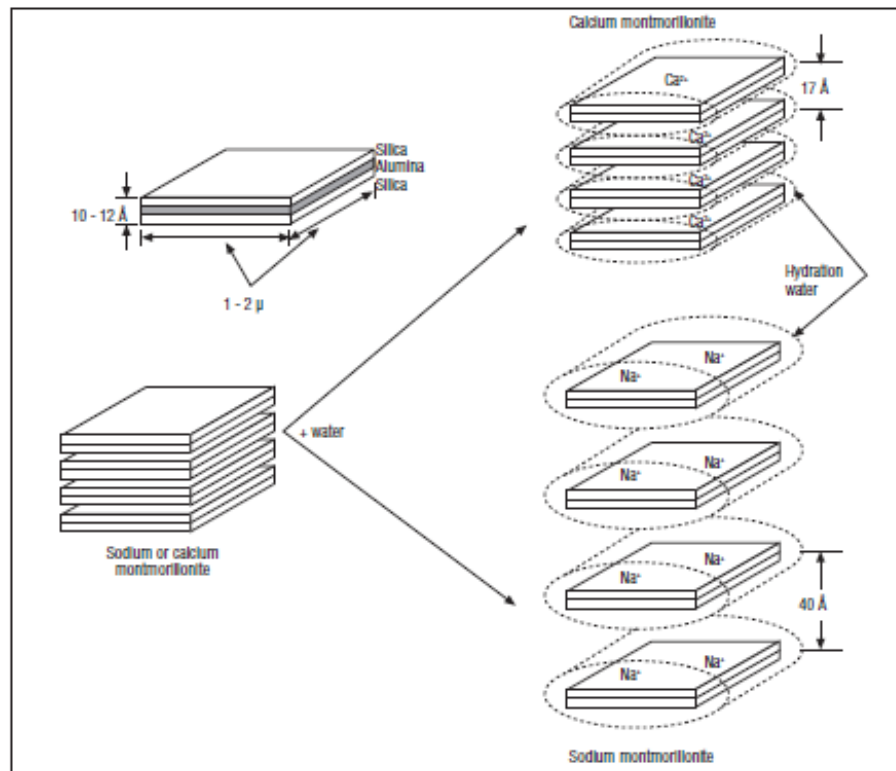


Figure 4.14: Swelling of clay platelets of Ca^{2+} and Na^{+} types when getting in contact with fresh water [132]

Table 4.4 shows the effect of adding clay to the water-based fluids. It is clear that clay particles contribute in the increase of the plastic viscosity as well as the yield stress of the fluids.

Table 4.4: Effect of adding clay on the rheological properties

	Without Clay	After adding 2 wt.% Cloisite Ca ⁺⁺
PV [mPa.s]	6.1	13.5
YP [Pa]	4.4	8.2
τ_0 [Pa]	3.4	7.6

The samples prepared with clay particles are then tested for their ability to withstand high temperature and high pressure conditions. Therefore, **Fig. 4.15** shows the variation of the plastic viscosity and the yield point of the WBM prepared with 2 wt.% of Cloisite Ca⁺⁺ at temperatures varying from 20 °C (68 °F) to 180 °C (356 °F). As described in the previous chapter, the pressure has a very slight effect of the rheological properties. Therefore, for all temperatures, the pressure was fixed at 75 bars (1071 psi).

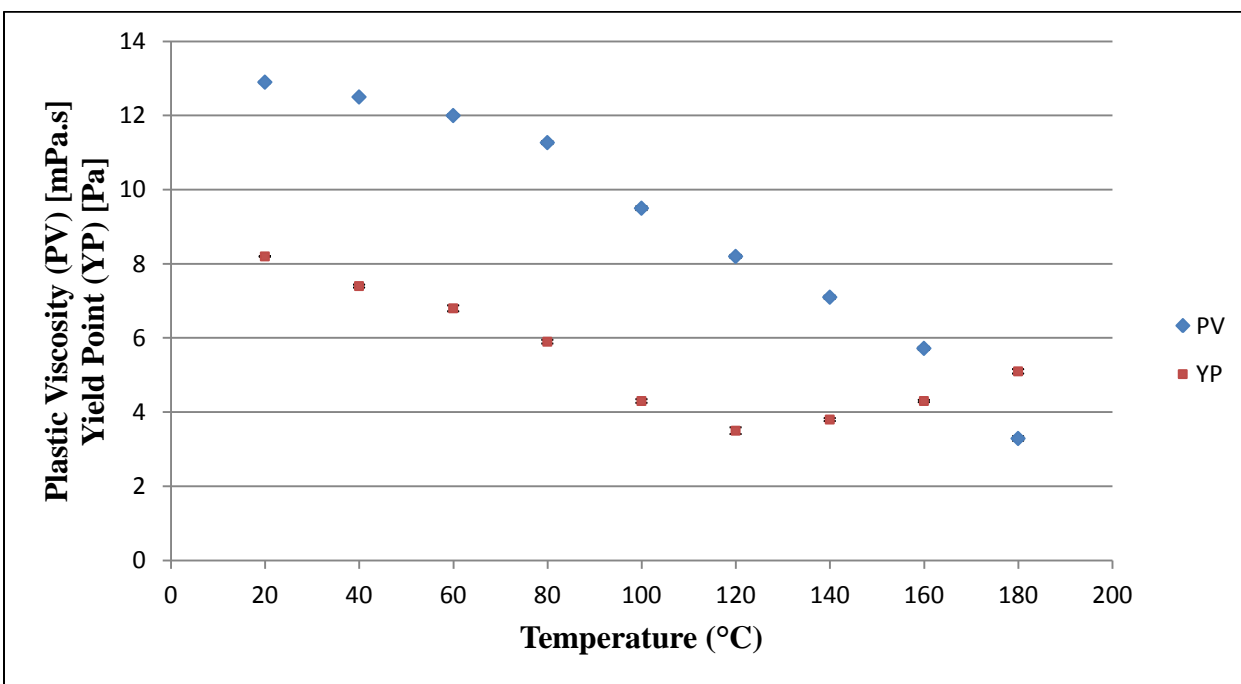


Figure 4.15: Effect of temperature and pressure on the plastic viscosity and the yield stress of WBM

The results obtained in **Fig. 4.15** are of great importance for the WBM market. As it can be seen at first, the samples held their entire stability to coalescence/sedimentation (or creaming) through the whole temperature variation range. Thus, no destabilization of the samples was seen even at temperature as high as 180 °C (356 °F). This property gives the newly prepared WBMs a great advantage over many OBM used nowadays that can't withstand such environmental conditions.

On the other hand, the viscosity of the fluids decreased with increasing temperature from 12.9 mPa.s at 20 °C (68 °F) and 75 bars (1071 psi) to 3.3 mPa.s at 180 °C (356 °F). However, the yield stress did not undergo the same changes. An increase in the yield point was obtained at temperatures higher than 120°C (248 °F). This might be due to the solidification that could start at such conditions stated by Tehrani [23-24]

It should be noted that microscopy images of the samples couldn't be done for the high density of the fluids and the presence of the clay particles.

Conclusion

- O/W emulsions were prepared using hydrophilic silica nanoparticles (AEROSIL 130, OX 50 and R816). It was stated that very hydrophilic silica particles (AEROSIL OX 50 and 130) were not able to stabilize the emulsions against creaming/sedimentation and/or coalescence for more than 24 hours. However, stable emulsions were prepared with surface modified with hexadecysilane silica nanoparticles (AEROSIL R816) which showed stability over 18 months at a concentration of 4 wt.%.

- The effect of changing the pH (from 1.4 to 13.4) and the salt concentration (from 0 wt.% to 10 wt.%) of the water phase was seen on the stability as well as the droplets sizes distribution of the emulsions. O/W stable emulsions were obtained at low pH values ($\text{pH} \leq 7.1$). However, silica nanoparticles tend to solubilize in water at high pH values destabilizing the emulsions. Salt concentrations did not have large effects on the stability to creaming/coalescence of the emulsions. However, depending on the salt used (NaCl, CaCl_2 and KCl), the emulsions tend to flocculate. Samples prepared with NaCl showed the highest yield stresses and the lowest plastic viscosity which is related to the high flocculation of the emulsions.

- Addition of clay/Bentonite (2 wt.% Cloisite Ca^{++}) to the emulsions for the preparation of WBMs was mandatory to maintain the fluids visco-elastic properties as well as main functions all along the drilling operation. Its effects on the stability as well as on the rheology of the emulsions were assessed. It was seen that a large increase in the plastic viscosity from 6.1 mPa.s to 13.5 mPa.s as well as the yield point from 4.4 Pa to 8.2 Pa was obtained after adding clay.

- The effect of the variation of temperature and pressure on the rheology as well as the stability of the emulsions was finally tested. It was seen that samples prepared with AEROSIL R816 were highly stable even at temperatures as high as 180 °C (356 °F). However, an increase in the yield stress was obtained at temperatures over 120 °C (248 °F) which might indicate a start of a solidification of the samples.

Conclusions

In this work two types of drilling fluids were prepared; Oil-Based-Mud (OBM) and Water-Based-Mud (WBM). For both, various types of silica nanoparticles were used.

OBMs consist of W/O emulsions, thus they were stabilized using hydrophobic silica nanoparticles (AEROSIL R104, HDK H17 and H20). Oppositely, WBMs are O/W emulsions, and for that, hydrophilic silica nanoparticles were used (AEROSIL OX50, 130 and R816).

The main objective of this work was the formulation of surfactant-free drilling fluids stabilized using only silica nanoparticles. The stability was firstly examined in terms of coalescence/sedimentation via the appearance of an oil phase on top of the emulsions for OBM and a water phase (cream oil phase) on the bottom (top) of the emulsions for WBM. However, for OBMs, the electrical stability showed a promising tool for measuring the conductivity of the emulsions. Emulsions showing stability for more than 24 hours were considered acceptable for further examination. Thereafter, the rheological profiles of the emulsions measuring their plastic viscosity as well as their yield stresses for their straight relation with the borehole cleaning as well as the carrying capacity of the fluids were measured. The gel structure of the fluids reflecting their visco-elastic properties mandatory for drilling fluids were measured too via amplitude sweep and thixotropy tests. Clay particles were used for their ability to generate viscosity as well as good gel structure. The Oil-Water-Ratio (OWR) of the emulsions was varied from 90:10 to 50:50, for one to test the eligibility of the fluids to hold higher amount of the internal phase which might be intentionally added or mixed with the fluids while drilling. Hence, the effect of changing the internal dispersed phase was assessed on the stability as well as the morphology of the emulsions through their mean droplet diameter measurements. The fluids were then tested for the ability to change the water phase composition in terms of pH and salt concentration for the possibility of affecting the emulsifying behavior of the solid particles as well as the flowability of the fluids.

Finally, for the possibility of using such fluids in deep and ultra-deep wells, they were aged at 350 °F (177 °C) and 500 psi (35 bars) for 16 hours. The effect of aging was reported on the droplet mean diameter as well as the rheology (plastic viscosity, yield stress and gel strength) and the stability of the emulsions via electrical stability tests (for OBM). The flow behavior of the fluids was then tested at reservoir depth conditions where the temperature was changed from 20 °C (68 °F) to 180 °C (356 °F) at a constant pressure of 75 bars (1071 psi). The flow curves (shear stress in function of the shear rate) were measured and the plastic viscosity as well as the yield stress of the fluids was reported.

For OBMs, three systems were established: 5 wt.% AEROSIL R104, 5 wt.% HDK H17 and 2 wt.% H20 where the W/O emulsions prepared showed good stability to coalescence for more than 12 months. However, systems prepared with surfactant started to show signs of instability (oil phase separating on top of the emulsions) after 24 hours.

Both R104 and H17 were able to emulsify water volume fractions up to 50 vol.%. However, with H20, a catastrophic inversion was obtained around an OWR 70:30 which is a very undesirable property for drilling fluids. This was related to the intermediate wettability of the particles that was assessed by the high drop in the electrical stability of the emulsions (from 1999V at an OWR 90:10 to 8V at 50:50).

Changing the salt concentration (CaCl_2) in the brine phase of the emulsions did not affect the stability nor the droplet size distribution of the fluids even at concentrations up to 25 wt.%. However, changing the pH of the water phase from 3.5 to 12 had an effect on the charging behavior of the particles and the stability of the emulsions. For both H17 and R104, increasing the pH of the water phase lead to a decrease in the droplet mean diameter, contrary to the H20 particles.

Addition of clay particles enhanced the stability of the three samples which was assessed by an increase in the electrical stability assuring a tight encapsulation of the water

droplets inside the oil continuous phase. The visco-elastic behavior of the samples was highly enhanced, representing the gel structure generated between the dispersed particles. This was given via amplitude sweep measurements reported by the loss and storage modulus (G' and G'') and the true yield stress.

Aging of the samples lead to a decrease in the electrical stability of the three samples, however, a simple re-homogenization of the fluids helped in the regeneration of the initial structures. The plastic viscosity as well as the yield stress of the emulsions decreased as well after aging, but remained high enough to avoid a destabilization of the systems. Thus, all samples did not show any sign of instability after aging contrary to surfactant stabilized fluids which showed a phase separation and did not re-emulsify even after re-homogenization.

The flow behavior of the samples representing their efficiency at reservoir levels through measuring their plastic viscosity as well as their yield stresses at various temperatures going from 20 °C (68 °F) to 180 °C (356 °F) showed very promising results. Especially to the fact that those prepared with clay particles showed plastic viscosities as high as 10 mPa.s even at 180 °C (356 °F) showing good borehole cleaning efficiency that surfactant-stabilized fluids could not offer under such conditions.

Finally for WBMs, the same reasoning in the characterization of the fluids was applied. For these fluids hydrophilic silica nanoparticles (AEROSIL OX 50, 130 and R816) were used. Very hydrophilic silica particles (OX50 and AEROSIL 130) could not stabilize the emulsions and showed phase separation in less than 24 hours. However, very good stability of the emulsions was obtained with 4 wt.% of R816 that were stable for more than 18 months.

Fluids prepared with R816, showed very good stability and no signs of coalescence or creaming even after changing the oil internal phase volume fraction from 10:90 to 50:50. However, these particles were very sensitive to pH changes of the water phase where the

stability decreased dramatically when approaching the alkaline region to give a phase separation at $\text{pH} = 13.4$.

Salt did not affect the stability of these emulsions but it had a big effect of the repulsive force of the particles which highly decreased leading to an increase in the yield stress of the emulsions. Three salts were used in this work (CaCl_2 , NaCl and KCl) and for the three salts, the AEROSIL R816 particles were able to indefinitely stabilize the emulsions.

Finally, clay particles added to the above system showed a doubling in the plastic viscosity and yield stress. They helped maintaining the visco-elasticity of the fluids even at temperatures as high as $180\text{ }^\circ\text{C}$ ($356\text{ }^\circ\text{F}$) and 75 bars (1071 psi) contrary to the Oil-Based surfactant stabilize fluids that showed hysteresis at temperatures above $120\text{ }^\circ\text{C}$ ($248\text{ }^\circ\text{F}$).

Perspectives

This work presented the high potential of Pickering-based drilling fluids in the future of the drilling industry. However, further work should be done in order to achieve a final product able to replace those existing today with highly optimized functionalities.

First, the already prepared systems should be tested for HTHP filtration properties to test the eligibility of such nanoparticles to enhance the quality of the mud cake produced and its ability to limit the leakage of fluids inside the formations. Some works were already done on this subject, showing the high importance of nanoparticles in the formation of a good filter cake at the formation able to block the pores inhibiting fluid loss [133-134].

In addition, the tribological (frictional) properties of the particles should be tested in order to address the possibility of using such particles as lubricant for the drilling tools via reducing the friction between the drilling bit and the rocks [references for nanotech. in oil and gas]. Nanoparticles are known for their ability to act as lubricants as well as their great heat conductivity helping in cooling the drilling tools and enhancing by that the drilling efficiency and time.

One must keep in mind that the possibility of using nanoparticles as inhibitors for hydrate formation is of high importance in the drilling industry as hydrates tend to form inside the drilling pipes halting the drilling operation. This is related to the high surface-to-volume ratio property that exist at the nanoscale, which enables the particles to interact as well with hazardous environments (acid gases such as H_2S) which represent a great danger for the personal as well as the equipments [135].

Finally, we hope that this work is an opening for a new generation of drilling fluids that can serve to solve many of the current oil and gas problems helping in the increase of the petroleum production to meet the energy incrementing needs.

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Titre : Stabilisation des Fluides de Forage de Type Pickering Pour Applications dans les Forages Profonds et Ultra-Profonds

Mots clés : Fluides de Forage, Emulsions Pickering, HTHP, Vieillissement, Nanoparticules, Silice

Résumé : Cette durable situation des prix du pétrole volatils a été considérée comme un recul et un défi à la fois pour l'industrie pétrolière. Il est au cours de cette crise, que les compagnies pétrolières ont la possibilité de se concentrer sur des solutions de production rentables, ce qui signifie très souvent l'apport des nouvelles technologies et en outre l'amélioration des processus.

Ce travail présente une nouvelle frontière pour la synthèse d'une nouvelle génération de fluides de forage pétrolier sans surfactants/émulsifiants pour des applications dans le forage des puits profonds et ultra-profonds. Cette nouvelle génération consiste à l'introduction des émulsions Pickering dans la formulation des fluides de forage. Ces dernières sont des émulsions stabilisées uniquement par des particules solides (dans ce cas des particules de silice). Différents types de nanoparticules de silice de différentes hydrophobicités ont été utilisés pour stabiliser des fluides de forage

de types huile-dans-l'eau et eau-dans-l'huile.

Ces fluides ont été conçus pour être utilisés dans des conditions hostiles de température et de pression. Par conséquent, une caractérisation concrète de leur stabilité ainsi que leurs propriétés rhéologiques sous ces conditions extrêmes étaient obligatoire. Par suite, les profils rhéologiques de ces fluides reflétant leurs capacités de nettoyage du trou, leur coulabilité ainsi que leurs capacités de transporter les débris jusqu'à la surface ont été établis. Les fluides ont été exposés à un processus de vieillissement qui permet d'étudier l'effet de l'environnement du réservoir hostile sur la stabilité et la rhéologie des nouveaux fluides préparés. Ces fluides de haute qualité ont été vus très fiables offrant une grande stabilité ainsi que de haute capacité à résister à des conditions extrêmes de réservoir donnant lieu à une nouvelle génération de fluides de forage permettant la rupture des frontières de réservoirs profonds et ultra-profonds.

Title : Pickering Stabilized Drilling Fluids for deep and ultra-deep Drilling Operations

Keywords : Drilling Fluids, Pickering Emulsions, HTHP, Aging, Nanoparticles, Silica

Abstract: This enduring situation of volatile oil prices has been seen as a decline and a challenge at the same time for the oil and gas industry. It is during this slump that the oil and gas companies own the opportunity to focus on cost-effective production solutions, which very often means bringing new technologies and further improving processes. This work presents a novel frontier of surfactant-free drilling and completion fluids for deep and ultra-deep wells. This new generation of drilling fluids is based on the principle of Pickering emulsions (emulsions stabilized solely by solid nanoparticles). Hydrophobic and hydrophilic silica nanoparticles were used to stabilize Oil-Based Mud and Water-Based Mud. These fluids were designed to be used under hostile conditions of temperature and pressure. Therefore, a concrete characterization of their

stability as well as their rheological properties under HTHP conditions was mandatory. Rheological profiles reflecting the flowability, hole cleaning capacity as well as cutting transport ability of the fluids were established. On the other hand, the electrical stability as well as the morphology (Droplet Size Distribution) of the emulsions were studied and compared with surfactant-stabilized drilling fluids. The fluids were exhibited to an aging process allowing one to study the effect of hostile reservoir environment on the stability and rheology of the new fluids prepared.

These high quality fluids were seen very reliable offering high stability as well as high capacity to withstand extreme reservoir conditions giving rise to a new generation of drilling fluids allowing breaking the frontiers of deep and ultra-deep reservoirs.