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INVESTIGATION OF LIGNITE EFFECT ON RHEOLOGICAL AND FILTRATION PROPERTIES OF WATER-BASED DRILLING MUDS

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ABSTRACT

Bentonite is a clay widely used – among others – as a low-cost additive in the drilling fluids to impart the desired plastic rheological properties to the mud. As drilling progresses, the clay particles tend to swell causing thickening problems. In this case, it is essential to treat the mud in order to sustain the drilling operation. Treatment with Drilling Mud Thinners is applied to control the dispersion properties and lower the viscosity. Lignosulfonate is a lignin-based polymer widely used to deflocculate clay-based muds. Lignite is often added in the drilling mud as a low-cost thinning agent to control the swelling behavior of the clay particles, to reduce the viscosity and to control the filtration properties of the mud. Especially, after a causticization treatment in alkaline solution, lignite can act as mud thinner reducing the thickening effect. Lignite can also affect the filtration properties essentially reducing the filtrate volume of the drilling fluid. Another type of lignite, namely leonardite, can also be used for the same purpose. Four low-rank coals (three lignites and one leonardite) were obtained from several deposits in Western Macedonia, Greece to investigate the benefits of their addition on the rheological and filtration properties of water-bentonite suspensions. The samples were causticized with two different methods and added in water-based mud mixtures. Rheological and filtration properties of the samples were proved strongly dependent on the type of causticization, as well as their humic acid content. This study is an attempt to develop a low-cost, environmental-friendly product from indigenous and very abundant raw material (lignite, leonardite) intending to explore in the post-lignite era one industrial, non-electrical application for this primary energy source.

ΠΕΡΙΛΗΨΗ

Ο μπεντονίτης είναι μια άργιλος, που χρησιμοποιείται μεταξύ άλλων ως χαμηλού κόστους πρόσθετο των ρευστών διάτρησης, προκειμένου να προσδώσει τις επιθυμητές πλαστικές ρεολογικές ιδιότητες στον πολφό. Όσο η διάτρηση προχωρά, τα σωματίδια της αργίλου τείνουν να διογκώνονται προκαλώντας αύξηση του ιξώδους. Σε αυτήν την περίπτωση είναι απαραίτητη η επεξεργασία του πολφού, ώστε να μειωθεί το πλαστικό ιξώδες και να διατηρηθεί ομαλή η διάτρηση. Η επεξεργασία γίνεται με αραιωτές πολφού, που συμβάλλουν στον έλεγχο των ιδιοτήτων διασποράς και στη μείωση του ιξώδους. Το Λιγνοσουλφονικό αποτελεί ένα ανιονικό πολυμερές με βάση τη λιγνίνη, που χρησιμοποιείται ευρέως για αραίωση μπεντονιτικών πολφών με βάση το νερό. Συχνά προστίθεται και λιγνίτης [σε ορισμένες περιπτώσεις μαζί με λιγνοσουλφονικά] στον πολφό διάτρησης ως χαμηλού κόστους παράγοντας αραίωσης για τον έλεγχο της διόγκωσης των σωματιδίων της αργίλου, τη μείωση του ιξώδους καθώς και τον έλεγχο των ιδιοτήτων διήθησης του πολφού. Συγκεκριμένα, μετά από καυστικοποίηση σε αλκαλικό διάλυμα, ο λιγνίτης μπορεί να λειτουργήσει ως αραιωτικός παράγοντας, μειώνοντας τα φαινόμενα πηκτώματος, που δημιουργούνται στους πολφούς. Επιπλέον μπορεί να επηρεάσει τις διηθητικές ιδιότητες μειώνοντας ουσιαστικά τον όγκο του διηθήματος του πολφού. Ένας άλλος τύπος λιγνίτη, ο λεοναρδίτης, μπορεί επίσης να χρησιμοποιηθεί για τον ίδιο σκοπό. Τέσσερα δείγματα χαμηλού βαθμού ανθράκων (τρεις λιγνίτες και ένας λεοναρδίτης) λήφθηκαν από συγκεκριμένα κοιτάσματα στη Δυτική Μακεδονία, για να αξιολογηθεί η επίδρασή τους στις ρεολογικές και διηθητικές ιδιότητες πολφού με βάση το νερό. Η παρούσα διατριβή αποτελεί μια προσπάθεια να αναπτυχθεί ένα χαμηλού κόστους, περιβαλλοντικά φιλικό προϊόν από μια εγχώρια και πολύ συνήθη πρώτη ύλη (λιγνίτης, λεοναρδίτης) με στόχο να διερευνηθεί μια βιομηχανική, έξω-ηλεκτρική χρήση αυτής της κατ’ εξοχήν ενεργειακής πηγής στη μεταλιγνιτική περίοδο.

SCOPE OF THE STUDY

Bentonite is a low-cost clay that is widely used in the drilling fluids. As drilling progresses, bentonite clay particles tend to swell and create thickening problems by changing the optimal rheological properties of the mud. Therefore, the right treatment of the mud is needed to sustain the drilling operation. This is usually achieved by reducing the Plastic Viscosity of the drilling mud and consequently increase the rate of penetration and reduce the required pump pressure to circulate the mud to the surface.

Drilling Mud Thinners are used in these conditions, to control the dispersion properties and lower the viscosity. Thinners are considered to adsorb on the clay particles surface reducing the attraction forces among them. Lignosulfonate (LS) is a highly anionic polymer used to deflocculate clay-based muds. Lignosulfonate is a complex mixture of small -to moderate-sized-polymeric compounds with sulfonate groups attached to the molecule. Iron-Chromium-LS (FCLS) was the most widely used as a thinning additive but due to its toxicity, it has been restricted. With the increase in environmental concerns regarding the use of conventional chemical additives, there is a demand for new environmentally friendly additives, which can enhance the effectiveness of the drilling mud with the least effects on the environment and the drilling personnel safety. Thus, there is constant research for alternative lignosulfonate-based thinners with environmental acceptability.

Lignite compounds are often added in the drilling muds [in some cases together with lignosulfonates] as a low-cost thinning agent to control the swelling behavior of the clay particles, reduce the viscosity, as well as control the filtration properties of the mud.

This thesis deals with the influence of the addition of Greek lignite and leonardite in water-based drilling mud.

Organic compounds, such as lignites, after a causticization treatment in alkaline solution, can act as a thinner reducing the thickening effects that occur in drilling muds with depth, and the changes in temperature and pressure conditions. It has also been widely reported, that they can affect the filtration properties reducing essentially the filtrate volume of the drilling fluid.

Another type of Low-Rank Coal – Leonardite – can also be used for the same purpose. However, leonardite addition is just mentioned in very few studies (Darley and Gray 1988; Hoffman et al. 1993; HSE 2000; Hudgins 1991; Neff 2005).

Additionally, no current studies have attempted to compare typical lignites and leonardite as drilling mud additives.

Greece is the fifth largest producer of lignite with EU countries (Euracoal, 2018) producing approximately 36 million tons of lignite per year (Euracoal, 2018). Considering the above and within the framework of seeking alternative uses for Greek low-rank coals, lignite, and leonardite samples from different mines in Western Macedonia, Greece were collected and their effect on the rheological and filtration properties of the water-based drilling muds was investigated.

This thesis aims to investigate the benefits of the addition of Greek lignite and leonardite on the rheological and filtration properties of water-bentonite suspensions in order to:

- Decrease the thixotropic behavior of the drilling mud which can lead to cost savings by reducing power consumption.
- Avoid the formation damage while drilling and produce a thin filter cake, which will help in avoiding the pipe sticking and consequently protect the environment.
- Develop a low-cost, environmental-friendly product from indigenous and very abundant raw material (lignite, leonardite) and explore in the post-lignite era one industrial, non-electrical application for this primary energy source.

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CHAPTER 1 - DRILLING AND DRILLING MUDS

1.1 Rotary drilling

Currently, rotary drilling is the most common drilling method concerning oil wells. The rotary drilling method uses tricone-type toothed bits or one-piece, such as diamond or PDC-Polycrystalline Diamond Compact bits. The disintegration of the rock occurs as a result of a concurrent rotation of the bit and applied pressure. Under the effect of the pressure, the bit penetrates the rock, while under that of the rotation it shears it. As presented in Figure 1, in rotary drilling rigs a link of mechanical parts is responsible for three initial functions:

- The **weight** application on the drill bit
- The **rotation** of the drill bit
- The **circulating system** of the drilling mud

The rotary drilling rig uses a *drill bit* to penetrate the underground geological formations. As the depth of the hole increases, new *drill pipes* are installed allowing the bit to reach greater depths. The *drill string* consists of the drill pipes and the drill bit. There are five essential parts in a drilling rig complex:

1. **Hoisting system**: It is responsible for the uplifting and launching of the drill string. As demonstrated in Figure 1, it consists of the derrick, the traveling block, the crown block, the drilling line, and the draw works. Derrick holds the drill string and the drill bit. It also holds the traveling block and the crown block, which are systems of pulleys that lift and launch the drill string when necessary.
2. **Rotating system**: It is the system which rotates the bit. There are two different ways of this procedure, with ***Kelly*** and with ***Top Drive***. The Kelly Drive is a long square or hexagonal steel bar with a hole drilled through the middle for a fluid path, which is used to transmit rotary motion from the rotary table to the drill-string while allowing the drill-string to be lowered or raised during rotation. The rotary table has an inside profile matching Kelly's outside profile (either square or hexagonal), but with slightly larger dimensions so that the Kelly can

freely move up and down inside. The Top Drive system is a motor that is suspended from the derrick, or mast, of the rig and allows the drilling rig to drill the longer section of a stand of drill pipe in one operation. When the bit progresses under a Kelly drive, the entire string must be withdrawn from the wellbore for the length of the Kelly to add one more length of drill pipe. On the other hand, with a Top Drive, the draw works only have to pick up a new stand from the rack and makeup two joints. Replacing the traditional Kelly or rotary table, the Top Drive lessens the manual labor involved in drilling, as well as many associated risks.

3. **Circulating system**: During the drilling procedure, a drilling fluid is used to transport the rock fragments from downhole and maintain the wellbore stability, as well as other drilling parameters. The circulating system is responsible – among others – for the circulation of the fluid downhole and it consists of the mud tanks, the mud pits, the mud pump, the shale shakers, as well as the mud-gas separator. Further details about the circulating system are given in Chapter 1.1.1.
4. **Power system**: Fuel tanks store large quantities of fuel for the rig generators which through electric cables transport the power in every place needed.
5. **Blow Out Preventer system (BOP)**: It is a safety system consisting of several valves that monitor and control the oil and gas wells. The BOP system is necessary for every drilling rig to prevent and control the huge pressures that occur during a “formation kick” situation.

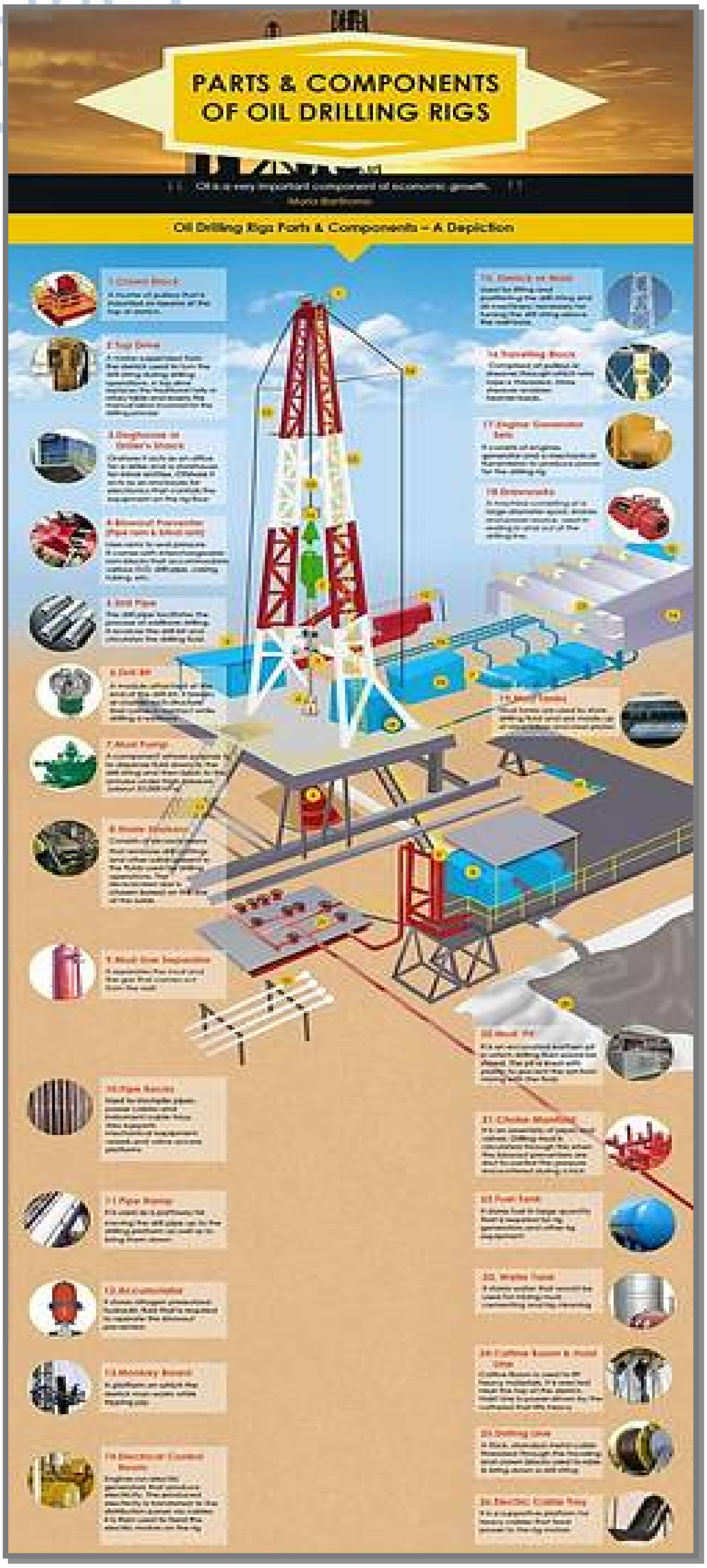


Figure 1. Parts and components of oil drilling rigs (Source: https://oilfieldteam.com/en/a/learning/partsandcomponentsofoildrillingrigs).

1.1.1. The rotary drilling circulation system

Drilling fluids were first used in the rotary drilling process between 1887 and 1901. Their primary function was to remove the cuttings from the well (Chilingarian and Vorabutr, 1983). Drilling fluid is a mixture of clay minerals (bentonite, attapulgite, etc.), a base fluid or gas (water, salt water, oil, foam, gas, etc.), weighting agents (barite, hematite, etc.), as well as other chemical compounds depending on the formations drilled. The drilling fluid or drilling mud is a ***colloidal clay system*** (Sarquis, 1980). Its consistency is critical. **It must be fluid enough to be pumped, yet it must be thick enough to keep the cuttings suspended**. A significant amount of studies has been published since then, focusing on the improvement of the drilling fluid functions (Abdo and Haneef, 2013; Averkina and Shakirova, 2019; Caenn et al., 2016; Calcada et al., 2011; Chilingarian and Vorabutr, 1983; Civan, 2015; Herzhaf et al., 2013; Kenny and Hemphill, 1996; Luckham and Rossi, 1999; L-Yami et al., 2019; Lyons and Plisga, 2016; Mark and Ramsey, 2019; Mitchel and Miska, 2011; Kelessidis et al., 2009; Kelessidis et al., 2006; Wang et al., 2019 Zhang et al., 2019).

In a complete circulation system, the drilling mud is mixed and conditioned in the *mud pits*. Mud is pumped from the mud pits by specially designed mud pumps and travels through either a swivel/Kelly system or a top drive system into the drill string. It is sprayed out of *nozzles* on the drill bit and returns to the surface carrying the crushed rock fragments.

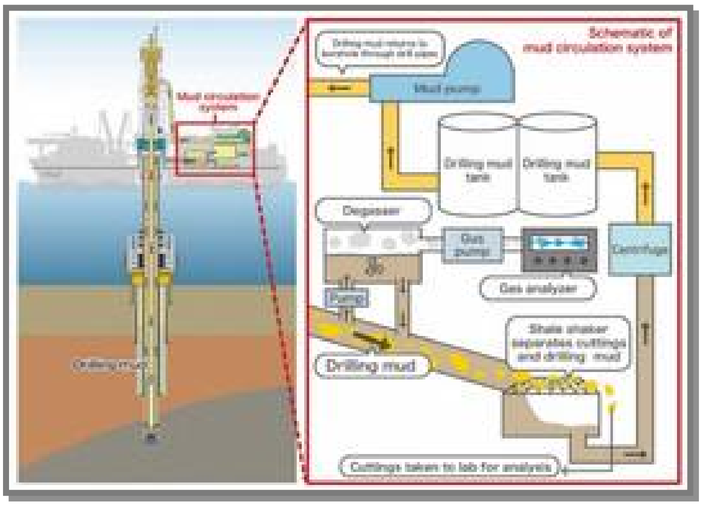


Figure 2. Overview of the circulation system of the drilling fluid in an oil well.

Before the mud re-enters the mud pits, cuttings are removed by the *shale shakers* or any other solids removal equipment. Since the solids have been removed the drilling mud is re-circulated inside the borehole. The drilling mud properties are constantly checked to ensure their maintenance under the same limits. Cuttings are sorted into size fractions with sieves. The properties of these fractions are measured and examined with optical and scanning electron microscopes providing the geologists with information about the downhole formations.

1.2 Drilling mud objectives and functions

There are many requirements placed on the drilling fluid. It is known (Caenn et al., 2016) that the first purpose of the drilling mud was only to remove the cuttings from the wellbore. **The main challenge in drilling fluids science is to maintain preferable properties while drilling**. Nowadays in rotary drilling, the essential drilling mud functions are to:

1. Control subsurface formations' pressure
2. Remove and transport drilled cuttings to the surface
3. Form filter cakes on walls of permeable formations
4. Maintain wellbore stability
5. Support part of the tubular weight
6. Cool, lubricate and support bit and drill string
7. Transmit horsepower to tools and bit
8. Ensure adequate formation evaluation
9. Minimize reservoir damage
10. Reduce corrosion of formations
11. Reduce pressure losses
12. Improve penetration rates
13. Minimize impact on the environment and improve the safety of drilling personnel

Control subsurface formations pressure. Drilling fluids play a significant role in the defense against wellbore control problems, by balancing or overcoming the formations pressures. This is achieved by adjusting the mud's density. The preferable density of the fluid is achieved with the addition of weighting agents such as barite, hematite, etc., to avoid overbalanced or underbalanced pressure conditions in the wellbore. Overbalanced conditions occur when the pressure of the drilling fluid overcomes the pressure of the formations, whereas underbalanced conditions occur when the pressure of the drilling fluid is lower than the formation pressure.

Abnormally pressured formations (or geopressured) are formations that their pressure exceeds the pressure column of water (normal pressure). For instance, during diagenesis procedure, when a clay formation is in proximity with sandstone that provides a permeable path to the surface, as the clay compacts it releases the water through this path. As the compaction of the formations continuous, a layer of low-permeability clay develops adjacent to the sand, restricting flow from the clay formation to the sand layer. Therefore, in a clay formation, the rate of compaction exerts the rate of water expulsion leading to an increase of the pressure above normal. In such a case, the mud density often must be greater than 2.32SG (SG= Specific Gravity) to control the pressures of the formation fluids (water, oil, gas).

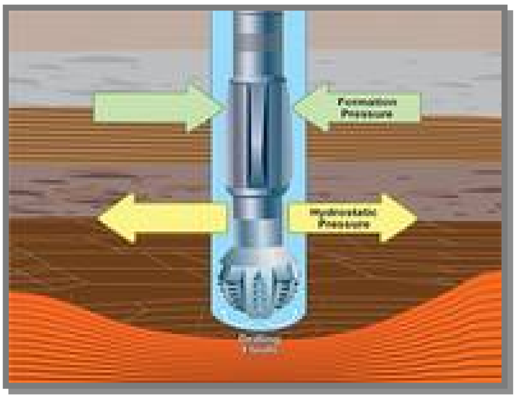


Figure 3. Formation and fluids (hydrostatic) pressures equilibrium inside the well.

Also, drilling operations often expose the producing horizons to the drilling fluid, and any solids and chemicals contained in that fluid. Some invasion of fluid filtrate and fine solids into the formation is inevitable. However, this invasion and the potential for damage to the formation can be minimized with a careful fluid design that is based on testing performed on samples (core plugs) of the formation of interest. Formation damage also can be curtailed by expert management of downhole hydraulics using accurate modeling software, as well as by the selection of a specially designed "drill-in" fluid, such as the systems that typically are implemented while drilling horizontal wells.

Remove and transport drilled cuttings to the surface. One of the primary functions of the drilling fluid is to remove rock fragments from beneath the drill bit and transport them to the surface for further investigation. The density and viscosity are essential properties of the drilling fluid which are responsible for the process of lifting the flowing solids against gravity. Drilling mud should also have a gel-like structure to keep the particles in suspension even when the circulation has stopped.

The carrying capacity of the drilling fluid plays a significant role in preventing cuttings from tumbling and disintegrating when they are not brought to the surface as soon as possible. In this case, cuttings increase the low-gravity solids content of the drilling fluid, affecting its properties. On the other hand, several properties of the drilling fluid such as density, viscosity and gel strength, annular velocity, as well as the particles' dimension affect the cuttings carrying amount of the drilling fluid (Hong Gao et al., 2013).

Form filter cakes on walls of permeable formations. Filter cake formation on permeable rock sections exposed in the wellbore is directly related to the filtrate loss properties of the drilling fluid. Filtrate usually invades the formations exposed in the borehole, leaving behind associated solids. Filter cake is a thin impermeable layer that sticks on the borehole wells and controls the filtrate loss of the fluid.

Maintain wellbore stability. Maintaining a stable borehole is one of the major challenges encountered when drilling. It is important to obtain the optimal density levels in the drilling fluid to prevent the uncased sections of the hole collapsing. However, the nature of the hole instability depends on the borehole environment. There are plenty of factors that affect the stability of the well such as, clay mineralogy, tectonic stress, pore pressure, dip of the formations, as well as the degree of the compaction (Caenn et al., 2016). Therefore, the ideal drilling mud to maintain hole stability varies, depending on the borehole conditions.

Cool, lubricate, and support bit and drill string. The bit and drill string rotate at relatively high revolutions per minute (rev/min) during actual drilling operations. In that way, heat is generated from mechanical and hydraulic forces at the bit and when the drill string rotates and rubs against casing and wellbore.

The drilling fluid should have the ability to cool and lubricate the drill string as it passes through, as well as the drill bit. It is also important to decrease the friction between metallic surfaces (bit) and geological formations, without affecting the drill bit life.

Transmit horsepower to tools and bit. Hydraulic energy provides power to mud motor for bit rotation, Measurement While Drilling (MWD), and Logging While Drilling (LWD) tools. Hydraulic programs base on bit nozzles sizing for available mud pump horsepower to optimize jet impact at the bottom well.

Ensure adequate formation evaluation. Drilling muds provide a medium for further examination of the formations drilled. Drilling fluid is in constant contact with the wellbore, revealing substantial information about the formations being drilled, and serving as a conduit for much data collected downhole by tools located on the drill string and through wireline-logging operations performed when the drill string is out of the hole. For instance, mud loggers examine cuttings for mineral composition, a visual sign of hydrocarbons and record mud logs of lithology, ROP, gas detection or geological parameters. At the same time mud helps to avoid the dispersion of cuttings and also to improve cutting transport, in order mud loggers to determine the depth of the cuttings originated. These cuttings also serve as a primary indicator of the physical and chemical condition of the drilling fluid. An optimized drilling-fluid system that helps produce a stable, in-gauge wellbore can enhance the quality of the data transmitted by downhole measurement and logging tools, as well as by wireline tools.

Minimize reservoir damage. A producing formation can be damaged by poor drilling fluid. Damage mechanisms include formation's fines migration, solids invasion, and wettability alterations. The identification of the potential damage mechanisms, and a careful selection of suitable drilling fluid can minimize the potential reservoir damage.

Reduce corrosion of formations. In the wellbore, there are often common contaminants that promote corrosion of the formations such as oxygen, carbon dioxide, hydrogen sulfide, etc. Hydrogen sulfide, carbon dioxide, and occasionally organic acids can become incorporated in the mud from formations drilled, bacterial action, and degradation of certain mud additives. The drilling fluid is a carrier of agents that counteract with corrosion agents and retard corrosion. Thus, corrosive agents introduced into the wellbore from the formation can be neutralized by the mud before they cause serious problems.

Reduce pressure losses. Surface equipment pressure demands can be reduced by designing a fluid to minimize pressure losses. The reduction in pressure losses also permits greater hydraulic efficiency at the bit and a lower equivalent circulating density (ECD).

Improve Penetration Rates. Proper fluid selection and control can improve the rate of penetration (ROP). The benefits of improved penetration rates are the reduced drilling time and fewer hole problems due to the limited open-hole exposure time. According to Chilingarian and Vorabutr (1983), specific weight, viscosity, filtrate loss, solids content, and oil content are the essential parameters that affect the penetration rates to a varying degree. For instance, while viscosity and density increase, there is an improvement in the penetration rates. However, it is inevitable to change one property without affecting the others and therefore, it is hard to evaluate the true impact of an individual parameter on penetration rate.

Minimize the impact on the environment and improve the safety of drilling personnel. Water-based drilling fluids have low toxicity, once they usually contain water, bentonite, and barite. However, when drilling in high depths and extreme conditions, diesel oil is used as a base fluid, which can be toxic for the environment. Furthermore, there are specific chemicals that can be used in water-based drilling fluids that alone can be corrosive and toxic, such as hydrochloric acid or sodium hydroxide (caustic). However, when mixed into water-based drilling fluids, these substances only affect the pH of the water to a more manageable level. Moreover, anhydrous lime, soda ash, bentonite, barite, and polymers are the most common chemicals used in water-based drilling fluids. Oil-based mud and synthetic drilling fluids can contain high levels of benzene and other possibly hazardous chemicals. In any case, drilling fluids require daily testing and continuous monitoring by specially trained personnel. They must be scrutinized to help ensure that the formulations in use comply with regulations established to protect both natural and human communities, where drilling takes place.

1.3 Classification of drilling muds

The complexity of drilling requires specific drilling fluid properties for each formation drilled. The type of fluid selected depends on anticipated well conditions or the specific interval of the well being drilled. There is a variety of drilling fluids, which are classified according to their main component (Figure 6). The most common types of muds are the **water-based muds (WBM)** and the **oil-based muds (OBM)**, while there are also **gas-based** and **synthetic muds**.

The three key factors that drive decisions about the type of drilling fluid selected for a specific well are:

1. **Cost**
2. **Technical performance**
3. **Environmental impact.**

The factors that mostly affect the cost of the drilling fluids are the type of the formation drilled, the hole size, the total depth, and logistics. The selection of the proper drilling fluid type is very important in reducing the cost. For instance, if a salt or cement contamination of the drilling fluid occurred, the use of oil-based drilling mud will eliminate the problems of cement and salt contaminations; however, it is very costly to change the mud type while drilling.

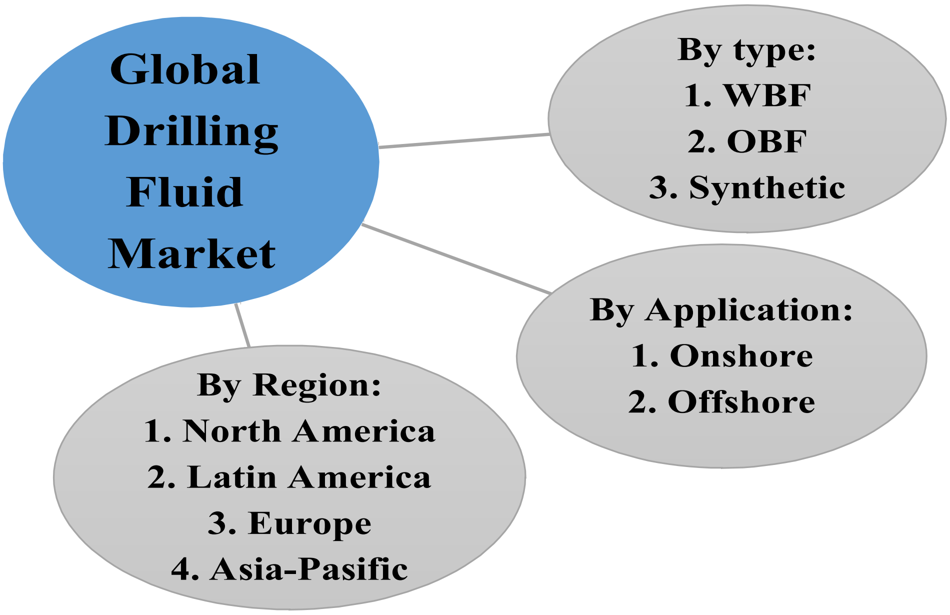


Figure 4. Distribution of drilling fluids in the global market. (Market Research Future, 2018, https://www.marketresearchfuture.com/reports/drilling-fluids-market-4329).

1.3.1. Water-based muds

Based on the type, water-based drilling fluid dominates the global drilling fluids market. **Water-based drilling fluid accounted for the largest market share of 55.90% in 2016** (Market Research Future, 2018) with a market value of USD 4,706 million which is projected to grow at the highest CAGR (Compound Annual Growth Rate) of 7.52% in the forecast period until 2023 (Market Research Future, 2018). Water-based mud is a drilling fluid, in which water or saltwater is the major liquid phase. General categories of water-based muds are freshwater, seawater, salt water, or solutions with lime, potassium, and silicate. Most water-based muds are composed of a combination of water, specific types of clays, and chemicals used to enhance parameters related to drilling performance in the well. Usually, water-based muds consist of clays such as attapulgite and bentonite. The most common kinds of water-based muds depending on the drilling situation are the following:

Non-dispersed: These fluids contain various muds and are generally used for shallow wells or top hole drilling. There is no addition of thinners or dispersants in this kind of water-based muds.

Dispersed: Dispersion is the act of breaking up large particles into smaller ones and distributing them throughout a liquid or gaseous medium. In higher depth when higher density and viscosity muds are required, or where hole conditions may be problematic, **muds are dispersed typically using lignosulfonates, lignites, or tannins**. These products are known as effective deflocculants and filtrate reducers. In dispersed water-based muds, these products act as a chemical means which degrade the clay materials into submicroscopic particles.

Calcium-treated: A water-based mud is often combined with divalent cations such as calcium and magnesium to prevent clay and shale swelling. Calcium-treated muds resist scale and any anhydrite contamination but may require further treatment to prevent gelation under the high temperatures of deep wells.

High performance: These muds are reformulated polymer systems containing specific additives to achieve shale stability, clay and cuttings inhibition, lubricity, and high penetration rates.

Low solids: In this kind of muds the total solids content should not range higher than about 6% to 10% by volume. Clay solids should be 3% or less. Consequently, the low-solids systems typically use polymer additive as a viscosifier or bentonite extender and are non-dispersed.

Spud Muds: This type of mud is prepared with available water and appropriate concentrations of bentonite or other commercial clays. They are chemically untreated, although lime, cement, or caustic soda is occasionally added to increase viscosity and give the mud the ability to seal possible lost return zones in unconsolidated upper hole surface formations. Spud muds are mostly used for drilling the surface hole. Their tolerance for drilled solids and contaminants is very limited (Lyons and Plisga, 2016).

Polymer muds: Polymer additives are generally used in muds either to encapsulate drill solids to prevent dispersion and coat shales for inhibition, or to increase viscosity and reduce fluid loss. The most common polymers available for these purposes include cellulose, natural gum-based products, and acrylamide. Frequently, inhibiting salts, such as KCl or NaCl, are used in drilling muds to provide greater shale stability. These systems usually contain a minimum amount of bentonite and may be sensitive to divalent cations, such as calcium and magnesium.

Saltwater mud systems: Saturated saltwater-based muds are used to drill salt formations. These muds are usually prepared from brackish water, seawater or produced water sources, and dry sodium chloride (or another salt, such as potassium chloride used for shale inhibition) is added. Various specialty products are also used to increase viscosity achieving better hole cleaning properties reduction of fluid loss, such as attapulgite, starch, or carboxymethyl cellulose (CMC). Saltwater muds ordinarily are classified as saltwater muds when they contain more than 10,000 mg/L of chloride (Caenn et al., 2016; Lyons and Plisga, 2016). They may be further classified according to the amount of salt present and/or the source of the water. Saltwater muds include the *seawater or brackish water muds* and the *saturated salt muds*.

Chemically treated muds: This type of mud has been conditioned with bentonite and treated with caustic soda and lignite or lignosulfonate (as a thinning agent). No inhibiting ions are found in this type of mud (Lyons and Plisga, 2016).

Lignite or Lignosulfonate Muds: In this kind of drilling mud, freshwater is used as a base fluid, conditioned with bentonite. Lignosulfonate is added as a thinner and lignite as a fluid loss agent. Other additives such as CMC or PAC can be used for additional filtration control in such conditions that the bottom-hole temperature does not exceed 121°C (250°F). This type of mud is applied at all mud weights and provides a relatively low pH system (pH values for calcium lignosulfonates are expected between 10.0–11.0). This type of mud is stable at reasonably high temperatures (325◦F) and has good resistance to contamination (Lyons and Plisga, 2016).

Advantages of water-based drilling muds

- ✓ Low cost
- ✓ Suitable for curing mud losses
- ✓ Simple configuration
- ✓ Multiple types available for selection
- ✓ Good protective effect of oil and gas layer

Disadvantages of water-based drilling muds

- × They are active in clays leading to time-dependent borehole problems
- × They cause hydration of shale formation
- × They dissolve salts when drilling in evaporates
- × Not efficient in high-temperature conditions
- × They interfere with the flow of oil and gas through porous rocks

1.3.2. Oil-based muds

The oil-based fluid was the second-largest market in 2016, valued at USD 2.248 million in 2016, projected to expand in CAGR of 6.66% until 2023 (Market Research Future, 2018). Oil-based systems are used in various applications and especially where fluid stability and inhibition are necessary, such as high-temperature wells, deep holes, and wherever sticking and hole stabilization are problems. There are two kinds of oil-based muds and fluids depending on their components, as well as the drilling conditions that occur:

Invert emulsion muds: This kind of muds are water-in-oil emulsions, typically with oil as the continuous phase and calcium chloride brine as the emulsified internal phase. They usually contain as much as 50% brine in the liquid phase. There is a variety of oil-based mud additives which control fluid loss, viscosity, and other essential parameters of drilling. These additives mostly include emulsifiers and wetting agents (commonly fatty acids and amine derivatives), amine-treated organic materials for filtration control, organic clays and polymers for viscosity, and lime for alkalinity.

All-oil fluids: The all-oil fluids are formulated only with oil as the liquid phase and are often used as coring fluids. All-oil systems require higher additional gelling agents for viscosity.

Advantages of oil-based drilling muds

- ✓ Lower friction
- ✓ Suitable for HP/HT wells
- ✓ They are not reactive towards shale formations
- ✓ They resist salt and calcium contamination
- ✓ High penetration rates
- ✓ Better corrosion control

Disadvantages of oil-based drilling muds

- × Higher cost
- × High-speed diesel as base fluid is hazardous
- × If circulation losses arise when drilling is difficult to stop the losses
- × They must have aromatic content <1% to be used in onshore drilling operations

1.3.3. Pneumatic drilling fluids

In this kind of drilling fluids, compressed air or gas are used instead of the typical drilling mud to circulate cuttings out of the wellbore. Four basic types are included in this specialized category:

Dry air: This situation involves injecting dry air or gas into the wellbore at rates capable of achieving annular velocities that will remove cuttings.

Mist: In this category there is an injection of a foaming agent into the air stream that mixes with produced water and coats the cuttings to prevent mud rings, allowing drill solids to be removed.

Foam: A high carrying-capacity foam is often formed using surfactants and possibly clays or polymers.

Aerated fluids: This type of drilling fluid relies on the mud with injected air to remove drilled solids from the wellbore.

Advantages of pneumatic drilling muds

- ✓ Low cost (dry air)
- ✓ They cause minimum damage to water-sensitive pay zones
- ✓ They have excellent ROP in dry competent formations
- ✓ Good thermal stability (foam)
- ✓ Hydrocarbon identification immediate and continuous

Disadvantages of pneumatic drilling muds

- × Excessive erosion near the top of the hole where expansion results in high annular velocity
- × Disposal of waste gas can be a hazard
- × Increased mud and chemical costs (foam)
- × May cause a downhole fire when hydrocarbons are encountered (Air drilling).

1.3.4. Synthetic drilling fluids

Synthetic drilling fluids are designed to mirror the behavior of oil-based muds, without environmental hazards. They primarily contain esters, ethers, and olefins.

Advantages of synthetic drilling muds

- ✓ Low toxicity and reduced irritant property
- ✓ Elimination of diesel reduces pollution hazards
- ✓ Highly biodegradable
- ✓ They have the effectiveness of OBM

Disadvantages of synthetic drilling muds

- × High cost
- × Kick detection
- × Not suitable in exploratory wells
- × Rubber parts tend to deteriorate.

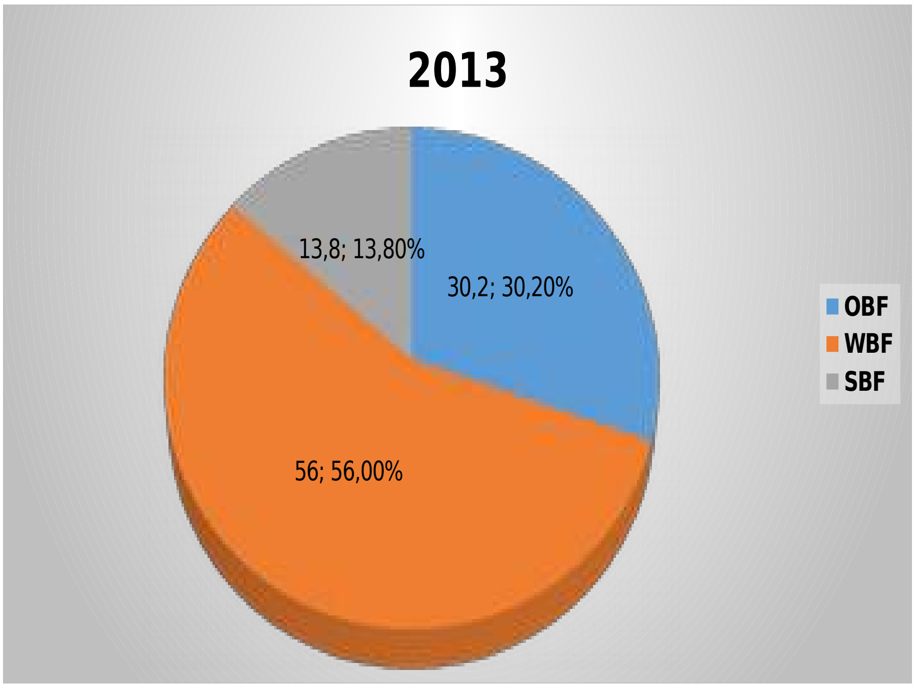


Figure 5. Drilling fluid market share by product in 2013 (Source: U.S Department of Energy, Company annual reports, Primary interviews, Grand view research).

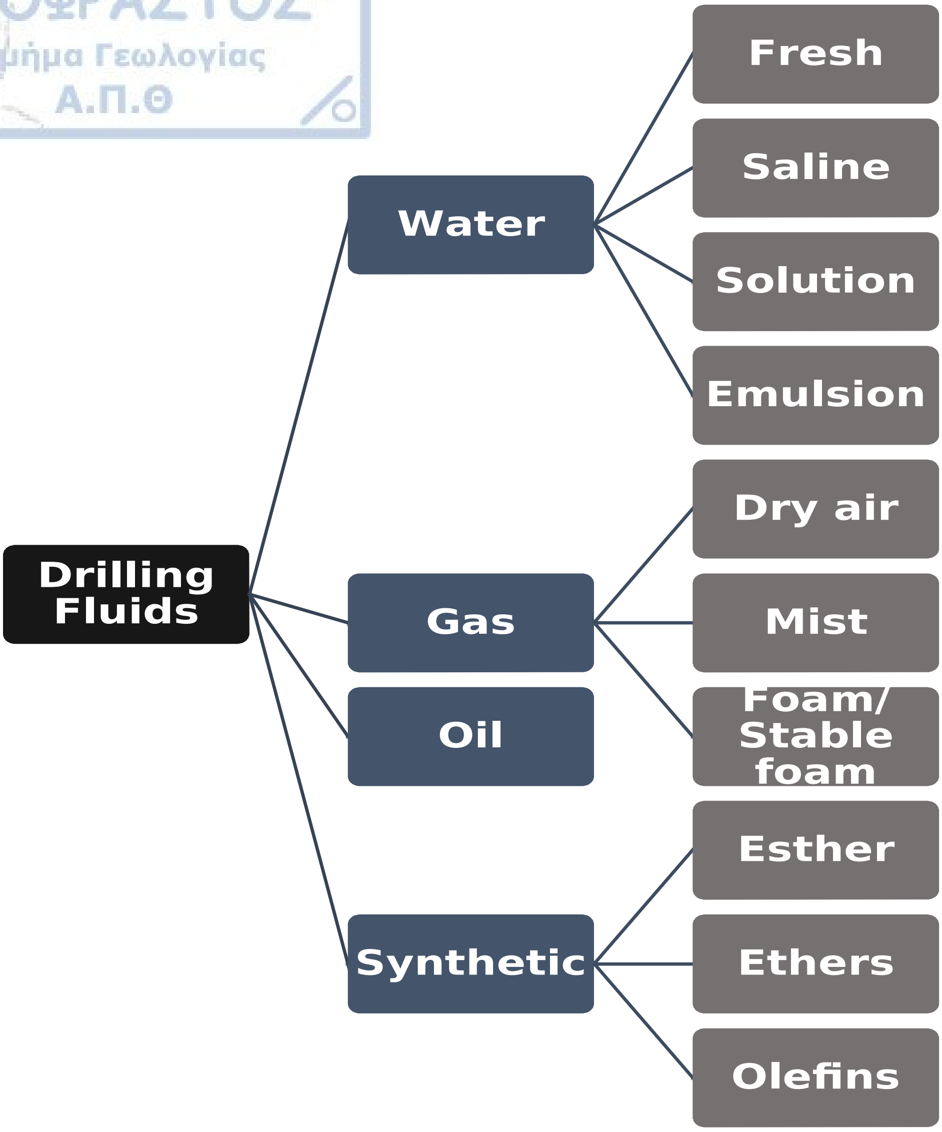


Figure 6. Classification of drilling muds and fluids.

1.4 Drilling mud properties

1.4.1. Density

The *density* of drilling mud is its weight per unit volume and compared to the weight of an equal volume of water is also expressed as *specific gravity*. The density affects the buoyant effect of the mud upon the drill cuttings. Specifically, an increase in mud density gives rise to an increase in carrying capacity and a synchronous retarding settling of the cuttings at the surface. The density of a drilling fluid is an essential parameter in wellbore pressure calculation, as well as for the success of drilling and completion operations (Kamari et al., 2017).

Excessive mud densities may cause fracturing on the borehole walls (Aadnøy et al., 2019; Aird, 2019). According to Cenn et al., (2016), the problem of maintaining mud density in high enough levels to control formation fluids but not so high to induce a fracture becomes acute when dealing with different formation pressures at the same time. Mud density is mostly controlled with weighting agents such as barite, hematite, galena, etc.

Table 1. Densities of common mud components after Cenn et al., (2016).

Material	Kg/m^3	Lbs/bbl
Water	1000	350
Oil	800	280
Barite	4100	1436
Clay	2500	874
Salt	2200	770

1.4.2. Rheology-Flow properties

The science of rheology describes the deformation and flow of solids, liquids, and gases. Especially, rheology deals with the relationship between flow pressure and flow rate, and their influence on the flow characteristics of the fluid. Generally, there are three fundamental flow regimes:

1. Laminar flow regime occurs at very low velocities when the flow is orderly, viscous and the pressure-velocity relation of the fluid is a function of the viscous properties of the fluid. The laminar flow equations are based on specific flow models called, Newtonian, Bingham plastic, Pseudoplastic, and Dilatant.

2. Turbulent flow regime prevails at high velocities, where the fluid elements move mostly disorderly, in countless eddies and swirls. Flow in a pipe turns from laminar to turbulent due to the increase of the velocity over a critical value. The flow depends on the inertia properties of the fluid and the flow equations are empirical.

3. Transitional flow regime is the intermediate flow between the laminar and the turbulent.

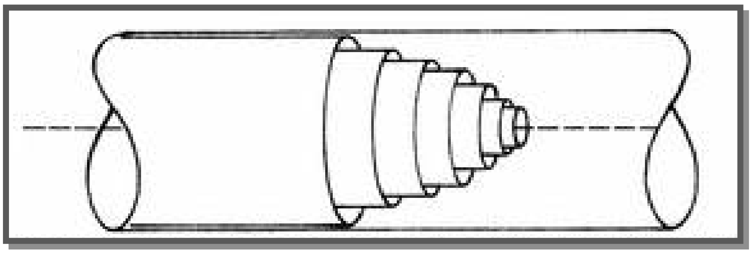


Figure 7. Schematic representation of the laminar flow of a Newtonian Fluid in a round pipe (Caenn et al., 2016).

The mathematical description of the drilling fluids rheology is related to the meanings of ***shear rate (γ)*** and ***shear stress (τ)***. These two parameters are widely used in the petroleum industry especially, in order to describe the type of drilling fluid flow. Shear rate is determined by the amount of force applied on the fluid, while shear stress is the resistance of the fluid to the applied rate of stress or force. The shear rate is described by the following equation:

$$\gamma = \mathrm{dv/dr} \quad (1.1)$$

where **v** is the velocity and **r** is the pipe radius. The shear stress is described by the following equation:

$$\tau = \mathrm{F/A} \quad (1.2)$$

where **F** is the applied force and **A** is the surface exposed to that force. The plot of shear stress versus shear rate is called ***flow model*** or ***consistency curve*** and its shape determines the nature of the fluid (Figure 9).

1.4.2.1. Rheological parameters

Apparent Viscosity (AV): The ratio of shear stress to shear rate is called *effective* or *apparent* viscosity and is a measure of the resistance to flow of a fluid. It is also, the result of the interaction of plastic viscosity and yield point.

Plastic Viscosity (PV): Plastic Viscosity represents the viscosity of the drilling fluid when extrapolated to an infinite shear rate -according to the mathematics of the Bingham model- and it is related to the concentration of solids in the fluid. Therefore, a high PV is caused by a viscous base fluid and by an excess of colloidal solids. On the other hand, low PV indicates that the mud is capable of drilling rapidly because of the low viscosity of mud exiting at the bit. To lower PV, a reduction in solids content can be achieved by dilution of the mud.

Yield Stress (YS or τ_0): Yield Stress is the initial stress required to move the fluid and it is related to the interparticle forces among the clay particles (Wang, 1992). In other words, it’s the attractive force between the colloidal particles of the fluid. It also indicates the ability of the drilling fluid to carry the cuttings to the surface. For water-based muds, Yield Stress increases with high temperature, contaminants (CO_2, anhydrite, salt, etc.) and treatment of mud with lime or caustic soda. For oil-based muds, an increase at Yield Stress is associated with the presence of drill solid, the excess of CO_2 in the mud, as well as the low temperature, which increases mud viscosity and therefore the Yield Stress.

Yield Point (YP or τ_γ): Yield Point is closely associated with the Yield Stress. Specifically, YP indicates the point that the fluid starts to move.

YP/PV ratio is a measure of the shear-thinning (the higher the ratio the greater the shear-thinning). In rheology, shear-thinning is the behavior of non-Newtonian fluids, whose viscosity decreases under an increase in shear stress.

Gel strength: Gel strength is a parameter that denotes the thixotropy of the mud at rest (Wang, 1992). Specifically, it is a measure of the inter-particle forces and indicates the gelling that will occur when circulation is stopped, which prevents the cuttings from settling in the hole (Caenn et al., 2016). To circulate a high gel mud, high pump pressure is required. Gel strength is measured in units of $lbs/100ft^2$ using a viscometer. The reading is obtained by noting the maximum dial deflection when the viscometer is turned at a 3 rpm rotor speed and after the mud has remained static for a specific period of time (10 seconds, 10 minutes, or 30 minutes). If the mud is allowed to remain static in the viscometer for 10 seconds, the maximum dial deflection obtained when the viscometer is turned on is reported as the initial gel. (API RP13B-1, 2017). If the mud is allowed to remain static for 10 minutes, the maximum dial deflection is reported as the 10-min gel.

1.4.2.2. Newtonian fluids

Newtonian fluids have constant viscosity at all shear rates, which is calculated by using the following equation:

$$\boldsymbol{\mu = \tau/\gamma} \quad (1.3)$$

where $\boldsymbol{\mu}$ is the viscosity of the fluid, $\boldsymbol{\tau}$ is the shear stress of the fluid, and $\boldsymbol{\gamma}$ is the shear rate of the fluids.

There is a straight-line relationship between shear rate and shear stress in Newtonian fluids (Figure 8), where the viscosity of the fluid is given by the calculation of the inclination of the straight line. Known Newtonian fluids are water, air, mineral oil, gasoline, etc.

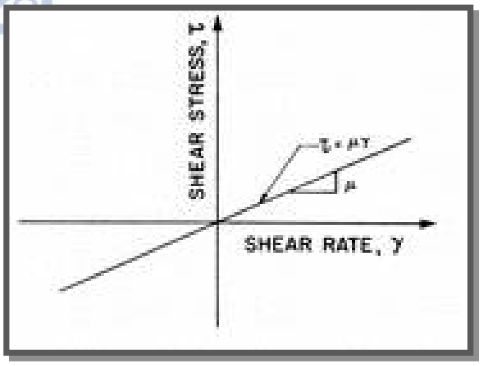


Figure 8. Shear stress -Shear rate relation for a Newtonian fluid.

1.4.2.3. Non-Newtonian fluids

Drilling fluids are usually non-Newtonian fluids, in which the ratio of shear rate/shear stress is not constant and depends on the composition of the fluid. Rheological models are used to predict fluid flow behavior across a wide range of shear rates.

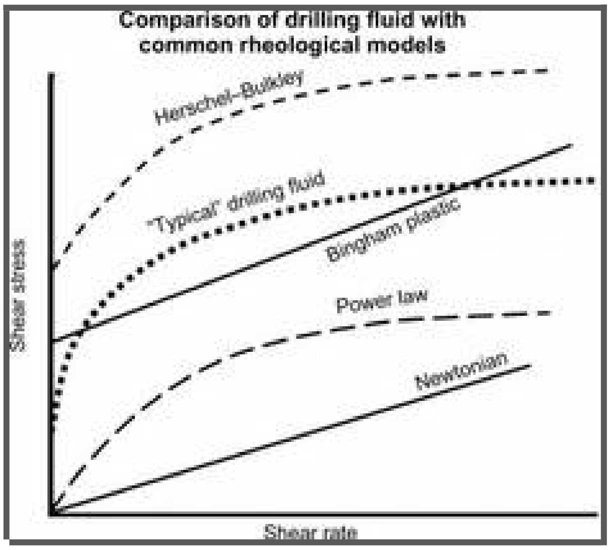


Figure 9. Summary illustration of primary oilfield rheology models after Texas Drilling Associates.

There are many models used to predict the viscosity of the drilling fluids. Traditionally, the oil and gas industry uses Bingham plastic and Power-law models in the field to calculate or predict the rheology of drilling fluids because of their simplicity. However, it is imperative to have rheological models spanning the full shear rate range (e.g. Hersey-Buckley model) and not only the high shear rates (e.g. Bingham model) (Herzhaft et al., 2003; Kenny and Hemphill, 1996).

Several mathematical models have been developed to describe the relationship between *shear stress* and *shear rate* of non-Newtonian fluids (Garakani et al., 2011). Fluids that exhibit Bingham plastic behavior are characterized by a yield point (τ_γ) and a plastic viscosity (n) (Malczewska et al., 2017).

1. Bingham plastic model: Bingham plastic fluid is defined as the fluid the yield point and plastic viscosity of which are the intercept and the slope, respectively, of a line drawn through the shear stress measurements at 600 and 300 rpm on the standard viscometer (Chilingarian, 1983). Specifically, the Bingham model curve is similar to Newtonian fluids except that it has an intercept on the shear stress axis, which is the **Yield Point (YP)**, while the slope of the line is the **Plastic Viscosity (PV)**. Therefore, a Bingham plastic model can be expressed by the following equation:

$$\boldsymbol{\tau} = \mathbf{n} \times \boldsymbol{\gamma} + \boldsymbol{\tau}_\gamma \quad (1.4)$$

where **n** is the behavior index (dimensionless) and $\boldsymbol{\tau}_\gamma$ is the Yield Point. In the Bingham model, the behavior index represents the PV of the fluid. So, the equation 1.4 can also be expressed as:

$$\boldsymbol{\tau} = \mathbf{PV} \times \boldsymbol{\gamma} + \mathbf{YP} \quad (1.5)$$

Plastic Viscosity and Yield Point can be calculated by the equations:

$$\mathrm{PV\ (cP)} = \theta_{600} - \theta_{300} \quad (1.6)$$

$$\mathrm{YP\ (lbs/100ft^2)} = \theta_{300} - \mathrm{PV} \quad (1.7)$$

2. Power-law model

The Power-law model is used in describing the rheological properties of shear-thinning fluids, such as polymer and foam solutions, in porous-medium flow. This model has two parameters to describe the behavior of the fluid. Equation 1.8, describes the behavior of a power-law fluid. (Rehm and Haghshenas, 2012)

$$\boldsymbol{\tau} = \mathbf{K} \times \boldsymbol{\gamma}^{\mathbf{n}} \quad (1.8)$$

where **K** is the flow consistency index in Pa × s^n.

In the Power-law fluid model, fluid starts to move as a shear rate applies to the fluid, which does not explain the thixotropic properties of the drilling fluid. In general, the power-law model presents issues in predicting the behavior of the drilling fluid at low shear rates because the model is forced to pass through the origin of a shear rate-shear stress plot (Rehm and Haghshenas, 2012).

The Power-law model suffers in the low shear rates region. Hence, it has been proved (Mark and Ramsey, 2019), that a Power-law model with the addition of a YP is more efficient at lower shear rates. Such a model was developed and is called the Herschel–Buckley model.

3. Herschel-Buckley Model

The Herschel-Buckley model is a modified Power-law model, in which there is the addition of **Yield Stress** to the equation. This model is one of the most complex models, which has three parameters and defines the behavior of the drilling fluids better than the other. API 13D (2009), recommends using the Herschel-Buckley model to predict fluid's behavior and pressure drop calculations more accurately for deep and complex wells (API 13D, 2009; Rehm and Haghshenas, 2012). A Herschel-Buckley fluid can be described mathematically as follows:

$$\tau = \tau_0 + K(\gamma)^n \quad (1.9)$$

where τ_0 is the Yield Stress of the fluid.

The Herschel-Buckley equation is preferred to Power-law or Bingham models because it results in a more accurate characterization of rheological behavior when adequate experimental data are available. The **consistency curve** and the **rheological model** it fits in are necessary to describe the rheology of a fluid, as well as the calculation of its rheological parameters: **Yield Stress (τ_0), K, and n**.

Table 2. Rheological models and their equations.

Model	Equation
Bingham plastic	$\tau = n \times \gamma + \tau_\gamma$

Power-law	$\tau=K\times\gamma^n$
Herschel-Buckley	$\tau = \tau_0 + K\times\gamma^n$

1.4.3. Filtration Properties

While drilling, muds tend to invade the permeable formations to prevent formation fluids from entering the borehole and result in damage. **To achieve that, the hydrostatic pressure of the mud column must be greater than the pressure of the fluids in the pores of the formations** (Caenn et al., 2016). The solids contained in the mud are filtered out onto the walls of the hole, forming a cake of relatively low permeability through which, only filtrate can pass.

Filtrate is the liquid portion of the mud system that is driven through the filter cake.

Filter cake is a thin layer of drilling mud solids that forms on the well-bore walls and controls the inflow of the filtrate into the formations by the differential between the hydrostatic pressure of the mud column and the formation pressure. The permeability of the filter cake is an essential parameter to maintain a stable borehole and to minimize the damage of potentially productive horizons. On the other hand, thick mud cakes result in a decrease in the hole's width, which can cause other problems in the drilling procedure. Thus, a lot of studies have been made dealing with suitable fluid loss and mud cake rates for each formation drilled, as well as new techniques to improve the filtration mechanisms. (Alsaba et al., 2018; Averkina et al., 2019; Black et al., 1985; Ezeakacha et al., 2019; Hassen, 1982; I-Tami et al., 2019; Kelessidis et al., 2007; Medvedev et al., 2018; Morenov and Leusheva, 2017; Wang et al., 2019; Wang et al., 2017; Xu et al., 2018).

1.4.3.1. Static and dynamic filtration

Filtration can occur both in ***static*** or ***dynamic*** conditions. When the circulation in the borehole is interrupted, a difference between the hydrostatic pressure in the wellbore and that in the reservoir is created, and from that point on static filtration begins. Static filtration rates are controlled by an undisturbed thickening of the mud cake. On the contrary, dynamic filtration occurs when drilling fluids are pumped through the well, and suspensions are flowing parallel to the filter cake (Caenn et al., 2016; Calcada et al., 2011; Outmans, 1963). In this process, the filter cake growth is limited by the shear stresses generated due to the fluid flow in the wellbore.

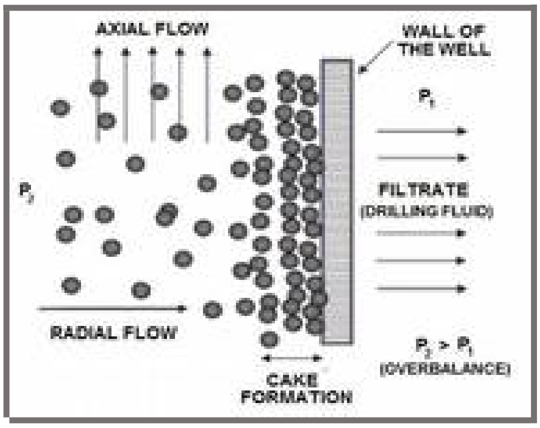


Figure 10.A schematic for the filter cake buildup in dynamic filtration (after Calcada et al., 2011).

1.4.3.2. Fluid invasion mechanisms

Understanding the fluid invasion mechanisms and predicting the filtration rates that occur during drilling and dynamic filtration has always been essential for the oil drilling operations, to guide the development and design of reservoir protection measures. (Lomba et al., 2002; Martins et al., 2003; Wang et al., 2019; Zhao et al., 2019). Prediction of the conditions that occur near and over the wellbore walls, such as mud filtrate and fines invasion and distribution, is essential for an accurate interpretation of the well-logs used for measurement and monitoring of the properties of the formations in proximity providing with an accurate estimation of the hydrocarbon content of the reservoirs (Civan and Engler, 1994; Phelps, 1995; Ramakrishnan and Wilkinson, 1997).

As presented in Figure 11, mud solids and filtrate can invade and damage the near-wellbore formation. The depth of filtrate invasion strongly depends on the type of muds, as it is less with oil-based muds, more with water-based muds, and moderate with emulsion muds applied to a water-wet formation (Civan, 2007).

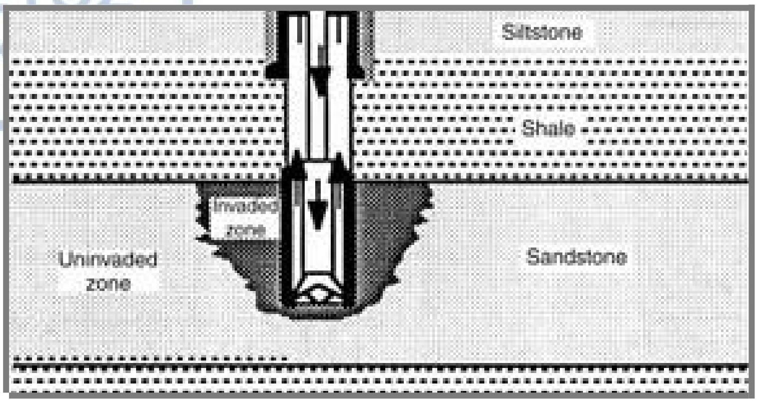


Figure 11. Mud-filtrate invasion in the near-wellbore formation (after Yao and Holditch, 1993).

During this process, the formation of a mud filter cake reduces the filtrate volume and the migration of fine particles into the porous formations (Figure 12). Simultaneously, there is an interaction among the reservoir fluids in porous media and the mud filtrate and fine particles of the fluid, which results in changes of fluid's initial properties such as density and viscosity.

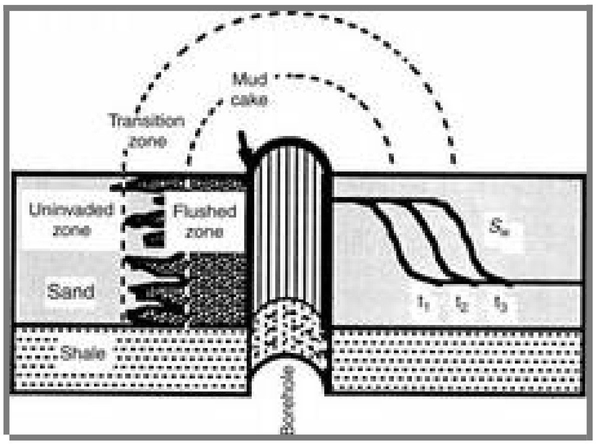


Figure 12. Detailed schematic of the various zones and the mud filtrate invasion profiles at different times in the near-wellbore formation (after Yao and Holditch, 1993).

Reservoir formation damage frequently occurs during drilling, completion, and production, and it reduces production capacity or even causes total reservoir shut down. It is frequently reported (Civan, 2015; Fjelde, 2009; Lopes et al., 2012; Sánchez et al., 2004; Zhao et al., 2019) that it can also delay the discovery and development of oil and gas fields. The implementation of formation protection measures by drilling and completion fluids would directly influence the safety, efficiency, and benefit of oil and gas development.

1.4.3.3. Filter cake

The filter cake is essential for stabilizing porous permeable formations. The ideal filter cake needs to be thin, tough, impermeable, and flexible. A cake with the ideal properties can easily isolate the wellbore fluids from the pore fluids at the wellbore wall. This is important in terms of wellbore stability and to prevent differential sticking. If there is poor or no filter cake, the pore pressure near the wellbore overcomes the hydrostatic pressure and causes a dangerous situation. In simple terms, the ideal filter cake provides a more stable wellbore. The chemical composition of the mud and the formation permeability control the filter cake quality and the time taken to form. (Aird, 2019).

1.4.4. pH

Measurement of pH values when drilling is constant and it is often an indicator of mud contamination. For instance, drilling muds usually have pH values between 8-10. If this value is changed when drilling, it indicates the contamination of the mud by other substances (e.g. cement, salts, etc.). Modifying pH values is also a way to influence the rheological properties of the mud. As an example, when adding caustic soda, an increase of the dispersion of clay particles is observed, followed by an increase of the rheological properties of the mud (AV, PV, YP). Monovalent cations, such as Na^+ give rise to a lesser attractive force and allow more water to penetrate between the clay platelets than divalent cations, consequently increasing the rheological characteristics of the mud (Al-Marhoun and Rahman, 1988; Ghassem and Teymoori, 2007).

1.4.5. Solids content

Solids content refers to the total soluble and insoluble amount of solids in the drilling mud, and it always increases while drilling ahead due to the enrichment of the mud with cuttings, as well as the addition of mud chemical additives and weighting material.

There are three types of solids in drilling muds; the soluble compounds such as salts, the insoluble high gravity materials such as weighting agents, and the insoluble low gravity solids such as drilled cuttings. The last type is the worst because it can alter the mud properties and when the size of the cutting is lower than 5 microns, it is rather impossible to remove them mechanically from the mud.

1.5 Drilling mud main constituents

1.5.1. Clays

Clay minerals are fundamental in drilling fluid technology as they provide the colloidal base of almost every aqueous muds, while they are also used in oil-based drilling fluids (Abdo and Haneef, 2013; Abu-Jdayil, 2011; Caenn et al., 2016). Clays are responsible for the thixotropic and gel-forming behavior of the drilling mud. Some of the essential properties of the clay minerals are as follows:

1. **Swelling:** Swelling is the moving apart or disjoining of the clay particles, especially those in a parallel arrangement until they reach their equilibrium separation under a given pressure (Chen et al., 1987). In bentonite, for instance, the absorption of specific cations can multiply the swelling ability of montmorillonite, as well as in other clay minerals such as vermiculite (Figure 13).

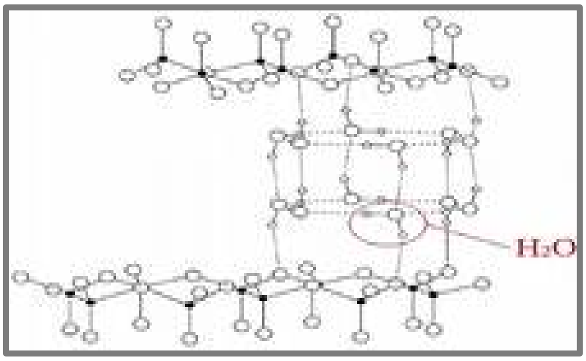


Figure 13. Combined water layers between layers of partially dehydrated vermiculite (modified after Hendricks and Jefferson, 1938).

2. **Flocculation & Deflocculation:** When suspended into pure water, clay minerals cannot agglomerate due to the high interference between the double layers of their structure. The phenomenon of flocculation occurs with the addition of electrolytes, which cause the compression of the double layers, increasing the attractive forces and leading to the agglomeration of the clay particles (Caenn et al., 2016). This property of clays causes the formation of a continuous gel structure, especially when

drilling salts. According to Van Olphen, (1977), clay particles are linked forming bonds with two different surfaces; the negatively charged **Face surface** and the usually positively charged **Edge surface**. As presented in Figure 14, the **Edge-to-Edge (EE)** and **Face-to-Edge (FE)** bonds are common in flocculation conditions, while **Face-to-Face (FF)** bond results in a deflocculated or aggregated condition of clay particles. FF structure corresponds to lower viscosity, while EE and FE structures lead to the higher viscosity of the fluid.

3. **Thixotropy:** Clay suspensions often show a time-dependent flow behavior, which is called thixotropy (Lucham and Rossi, 1999). After mixing the suspensions with water the Plastic Viscosity and Yield Stress increase with time, forming a gel-like structure in the mud. After mixing, the clay particles (which were separated due to mixing) are linked again due to FE or EE forces, forming a three-dimensional network (Lucham and Rossi, 1999).
4. **Cation exchange ability:** Cations are absorbed on the surface of clay particles. Cation Exchange Capacity (CEC) is the total amount of cations absorbed, expressed in meq/gr of dry clay. This property of clay minerals allows the treatment of clays with various cations. As an example, Greek bentonite clay from Milos island is usually activated with Na_2CO_3, where Na^+ substitutes the Ca^+ in montmorillonite structure to achieve the desirable properties of sodium montmorillonite with huge economical and industrial applications.

Table 3. Base exchange capacities of clay minerals (Weaver and Pollard, 1973).

Meq/ 100 gr of dry clay	
Montmorillonite	70-130
Vermiculite	100-200
Illite	10-40
Kaolinite	3-15
Chlorite	10-40
Attapulgite	10-35

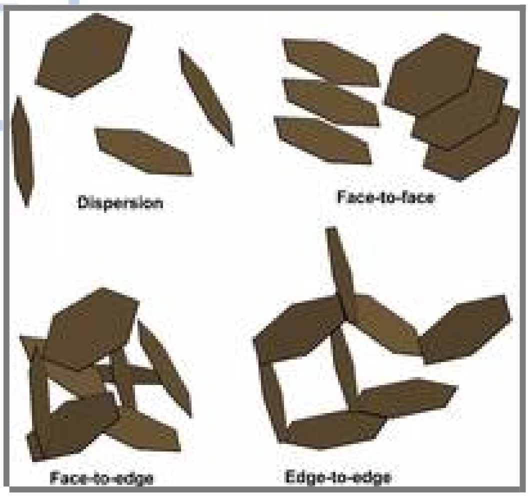


Figure 14. The structures of Montmorillonite in water (After Zhuang et al., 2019).

The above properties are deeply associated with colloidal systems behavior and make clay minerals suitable as the colloidal base in a drilling fluid. In colloidal systems, several properties (e.g. viscosity) are controlled by surface phenomena. These phenomena are easily applied to clay minerals due to the greater **specific surface** of their particles (Sarquis, 1980).

Montmorillonite is the best-known member of the Smectite group and is the principal mineral phase of bentonite. The special structure and features of this mineral lead in large specific surface area, swelling properties in polar solvents, adsorptive properties, and suitable rheological properties for drilling muds (Zhuang et al., 2019). Due to its expanding lattice, montmorillonite swells easily. For instance, when mixed with water, its high charge and fine particle size result in a very high viscosity of the fluid.

1.5.2. Additives

Drilling mud additives are specific compounds that are used to control or treat the drilling mud functions. Depending on the mud system and the conditions on the borehole, there is a huge variety of drilling mud additives suitable for each one of the drilling mud properties.

Alkalinity control agents: These agents may increase or decrease the alkalinity within the drilling fluid. Alkalinity agents help provide fluid stability, improve polymer hydration and performance, and treat out contaminants like cement, CO_2, and H_2S encountered in mixed waters or while drilling. Some of these products are Lime (CaO), Caustic soda (NaOH), Soda ash (Na_2CO_3), Citric acid, etc.

Filtration reducers: Fluid loss during drilling operations has a very significant effect on both reservoir formation damage and monetary terms. There are many additives to control this unwanted phenomenon. **The filtration reduction is achieved by improving the filter cake quality**. Bentonite, various polymers, asphaltic resins, polyanionic cellulose, or lignite are some of the compounds which act as filtration control agents.

Thinners and Dispersants: Thinners are added to mud to reduce flow resistance and gel development. Specifically, they modify the relationship between the viscosity and the solids in the drilling fluid. However, several thinner agents perform other functions. They reduce filtration and cake thickness, counteract the effects of salts, minimize the effect of water on the formations drilled, emulsify oil in water, and stabilize mud properties on elevated temperatures (Caenn et al., 2016). Thinners act by reducing the attractive forces on clay particles without affecting the hydration of the clay. Materials commonly used as thinners are plant tannins, lignite compounds, polyphosphates, and lignosulfonates.

Lignosulfonate (LS) is a highly anionic polymer used to deflocculate clay-based muds. It is a byproduct of the sulfite method for manufacturing paper from wood pulp. In some cases, it is called *sulfonated lignin*. Lignosulfonate is a complex mixture of small -to moderate-sized polymeric compounds with sulfonate groups attached to the molecule. LS became a popular deflocculant in the late 1950s as a replacement for quebracho. Chromium and iron compounds were admixed to get stability benefits at a higher temperature. These were called *chrome lignosulfonates* (CLS) and *ferrochrome lignosulfonates* (FCLS) (Schlumberger Oilfield Glossary, 2019).

Weighting agents: These agents are used to increase drilling mud density, control the formation fluid pressure, prevent blowouts, prevent formation caving, and facilitate the pulling of dry pipe. Common weighting agents are barite (API 13A, 1993), hematite (API 13A, 1993), galena, ilmenite (Saasen et al., 2001), siderite, etc.

Viscosifiers: Viscosifiers (or thickeners), are mostly polymer compounds designed to increase drilling mud viscosity, and to improve the hole-cleaning and solids-suspension capabilities of drilling fluids. Thickener polymers include polyurethanes (PUs), polyesters, polyacrylamides (PAMs), natural polymers and modified natural polymers (Caenn et al., 2016; Doolan and Cody, 1995).

Shale stabilizers: While drilling, it is important to maintain wellbore stability, especially when drilling water-sensitive formations, such as shales. These kinds of rocks tend to absorb the water of the drilling fluid, which leads to a swelling behavior and therefore a wellbore collapse (Chen et al., 2010; Van Oort, 1997). Shale stabilizers are compounds such as polymers, hydroxy-aldehydes / hydroxy-ketones, quaternary ammonium carboxylates, which deal with this issue.

Surfactants: These compounds reduce the interfacial tension between water/oil, water/solid, water/air, and other contacting surfaces. They are organic compounds whose molecular structure is made of two dissimilar groups having opposing solubility tendencies (hydrophilic/hydrophobic). They act as emulsifiers, foamers, defoamers, lubricants, and corrosion inhibitors as well (Caenn et al., 2016). These additives are very important constituents of oil-based muds because they serve as emulsifiers, stabilizers, and oil-wetting agents.

Lubricants: Lubricant chemical products are formulated to reduce the coefficient of friction in the drilling fluids. They minimize torque and drag, reduce stuck pipe risk, and increase ROP. Fatty acids, esters, black coal (Runov et al., 1992) asphaltic compounds, olefins, phospholipids (Garyan et al., 1998), extreme-pressure lubricants, synthetic oils, and long-chain alcohols are used to impart lubricity on drilling fluids.

There is a constant worldwide research on several compounds concerning the improvement and the invention of new drilling fluid additives to improve the drilling performance and reduce the cost of drilling operations (Aadnøy and Looyeh, 2019; Abdo and Haneef, 2013; Al-Marhoum and Rahman, 1988; Browning, 1969; Chen et al., 1987; Chu et al., 2012; Garyan et al., 1998; Ghassem and Teymoor, 2007; Kosynkin et al., 2012; Liu et al., 2015; L-Yam et al., 2019).

CHAPTER 2 - MATERIALS AND METHODS

2.1 Materials

Commercial bentonite: The bentonite used was a Na_2CO_3 activated Greek commercial Zenith® bentonite. It is a <75μm powder from Milos island, with pH ranging from 8 to 10. After the X-Ray Diffraction analysis, it consists mostly of montmorillonite, natrite, calcite, and plagioclase.

Low-rank Coals: Four low-rank coals were obtained from the Florina-Ptolemais-Kozani lignite basin in NW Greece. There are three *typical matrix lignite* samples from Kardia, Mavropigi, and Northern Field mines, as well as a *leonardite* from Achlada mine (Table 4). The lignite samples were obtained from the seams of the highest quality and highest calorific value of each mine.

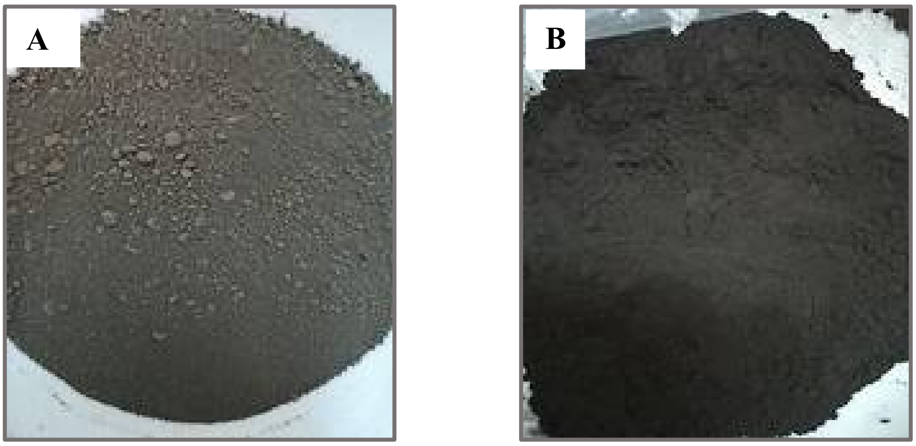


Figure 15. A: Leonardite powder from Achlada mine. B: Lignite powder from Kardia mine.

Table 4. Low-rank coals used and their description.

Sample	Lithotype	Location
KA	Matrix lignite	Kardia lignite mine, Western Macedonia Greece
MA	Matrix lignite	Mavropigi lignite mine, Western Macedonia, Greece
NF	Matrix lignite	Northern Field, lignite mine, Western Macedonia, Greece
LE	Leonardite	Achlada lignite mine, Western Macedonia, Greece
CLIG	Commercial causticized matrix lignite	Gumpro LTD, India

Leonardite is a low-rank coal type that usually derives either from lignite that has undergone oxidation during surface exposure or it represents sediments enriched in humic acids that were leached from topsoil or overlain lignite (Kalaitzidis et al., 2003). Generally, there are three types of leonardite (Browning, 1969). Type I is a soluble to alkali hydroxides colloidal black material analogous to native humic acid. Type II is a mixture of leonardite and lignite found in the topsoil formations above lignite seams, where humic acids from lignite are leached and enriched in the topsoil, while Type III leonardite is a laboratory precipitated product. Greek leonardites have been found in Achlada, NW Greece, and Zeli Central Greece (Kalaitzidis et al., 2003) and they are sorted as Type II leonardite.

Commercial causticized lignite: Commercial causticized lignite provided by Gumpro Drilling Fluids LTD was also used in the experiments as reference material.

Table 5. Certificate of analysis for causticized lignite as received by Gumpro Drilling Fluids Pvt. Ltd.

Commercial Causticized Lignite properties	
Appearance	Black free-flowing powder
pH of 2% solution	10.0
Moisture	5.20 %
Solubility in water	76.15 %

Figure 16. Commercial Causticized lignite powder.

Proximate analysis of all low-rank coal samples was held according to ASTM D3172-13, to determine their **moisture, ash, volatile matter,** and **calorific value** (both net and gross). The preparation of the coal samples involved drying at 45°C, where they lost most of their moisture content (approximately 55%). Afterward, they were grounded to particles less than 75 μm and air-dried at 105°C for 2 hours to eliminate the rest of their moisture content. Ash content, as well as volatile matter (CO_2, SO_x), were calculated on a dry basis. The total moisture content of the samples came up by summing the two moisture measurements after the 45°C and 105°C drying.

The lignite samples (MA, NF, KA) presented high moisture content between 56-60%, while leonardite (LE) is the sample with the lowest moisture content with 24.6% (Table 6). The ash content of the lignite samples was measured in dry basis (d.b.) and it was between 18-21%, lower than the average ash content of Greek lignites (Iordanidis and Georgakopoulos, 2003; Kolovos et al., 2005; Kolovos et al., 2002a), while the leonardite ash content was significantly higher at 62.5%. Gross and net calorific values were also measured on a dry basis and were higher than the average gross calorific values of the Ptolemais lignites (Kolovos et al., 2002b). Lignite samples had higher calorific values compared to the leonardite one.

The higher ash content of the leonardite sample indicated a higher concentration of inorganic compounds than in the other lignite samples, which was also reflected in the calorific value. The volatile matter content of all samples was low. For CO_2 the values were between 0.8-1,6%, while for sulfur the values were approximately 1-2%.

Table 6. Proximate analysis results of the low-rank coals used in the present study.

Samples	Total Moisture (%)	Ash content d.b. (%)	CO2 content d.b.(%)	Gross Calorific Value d.b. (cal/gr)	Net Calorific Value d.b. (cal/gr)	S content d.b.(%)
MA	59.3	19	1.2	5045	1610	1.28
NF	56	21.1	0.8	4983	1760	2.06
KA	60.2	18.1	1.5	5016	1553	1.27
LE	24.6	62.57	1.61	2146	1392	1.18

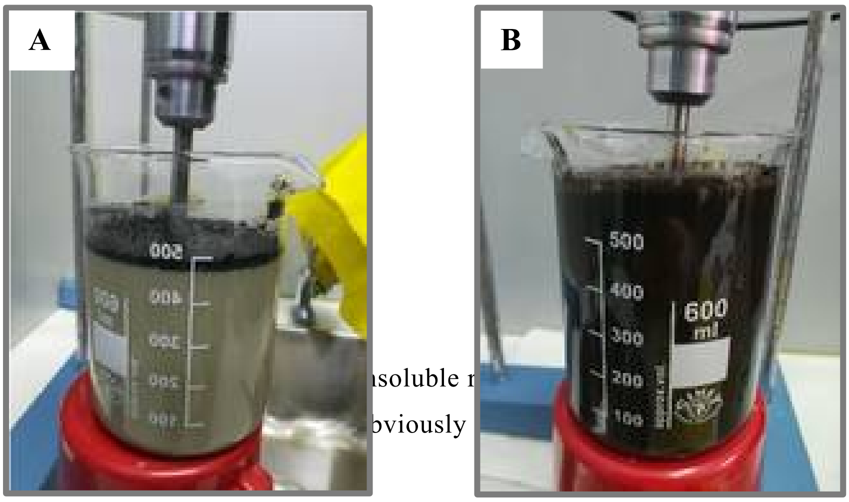
2.2 Methods

2.2.1. Causticization

Causticization is the chemical treatment of the samples with an alkaline solution. This procedure is essential for the coal samples, to release their **humic acid content**, increase their solubility, and control their pH values. Figure 17, shows coal samples before and after the causticization, where it is obvious that causticization affects the coal solubility in the drilling fluid.

Humic acids are organic carboxylic acids of complex molecular structure (aromatic and phenolic). The water solubility of lignite depends on its humic acid content. Decarboxylation of humic acid groups by hydrolysis in alkaline muds is a major source of carbonate and bicarbonate anions in water muds. Humic acids can be used as a **fluid loss additives** in an oil base and water-base drilling fluids. **Humic acids have three types of functions when used in drilling fluids:**

- They reduce viscosity and gel strength.
- They function as thinners, deflocculants, dispersants, and as rheological control agents.
- They also act, as stated above, as fluid loss agents and emulsifiers.



soluble r B: Addition of causticized
bviously mud.

Two different methods of causticization were examined in this study. The first one was performed with the addition of NaOH, while the second one was performed with a mixture of KOH, NaOH, and $ZnSO_47H_2O$.

1. **NaOH causticization:** In this method, the causticization was held with the addition of a NaOH 0.3M solution to the coal samples according to Shen and Zang (2018). In the experiment, 50 gr of each coal sample and 200 mL of a 0.3M NaOH solution were mixed. Coal samples were treated with the caustic solution at a temperature of 80°C±2°C for 2 hours and then cooled to a temperature of 60°C.
2. **Organic Zinc Complex causticization (OZC):** In the second method samples were causticized according to Browning, (1969) US patent. The preparation of the Organic Zinc Complex (OZC) was accomplished by solubilizing 82.7 gr of each sample in a caustic solution of 6.6%w/v KOH and 6.6%w/v NaOH. After the sample had sufficient time to solubilize in the caustic mix, 4.1 gr of zinc sulfate ($ZnSO_4 \times 7H_2O$) were added. The solution was kept hot at 78±2°C to facilitate the reaction and remain in a fluid state. After the zinc sulfate had been effected, the product was dried at 120°C.

After drying, all samples from both procedures were grounded to particles of 75μm and were ready for use as a drilling mud additive.

2.2.2. Preparation of the drilling muds

For the preparation of the studied mixtures, 32.1 gr of Zenith® bentonite were added in 500mL deionized water to create a **6.42% w/w** water-bentonite mixture according to API 13A, (1993) suggested proportions. Each mixture was stirred at 750 rpm for 30 min to homogenize. Afterward, **3% w/w** of each one of the causticized samples was added in the mixture and stirred for 15 min in 750-800 rpm to homogenize the fluid. Table 7, presents the drilling fluids which were prepared and examined.

Sample	Deionized water (mL)	Bentonite (gr / %)	Lignite or Leonardite (gr / %)
1. BH	500	32,1 /6.42	-
2. CKA	500	32,1/6.42	15 / 3
3. CMA	500	32,1/6.42	15 / 3
4. CNF	500	32,1/6.42	15 / 3
5. CLE	500	32,1/6.42	15 / 3
6. ZKA	500	32,1 /6.42	15 / 3
7. ZMA	500	32,1/6.42	15 / 3
8. ZNF	500	32,1/6.42	15 / 3
9. ZLE	500	32,1/6.42	15 / 3
10. CLIG	500	32,1 /6.42	15 / 3

Table 7. All drilling fluids examined and their concentrations. B: Bentonite, KA: Kardia, MA: Mavropigi, NF: Northern field, LE: Leonardite, CLIG: Commercial causticized lignite, C: Causticized lignite with NaOH, Z: Organic Zinc Complex causticized lignite.

The following experiments were performed on the above-mentioned drilling fluid samples to determine their properties.

- **Rheology - Viscosity measurements** (Fann 35A Viscometer)
- **Gel strength measurements** (Fann 35A Viscometer)
- **Filtration volume/ Filter cake thickness** (API LP/LT Filter Press)
- **pH measurements**
- **X-Ray Powder Diffraction (XRD)** was performed in all the initial raw samples (both bentonite and lignites), in the causticized samples, as well as in the filter cakes received from the filter press experiments.
- **Scanning Electron Microscopy (SEM)** was performed in the raw bentonite, in the causticized samples, as well as in the filter cakes received from the filter press experiments.

Usually, water based muds with bentonite are examined under several ageing techniques (hydration, static thermal ageing, dynamic thermal ageing, etc.). In the present thesis, the mixtures were examined without any ageing procedure. The aim of the study is the evaluation of low-rank coals as drilling mud additives without any ageing of the samples and not the evaluation of bentonite performance.

2.2.3. Rheology

Flow properties of the drilling fluids were measured at the Drilling Mud Laboratory of the Department of Mineralogy – Petrology – Economic Geology, School of Geology, Aristotle University of Thessaloniki. The experiments were performed using a six-speed (3, 6, 100, 200, 300, 600 rpm), rotational **Fann 35A model Viscometer**. The Fann direct-indicating viscometers are equipped with the standard R1 rotor sleeve, B1 Bob, F1 torsion spring, and stainless steel sample cup (Fig. 19). The outer rotating cylinder (R1) has a diameter of 1.8415 cm, while the inner cylinder (B1) has a diameter of 1.7245 cm. The procedure followed in the experiments is based on API RP13B-1, 2017 specifications.

The flow curve data reported in this study were obtained in θ° degrees through viscometer dial reading and **a model was developed to convert them, calculate the rheological parameters n, K, τ_0, PV and YP and investigate the rheological model that each sample fits in**, by solving the Herschel-Buckley (HB) rheological equation (API 13D, 2009).

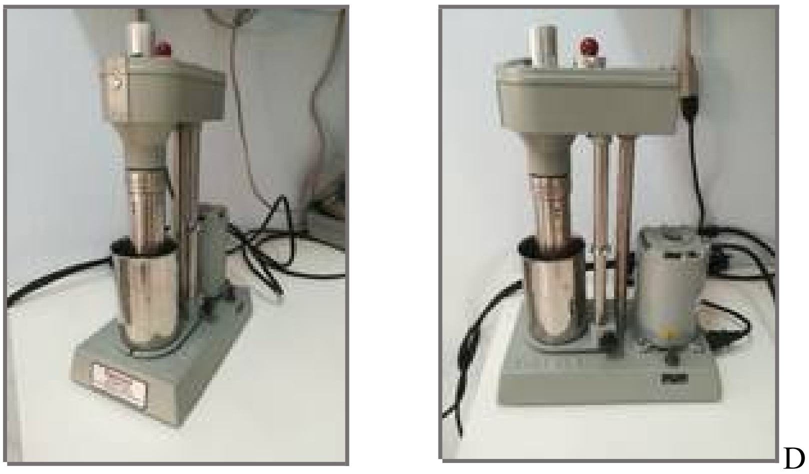
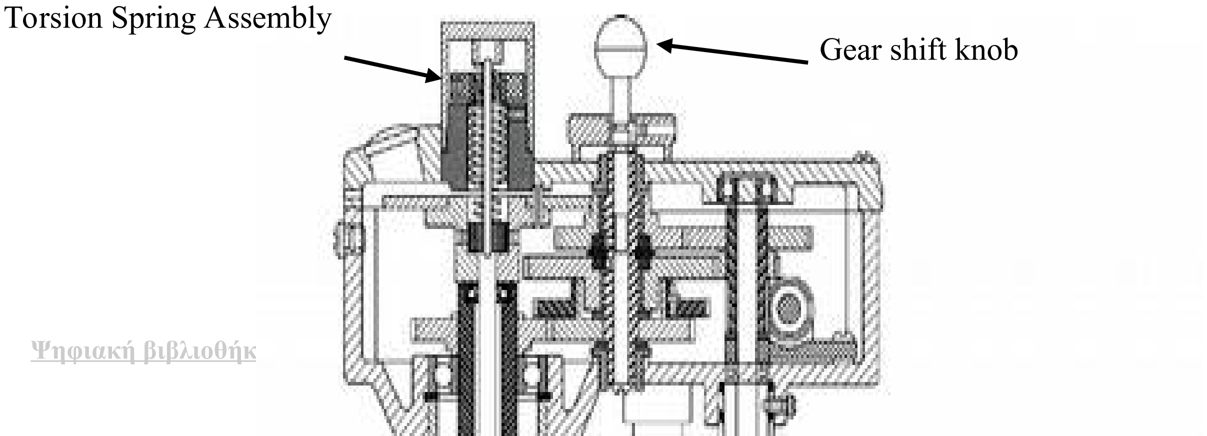


Figure 18. Fann 35A Viscometer apparatus used in the experiments.



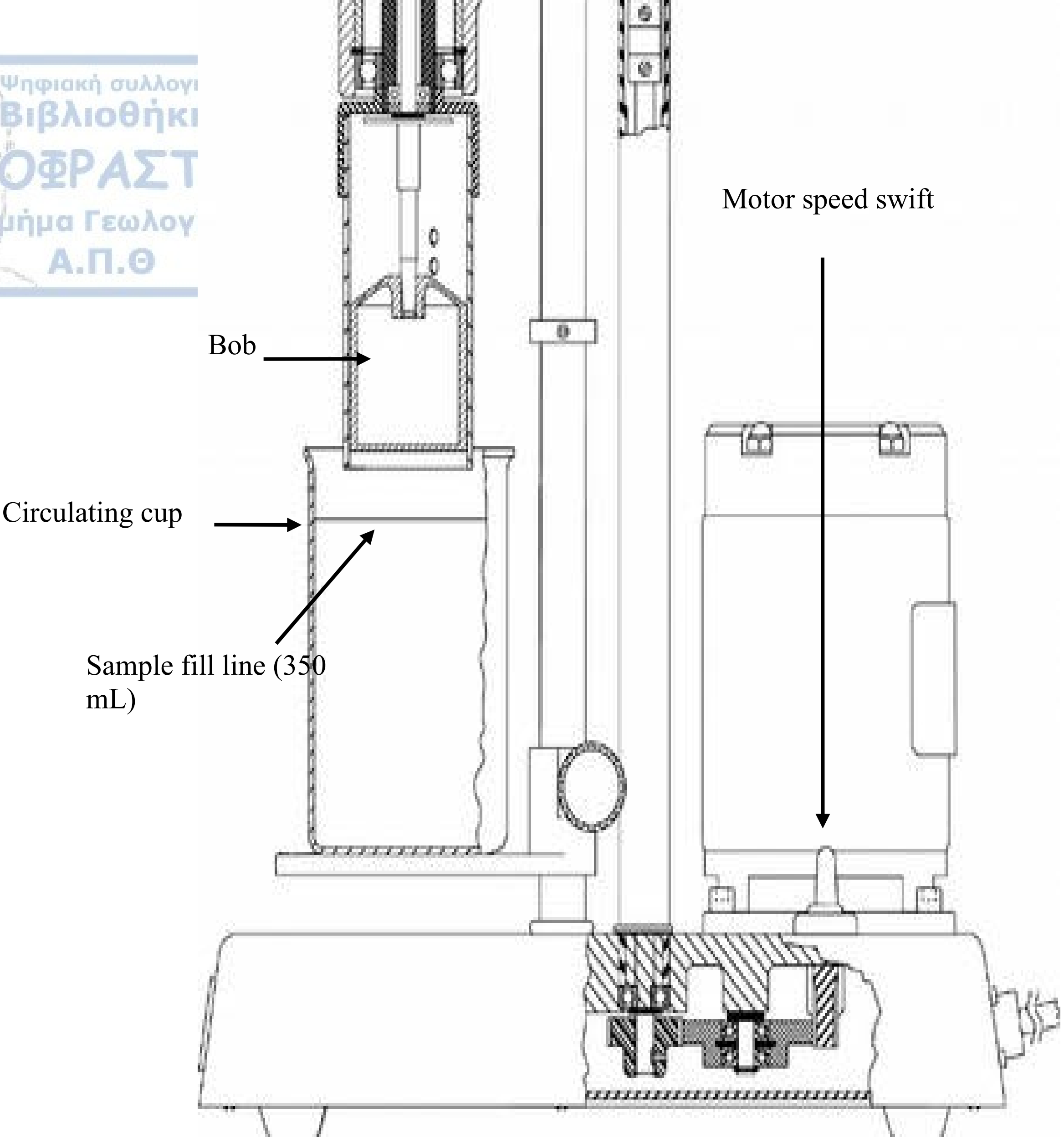


Figure 19. Fann 35A Viscometer, schematic.

The developed model was used at first, to convert the dial reading measurements (θ^o) to shear stress (Pa) by following the calculations:

Dial reading measurement (θ^o) × 1.066 = Shear stress (lb/100ft^2)

Shear stress (lb/100ft^2) × 0.4788= Shear stress (Pa)

and the speed of the viscometer (rpm) to shear rate (1/s) by the calculations:

Speed (rpm) × 1.703=Shear rate (1/s)

At the same time, for the given shear rates (γ) –which correspond to the six different speeds that were applied by the Viscometer in the experiments– the model generates (Table 9) **random numbers n, K, and τ_0 and calculates random shear stress values**. In this way, random shear stress (τ) is calculated. Both calculated and measured data are plotted on an x-y diagram with the shear rate on the x-axis and shear stress on the y-axis (Figure 20).

Table 8. The Herschel-Buckley rheological equation.

$$\tau = \tau_0 + K \times \gamma^n$$

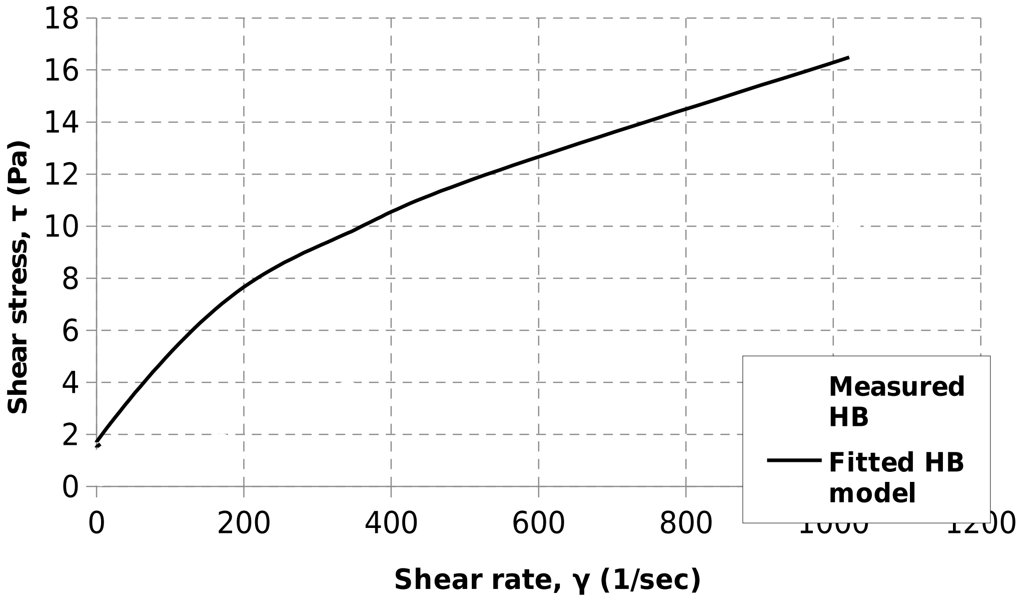


Figure 19. Example of the deviation between the measured and the calculated data that were produced from random rheological parameters in the model.

As can be noticed at the example in Figure 20, **the calculated shear stress does not fit the measurements, due to the random rheological parameters that the model initially generates.** Thus, the next step was to find the right parameters that will lead to the smallest possible residue between the measured and the calculated data.

Table 9. Demonstration of the calculated rheological parameters as calculated for random numbers.

Results

Determined Rheological Parameters

to (Pa)	**0.005**	**Random** - Shear stress at zero shear rate
K (Pa.sec^n)	**0.005**	**Random** - Consistency index
n (-)	**0.005**	**Random** - Flow behavior index
PV (cP)	7	Plastic Viscosity
YP (lbf/100ft^2)	3	Yield Point
PV (Pa.sec)	0.007	Plastic Viscosity
YP (Pa)	1.4364	Yield Point
Optimized Minima	**118.1878**	**Fitting error**

In Table 9, the results received for random numbers are demonstrated showing a very high fitting error value. **New shear stress data were produced by the non-linear solution of the HB equation for the rheological parameters n, K, and τ_0 that will give the minimum error (= the minimum residue from the measured data).** In that way, all the essential rheological parameters were obtained, for each one of our samples. In Table 10, an example of the final results received every time the model was solving the HB equation, is demonstrated. It is noticed also that there is an acceptable fitting error. In Figure 21, the final fitting of the calculated and measured results is graphically demonstrated.

Table 10. An example of the calculated rheological parameters in the form that were finally received from the model.

Results

Determined Rheological Parameters

to (Pa)	**0.023**	**Shear stress at zero shear rate**

K (Pa.sec^n)	**0.036**	**Consistency index**
n (-)	**0.792**	**Flow behavior index**
PV (cP)	7	Plastic Viscosity
YP (lbf/100ft^2)	3	Yield Point
PV (Pa.sec)	0.007	Plastic Viscosity
YP (Pa)	1.4364	Yield Point
Optimized Minima	**0.097027**	**Fitting error**

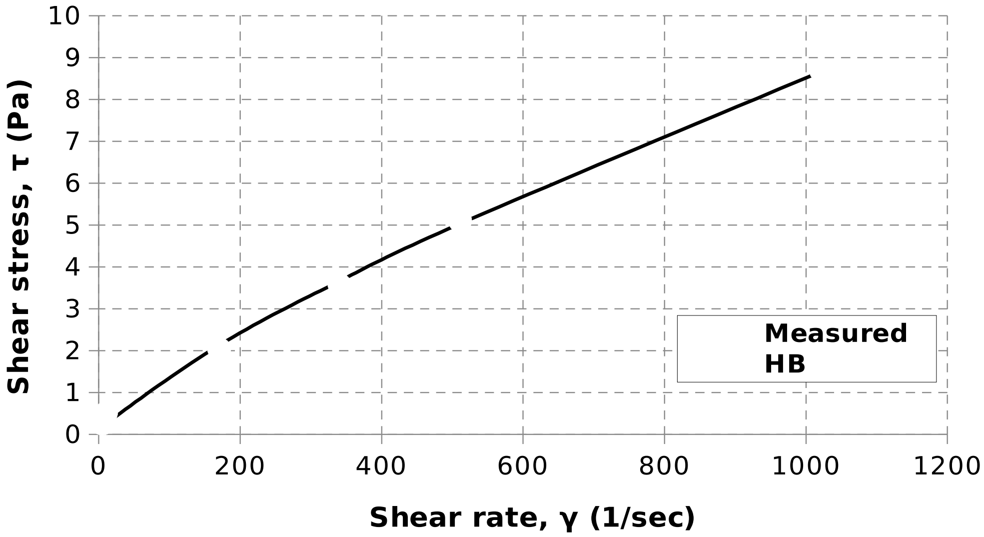


Figure 20. An example of graphical fitting of the calculated and the measured rheological data after the non-linear solution of the HB equation.

2.2.4. Gel strength

This experiment measures the ability of the drilling mud to create a gel, which is an unwanted situation when drilling, caused by several parameters that affect the fluid. **The gel strength is the maximum value measured before the gel breaks**. The procedure followed for measuring the gel strength is based on API RP13B-1, (2017) specification for **10s and 10min**. At first, the sample was stirred thoroughly at 600 rpm. The gear shift knob was set to the 3 rpm position for a few seconds, and then the motor was set to the OFF position. After the desired wait time, the motor was turned to the ON position at 3 rpm. The dial at the moment the gel breaks are noted by a peak dial reading, which is the measured gel strength of the sample. The gel strength units are lbs/100ft^2.

2.2.5. Filtration

Measurement of the filtration properties and the filter cake characteristics of drilling mud are fundamental to the treatment and control of a drilling fluid. Filtration properties of drilling fluid are affected by the quantity, type, and size of solid particles in the drilling fluid, and by properties of the liquid phase. The interactions of these various components can be affected by temperature and pressure. Filtration tests can be run under static or dynamic conditions at both low pressure/low temperature and high pressure/high-temperature conditions, and each procedure requires different equipment and techniques.

In this study, the static filtration properties of the samples were measured at the Drilling Mud Laboratory of the Department of Mineralogy – Petrology – Economic Geology, School of Geology, Aristotle University of Thessaloniki. The experiments were performed in LP/LT conditions with a **Fann LP/LT filter press** apparatus and with CO_2 as the mean of pressure, as recommended by API RP13B-1, (2017) specification.

Category	Specification
Pressure	100psi (690kPa)
Filtering area	45.8 cm^2
Dimensions (width×depth×heigth)	22.86 x 22.86 x 50.8 cm
Weight	6.8 kg

Figure 21. Fann LP/LT filter press Basic Assembly Specifications.

Preparation of the equipment was held by placing a gasket in the base cap, putting the screen on top of the gasket, and then placing the filter paper on top of the screen. Next, the sealing gasket was placed on top of the paper, and the cell was assembled. Finally, the drilling fluid sample was poured into the cell to 12 mm (0.5 in.) of the top. The cell was then sealed and a clean dry graduated cylinder was placed under the drain tube to collect the filtrate. A pressure of 100 psi (690kPa) was applied by closing the relief valve. The test lasts 30 min. At the end of the 30 min-test period, the filtrate volume was recorded and measured, as well as the mud cake thickness and properties.

2.2.6. Powder X-Ray Diffraction

Powder X-Ray Diffraction (PXRD) was performed on twenty-four samples, including raw materials (bentonite, lignites, and leonardite), causticized samples, and mud cakes received from the filtration tests. The tests were performed using the equipment of the Department of Mineralogy – Petrology – Economic Geology, School of Geology, Aristotle University of Thessaloniki.

A Philips (PW1710) diffractometer with Ni-filtered Cu K_α radiation was used. The samples were scanned over the 3–63° 2θ interval at a scanning speed of 1.2°/min. Interpretation of the PXRD diffractograms was held at both the Department of Mineralogy – Petrology – Economic Geology, School of Geology, Aristotle University of Thessaloniki, and the Geology Department of the University of Silesia, Poland. Semi-quantitative estimates of the abundance of the mineral phases were derived from the PXRD data, using the HighScore software, version 4.8, produced by Madvel Panalytical B.V., equipped with ICSD (Inorganic Crystal Structure Database).

2.2.7. SEM– EDS

Structure, morphology and chemical composition of the bentonite, the causticized samples, as well as the mud cakes received, were examined using a JEOL JSM-840 scanning electron microscope JEOL JSM-840 type of Aristotle University of Thessaloniki, equipped with an INCA 300 energy-dispersive X-ray spectrometer (EDS) with 20 kV accelerating voltage and 0.4 mA probe current. The samples were carbon-coated to acquire conductance.

CHAPTER 3 - RESULTS AND DISCUSSION

3.1 Rheological properties of the drilling muds

As already mentioned, when drilling in extreme conditions (elevated temperatures, high salinity, etc.) bentonite clay particles tend to swell and create thickening problems. In such a case, it is important to reduce the Plastic Viscosity of the drilling mud to improve the rate of penetration and to reduce the required pump pressure to circulate the mud to the surface. This will consequently help to sustain the drilling operation.

Organic mud thinners are used in these conditions, to control the dispersion properties and lower the viscosity. Thinners are considered to adsorb on the clay particles surface reducing the attraction forces among them. **Lignite compounds are often added in the drilling muds as thinning agents to control the swelling behavior of the clay particles and reduce the viscosity.** The organic molecules derived from the lignites are adsorbed on the surface of the clay particles and increase the negative charge, increasing the mutual repulsion among the particles and maintaining the stability of the suspension in high-temperature conditions. This mechanism is strongly associated with the fulvic and humic acids of the coal samples, as well as with their oxygen content.

3.1.1. Flow curves – Rheograms

Flow curves of each one of the studied samples along with tables of the measured and calculated properties are presented in the next pages. Each sample is compared to the control sample (BH) and is evaluated based on the improvement of the rheological properties that the addition of lignite offers.

1.Drilling mud - BH.

This mixture consists only of bentonite clay and water and it is the control sample. As shown in Figure 23, BH mud has a low shear stress value close to the origin –but not zero–, while the curve is of the **Herschel-Buckley rheological model** ($\tau_0 \neq 0$, $n \neq 1$). Apparent and Plastic Viscosity, as well as Yield point as measured through the experiments, are given in Table 11.

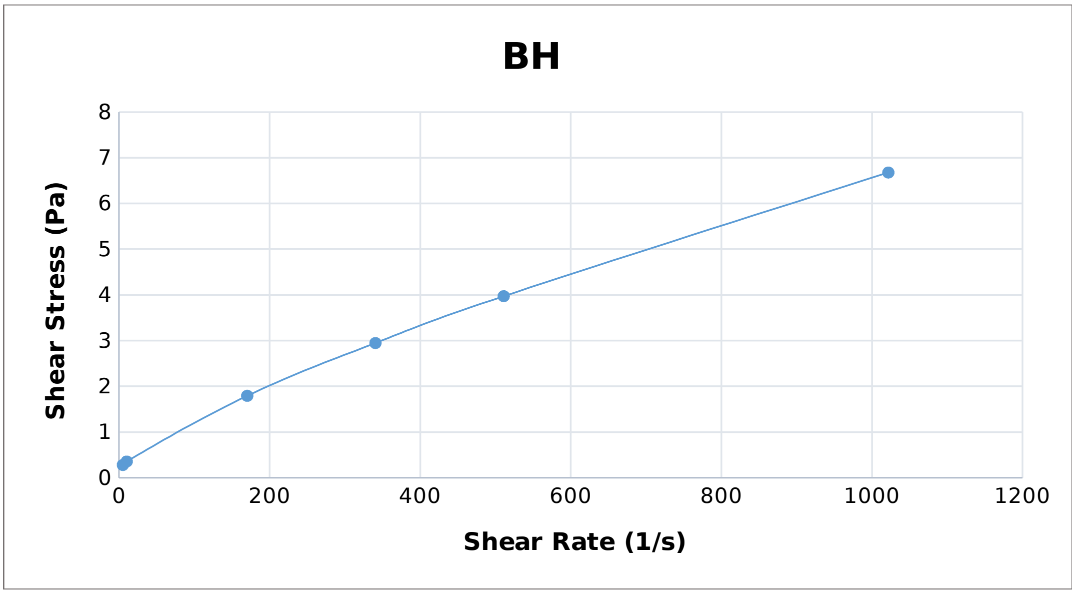


Figure 22. Flow curve diagram of the water-bentonite control sample.

Table 11. Apparent Viscosity, Plastic Viscosity and Yield point of BH mud, as measured by the experimental procedure.

BH	
Apparent Viscosity (cP)	8.0
Plastic Viscosity (cP)	5.0
Yield point (lbs/100ft^2)	3.0

2. Drilling mud CKA.

This mixture consists of water, bentonite clay, and 3% of CKA causticized lignite. As demonstrated in Figure 24, CKA lignite acts as a thinning agent, by decreasing the yield stress and the viscosity (Table 12) of the control drilling mud (BH). The Yield Stress of CKA mud is zero, which at first should indicate **Power-law rheology** but, as observed in Figure 24, the sample's rheogram is almost linear passing through the origin (τ_0=0, n~1), approaching the **Newtonian fluid behavior**.

The addition of CKA lignite decreases the Apparent viscosity and the Yield point of the original drilling mud (Table 12), while Plastic Viscosity values are the same with the BH sample.

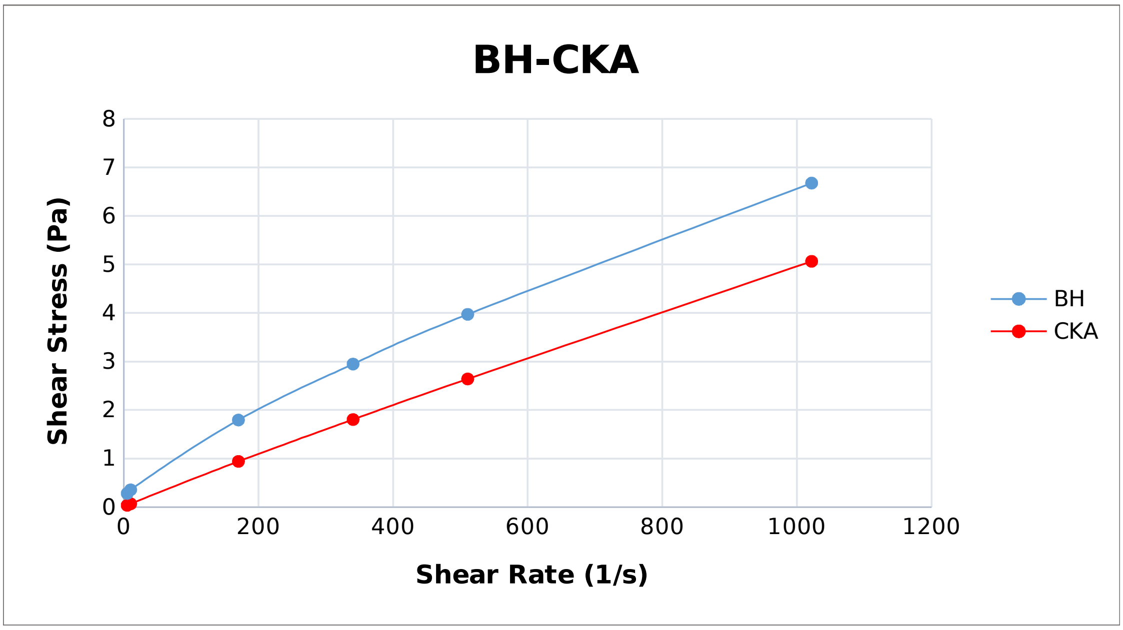


Figure 23. Comparative flow curve diagram of BH and CKA drilling muds.

Table 12. Apparent Viscosity, Plastic Viscosity and Yield point of CKA mud, as measured by the experimental procedure.

CKA	
Apparent Viscosity (cP)	5.0
Plastic Viscosity (cP)	5.0
Yield point (lbs/100ft^2)	0.0

3. Drilling mud CMA.

The CMA mixture consists of water, bentonite clay, and 3% of CMA causticized lignite. In Figure 25, it is observed that the addition of CMA lignite affects the flow curve of the control sample by **decreasing the Apparent viscosity and the Yield point**. Plastic Viscosity values remained the same.

According to the calculated rheological parameters, CMA mud is characterized by **Herschel-Buckley rheology**, but as demonstrated in the diagram, the sample's rheogram is almost a straight line, that intercepts the y-axis ($\tau_0 \neq 0$, $n \sim 1$), approaching the **Bingham plastic rheological model.**

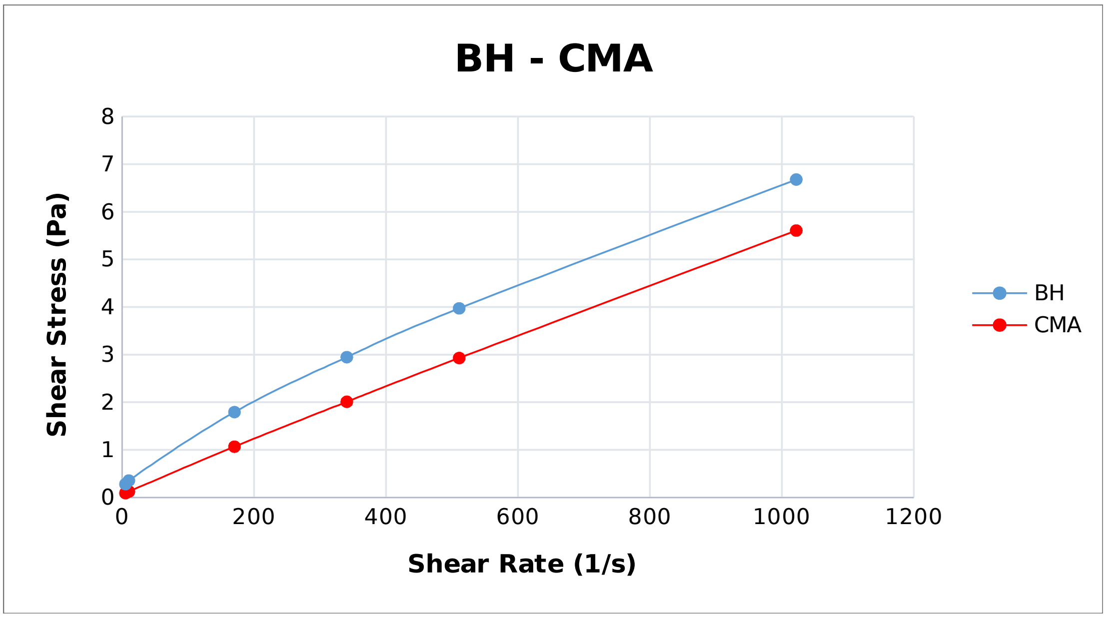


Figure 24. Comparative flow curve diagram of BH and CMA drilling muds.

Table 13. Apparent Viscosity, Plastic Viscosity and Yield point of CMA mud, as measured by the experimental procedure.

CMA	
Apparent Viscosity (cP)	6.0
Plastic Viscosity (cP)	5.0
Yield point (lbs/100ft^2)	1.0

4. Drilling mud CNF.

The CNF drilling mud is a mixture of water bentonite, and 3% of CNF causticized lignite. Figure 26 demonstrates the rheograms of both BH and CNF samples and it is observed that both samples behave as **Herschel-Buckley fluids** ($\tau_0 \neq 0$, $n \neq 1$).

The addition of CNF lignite affects the Apparent Viscosity, as well as the Yield point by decreasing their values (Table 14). It is important that with CNF lignite addition a decrease in Plastic Viscosity is also achieved.

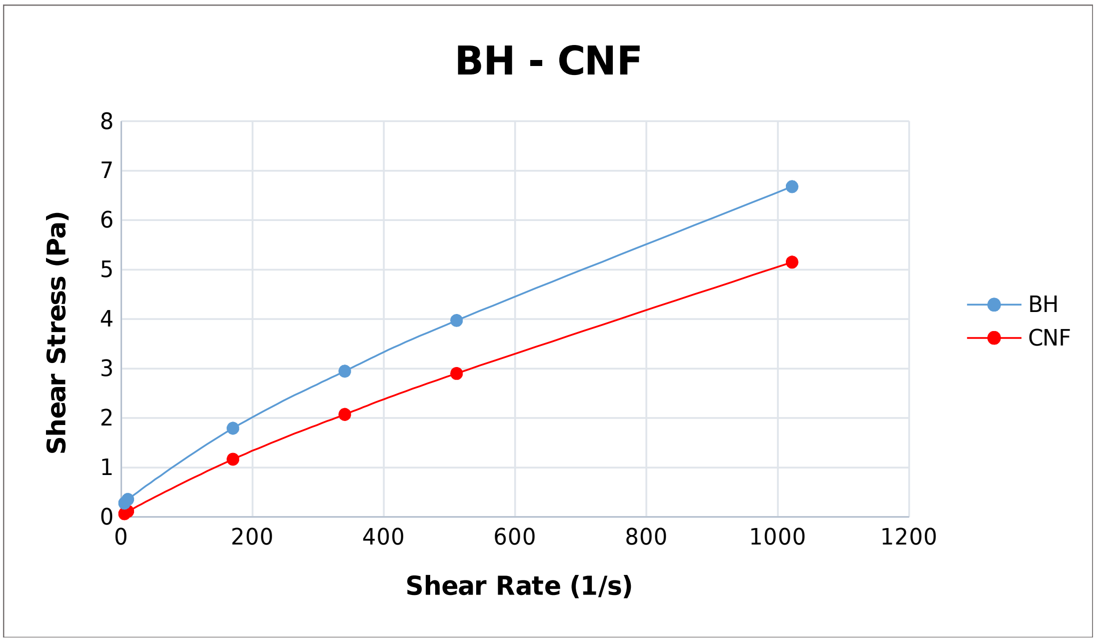


Figure 25. Comparative flow curve diagram of BH and CNF drilling muds.

Table 14. Apparent Viscosity, Plastic Viscosity and Yield point of CNF mud, as measured by the experimental procedure.

CNF	
Apparent Viscosity (cP)	6.0
Plastic Viscosity (cP)	4.0
Yield point (lbs/100ft^2)	2.0

5. Drilling mud CLE.

The CLE mixture consists of water, bentonite clay, and 3% of CLE causticized leonardite. As demonstrated in Figure 27, the CLE rheogram is a non-linear line that intercepts the y-axis, which is characteristic of **Herschel-Buckley rheology** ($\tau_0 \neq 0$, $n \neq 1$).

It is worth mentioning that CLE affects in a very different way the properties of the drilling mud compared to the rest of the lignites causticized with the same method. Specifically, **the addition of CLE leads to an undesired increase in the Apparent and Plastic Viscosity** of the original mud (Table 15), while it does not affect the Yield point value. This can also be observed graphically, as the CLE curve is located above the BH one, indicating greater viscosity values for the CLE sample (Figure 27).

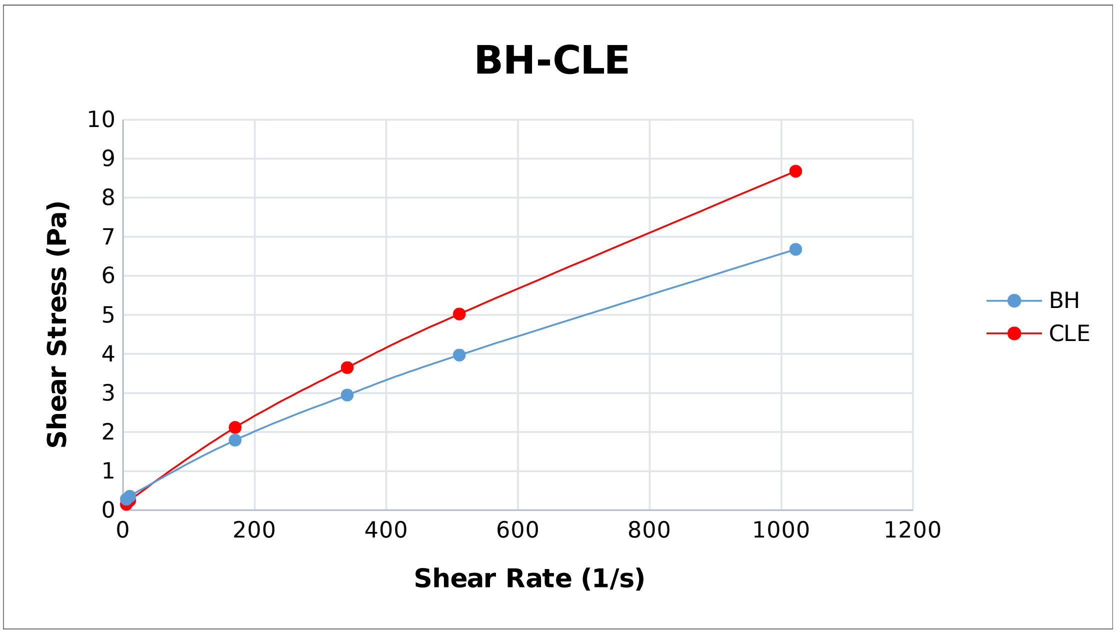


Figure 26. Comparative flow curve diagram of BH and CLE drilling muds.

Table 15. Apparent Viscosity, Plastic Viscosity and Yield point of CLE mud, as measured by the experimental procedure.

CLE	
Apparent Viscosity (cP)	10.0
Plastic Viscosity (cP)	7.0
Yield point (lbs/100ft^2)	3.0

6. Drilling mud ZKA.

The ZKA drilling mud consists of water, bentonite clay, and 3% of ZKA causticized lignite. As it is shown in Figure 28, the ZKA rheogram is a non-linear line that intercepts the y-axis, which indicates -as already mentioned- **Herschel-Buckley rheology** ($\tau_0 \neq 0$, $n \neq 1$).

Organic Zinc Complex (OZC) causticization affects in a different way the behavior of Kardia lignite as a rheological control agent. It is noticed that with the addition of ZKA lignite in the drilling mud there is **an increase of the Apparent and Plastic viscosity**, which is also pointed out graphically as the ZKA curve is located higher than the BH one. The Yield point values are the same, indicating that the change in the causticization type impacts mainly the viscosity and less the Yield point (Table 16).

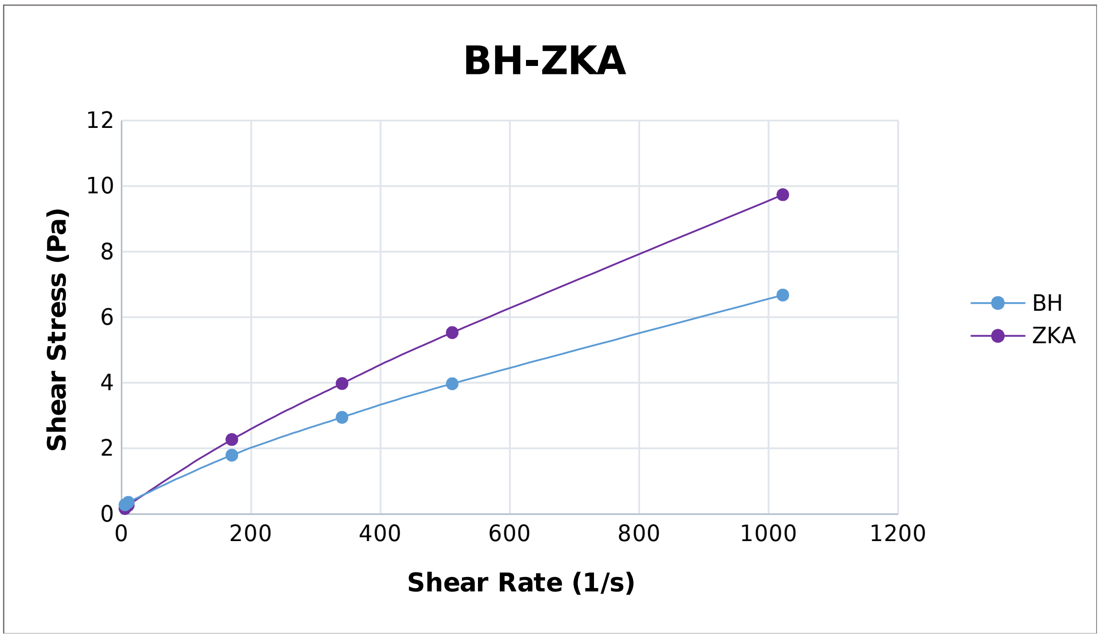


Figure 27. Comparative flow curve diagram of BH and ZKA drilling muds.

Table 16. Apparent Viscosity, Plastic Viscosity and Yield point of ZKA mud, as measured by the experimental procedure.

ZKA	
Apparent Viscosity (cP)	11.0
Plastic Viscosity (cP)	8.0
Yield point (lbs/100ft^2)	3.0

7. Drilling mud ZMA.

The ZMA drilling mud consists of water, bentonite clay, and 3% of ZMA causticized lignite. As pointed out previously with ZKA sample, also with ZMA, different behavior of the sample after the OZC causticization is observed. Particularly, in Figure 29, it is shown that the ZMA drilling mud curve is above the BH one, indicating that the addition of ZMA lignite in the original sample leads to an **increase in the Apparent and Plastic Viscosity**. This is also observed in the values of AV and PV parameters, as they were measured from the experiments (Table 17). However, with the addition of ZMA lignite, there is a small **decrease in the Yield point** (Table 17).

From Figure 29 it is also concluded that ZMA drilling mud behaves as a **Herschel-Buckley fluid** ($\tau_0 \neq 0$, $n \neq 1$).

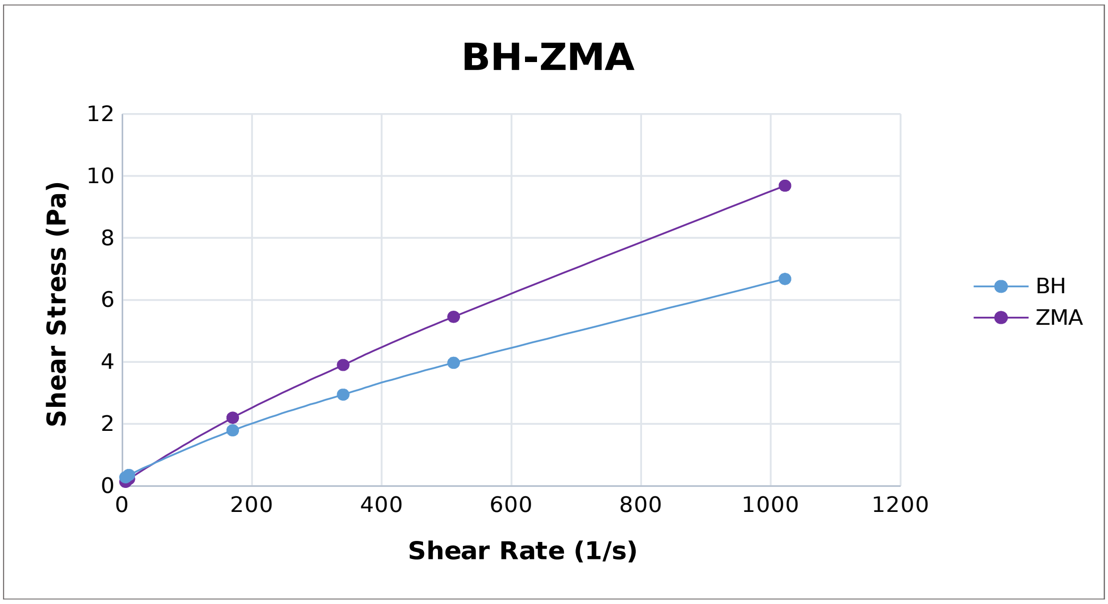


Figure 28. Comparative flow curve diagram of BH and ZKA drilling muds.

Table 17. Apparent Viscosity, Plastic Viscosity and Yield point of ZMA mud, as measured by the experimental procedure.

ZMA	
Apparent Viscosity (cP)	10.5
Plastic Viscosity (cP)	8.5
Yield point (lbs/100ft^2)	2.0

8. Drilling mud ZNF.

ZNF mixture consists of water, bentonite clay, and 3% of ZNF causticized lignite. In Figure 30, it is noticed that the ZNF drilling mud rheogram is a non-linear line ($n \neq 1$), that passes through the origin of the diagram, which is characteristic of **Power-law rheology** ($\tau_0 = 0$, $n \neq 1$).

The addition of ZNF lignite in the original drilling mud **increases the Apparent and Plastic Viscosity**. A small increase is also observed in the Yield point (Table 18). This is also visible graphically with the ZNF curve located above the BH curve (Figure 30).

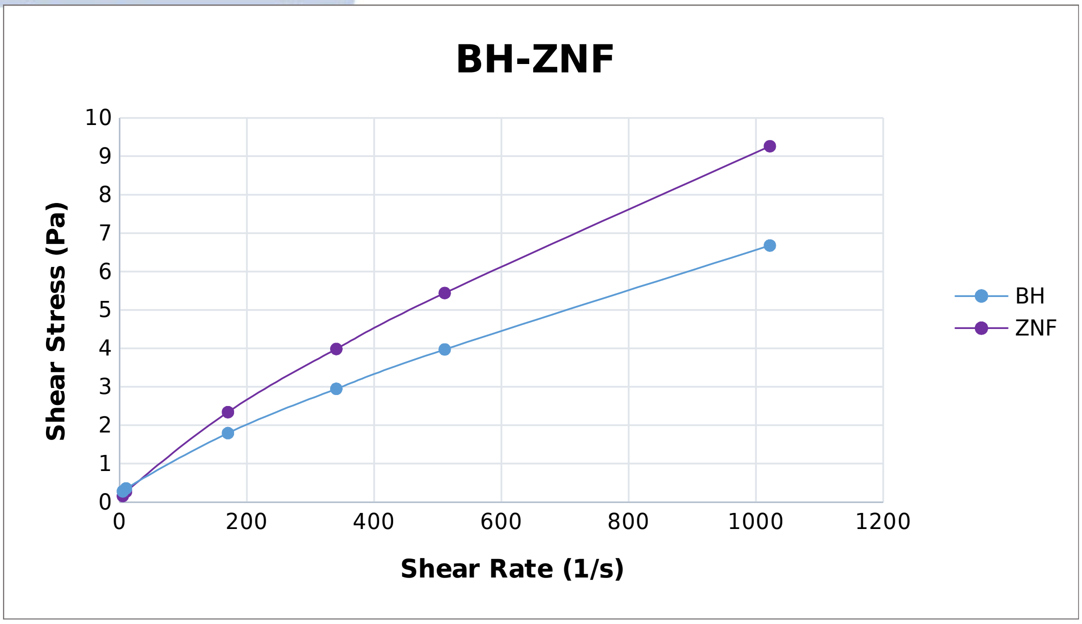


Figure 29. Comparative flow curve diagram of BH and ZNF drilling muds.

Table 18. Apparent Viscosity, Plastic Viscosity and Yield point of ZNF mud, as measured by the experimental procedure.

ZNF	
Apparent Viscosity (cP)	11.0
Plastic Viscosity (cP)	7.0
Yield point (lbs/100ft^2)	4.0

9. Drilling mud ZLE.

On the other hand, ZLE drilling mud, consisting of water, bentonite clay, and 3% of ZLE causticized leonardite, behaves in a very different way compared to all the other samples causticized with OZC causticization. As demonstrated in Figure 31, the ZLE curve is located **below** the BH curve, indicating that with the addition of ZLE leonardite in the mixture, there is a decrease in viscosity. Specifically, as shown in Table 19 **a decrease in Apparent and Plastic**

Viscosity is noticed after ZLE addition, while Yield point values remain the same.

The ZLE rheogram is a non-linear line that passes through the origin of the diagram, indicating **Power-law rheology** ($\tau_0=0$, $n\neq1$).

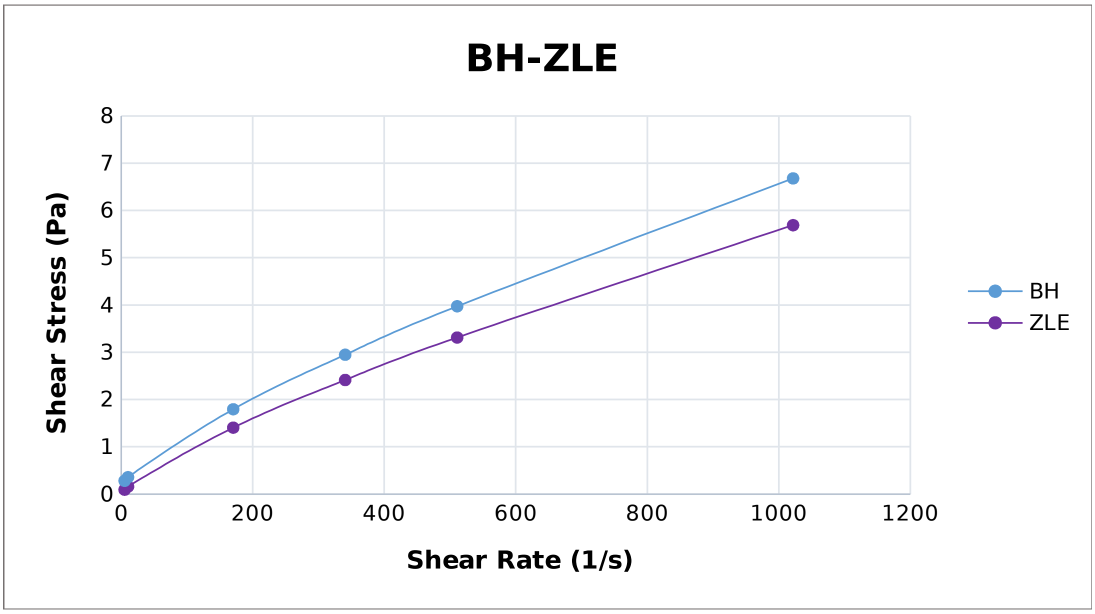


Figure 30. Comparative flow curve diagram of BH and ZLE drilling muds.

Table 19. Apparent Viscosity, Plastic Viscosity and Yield point of ZLE mud, as measured by the experimental procedure.

ZLE	
Apparent Viscosity (cP)	7.0
Plastic Viscosity (cP)	4.0
Yield point (lbs/100ft^2)	3.0

10. Drilling mud CLIG.

This mixture consists of water, bentonite clay, and 3% of the **commercial causticized CLIG lignite** provided by Gumpro LTD. From Figure 32, it is obvious that this drilling mud behaves as a **Newtonian fluid**, as the curve is a straight line passing through the origin of the diagram ($\tau_0=0$, $n\sim1$). With the addition of the commercial lignite, **a significant decrease in Apparent and Plastic Viscosity, as well as in Yield point is achieved** (Table 20).

This mixture is used as a reference in evaluating the behavior of all previously mentioned drilling muds.

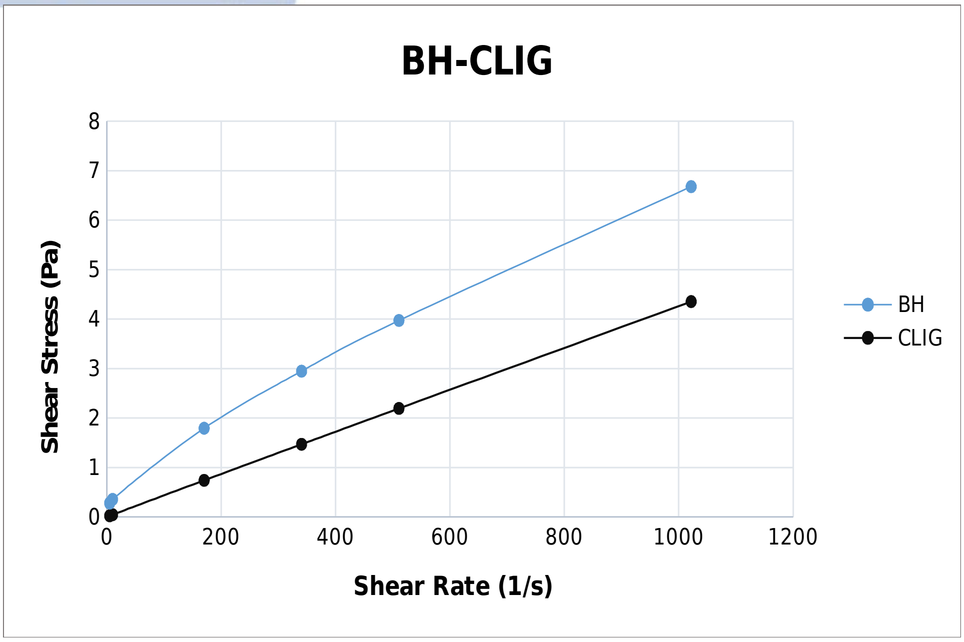


Figure 31. Comparative flow curve diagram of BH and CLIG drilling muds.

Table 20. Apparent Viscosity, Plastic Viscosity and Yield point of CLIG mud, as measured by the experimental procedure.

CLIG	
Apparent Viscosity (cP)	4.5
Plastic Viscosity (cP)	4.0
Yield point (lbs/100ft^2)	1.5

It is observed that concerning the viscosity –both Apparent and Plastic–, there are two groups of samples. One that positively affects viscosity by decreasing its values and a second one that increased the viscosity of the original mud. Specifically,

- Lignites causticized with NaOH **[CKA, CMA, CNF]**, **decrease** drilling mud's viscosity when added to the mixture.
- Leonardite causticized with Organic Zinc Complex **[ZLE]**, **decreases** drilling mud's viscosity when added to the mixture.
- Lignites causticized with Organic Zinc Complex **[ZKA, ZMA, ZNF]**, **increase** drilling mud's viscosity when added to the mixture
- Leonardite causticized with NaOH **[CLE] increase**s drilling mud's viscosity when added to the mixture
- Commercial lignite **[CLIG]** has the best performance of all samples by

In the above, it is denoted that causticization procedure affects in different way the lignites and the leonardite. Lignites causticized with NaOH are the most effective concerning viscosity reduction, while for leonardite, Organic Zinc Complex causticization is the one that gives the desired result on the mud's viscosity values. Differences in free humic acids, as well as in the inorganic content between these two different low-rank coal types may play an important role in the way that causticization procedure affects them.

Figure 33 and Figure 34 show the comparative rheograms of all the studied samples. Especially, Figure 33 demonstrates the raw measurements as they were obtained directly from the experiments, while Figure 34 shows the calculated results after the curve fitting that was held through the model.

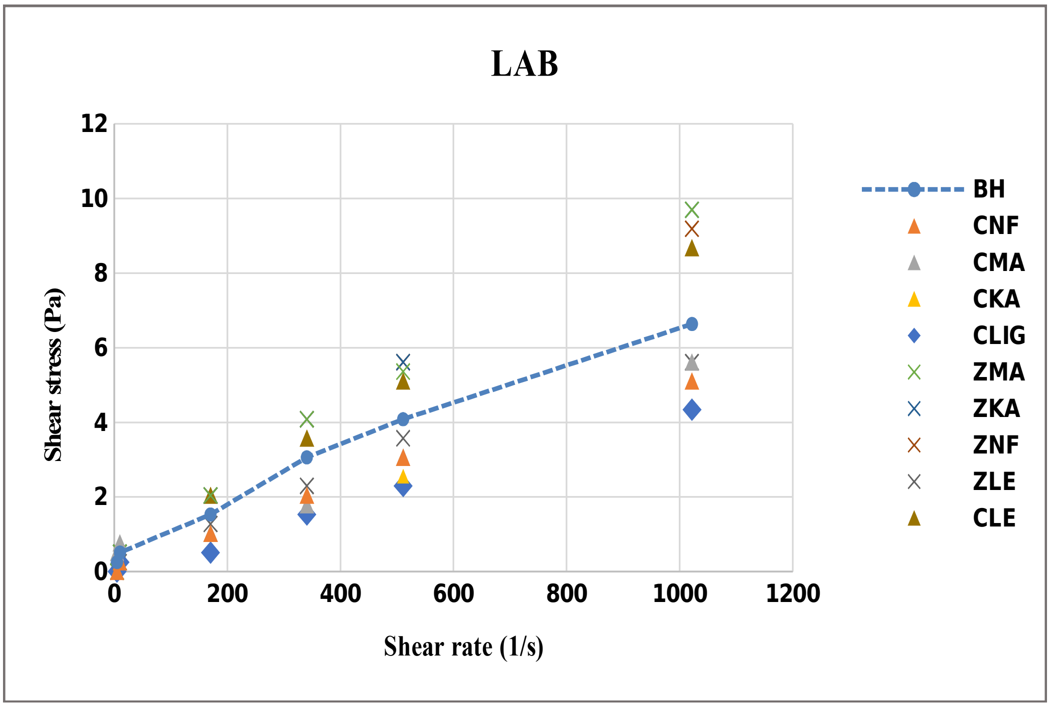


Figure 33. Comparative flow curve diagram of the experimental data of all the studied samples.

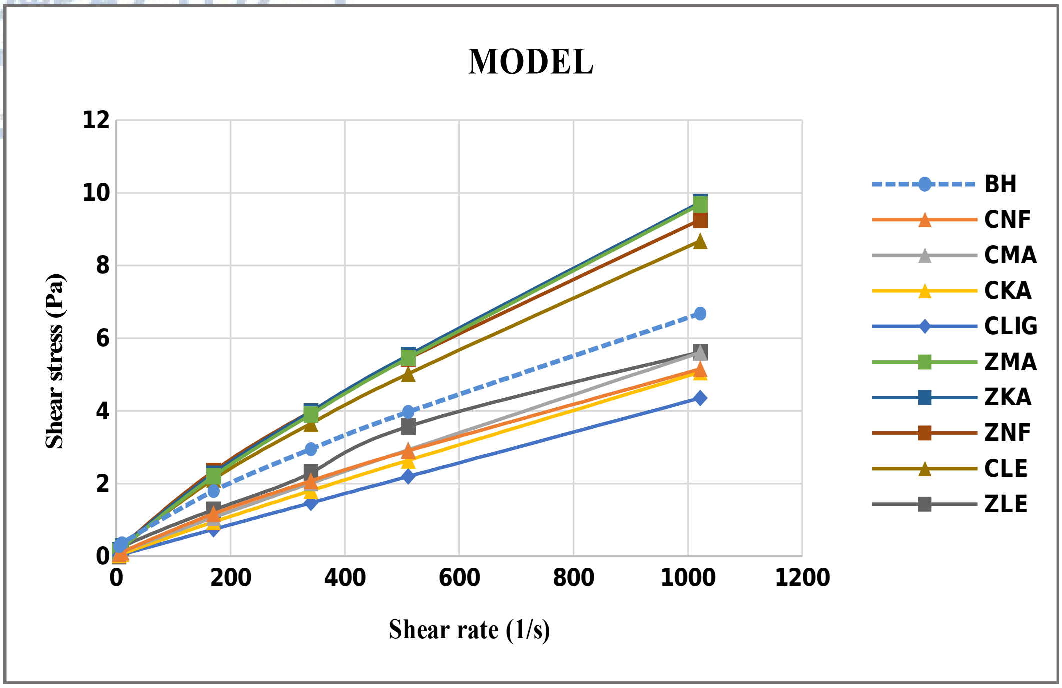


Figure 34. Comparative flow curve diagram of the calculated data of all the studied samples through the Herschel-Buckley equation model.

The diagrams present the different behavior of two groups of samples; one group with higher viscosity values with curves located above the BH one and a second group, with lower viscosity values with the curves of the samples located below the BH one. It is also observed that all curves start close to the origin indicating low Yield Stress values. However, **the addition of lignite and leonardite decreases significantly the YS values** of the muds. This is translated to a lower amount of stress required to move the fluid. The decrease of the YS values in Figure 34 is graphically visible only if we change the scale of the diagram. In Figure 35, it is obvious that all of the samples studied play an essential role in decreasing the YS of the drilling muds. Since YS is the stress required to move the fluid, it can be indicated graphically by the start-point of the curve. So, as demonstrated in Figure 35, all rheograms begin from lower points than the BH sample.

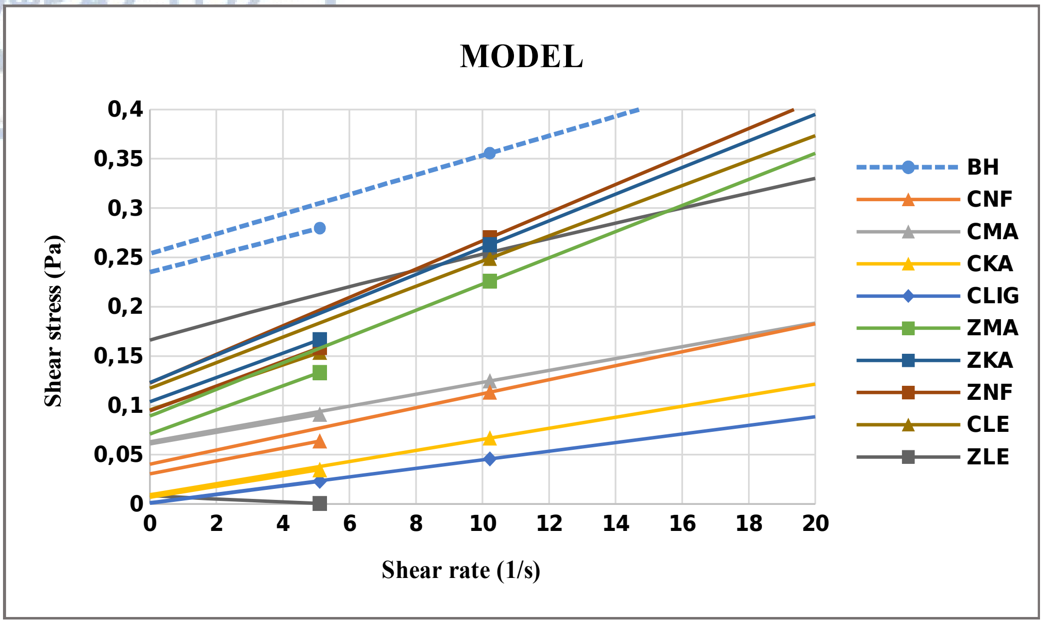


Figure 35. Comparative flow curve diagram of the calculated data of all the studied samples, with modified both x-axis and y-axis scale.

3.1.2. Rheological parameters

Rheological parameters measured for all drilling muds are demonstrated in Table 21. These parameters were derived through the model calculations, as they were described in chapter 2.2.3. Rheological parameters are essential for the characterization of the drilling mud since they are necessary for the construction of the rheological model equation that each sample fits in.

It has been observed that drilling fluids do not flow unless subjected to certain stress, which is called **Yield Stress.** Yield Stress is a key rheological parameter that the drilling industry has recognized as critical to the performance of drillings fluids (Power and Zamora, 2003). The Yield Stress can be described as the necessary stress applied to a material to initiate flow. If the applied stress is below the Yield Stress of the fluid, then it will display strain recovery, when the stress is removed. Once the yield stress has been exceeded, the fluid displays viscous flow characteristics (Power and Zamora, 2003). Yield Stress is closely related to the Viscosity and Thixotropy of the fluid. Especially, thixotropy and Yield Stress are usually properties of the same type of fluids. The same microstructure present in a fluid that resists large rearrangements (which is responsible for the Yield Stress), when broken by flow, is believed to be the origin of thixotropy (Peder et al., 2006).

Table 21. Rheological parameters of the studied samples as calculated by the Herschel-Buckley equation model.

	BH	**CNF**	**CKA**	**CMA**	**CLIG**	**CLE**
Parameters						
τ_0 (Pa)	**0.173**	0.010	0.000	0.055	0.000	0.023
K (Pa.sec^n)	**0.030**	0.016	0.008	0.008	0.005	0.036
n (dimensionless)	**0.776**	0.832	0.940	0.950	0.989	0.792
PV (cP)	**5.000**	4.000	5.000	5.000	4.000	7.000
YP (Pa)	**1.436**	0.958	0.000	0.479	0.239	1.436

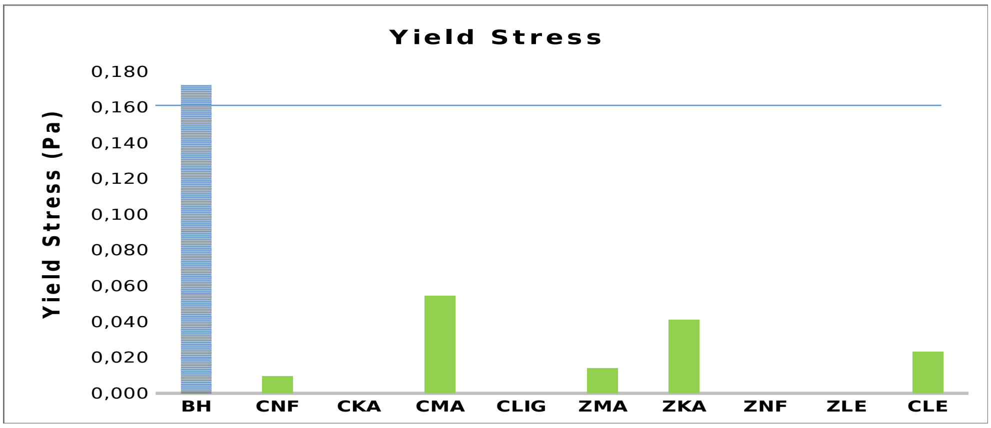
	BH	**ZMA**	**ZKA**	**ZNF**	**ZLE**
Parameters					
τ_0 (Pa)	**0.173**	0.014	0.041	0.000	0.000
K (Pa.sec^n)	**0.030**	0.031	0.033	0.045	0.025
n (dimensionless)	**0.776**	0.830	0.820	0.768	0.781
PV (cP)	**5.000**	8.500	8.000	7.000	4.000
YP (Pa)	**1.436**	0.958	1.436	1.436	1.915

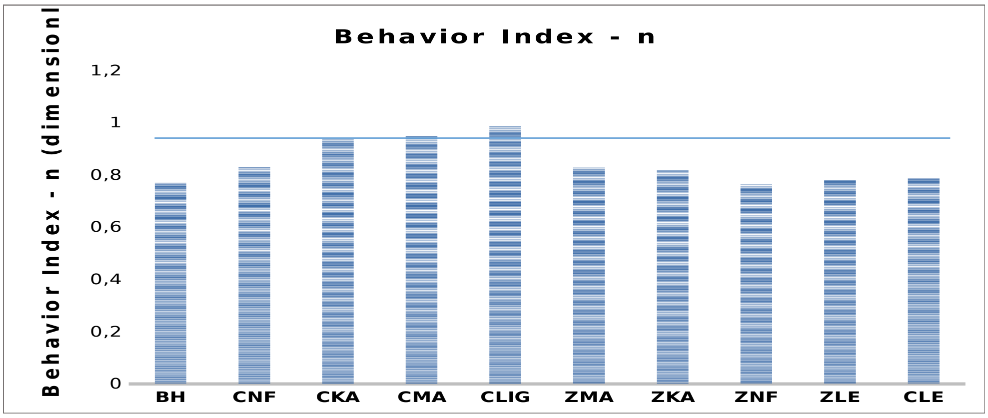
The **Yield Stress (YS)** of raw bentonite sample [BH], was calculated at 0.173 Pa. The addition of 3% of all causticized low-rank coal samples led to a significant decrease in the Yield Stress of the mud, with close to zero values. Especially, with the addition of CKA, CLIG, ZNF, and ZLE sample, the Yield stress of the mud is eliminated (Table 21). In Figure 33, it is visible that the addition of all lignite and leonardite samples affects to a significant degree the Yield Stress of the mud compared to the initial [BH] drilling mud.

Behavior index (n), was calculated at 0.776 in the BH control sample, while all of the muds presented an increase or remained equal with the addition of causticized samples. The greater increase of n index was achieved by the addition of CKA, CMA, and CLIG. It should be noted that in CLIG and CKA samples behavior index values are close to 1 (n~1), which indicates that the sample approaches Newtonian fluid behavior.

Flow consistency index (K), was calculated at 0.030 Pa×sec^n, before the addition of the causticized samples. Drilling muds with the addition of ZMA, ZKA, ZLE, and CLE presented a small increase in K values, while muds with the addition of CNF, CKA, CMA, CLIG, and ZLE showed decreased K values.

Regarding **Plastic Viscosity (PV),** it is noticed that lignites causticized with Organic Zinc Complex (ZMA, ZKA, ZNF), as well as leonardite causticized with NaOH (CLE), increase the PV values when added in the drilling mud. On the other hand, only one lignite sample causticized with NaOH (CNF), leonardite causticized with Organic Zinc Complex (ZLE), and commercial lignite (CLIG) decrease the PV values, while the rest of the samples (CMA, CKA) keep the PV values in the same level.


Yield Stress
Yield Stress (Pa)
0,180
0,160
0,140
0,120
0,100
0,080
0,060
0,040
0,020
0,000
BH
CNF
CKA
CMA
CLIG
ZMA
ZKA
ZNF
ZLE
CLE


Behavior Index - n
Behavior Index - n (dimensionl
1,2
1
0,8
0,6
0,4
0,2
0
BH
CNF
CKA
CMA
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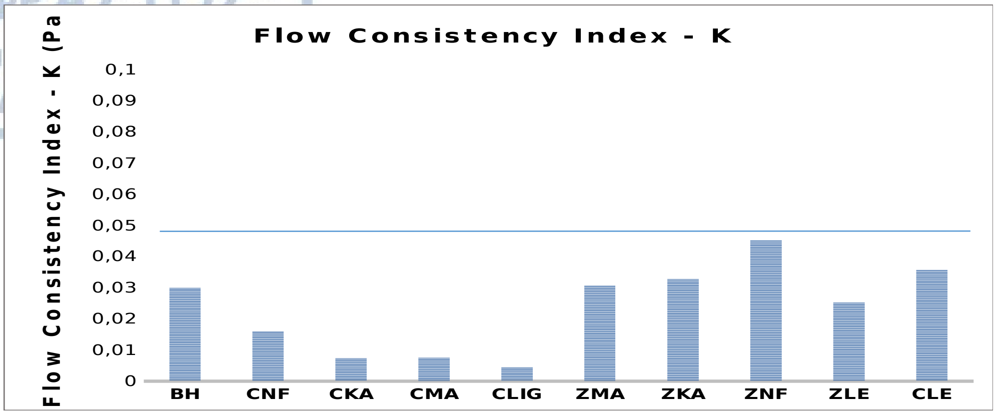
ZMA
ZKA
ZNF
ZLE
CLE



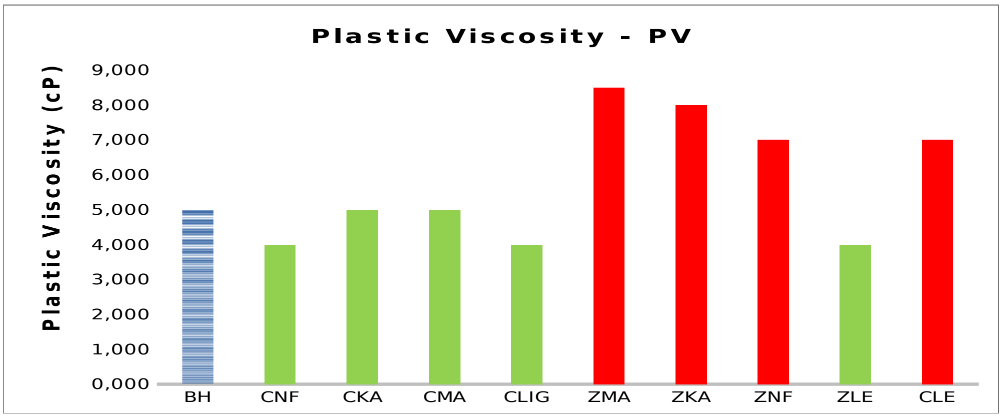


Figure 36. Effect of the lignite and leonardite addition on the Yield Stress, Behavior index, Flow consistency index, and Plastic Viscosity on the initial drilling mud mixture.

3.1.3. Model characterization

As already mentioned (see chapter 1.4), usually three rheological models have been applied in drilling fluid hydraulics and rheological analyses: **Bingham plastic**, **Power-law**, and **Herschel-Buckley**. These models adequately cover the range of rheology values that are encountered in the field. The Power-law represents the case of a zero Yield Stress (τ_0=0), while on the other hand, the Bingham plastic model covers the case where the Yield Stress (τ_0) equals the yield point (YP). The Herschel- Buckley model covers both these conditions, as well as all cases in between (Power and Zamora, 2003).

Table 22. Completed rheological characterization of each studied sample.

Sample	Model Equation	Characterization

BH	$\tau = 0.173 + 0.03\dot{\gamma}^{0.776}$	Herschel- Buckley
CNF	$\tau = 0.01 + 0.016\dot{\gamma}^{0.832}$	Herschel- Buckley
CKA	$\tau = 0.008\dot{\gamma}^{0.94} \Leftrightarrow$ $\tau = 0.008\dot{\gamma}^{1} \Leftrightarrow$ $(n \to 1)$	Power Law but may behave as Newtonian
CMA	$\tau = 0.055 + 0.08\dot{\gamma}^{0.95} \Leftrightarrow$ $\tau = 0.055 + 0.08\dot{\gamma}^{1} \Leftrightarrow$ $(n \to 1)$	Herschel- Buckley may behave as Bingham Plastic
ZMA	$\tau = 0.014 + 0.031\dot{\gamma}^{0.83}$	Herschel- Buckley
ZKA	$\tau = 0.041 + 0.033\dot{\gamma}^{0.82}$	Herschel- Buckley
ZNF	$\tau = 0.045\dot{\gamma}^{0.768}$	Power Law
ZLE	$\tau = 0.025\dot{\gamma}^{0.781}$	Power Law
CLIG	$\tau = 0.005\dot{\gamma}^{0.989} \Leftrightarrow$ $\tau = 0.005\dot{\gamma}^{1} \Leftrightarrow$ $(n \to 1)$	Behaves essentially as Newtonian
CLE	$\tau = 0.025 + 0.036\dot{\gamma}^{0.792}$	Herschel- Buckley

The calculated rheological parameters through the developed model were used to construct each sample's rheological equation and therefore to develop their model characterization. Each sample's equation and characterization are demonstrated in Table 22.

3.1.4. Thinning mechanism

Although humic acids are normally considered as aggregating agents in clays, several studies report that humic substances are also capable of dispersing clay particles and especially in clay-water systems (Canarutto et al., 1996; Visser and Cailler, 1988). Other studies (Narkis et al., 1970) also showed that Na-humates can cause dissociation of montmorillonite tactoids in suspension. Canarutto et al., (1996) mention disruption of soil aggregates **caused by humic acids from leonardite** at the rates of 4000 to 8000 $mg \times kg^{-1}$, while at the same time they observe the mean diameter of the soil particles markedly decreased. Visser (1982), also observed that the minimum concentration at which maximum surface tension depression occurs in fulvic and humic acid solutions is normally between 10 and 100 $mg \times L^{-1}$.

Thinning agents act by enhancing the deflocculation and dispersion of the clay particles in the mud. Especially according to Van Dyke (2000), the deflocculation is achieved due to thinner's particles forming a coating around the clay particles, rendering the electrochemical forces that cause flocculation ineffective (Figure 36). It is known that the flocculation procedure of montmorillonite clay particles can be affected by the addition of humic and fulvic substances, which usually act as thinners. However, **the flocculated and deflocculated structures of the clay particles are also strongly dependent on the pH values** of the mixture. This can be associated with the sign and extent of charge at the clay edges, as well as the configuration and charge of humic and fulvic substances, that both change with pH. In Tarchitzky et al., (1993) study is demonstrated that as pH increases (from 8 to 10), humic and fulvic acids tend to increase the flocculated structure of the clay particles. Of course, the flocculation of the clay particles also depends on the concentration of the humic acids added.

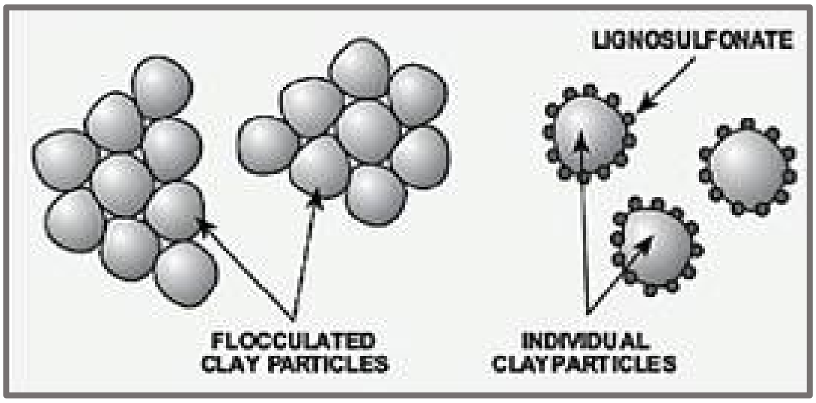


Figure 36. The action of deflocculation agents, after (Van Dyke. 2000).

In the present study, is not possible to know the exact concentration of humic and fulvic acids that lignite and leonardite samples contained. However, it can be suggested that the concentration of humic acids together with the pH values are responsible for the different behavior of the causticized samples, concerning rheology results.

Table 23. pH values as measured on the samples under study.

Sample	pH values
BH	11.0
CKA	10.0
CMA	10.2
CNF	10.0

CLE	10.6
ZKA	11.3
ZMA	11.4
ZNF	11.0
ZLE	11.4
CLIG	12.5

As demonstrated in Table 23, the lignite samples with the best rheological behavior [CKA, CMA, CNF] are the ones that also decreased the pH values compared to the control sample. On the other hand, the lignite samples that gave negative results concerning viscosity [ZKA, ZMA, ZNF] are the ones that increase or keep in equal values the pH. As far as leonardite samples are concerned, there is an opposite behavior concerning pH values, which may be attributed to the usually higher concentration of leonardite in humic and fulvic acids compared to typical lignites. Finally, concerning the commercial lignite, it is obvious that it has the greatest pH values of all samples, but it cannot be taken into account given that its specific composition, causticization procedure, and humic & fulvic acid content are unknown.

3.2 Gel strength

The gelation and thickening of drilling mud as drilling operation progresses causes problems in drilling deep wells. Thickening effects can lead to increased pump pressures to circulate the mud. It can also keep the gas from breaking out or the cuttings from settling out of the mud. At the same time, it can slow down the drilling rate and may, in severe cases, make circulation nearly impossible. In such cases, muds should be treated with organic thinners to reduce the thickening effects and stop the gelation procedure (Abu-Jdayil, 2011; Borst and Shell, 1971; Caenn et al., 2016; Sheng and Zang, 2018).

Table 24. Gel strength values as measured for 10'' and 10' for each one of the studied samples.

Sample	10s (lbs/100ft^2)	10min (lbs/100ft^2)
BH	0.00	18.12
CKA	0.00	2.13
CMA	0.00	3.20
CNF	0.00	2.13
CLE	0.53	11.73
ZKA	0.00	15.99
ZMA	0.00	15.99

ZNF	0.00	13.86
ZLE	0.00	6.40
CLIG	0.00	0.53

The addition of causticized lignites as thinning agents led to positive results in all samples by decreasing the gel strength values. Especially, with the addition of samples **CKA, CMA, CNF, and ZLE** the decrease in 10-minutes gel strength experiment is rather high. Comparing gel strength results with rheology ones it is enhanced that these four samples [CKA, CMA, CNF, ZLE] are probably quite suitable as thinning agents since they reduce both Viscosity and Gel strength values when added in the drilling mud. As demonstrated in Table 24, in a 10-seconds gel strength experiment, almost no sample shows a gel-like structure development.

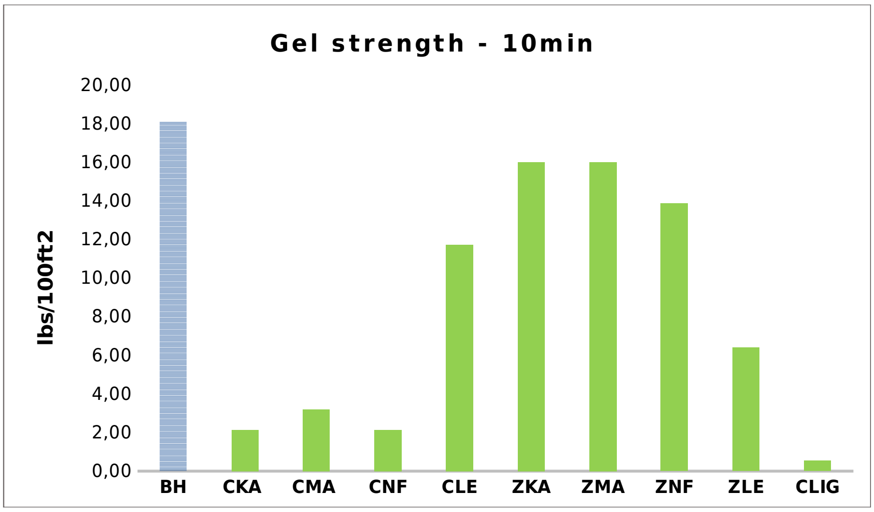


Figure 37. Effect of the lignite and leonardite addition on the Gel Strength of the initial drilling mud mixture.

3.3 Filtration Properties of the drilling muds

3.3.1 Filtrate Volume

The influence of Greek lignites and leonardite on the filtration characteristics of water–bentonite suspensions and on minimizing formation damage at high temperatures was examined in this stage. According to API RP13B-1, (2017), the **filtrate volume of the drilling muds must be kept under 15mL**. Results of fluid loss after the addition of causticized lignites and leonardite are given in Figure 38.

The factors that affect the fluid loss of the drilling muds are divided into the organic constituents [e.g. humic & fulvic acids, polymers, etc.] and the inorganic constituents [e.g. calcium carbonate or micas as bridging materials]. Lignites that were causticized with the NaOH method [CKA, CMA, CNF] **increased the filtrate volume**, exceeding the API RP13B-1, (2017) specification limits. On the other hand, Organic Zinc Complex treated lignites [ZKA, ZMA, ZNF] **sufficiently decrease the filtrate volume received**, below 15mL, as required (API RP13B-1, 2017). As it can be observed, a greater decrease is achieved by the commercial lignite. However, **the performance of Organic Zinc Complex treated lignites is significantly approaching the commercial lignite's effect on the filtrate volume**. In addition to that, it can be noticed that the filtration volume is positively affected by the addition of leonardite in the mixture, causticized by both methods.

The fact that leonardite samples act as fluid loss agents -causticized by both methods- while on the other hand for lignite only the Organic Zinc Complex causticization works indicate that the NaOH causticization is not efficient on lignite samples, as far as filtration properties are concerned.

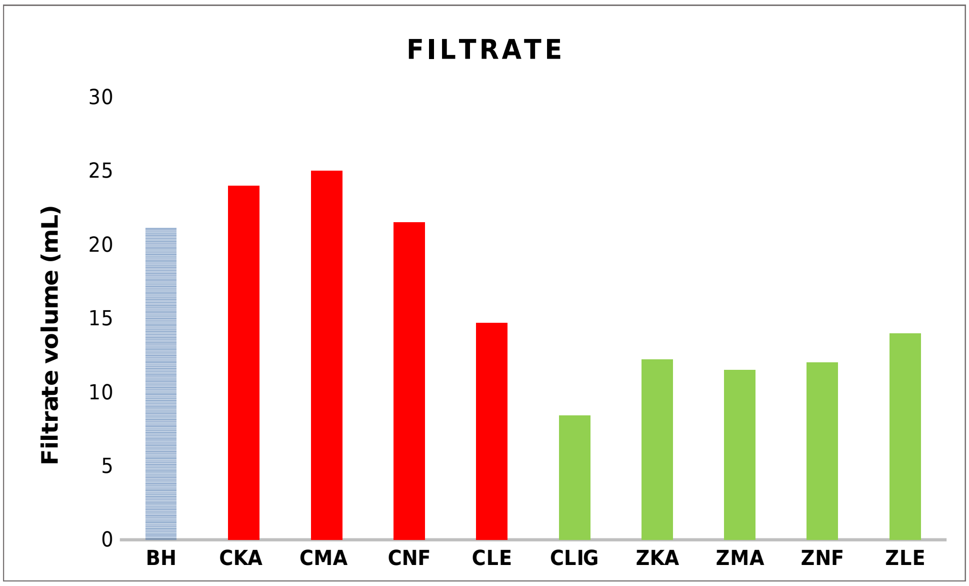


Figure 38. Filtrate volume as received from the samples under study.

This can be attributed to the fact that leonardite has a significantly higher inorganic matter content compared to lignites. Especially, as demonstrated in Table 6, (see chapter 2.1), lignites contain 18-21% total ash content, while leonardite has **62%** ash content. As previously mentioned inorganic compounds can act as bridging materials controlling filtration properties when required. These materials in some cases are minerals such as calcium carbonates and micas (Fink, 2015). These minerals are abundant in coals and especially lignites. Since leonardite has a significantly higher inorganic matter content compared to the typical lignites, it can be associated with the positive effect on filtration properties with both methods. Moreover, leonardite is known for its high humic acid content. Therefore, this is a factor that can also explain why leonardite has a better performance with both causticization treatments. On the other hand, lignites when treated with Organic Zinc Complex behave in a different way by decreasing fluid loss. The addition of Zn together with a higher degree of causticization (using both KOH and NaOH) has an important role in the improvement of filtration properties of lignites.

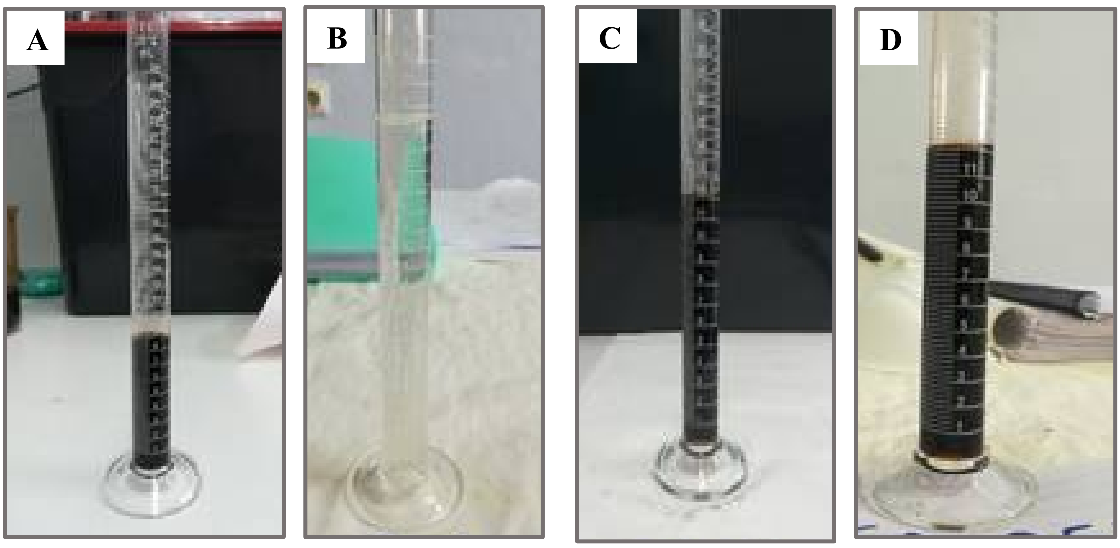


Figure 39. Filtrate volume as received from several samples. A: Commercial Lignite mixture, B: BH control sample, C: ZMA mixture, D: ZKA mixture.

The improvement index of the filtration properties with the lignite/leonardite addition was calculated as described by the following (3.1) equation:

$$n = \frac{V_{BH} + V_x}{V_{BH}} \times 100 \quad (3.1)$$

where V_{BH} is the filtrate volume of the control sample and V_x is the filtrate volume received with the addition of lignite/leonardite. The improvement index results are given in Table 25 and there were calculate only for the samples that had a positive effect on the filtration properties of the drilling mud. Especially, commercial lignite is the one that had the greatest improvement index value, followed by the Organic Zinc Complex causticized lignite with values among 42-45%. Leonardite had also a significant improvement with values between 30-34%. Generally, it can be noticed that Organic Zinc Complex causticization method leads to a more effective performance of the coal samples concerning the filtration properties of the drilling fluids.

Table 25. Filtration properties and improvement index of the drilling muds under study.

	Filtrate Volume (mL)	Improvement Index (%)	Filter cake thickness (mm)
BH	21.2	-	4.0
CKA	24.0	no improvement	2.5
ZKA	**12.2**	42.5	2.0
CMA	25.0	no improvement	2.5
ZMA	**11.5**	45.8	3.5
CNF	21.5	no improvement	3.0
ZNF	**12.0**	43.4	2.5
CLE	**14.7**	30.7	2.0
ZLE	**14.0**	34.0	2.5
CLIG	**8.4**	60.4	5.0

3.3.2. Filter Cake

Filter cake of the control sample [BH] was rather thick and of a gel-colloidal nature. Its color, as expected, was similar to the bentonite clay (Figure 40A). Filter cakes with lignite and leonardite addition (Figure 40C, 40D) had a dark brown to black color while both coarser and finer particles were noticed, indicating a medium-poor sorting of the particles' size. Their thickness was lower than the thickness of the control sample. The filter cake of the mud with the commercial lignite (Figure 40B) was brown, also with both coarse and fine particles, while its thickness was the highest of all filter cakes measured.

After filter cakes were left to dry, it was easy to notice a vertical separation of their constituents. This was only observed at the cakes with the addition of lignite/leonardite and it is related to the specific weight of each constituent. The samples seemed to keep the organic constituents (black color) on their upper part's surface, while bentonite was concentrated at the lower part's surface (light brown color). A better investigation of this phenomenon was held by Scanning electron microscopy (see Chapter 3.4).

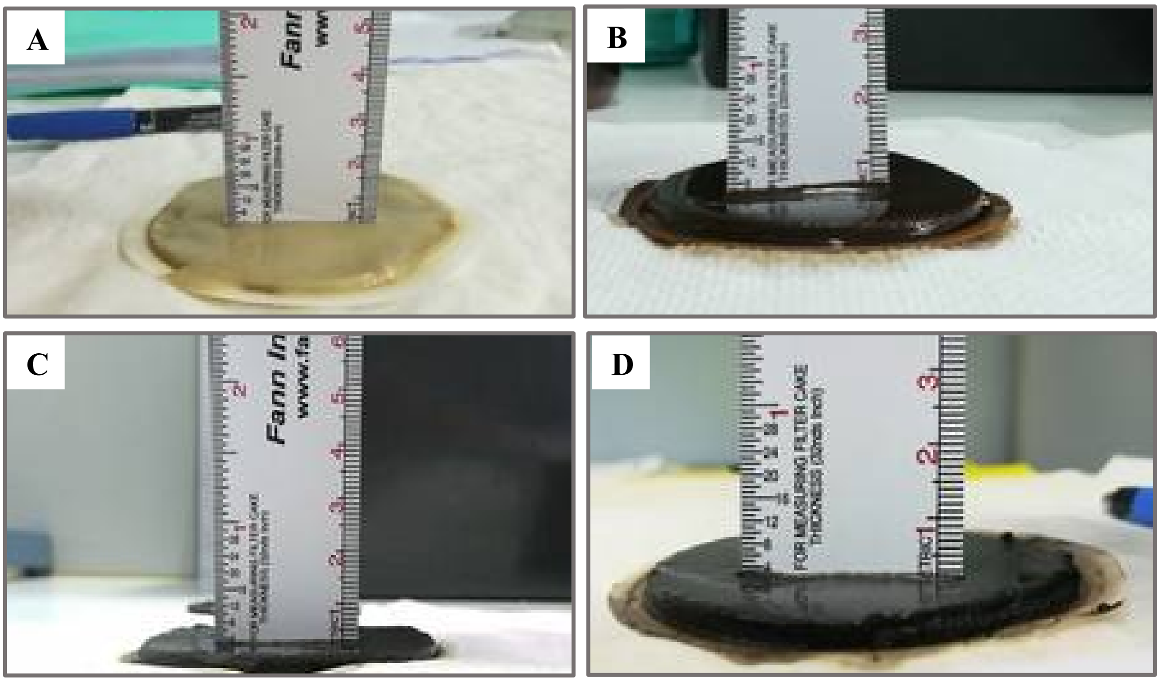


Figure 40. Filter cakes as received and measured. A: BH control mud, B: CLIG (commercial) mixture, C: ZMA mixture, D: ZKA mixture.

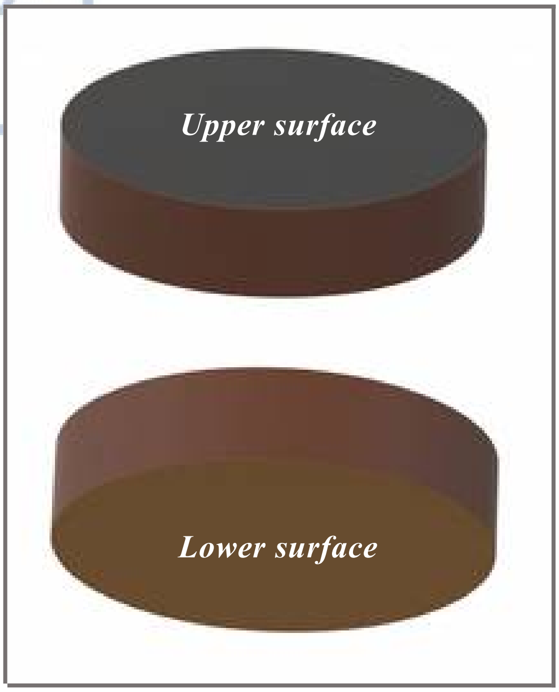


Figure 41. Schematic representation of the vertical separation that occurred in the filter cakes' constituents after they were left to dry for a small period.

Filter cake characterization is an important parameter in the drilling mud science, however, it should be combined with permeability tests to have a better understanding of the way the cake will behave during the drilling operation.

Moreover, it must be taken into account that there are few limitations to these experiments. Specifically, static filtration experiments can be reliable, concerning information on the fluid loss behavior in certain stages of a cementation process, in particular when the slurry is at rest. For further information about the behavior of the fluid during flow and the erosion parameters of the filter cake, dynamic filtering experiments are required.

3.4. Mineralogical composition

According to several studies, XRD is a suitable technique for the phase identification of filter cake (Al-Otaibi et al., 2008; Bageri et al., 2013; Nasr-El-Din et al., 2007). X-ray diffraction analysis was carried out on lignites, bentonite, causticized lignites, and filter cakes to investigate the mineral composition of the samples and identify any changes caused by causticization or filtration procedures. Representative diffractograms are demonstrated in Figures 43-48. In Table 26, the semi-quantitative mineral composition of each studied sample is demonstrated.

Table 26. Semi-quantitative estimation of the mineral composition of the studied samples after Powder X-ray Diffraction Analysis. Mt: Montmorillonite, Cc: Calcite, Qt: Quartz, Pl: Plagioclase, Nt: Natrite, Py: Pyrite, Th: Thenardite, Gy: Gypsum.

Semi-Quantitative Mineral Composition (%)

Sample	Amorphous	Crystallinity	Mt	Cc	Qt	Pl	Nt	Clay Minerals	Py	Th	Gy
B	8	92	19	21	14	22	16	-	-	-	-
BH	7	93	53	14	-	11	15	-	-	-	-
KA	78	22	1	2	2	-	-	16	-	-	-
MA	81	19	-	-	2	-	-	16	1	-	-
NF	80	20	-	-	2	-	-	17	2	-	-
LE	63	37	-	-	8	10	-	42	-	-	-
CKA	74	26	-	3	4	-	-	19	1	-	-
CMA	73	27	-	4	3	-	-	20	-	-	-
CNF	76	24	-	-	2	-	-	20	2	-	-
CLE	57	43	-	-	8	15	-	20	-	-	-
CLIG	65	35	-	-	2	-	-	16	-	13	4
ZKA	68	32	-	8	3	-	-	20	1	-	-
ZMA	71	29	-	5	2	-	-	20	1	-	
ZNF	67	33	-	8	3	-	-	20	1	-	-
ZLE	16	84	-	2	15	25	-	41	-	-	-
Filter cakes											
CKA25	47	53	12	12	14	14	-	-	-	-	-
CMA25	33	67	28	33	2	3	-	-	-	-	-
CNF25	42	58	23	14	6	16	-	-	-	-	-
CLE25	19	81	13	13	8	14	-	33	-	-	-
CLIG25	14	86	16	30	-	38	-	-	-	1	-
ZKA25	12	88	56	17	-	3	11	-	-	-	-
ZMA25	5	95	39	13	2	24	17	-	-	-	-
ZNF25	18	82	44	15	15	-	8	-	-	-	-
ZLE25	21	79	7	15	6	12	-	39	-	-	-

Raw bentonite [B], as well as filter cake of bentonite mud [BH], **have very low amorphous** matter content. Raw bentonite consists mainly of montmorillonite and calcite, while there is also quartz, plagioclase, and natrite in significant amounts. The presence of calcite in such amount indicates that this is natural calcium bentonite. **Calcium bentonite is often converted to sodium bentonite (sodium activation) to exhibit many of sodium bentonite's properties by an ion exchange process.** The Greek bentonite is sodium activated with natrite in order to gain the preferable properties. Na^+ ions of natrite enter the interlayer of Montmorillonite particles, while calcium carbonate precipitates outside, as presented in Figure 42. Usually, water is used to facilitate the reaction, and in the case of Greek bentonite, salt water is used, which offers extra Na^+ ions

$$\mathbf{Na_2CO_3 + Ca\text{-}Montmorillonite \rightarrow Na\text{-}Montmorillonite + CaCO_3}$$

Figure 42. Sodium activation of Bentonite.

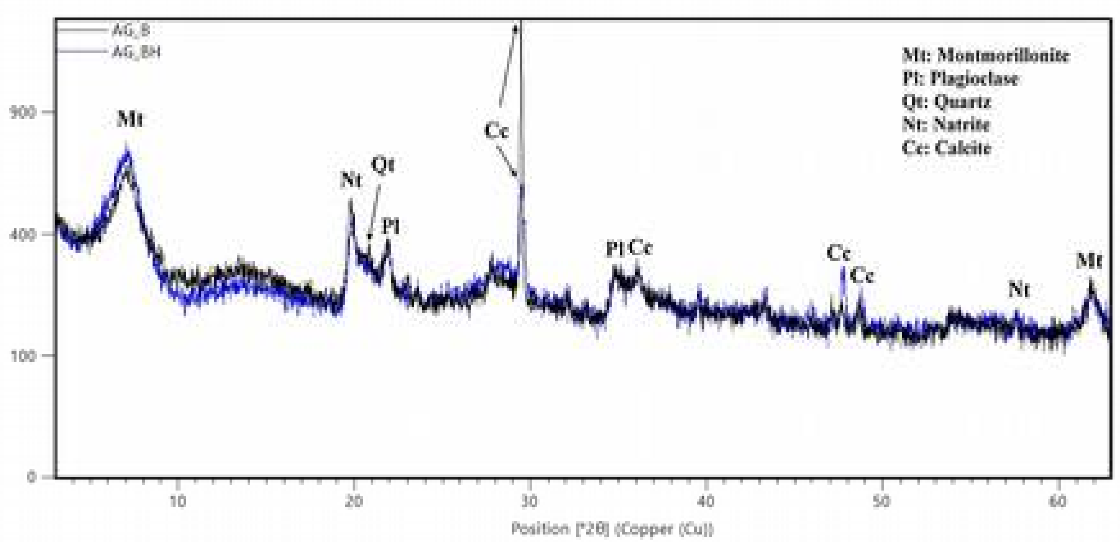


Figure 43. Comparative Diffractogram of raw bentonite [B] and filter cake of the control sample [BH].

Typical lignite samples [KA, MA, NF] are rich in amorphous matter content, compared to leonardite [LE], which is richer in mineral matter. This is also confirmed by the results of the proximate analyses of lignites, in which leonardite is significantly richer in ash (which mostly consists of minerals) compared to typical lignites. Consequently, this is imprinted in the amorphous content of these samples. The mineral composition of typical lignites is almost identical (Figure 45). They consist mostly of clay minerals and quartz. Kardia [KA] lignite has also small amounts of calcite, while traces of pyrite are also noticed in Mavropigi [MA] and Northern Field mine [NF] samples. On the other hand, leonardite is rich in clay minerals, plagioclase, and quartz.

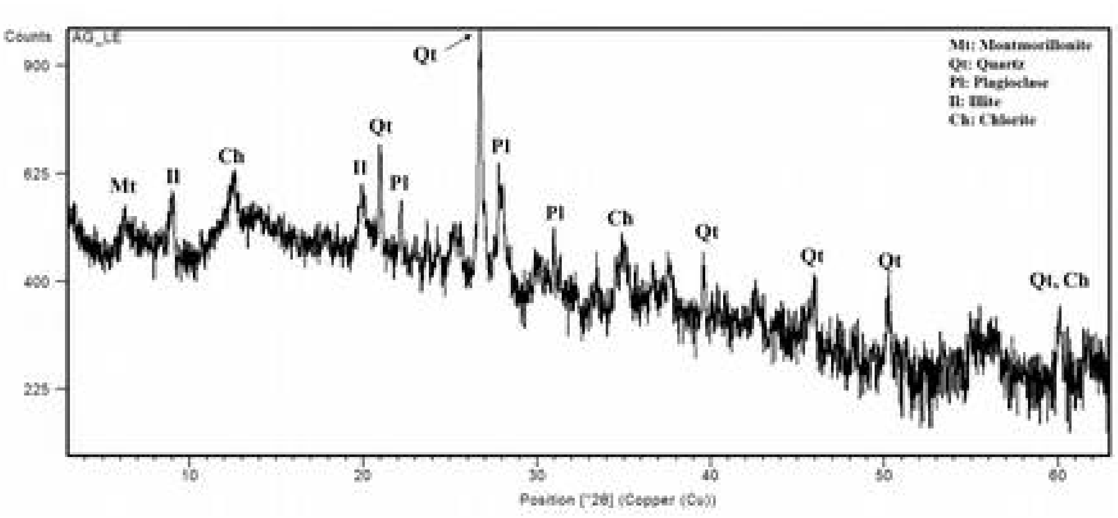


Figure 44. Leonardite [LE] Diffractogram.

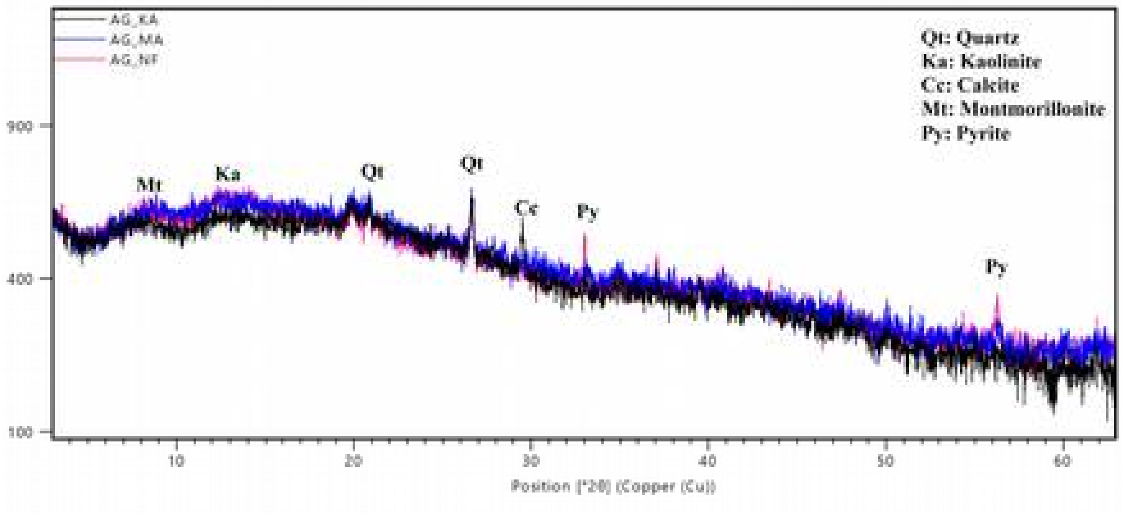


Figure 45. Comparative Diffractogram of the three typical lignites [KA, MA, NF].

Causticized lignites [CKA, CMA, CNF, CLE, ZKA, ZMA, ZNF, ZLE] are also rich in amorphous matter content. **However, an increase in percent crystallinity after causticization was observed in all lignite samples** (see Table 26). Part of the amorphous content of the lignite is of organo-mineral complexes and bonds. During the causticization procedure, part of these bonds has been cracked releasing the Humic and Fulvic acids. At the same time, it is possible that some of the organic matter is burned out leading to a decrease in the amorphous content and therefore to a percent increase in the crystallinity of the causticized lignites.

Filter cakes present a higher crystallinity percentage. Filter cakes have resulted from the filtration procedure of drilling muds, composed by water, bentonite and lignite/leonardite. Consequently, the addition of bentonite plays an important role in the mineralogical composition of the filter cakes. Montmorillonite is the main mineral component of filter cakes along with calcite. Several samples are also rich in quartz, plagioclase and clay minerals.

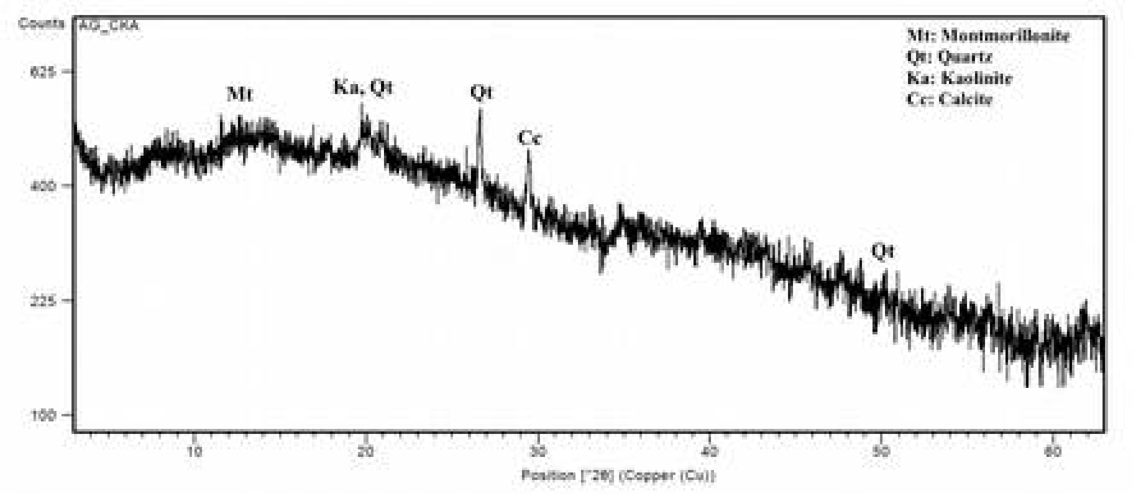


Figure 46. Causticized Kardia lignite [CKA] Diffractogram.

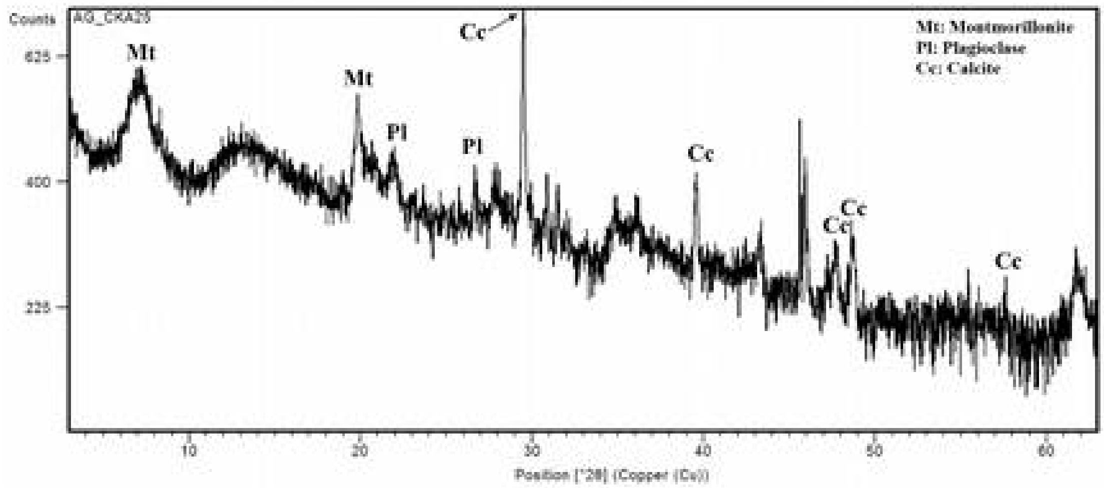


Figure 47. Diffractogram of filter cake with the addition of the causticized Kardia lignite.

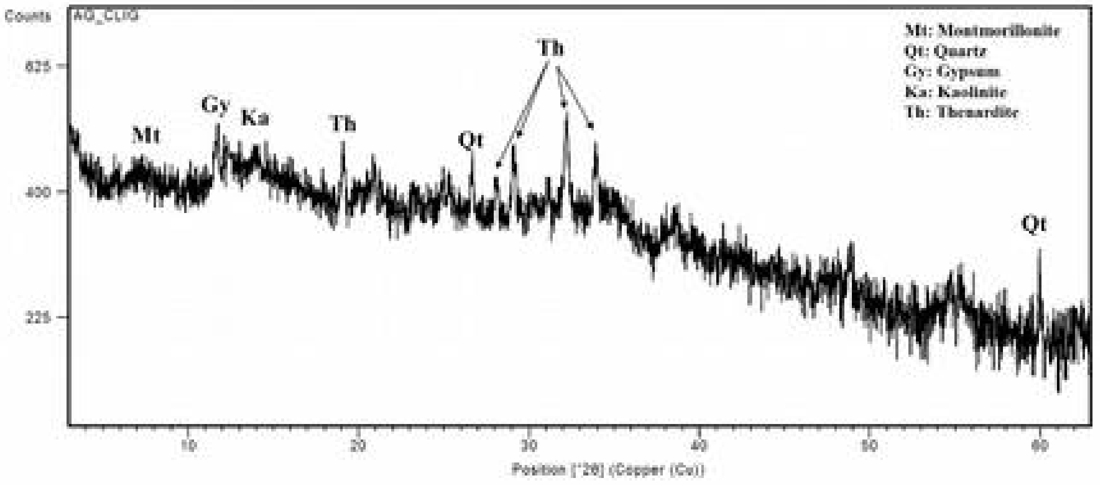


Figure 48. Commercial causticized lignite [CLIG] Diffractogram.

Commercial causticized lignite [CLIG] has higher crystallinity than the typical lignites but lower than leonardite. Its mineral composition is rather different than the other samples. **It is rich in clay minerals and thenardite, which is an anhydrous sodium sulfate mineral.** It also consists of quartz and gypsum. The mineral composition of CLIG indicates a high sulfur content, which is also confirmed by the elemental analysis performed by SEM-EDS (see chapter 3.5.3).

3.5. Chemical composition, morphology, and structure.

Scanning electron microscopy was used as a tool for investigating the morphology and structure of raw bentonite and specific filter cakes, while Energy Dispersive Spectrometry was used for the determination of the chemical composition of all the samples.

3.5.1 Filter cakes

As demonstrated in Figures 49 and 50, the structure of the upper and the lower part of the filter cakes present some differences. It can be noticed that the upper part has a more solid and impermeable structure, while the lower part is more porous with some of the pores being rather large (Figure 49A).

Particularly, in the upper part, it seems that lignite has been absorbed on the bentonite particles, constructing a more solid structure by decreasing the permeability of the cake. This effect of the organic compounds, such as lignite on the filter cake is also described by other studies (Rugang et al., 2014; Zhang et al. 2016). On the other hand, in the lower part, where most of the bentonite is concentrated we can observe the pores that were made up of the clay particle-clay particle structure.

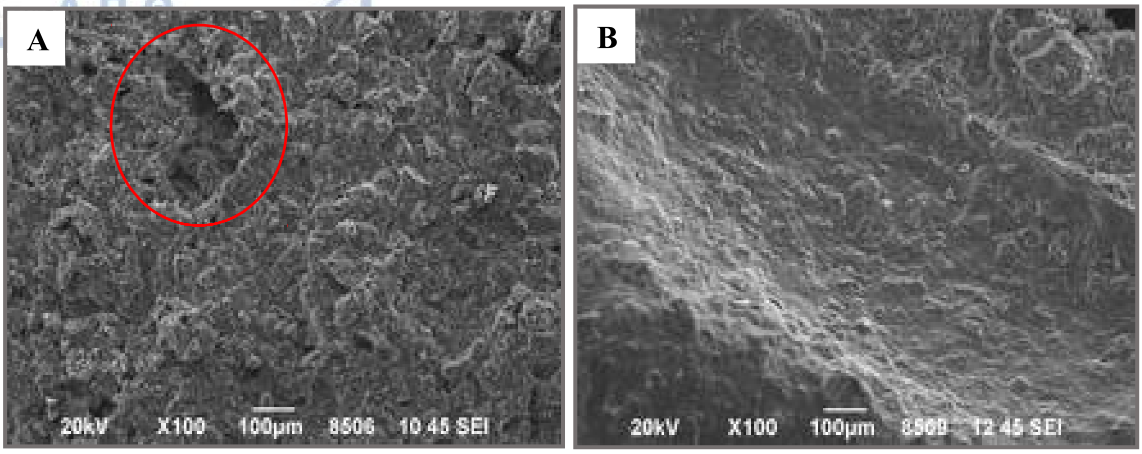


Figure 49. SEM images of filter cake with the addition of CLE Leonardite. A: lower part of the filter cake, B: upper part of the filter cake.

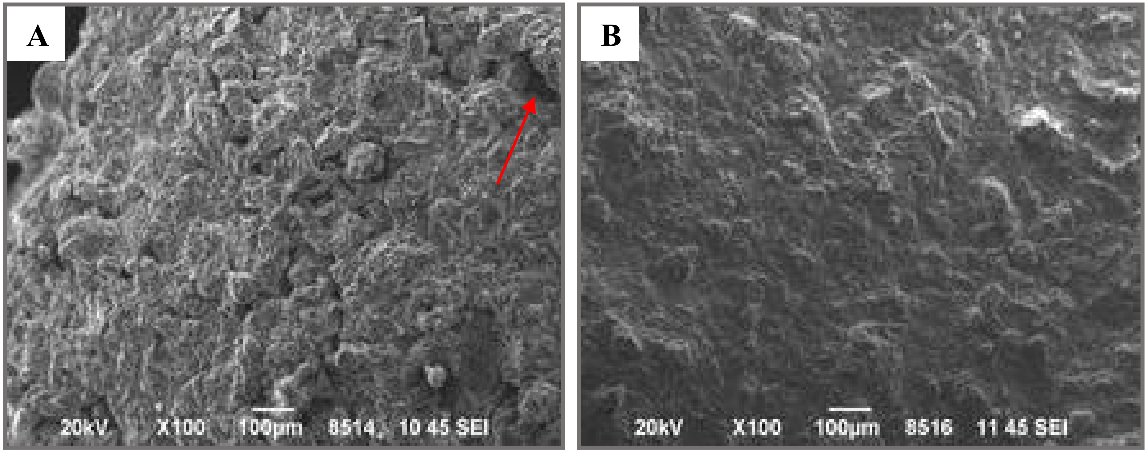


Figure 50. SEM images of filter cake with the addition of ZLE Leonardite. A: lower part of the filter cake, B: upper part of the filter cake.

3.5.2. Bentonite

Bentonite clay particles were also examined under the SEM microscope. Figure 48 demonstrates some representative images of bentonite under SEM. It can be also observed in Figures 51A and 51B the points where the chemical analysis was performed. Regarding morphology, higher magnification images (Fig. 51C and 51D) show that the micro-size particles of bentonite are composed of individual platelets, which conglomerate into large size particles.

Elemental analysis of the bentonite was carried out in selected points on the platelets and the results are given in Table 27. It can be noticed that the distribution of major oxides is almost identical for all the points and it is characteristic for bentonite. The presence of CaO indicates that this is calcium bentonite, but it can also be related to the presence of calcite composed by the sodium activation of Ca-montmorillonite. This procedure is also reflected in the chemical composition by the presence of Na_2O.

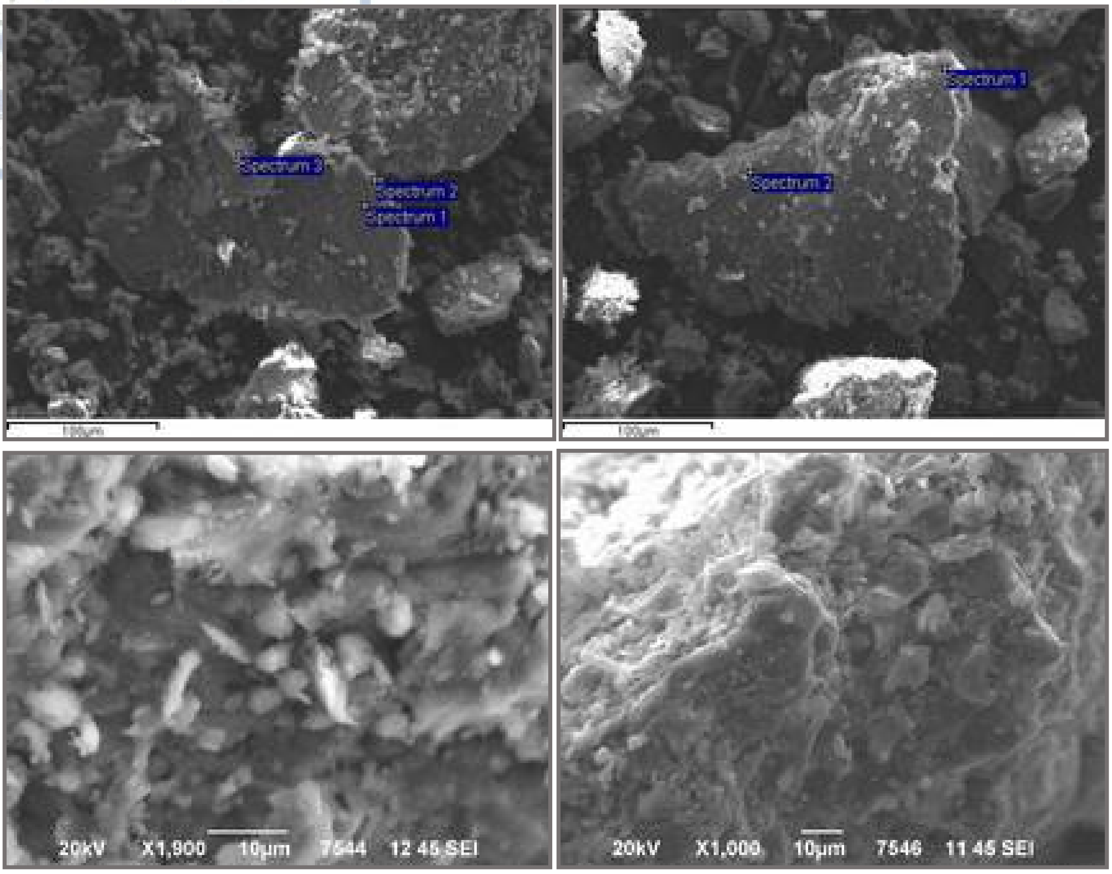


Figure 51. SEM images of Raw bentonite particles.

B

Table 27. Chemical composition in major oxides of the bentonite clay.

Major Oxides	**Bentonite (Figure 48A)** **Spectrum 3 (wt%)**	**Bentonite (Figure 48B)** **Spectrum 1 (wt%)**	**Spectrum 2 (wt%)**
SiO_2	67.25	67.07	67.31
Al_2O_3	18.47	18.13	17.30
FeO	3.58	3.98	6.46
CaO	0.91	0.95	1.39
MgO	6.16	6.28	4.66
Na_2O	2.45	2.32	1.23
K_2O	1.18	1.25	1.65

3.5.3 Commercial causticized lignite

Commercial causticized lignite was also examined under SEM in order to determine its morphology, as well as its chemical composition. Commercial lignite seems to be rich in Na_2O, SO_3, Al_2O_3, CaO, and SiO_2, while in some grains P_2O_5 and MoO_3 concentration were also measured. Part of sodium oxides is probably associated with the causticization treatment followed by the manufacturers of the commercial product.

Table 28. Chemical composition in major oxides of Commercial causticized lignite.

	Commercial causticized lignite - Spectrums							
Major Oxides	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
SiO_2	73.42	-	5.16	3.23	14.64	17.06	-	19.55
Al_2O_3	5.2	12.3	4.21	3.07	13.2	13.83	-	13.75
CaO	-	-	23.99	30.89	-	-	34.63	2.8
Na_2O	21.38	34.34	20.89	20.21	47.28	24.28	42.44	48.75
MoO_3	-	-	-	-	24.88	-	-	-
P_2O_5	-	12.16	-	-	-	-	-	-
SO_3	-	20.55	45.75	42.6	-	44.82	22.93	15.14

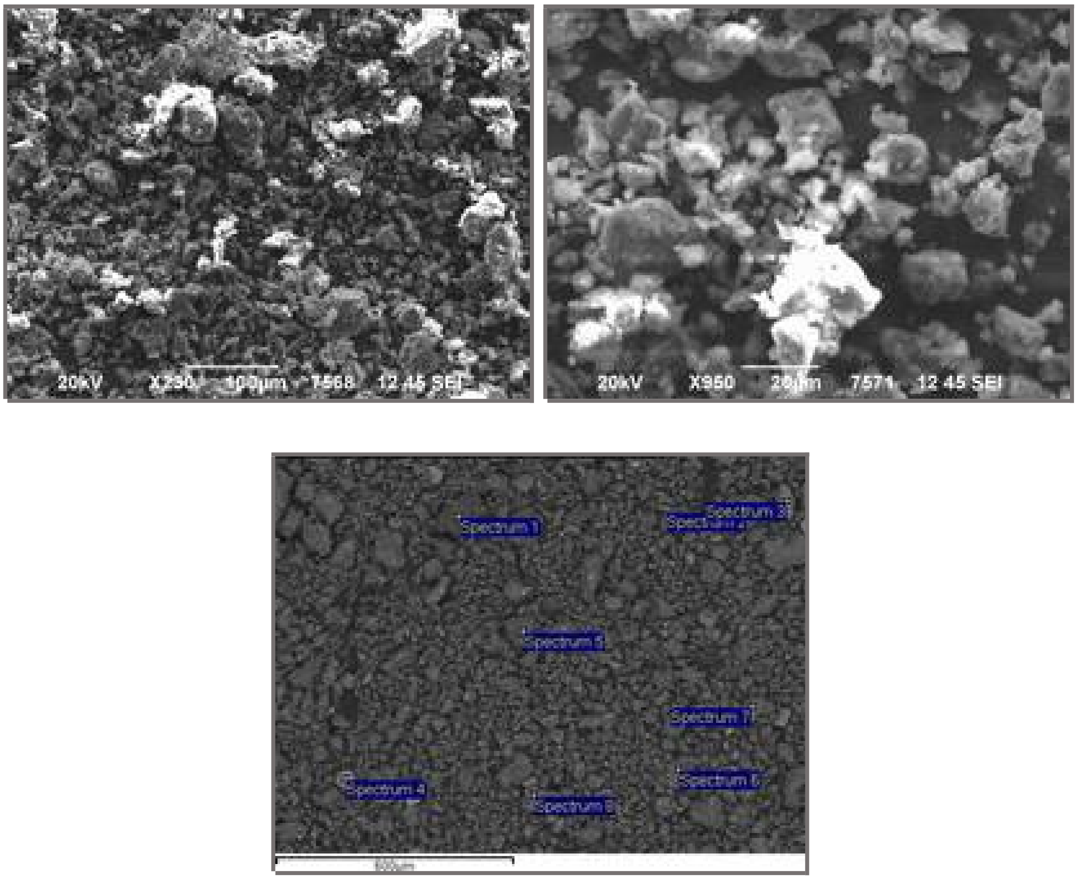


Figure 52. SEM images of the commercial causticized lignite with different magnifications.

The high concentration of sodium can explain the high performance of the product as drilling fluid additive, as well as the high pH values that its addition resulted in. Calcium, silica, aluminum, sulfur, and part of the sodium oxides are probably related to mineralogy. Specifically, XRD results indicated the presence of **gypsum** ($CaSO_4$ x $2H_2O$) and **thenardite** (Na_2SO_4) explaining the presence of calcium, sulfur, and part of sodium oxides. Also, the silica oxides can be associated with quartz (SiO_2), as it is indicated by mineralogy. Aluminum oxides are linked to clay minerals, such as kaolinite and montmorillonite. However, the presence of phosphorous and molybdenum oxides is quite peculiar. One explanation could be that these compounds are linked to the treatment procedure of lignite and were added to impart some properties to result in an advanced performance of the product as a drilling mud additive. Specifically, phosphoric acid has been found as an optional drilling mud additive (Bochenova and Korolev, 1983; Zollar and Moore, 1978 US Patent). According to Zollar and Moore (1978): "*The product is useful as a source of phosphoric acid, and in combination, it produces a new animal feed ingredient material*, ***a new drilling mud additive,*** *and other novel products*."

4. Further research

At the next steps, it is important to shed light on the performance of the studied samples under the extreme temperature and pressure conditions that occur when drilling in higher depths. The properties of drilling mud at surface conditions are easy to determine. Unfortunately, these properties do not represent bottom-hole conditions because they radically change due to elevated temperature and ageing time at the subsurface. This may cause a series of downhole problems.

Further research will be concentrated on the effect of Greek lignite and leonardite addition on rheological and filtration properties of the water-based drilling fluid **after applying a dynamic thermal ageing procedure.**

Drilling fluid ageing is the process in which a drilling fluid sample, previously subjected to a period of shear, is allowed to more fully develop its rheological and filtration properties. The period needed to more fully develop properties varies from as little as several hours (usually 16 hours) to as much as several days. Ageing is done under conditions which vary from static to dynamic and from ambient to highly elevated temperatures. Dynamic thermal ageing procedure includes a laboratory investigation of the effects of temperature while ageing time on water-based mud is achieved with an ageing cell and an oven. The temperatures selected are usually near the estimated bottom-hole temperatures. To achieve the experiments, ageing cells designed and constructed in such a way as to meet, or even exceed, the pressure and temperature requirements of the ageing tests are used.

It is to be noted that since leonardite addition has not yet been extensively studied especially in such conditions, important conclusions can be drawn from the results of dynamic thermal ageing.

CHAPTER 4 – CONCLUSIONS

Drilling fluids used in drilling operations are responsible for controlling subsurface formations pressure, removing and transporting drilled cuttings to the surface, maintaining wellbore stability, and reducing pressure losses. **The main challenge in drilling fluids science is to maintain their properties while drilling.**

Matrix lignite and leonardite from several deposits in Western Macedonia, Greece were collected. Leonardite is a low-rank, low-grade coal type, which usually derives either from lignite that has undergone oxidation during surface exposure or it represents sediments enriched in humic substances that were leached from topsoil or overlain lignite (Browning, 1969; Kalaitzidis et al., 2003). Additionally, a commercial causticized lignite product –CLIG– was used as reference material.

The collected samples were examined after the proximate analysis. **Leonardite is richer in inorganic matter content and thus has the lowest calorific value compared to typical lignites, while it has the lowest moisture content (24.6%).**

The water solubility of lignite and its performance as a drilling mud additive depends on its humic acid content. Humic acids can be used as a fluid loss additive in oil- and water-based drilling fluids. Humic acids have three types of functions when used in drilling fluids:

- They reduce viscosity and gel strength,
- They act as thinners, deflocculants, dispersants, and rheological control agents,
- They also act as fluid loss agents and emulsifiers.

Before the addition in the drilling mud, low-rank coals require a causticization treatment. **Causticization is the chemical treatment of the samples with an alkaline solution. It involves the dissolution of the coal sample into an alkaline solution (usually with NaOH or KOH) while heat is provided**. Causticization treatment was held with two different methods to examine their differences and their effect on the coal samples. The initial difference of the two methods lies on the strength of causticization and on the type of reactants used, as in the first one a solution of low molarity NaOH was used, while in the second one both NaOH and KOH with higher molarities were used together with $ZnSO_4 \times 7H_2O$ as a catalyst.

Ten drilling mud mixtures were composed and analyzed. The mixtures consisted of 6.42% of bentonite and 3.00% of causticized lignite dissolved in 500mL of deionized water.

It is important to mention that the commercial lignite CLIG had the best performance in all experiments.

Rheological models were used to predict fluid flow behavior. Traditionally, three rheological models have been applied in drilling fluid hydraulics and rheological analyses: *Bingham plastic, Power-law, and Herschel-Buckley*. These models adequately cover the range of yield-stress values that are encounter in the field. Drilling muds derived from the present study are characterized by all the above models, while there were a few that were approaching Newtonian fluid behavior. **Concerning the performance of the lignites as viscosity reducers:**

- **Lignites causticized with NaOH [CKA, CMA, CNF] and leonardite causticized with Organic Zinc Complex [ZLE], decreased drilling mud's viscosity when added to the mixture**.
- **Lignites causticized with Organic Zinc Complex [ZKA, ZMA, ZNF], and leonardite causticized with NaOH [CLE] increased drilling mud's viscosity when added to the mixture**
- Commercial lignite [CLIG] has the best performance of all samples by significantly decreasing both types of viscosity.

Consequently, it is derived that samples CKA, CMA, CNF and ZLE can act as viscosity reducers.

The gelation and thickening of the drilling mud, as drilling operation progresses, also causes problems in drilling deep wells. Thickening effects can lead to increased demand in pump pressures to circulate the mud. In such cases, **organic thinners** play an essential role in reducing the thickening effects and stop the gelation procedure. **All of the drilling muds after lignite/leonardite addition presented a significant decrease in their gel-structure reducing the gel-strength below 16.00 lbs/100ft^2. Especially samples CKA, CMA, CNF,**

ZLE had the best performance by reducing the gel-strength below 7.00 lbs/100^2.

Furthermore, several studies indicate that humic acid rich compounds (such as lignites and especially leonardite) are capable of dispersing clay particles and especially in clay-water systems (Canarutto et al., 1996; Narkis et al., 1970; Van Dyke, 2000; Visser 1982; Visser and Cailler, 1988). **It is important that flocculated and deflocculated structures of the clay particles are also strongly dependent on the pH values of the mixture.** This can be associated with the sign and extent of charge at the clay edges, as well as the configuration and charge of humic and fulvic substances, that both change with pH. The lignite samples with the best rheological behavior are the ones that also decreased the pH values compared to the control sample. On the other hand, the lignite samples that resulted in negative results concerning viscosity are the ones that increase or keep in equal values the pH. For leonardite, the opposite effect occurred for pH values. This can be attributed to the usually higher concentration of leonardite in humic and fulvic acids compared to typical lignites. From the results of the present study, it can be concluded that **the concentration of humic acids together with the pH values are responsible for the different behavior of the causticized samples, concerning the rheology performance.**

Understanding of the fluid invasion mechanisms and predicting the filtration rates that occur during drilling and dynamic filtration is always essential for the oil drilling operations, to guide the development and design of reservoir protection measures. To achieve that, the hydrostatic pressure of the mud column must be greater than the pressure of the fluids in the pores of the formations. Keeping filtrate volume under specific limits - as they are proposed by API specifications - is essential in avoiding the formation damage because the filtrate will couple with the existing formations pressure, the effective stresses will be reduced and as a direct result the rock formations will be damaged which can be detrimental not only to drilling activity but also later during production. It is also important to produce an appropriate thin filter cake, which will help in avoiding pipe sticking and consequently protect the environment. All causticized lignites did not have the same performance under filtration experiments. Especially, causticized lignites with NaOH presented very high filtration volumes which make them unsuitable as fluid loss agents. On the other hand, Organic Zinc Complex causticized lignites when added to the mixture, significantly decrease filtrate volume, below the 15mL limit, as recommended by API specification. Regarding leonardite, the addition of both samples resulted in a decrease of the filtrate volume received below the API limit. **Consequently, leonardite causticized by both methods, as well as lignites causticized with Organic Zinc Complex sufficiently behave as fluid loss additives.**

The above results support the conclusion that the better effect of Organic Zinc Complex causticized samples lies on the higher strength of the causticization and the higher molarity of the alkaline solution used that may have resulted into a higher release in humic acids content of the low-rank coals used.

Filter cakes' thickness varied between 2.0-5.0mm. A vertical separation of their ingredients was observed after drying and was examined under the Scanning Electron Microscope. It was noticed that the upper and the lower part of the cakes had several differences. Particularly, in the upper part, lignite was absorbed on the bentonite particles, creating a more solid structure and potentially decreasing the permeability of the cake. On the other hand, in the lower part, where most of the bentonite was concentrated, the pores that were made up of the clay particle-clay particle structure and a lot of open holes were observed.

The elemental analysis of the samples was in accordance with the mineralogical analysis. Specifically, XRD results indicated that causticization procedure probably resulted in “burning” a part of the organic amorphous content of the lignites, which was observed by a percentage increase of the crystallinity in the causticized samples. Elemental and XRD analyses also provided us with information about the nature of the commercial causticized samples. The CLIG lignite consists of a high amount of sulfur as indicated by the presence of gypsum and thenardite minerals. This may be associated with its great performance as a drilling mud additive, considering that Organic Zinc Complex causticization that had positive results, also had the addition of sulfur by the form of hydrated zinc sulfate.

However, there is a lot of research needed to deeply understand the way causticization procedure affects low-rank coals' structure. Several questions remain on how different physicochemical properties (such as pH, humic and fulvic acid content, presence of specific elements, clay particles nature, etc.) influence the performance of low-rank coals as drilling fluid additives.

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APPENDIX

EXPERIMENT No. 1

SAMPLE: BH

Preparation

Bentonite added (gr): 32.2 Water (mL): 500

Bentonite added (%): 6.42

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 ºC

Speed	Dial reading (θ)
3	0.5
6	1
100	3
200	6
300	8
600	13

Viscosity =θ_{300} = 8 cP

Plastic Viscosity = θ_{600}-θ_{300} = 5 cP

Yield point = θ_{300}- PV = 3 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	17

2. Filter press

Temperature	25 ºC
Filtrate 30 min	21.2 mL
Mud cake 30 min	4.0 mm
Hardness of filtrate	25 ppm

3. pH: 11

EXPERIMENT No. 2

SAMPLE: CKA

Preparation

Bentonite added (gr): 32.13 Water (mL): 500

Bentonite added (%): 6.42

Lignite (CKA) added (gr): 15.0

Lignite (CKA) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	0.5
100	2
200	3.5
300	5
600	10

Viscosity = θ_{300} = 5 cP

Plastic Viscosity = θ_{600}-θ_{300} = 5 cP

Yield point = θ_{300}- PV = 0 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	2

2. Filter press

Temperature	25 °C
Filtrate 30 min	24 mL
Mud cake 30 min	2.5 mm
Hardness of filtrate	120 ppm

3. pH: 10

EXPERIMENT No. 3

SAMPLE: CMA

Preparation

Bentonite added (gr): 32.13 Water (mL): 500

Bentonite added (%): 6.42

Lignite (CMA) added (gr): 15.0

Lignite (CMA) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	1
6	1
100	2
200	3.5
300	6
600	11

Viscosity = θ_{300} = 6 cP

Plastic Viscosity = θ_{600}-θ_{300} = 5 cP

Yield point = θ_{300}- PV = 1 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	3

2. Filter press

Temperature	25 °C
Filtrate 30 min	25 mL
Mud cake 30 min	2.5 mm
Hardness of filtrate	120 ppm

3. pH: 10.2

EXPERIMENT No. 4

SAMPLE: CNF

Preparation

Bentonite added (gr): 32.13 Water (mL): 500

Bentonite added (%): 6.42

Lignite (CNF) added (gr): 15.0

Lignite (CNF) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	0
100	2
200	4
300	6
600	10

Viscosity = θ_{300} = 6 cP

Plastic Viscosity = $\theta_{600}-\theta_{300}$ = 4 cP

Yield point = θ_{300}- PV = 2 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	2

2. Filter press

Temperature	25 °C
Filtrate 30 min	21.5 mL
Mud cake 30 min	3 mm
Hardness of filtrate	120 ppm

3. pH: 10

EXPERIMENT No. 5

SAMPLE: CLE

Preparation

Bentonite added (gr): 32.10 Water (mL): 500

Bentonite added (%): 6.42

Lignite (CLE) added (gr): 15.0

Lignite (CLE) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0.5
6	1
100	4
200	7
300	10
600	17

Viscosity = θ_{300} = 10 cP

Plastic Viscosity = θ_{600}-θ_{300} = 7 cP

Yield point = θ_{300}- PV = 3 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0.5	11

2. Filter press

Temperature	25 °C
Filtrate 30 min	14.7 mL
Mud cake 30 min	2 mm
Hardness of filtrate	120 ppm

3. pH: 10.6

EXPERIMENT No. 6

SAMPLE: CLIG

Preparation

Bentonite added (gr): 32.10 Water (mL): 500

Bentonite added (%): 6.42

Lignite (CLIG) added (gr): 15.0

Lignite (CLIG) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	0
100	1
200	3
300	4.5
600	8.5

Viscosity = θ_{300} = 4.5 cP

Plastic Viscosity = θ_{600}-θ_{300} = 4 cP

Yield point = θ_{300}- PV = 1.5 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	0.5

2. Filter press

Temperature	25 °C
Filtrate 30 min	8.4 mL
Mud cake 30 min	5 mm
Hardness of filtrate	120 ppm

3. pH: 12.5

EXPERIMENT No 7

SAMPLE: ZKA

Preparation

Bentonite added (gr): 32.10 Water (mL): 500

Bentonite added (%): 6.42

Lignite (ZKA) added (gr): 15.0

Lignite (ZKA) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	1
100	4
200	8
300	11
600	19

Viscosity = θ_{300} = 11 cP

Plastic Viscosity = θ_{600}-θ_{300} = 8 cP

Yield point = θ_{300}- PV = 3 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	15

2. Filter press

Temperature	25 °C
Filtrate 30 min	12.2 mL
Mud cake 30 min	2 mm
Hardness of filtrate	120 ppm

3. pH: 11.3

EXPERIMENT No. 8

SAMPLE: ZMA

Preparation

Bentonite added (gr): 32.10

Water (mL): 500

Bentonite added (%): 6.42

Lignite (ZMA) added (gr): 15.0

Lignite (ZMA) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	1
100	4
200	8
300	10.5
600	19

Viscosity = θ_{300} = 10.5 cP

Plastic Viscosity = θ_{600}-θ_{300} = 8.5 cP

Yield point = θ_{300}- PV = 2 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	15

2. Filter press

Temperature	25 °C
Filtrate 30 min	11.5 mL
Mud cake 30 min	3.5 mm
Hardness of filtrate	120 ppm

3. pH: 11.4

EXPERIMENT No. 9

SAMPLE: ZNF

Preparation

Bentonite added (gr): 32.10 Water (mL): 500

Bentonite added (%): 6.42

Lignite (ZNF) added (gr): 15.0

Lignite (ZNF) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	1
100	4
200	8
300	11
600	18

Viscosity = θ_{300} = 11 cP

Plastic Viscosity = θ_{600}-θ_{300} = 7 cP

Yield point = θ_{300}- PV = 4 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	13

2. Filter press

Temperature	25 °C
Filtrate 30 min	12 mL
Mud cake 30 min	2.5 mm
Hardness of filtrate	120 ppm

3. pH: 11

EXPERIMENT No. 10

SAMPLE: ZLE

Preparation

Bentonite added (gr): 32.10 Water (mL): 500

Bentonite added (%): 6.42

Lignite (ZLE) added (gr): 15.0

Lignite (ZLE) added (%): 3

Measurements

1. Rheology & Viscosity - Fann 35A instrument

Temperature: 25 °C

Speed	Dial reading
3	0
6	0.5
100	2.5
200	4.5
300	7
600	11

Viscosity = θ_{300} = 7 cP

Plastic Viscosity = θ_{600}-θ_{300} = 4 cP

Yield point = θ_{300}- PV = 3 lb/100ft^2

Gel Strength:

Waiting Time	10 s	10 min
Dial Reading	0	6

2. Filter press

Temperature	25 °C
Filtrate 30 min	14 mL
Mud cake 30 min	2.5 mm
Hardness of filtrate	120 ppm

3. pH: 11.4