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Review

Application of Organoclays in Oil-Based Drilling Fluids: A Review

Ali Mahmoud, Rahul Gajbhiye,* and Salaheldin Elkatatny

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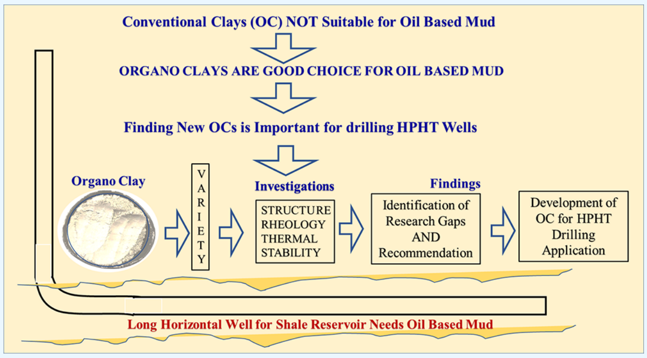

ABSTRACT: Organoclays (OCs), formed by surface modification of clay minerals using organic compounds, are typical additives for providing rheology for oil-based drilling fluids (OBDFs). There are different studies on the effect of OCs on the rheological properties of oil-based systems under high-pressure, high-temperature (HPHT) conditions, but finding new OCs as rheology control agents is attractive for drilling fluid engineers. This work reviews different OCs used in OBDFs, namely, organo-montmorillonite (OMMT), organo-sepiolite (OSEP), and organo-palygorskite (OPAL). Furthermore, the structure of OCs in OBDFs, their rheological properties, and the thermal stability of OCs were investigated. Besides, the role of fibrous and layered OCs in enhancing the rheological properties of OBDFs is illustrated. Finally, the synergistic use of different OCs to enhance the thermal stability and rheological properties of the OBDFs is presented. The study highlights research gaps and recommendations for research approaches and potential areas that need further investigation. The application of OCs in OBDFs is a wide field and has huge potential to be developed. The use of OCs in OBDFs will promote development in the oil and gas industry.

1. INTRODUCTION

The demand for energy resources from the oil and gas industry is increasing to a level that is difficult for conventional hydrocarbon reservoirs to fulfill. Oil and gas companies are in search of novel ways to exploit the potential of unconventional reservoirs. Using a proper drilling fluid is critical for any successful drilling operation. High-performance drilling fluids must be used while drilling unconventional hydrocarbon reservoirs due to the high-pressure, high-temperature (HPHT) conditions encountered and the requirement of long horizontal/multilateral drilling for maximum reservoir contact (MRC).

Drilling fluids are used to drill oil and gas wells and are considered to be a crucial part of any drilling operation. These complex fluids correspond to 15−18% of a well's total cost.[1] Figure 1 shows a schematic of the drilling operation including main constituents, main function, and classification of drilling fluid. They have several purposes that must be adjusted to ensure safety and minimize hole problems. Some of these functions include the removal of the cutting downhole, providing wellbore stability, cooling and lubricating the drill string and bit, controlling the downhole formation pressures, and preventing formation damage by creating a filter cake that seals the rock pores.[2−4] Any failure of the drilling mud to meet its required functions can prove extremely costly and can jeopardize the success of the drilling operation. When selecting the optimal drilling fluid, the cost of the drilling fluid, environmental regulations, and shale inhibition characteristics are key factors to consider.[5]

Drilling fluids are categorized into water-based drilling fluids (WBDFs) and oil-based drilling fluids (OBDFs) depending on whether the continuous phase is water or oil. The oil base can be diesel, crude oil, or mineral oil.[6] In most cases, WBDFs are used because of their low cost and minimal environmental impact.[7] On the other hand, WBDFs have significant disadvantages, including interfering with oil flow through porous rocks and dissolving salts.[8] In addition, WBDFs have limitations under HPHT conditions. OBDFs are complex fluids composed of water, oil, different additives, and organophilic clays.[9] For HPHT wells, OBDFs are used due to their superior performance. Also, OBDFs provide higher lubricity, thermal stability, and shale inhibition; better wellbore stability; and higher rates of penetration and achieve lower filter loss and a thin filter cake.[1−3,10] Hydraulic fracturing is the most common technique to extract hydrocarbons in shale formations.[11] For shale formations, OBDF is used to eliminate

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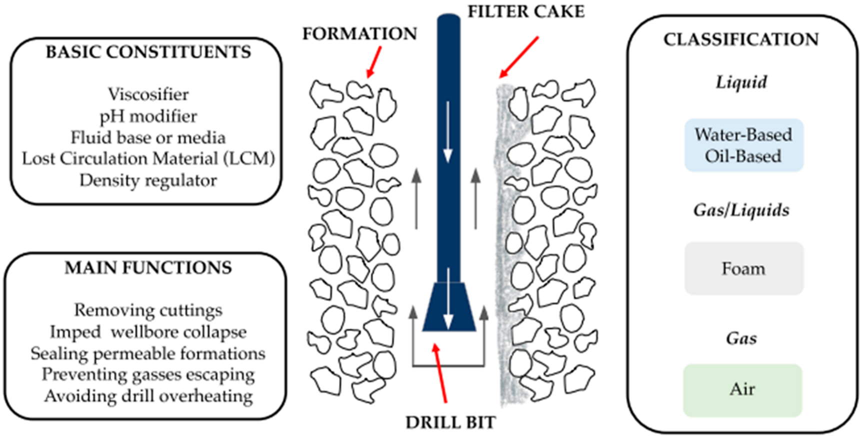

Figure 1. Schematic of the drilling operation, including main constituents, main function, and classification of drilling fluid. Reprinted with permission from Zamora-Ledezma et al.[5] Copyright 2022 ACS Publications.

the water-sensitive shale's problems of hydration and swelling.[12]

The complex drilling fluids are non-Newtonian thixotropic shear-thinning fluids.[4,10] Their behavior varies depending on the temperature and pressure. Drilling fluid exhibits low viscosity when sheared, and it thickens to hold the cuttings in place when shearing is halted. Different models are used to describe the rheology of drilling fluids, such as the Bingham plastic model, the Herschel−Bulkley model, and the Casson model.[13] Various additives are added to drilling fluids to adjust their density or chemical properties.[13−15]

1.1. Organoclays (OCs). OCs are formed naturally by modifying clay materials with organic ammonium salts and are widely used in industrial applications as rheology modifiers, such as grease, and cosmetics, as well as in the preparation of OBDFs.[16] OCs are a crucial additive in the preparation of drilling fluids' preparation. The interlayer cations of clay are replaced by organic molecules, such as alkyl ammonium cations. Due to its favorable dispersing properties in the oil phase and filtration characteristics, organophilic bentonite has been used extensively.[17] OCs have several advantages when added to OBDFs, such as the ability to swell in an organic medium, high thermal stability, and favorable rheological properties.[15,18−24] Ogawa and Kuroda[25] discussed the preparation of inorganic−organic nanocomposites through the intercalation of organoammonium ions into layered silicates. The authors developed a method to create tiny particles that are composed of both inorganic and organic materials. This process creates a new material that has unique properties and can be used in a variety of applications, such as in the production of plastics, coatings, and other materials.

1.2. Common Organoclays (OCs) Used in Oil-Based Drilling Fluids (OBDFs). Montmorillonite (MMT),[2,3,26,27] palygorskite (PAL),[28−33] and sepiolite (SEP)[31,34−36] are the most widely used clay minerals in WBDFs due to the formation of network structures in water. In OBDFs, OCs are used as rheological additives. OCs thicken the organic compositions.[13] In addition, appropriate colloidal and rheological properties for OBDF systems are obtained by adding OCs.[13] Moreover, adding OCs to the continuous phase of the drilling fluid enhances the fluid properties.[19,37] Recently, scientists have studied the application of OCs in OBDFs. The search for new OCs with favorable properties for use in OBDFs is an area of active research. This review presents the application of OMMT, OSEP, and OPAL. Furthermore, the structure, colloidal and rheological properties, and thermal stability of OCs in OBDFs are summarized. Also, recent developments in nanotechnology have opened a route for developing OCs for OBDF applications.

2. MONTMORILLONITE (MMT)

MMT is the main component of bentonite. It belongs to the general family of clay minerals. The structure of MMT is made of two continuous (SiO_4) tetrahedral sheets and an AlO_6 octahedral sheet.[38,39] MMT is negatively charged due to isomorphism. Due to the substitution of Mg^{2+} and other lower-charge cations for Al^{3+} in octahedral sites, a negative charge layer is formed.[38,40] Thus, some exchangeable cations present in the interlayer space, such as Na^+ and Ca^{2+}, counterbalance the deficit of positive charges.[38,41,42] The fluid has a very high viscosity due to MMT's high charge and fine particle size. MMT is mainly used in WBDFs, while OMMT is used in OBDFs.

2.1. Organo-Montmorillonite (OMMT). Organic cations can intercalate into the interlayer space due to the exchangeable cations.[16] This results in an expansion of the interlayer space. Besides, organic cations also coat the surface of MMT, which results in increased hydrophobicity.[7,8] Several organic compounds can be used to prepare OMMT, e.g., cationic surfactants,[43−48] anionic surfactants,[49−52] and non-ionic surfactants.[53−59] OMMT modified using cationic surfactants is widely used because of its low cost, easy reaction, and controllable hydrophobicity.[14] Additionally, mixtures of these organic compounds can be used, such as cationic and anionic surfactants,[60−65] cationic and nonionic surfactants,[8,59,66] and nonionic and anionic surfactants.[8,66,67] Some properties of OMMT can be modified using two or more types of surfactants by changing the type and concentration of surfactants.[13]

2.2. Application of Organo-Montmorillonite (OMMT) in Oil-Based Drilling Fluids (OBDFs). Jordan[17] used OMMT as a thicker organic solvent. The authors investigated the conversion of clay from a highly hydrophilic condition to an organophilic condition. The organocation used in this study is octadecylammonium. OMMT is the most popular commercial rheological additive used in OBDF. Due to its hydrophobicity and large basal spacing, OMMT controls the rheological behavior of an OBDF by dispersing, swelling, and

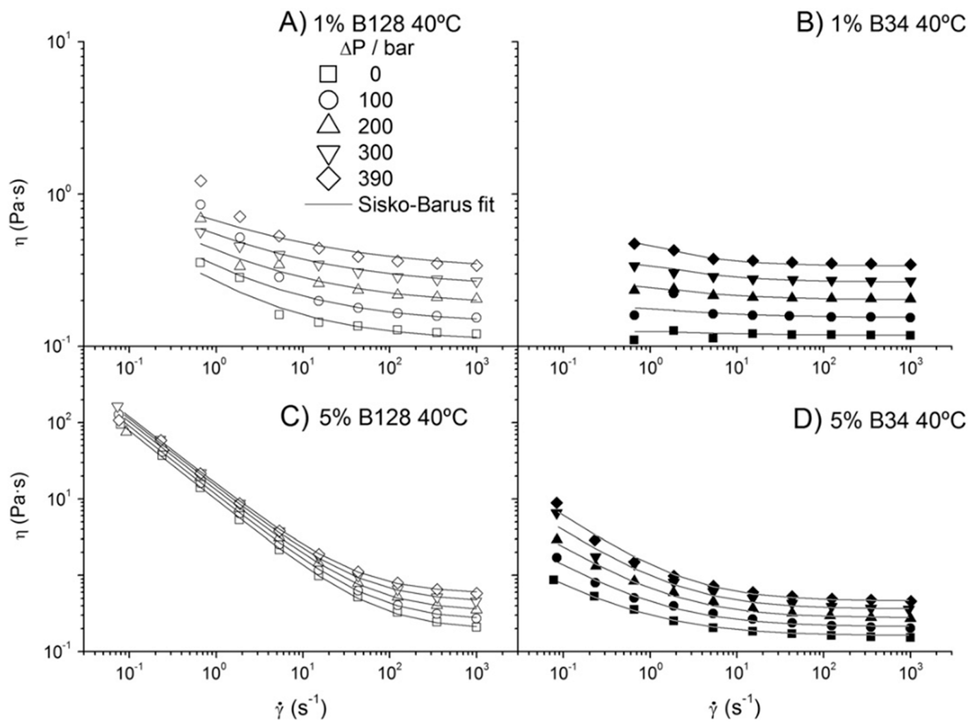

Figure 2. Experimental viscous flow curves and Sisko−Barus model fitting for the different OMMT/oil fluids studied as a function of pressure at 40 °C: (A) viscous flow curve for the lowest B128 concentration, (B) viscous flow curve for the lowest B34 concentration, (C) viscous flow curve for the highest B128 concentration, and (D) viscous flow curve for the highest B34 concentration. Reprinted with permission from Hermoso et al.[19] Copyright 2014 Elsevier.

exfoliation in a base oil.[13] This study provides insights into the factors involved in the conversion process and the extent of the conversion.

Silva et al.[58] used OMMT with nonionic surfactants as dispersants in organic-based drilling fluids. The paper discusses the use of nonionic surfactants, specifically Ultramina 20 (TA20) and Ultramina 50 (TA50), as OC modifiers for use in organic-based drilling fluids. The study shows that the nonionic surfactants effectively intercalate in the OCs, and the content of incorporated surfactants was quantified. The swelling results demonstrate the chemical compatibility between diesel and kerosene organic media and the OCs produced. The authors highlighted that nonionic surfactants are superior to ionic surfactants, as they enhance the thermal stability and chemical properties of OCs and are eco-friendly. Furthermore, the results indicate efficient intercalation of nonionic surfactants in OCs. In addition, OCs considered poor in WBDFs showed great potential with organic-based drilling fluids. However, there was no direct correlation between apparent viscosity and swell indices, and the swell index should be used only for a qualitative analysis of the solvent−OC interaction and not as an indication of the viscosity of the dispersion to be used as a drilling fluid.

Recently, Hermoso et al.[19] studied the influence of the viscosity modifier and concentration on the rheological properties of OBDFs with two commercial OMMT samples (B34 and B128) as additives at different pressures. The authors used a controlled-stress rheometer to measure the fluids' viscous flow behavior as a function of the OC concentration, OC nature, and pressure. They concluded that the nature and concentration of the OC strongly influenced the viscous flow behavior of OBDFs (Figure 2). Also, a Sisko−Barus model can be used to calculate pressure losses in different sections of the bore. In addition, higher concentrations of OMMT increased the viscosity. Moreover, the experimental pressure−viscosity data were fitted in to a Sisko−Barus model, which considers shear and pressure effects. The study also found that the microstructure of the OC dispersions is related to the cohesion energy between microgel domains and that the pressure−viscosity behavior of these dispersions is mainly influenced by the piezo-viscous properties of the oil and the properties of the continuous phase.

Hermoso et al.[37] studied the effect of OC concentration (1 and 3 wt %) and aqueous phase volume fraction on the rheology of OMMT in invert-emulsion OBDFs. The OC used in this study was Bentone 128, which was modified by a cationic exchange reaction between bentonite clay and dimethyl-benzyl-hydrogenated tallow. The authors concluded that, at low concentrations of OC, the yield stress varied linearly; on the other hand, at high OC concentrations, the yield stress varied according to a power law model. The study found that increasing the aqueous phase volume fraction led to a decrease in the viscosity, while increasing the OC concentration led to an increase in viscosity, confirming previous research results.[68,69] Moreover, the emulsion's stability increased due to a decrease in mean droplet diameter due to the increase in the concentration of OC, as has been reported earlier.[70]

Zhuang et al.[8] compared cationic-organo-montmorillonite (CO-MMT), cationic-nonionic-organo-montmorillonite (CN-OMMT), and nonionic-organo-montmorillonite (N-OMMT) intended to be used in OBDFs. The study involved the preparation and characterization of the organo-montmorillonites using various techniques such as X-ray diffraction, differential thermal analysis, thermogravimetric analysis, the contact angle test, and the swell index. The results of the study

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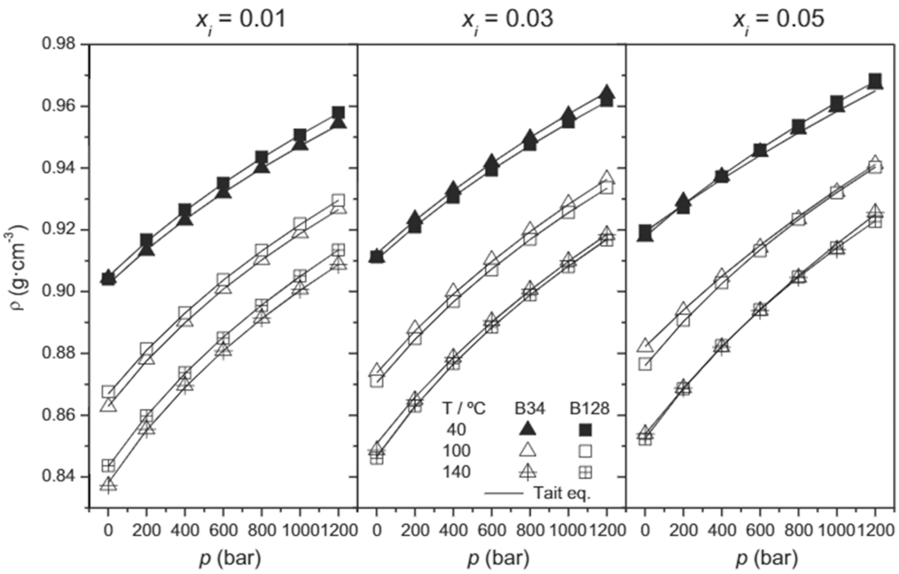

Figure 3. Evolution of the experimental density with pressure at different temperatures for OMMT/oil fluids. Reprinted with permission from Hermoso et al.[71] Copyright 2017 Elsevier.

indicated that both cationic and nonionic surfactants can intercalate into the interlayer spaces of MMT, and the order of their thermal stability was CN-OMMT > CO-MMT > NO-MMT. The order of surface lipophilicity and swelling indices in oils was CN-OMMT > CO-MMT > NO-MMT. Moreover, CN-OMMT presented a novel potential rheological control additive for OBDF, especially for fluids with high oil/water ratio (OWR).

Zhou et al.[22] studied the rheological and filtration properties of OBDFs using OMMT modified by cationic and anionic surfactants. The authors first modified the MMT through mechanochemistry and studied the fluids' structures and properties by using various techniques such as X-ray diffraction, thermal analysis, contact angles, and dispersion. They found that the cationic and anionic surfactants had intercalated into the interlayer spaces of MMT, resulting in higher surface polarity, better thermal stability, and better dispersion in highly polar solvents than those of cationic OMMT alone. The authors studied the thixotropic behavior, viscosity properties, gel properties, and filtration loss at ambient and elevated temperatures (200−220 °C). It was concluded that cationic and anionic OMMT have better thixotropy, enhanced rheological properties, and less filtration loss compared to commercial cationic OMMT in OBDFs with different OWRs.

Hermoso et al.[71] investigated the influence of two types of OCs and their concentration on the density of OC suspensions at a wide range of pressures and temperatures. The study found that the addition of OC to the liquid matrix resulted in a significant increase in density values across the range of temperatures and pressures evaluated (Figure 3). The volumetric behavior of these suspensions was found to be influenced by the nature of the OC and dampened by increasing pressure. The Tait equation was used to model the pressure−temperature dependence of the volumetric properties.

Zhuang et al.[7] studied the structure of OMMT and OMMT/oil gels and the rheology of OMMT/oil fluids aged at different temperatures. The results demonstrated that surfactant loading influenced the structure and surface properties of the OMMT. Furthermore, the authors discovered that the structure of OMMT in oil went through four stages with increasing temperature: swelling, continuous swelling, exfoliation, and shrinking, respectively. The enwinding, absorption, and other attractions among absorbed surfactants bridged individual OMMT sheets, particles, and aggregates, forming the gel structure. The swelling and gel formation of OMMT/oil were influenced by the surface properties, basal spacing, surfactant loadings, and temperature. Moreover, the rheological studies indicated that the fluid followed the Bingham plastic model at a high shear rate ($\geq 20\ s^{-1}$), while deviation emerged at a low shear rate range (Figure 4). The

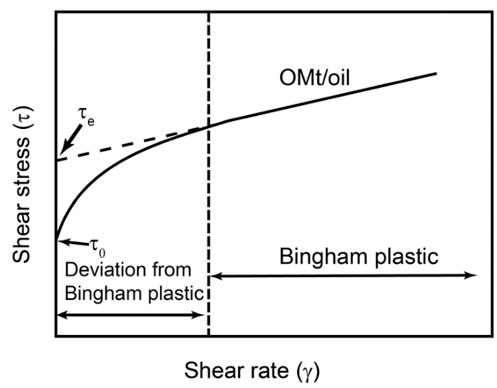

Figure 4. Interpretative diagram of the rheological model of the OMMT/oil fluid. Reprinted with permission from Zhuang et al.[7] Copyright 2016 Elsevier.

viscosity, gel strength, and thixotropy of the OMMt/oil were relevant to the structure, which was influenced by multiple elements, such as surface properties, basal spacing, surfactant loadings, temperature, etc. The best performance of individual elements did not automatically lead to the greatest rheological properties. For oil-based drilling fluids containing OMMT prepared with cetyltrimethylammonium bromide (CTAB), the recommended operating temperature was below 150 °C.

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Several rheological studies conducted show that, at elevated temperature and pressure, the Herschel−Bulkley and Casson models fit the flow behavior of OBDFs fairly well.[19,72−75] The Casson rheological model accurately predicts the drilling fluid behavior across low and high shear rates. In addition, it is preferred to the Herschel−Bulkley rheological model due to the correction factor that is introduced to the yield stress and PV.

3. SEPIOLITE (SEP) AND PALYGORSKITE (PAL)

SEP and PAL are used in many technological applications due to their unique adsorptive, colloidal, and rheological properties.[13] These clay minerals contain a continuous two-dimensional tetrahedral sheet but lack continuous octahedral sheets. The structure of SEP and PAL clay minerals is shown in Figure 5. Also, a variable amount of zeolitic water is contained in the channels of SEP and PAL.[76−78] SEP and PAL clay minerals exhibit extra negative charges that are balanced by cations in the channels due to isomorphism substitution. These clay minerals are used in paints, adhesives, sealants, fertilizer dispersions, and cosmetics.[31,32] They are also used in OBDFs.[26,28−30,33,35,36]

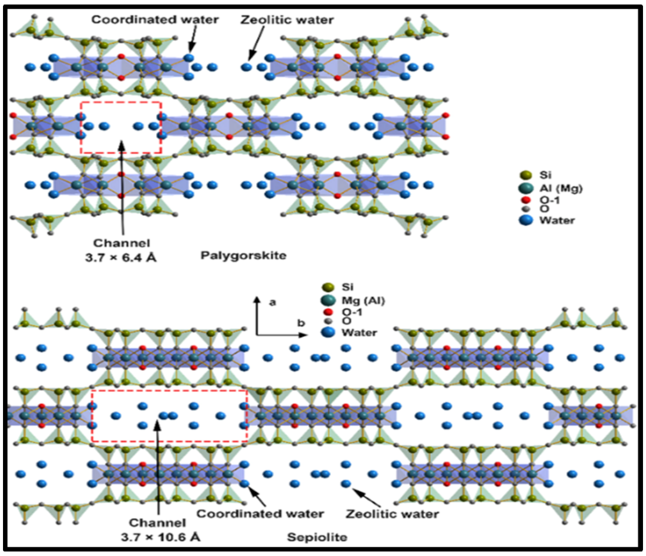

Figure 5. Crystal structures of PAL and SEP. Reprinted with permission from Zhuang et al.[13] Copyright 2019 Elsevier.

3.1. Organo-Sepiolite (OSEP) and Organo-Palygorskite (OPAL).

In some applications, the organic modification of SEP and PAL is due to poor compatibility between these clay minerals and organic compounds. The modifiers include cationic surfactants, amines, polymers, and organosilanes. Table 1 summarizes the syntheses of OSEP and OPAL.

3.2. Application of Organo-Sepiolite (OSEP) and Organo-Palygorskite (OPAL) in Oil-Based Drilling Fluids (OBDFs).

In the presence of dissolved salts, PAL and SEP remain a viscous dispersion, unlike MMT.[26,28,31] PAL and SEP develop a haystack structure by organizing the nanofibers. PAL and SEP are organically modified due to the poor compatibility between the clay surface and base oil.

Zhuang et al.[79] investigated the effects of different surfactants on the properties of OPAL in OBDFs. In this study, three different quaternary ammonium salts with different lipophilicity were used to organically modify PAL. The study found that the surfactants' lipophilicity affects the dispersity of OPAL in oil, with better lipophilicity leading to better dispersity. However, excellent dispersity does not necessarily contribute to high viscosity and gel strength. A little polarity is beneficial for promoting the rheological properties of OBDFs. The authors concluded that rising temperatures facilitate the disaggregation of OPAL in oil, but high temperatures may result in the thermal decomposition of surfactants on the surface of PAL (Figure 6). The content of sequestrated oil in the interspace of the OPAL units affects the network structure of the OPAL in oil, with more sequestrated oil resulting in a stronger network structure.

Table 1. Synthesis of OPAL and OSEP, Modified after Zhuang et al.[13]

Clay mineral	Modifiers	Method	Reference
PAL	Series of quaternary ammonium salts	Reacting in water	Zhuang et al.[79,80]
PAL	Chitosan	Stirring in toluene at 60 °C	Peng et al.[81]
PAL	Octadecyl trimethyl ammonium chloride (OTMAC)	Reacting in water with ultrasonication	Huang et al.[82]
PAL	Hexadecyl trimethyl ammonium bromide (HDTMAB)	Reacting in water with ultrasonication	Lei et al.[83]
SEP	Series of quaternary ammonium salts, amines, and organosilanes	Adsorption and grifting	Tartaglione et al.[84]
SEP	Series of quaternary ammonium salts	Reacting in water	Zhuang et al.[15,85]
SEP	Series of quaternary ammonium salts and sodium dodecyl sulfate (SDS)	Reacting in water	Weng et al.[21]
SEP	Alkoxysilane	Reacting in water	Garcı́a et al.[86]

Zhuang et al.[80] characterized the structure of OSEP and evaluated its rheological properties in OBDFs. SEP was modified with benzyl dimethyl octadecyl ammonium chloride to create OSEP samples. The authors used different techniques such as X-ray diffraction, scanning electron microscopy, specific surface area, and thermal analysis to characterize the structure of OSEP. The surfactants coat the surface of SEP and are inserted into the channels and tunnels, resulting in lipophilicity and a decline in the surface area of OSEP. The rheological properties of OSEP/oil fluids were evaluated by using viscosity, yield point, dynamic rheological behavior, and thixotropy. The authors concluded that the addition of surfactants to OSEP promoted its rheological properties, but extremely high surfactant loading levels resulted in a decrease in rheological properties. OSEP modified with a 35% surfactant showed the best rheological properties. Furthermore, rising temperatures promoted the rheological properties of OSEP/oil fluids by changing the organization of OSEP. However, extremely high temperatures resulted in deterioration of the rheological properties. The authors concluded that OSEP is a potential rheological additive in OBDFs with excellent rheological properties. However, an alternative organic modifier with a high thermal stability is recommended to improve the thermal stability of OSEP/oil fluids.

Zhuang et al.[87] characterized the structure and properties of OPAL with three different cationic surfactants and evaluated its effectiveness in OBDFs. The three different cationic surfactants used were octadecyl trimethylammonium chloride (C18-A), benzyl dimethyl octadecyl ammonium chloride (C18-B), and dimethyl dioctadecyl ammonium chloride

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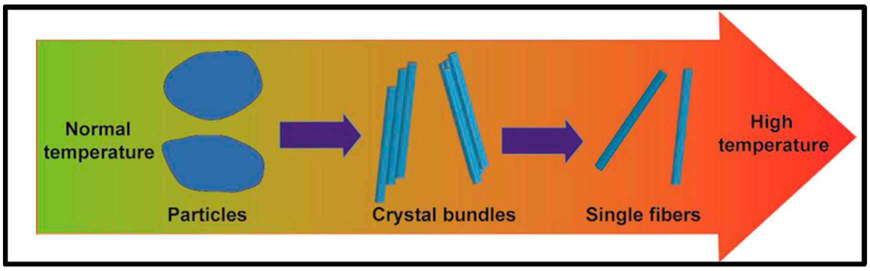

Figure 6. Organization change of OPAL in oil with the temperature rising. Reprinted with permission from Zhuang et al.[79] Copyright 2017 Elsevier.

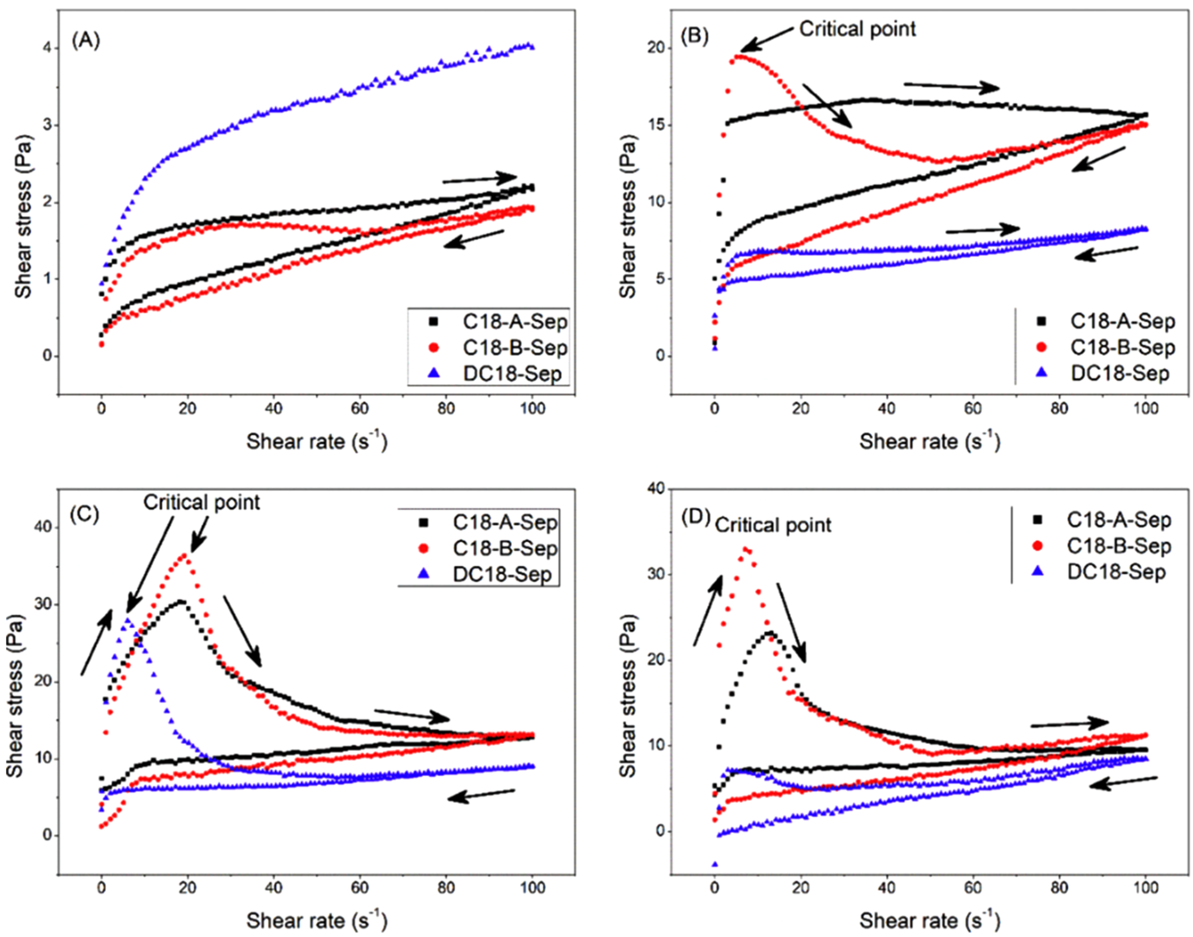

Figure 7. Dynamic rheological curves of OSEP/oil fluids aged at (A) 66 °C, (B) 150 °C, (C) 180 °C, and (D) 200 °C for 16 h. Reprinted with permission from Zhuang et al.[87] Copyright 2018 Elsevier.

(DC18) (Figure 7). The authors found that the surfactant modification did not change the crystal structure of PAL, but it did change the aggregation of the fibers. Also, the surfactants mainly coated the surface of the PAL, but the details of the coating were influenced by the molecular scale of the surfactants and the coating level. Furthermore, OPAL was effective at increasing the viscosity of OBDFs and showed excellent thixotropy at temperatures above 150 °C. Moreover, the rheological properties of the OPAL/oil fluids were influenced by the nature of the surfactants, coating level, and temperature. The researchers found that OPAL is a promising rheological additive for OBDFs, with potential applications in the oil and gas industry.

Weng et al.[21] studied the rheological properties and structure of cationic organo-sepiolite (CO-SEP) and cationic-anionic organo-sepiolite (CA-OSEP) to be used in OBDFs. The authors discussed the preparation and characterization of CO-SEP and CA-OSEP. The researchers used surfactants to modify the SEP and studied the effect of the dosage and chain length of surfactants as well as the ratio of cationic to anionic surfactants on the properties of the modified SEP. They found that CA-OSEP had higher surface polarity and better thermal stability than CO-SEP. The authors concluded that long-chain cationic surfactants had superior adhesion to the surface of the SEP compared to short-chain surfactants. Furthermore, the thermal stability of CA-OSEP was better than that of CO-SEP. Moreover, CA-OSEP had a higher surface polarity and improved rheological properties compared to CO-SEP. CA-OSEP presents a new kind of potential rheological control

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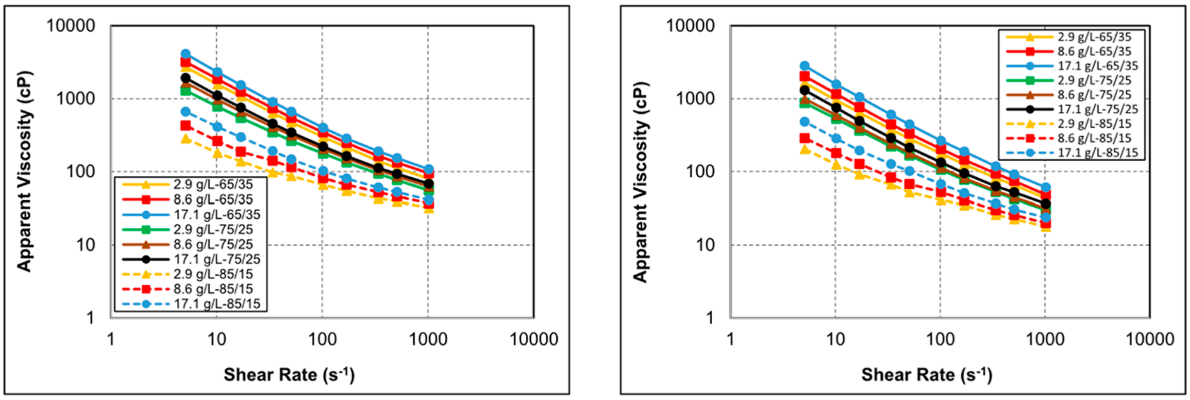

Figure 8. Effects of OC concentration and OWR on the apparent viscosity of the OBM at 52 °C (right) and 79 °C (left). Reprinted with permission from Fakoya and Ahmed.[93] Copyright 2018 Elsevier.

additive for oil-based drilling fluids that would exhibit excellent thermal stability.

According to Zhuang et al.,[13] OPAL forms a network structure in oil easily due to its fibrous morphology. In addition, compared to the house of cards structure of OMMT, OPAL exhibits excellent thermal stability due to the haystack structure in OBDFs.[79,88]

de Brito Buriti et al.[89] discussed the synthesis and characterization of OPAL using cationic and nonionic surfactants for use as an additive in OBDFs. The objective of the study was to determine the rheological properties and thermal stabilities of the resulting dispersions. The authors used Praepagen WB as the cationic surfactant and Ultramina TA50 and Ultramina TA20 as the nonionic surfactant. The OPAL was obtained using a proportion of 15% surfactants. The results showed that the surfactants coated the clay surface without changing the crystal structure and morphology. The incorporation of surfactants was found to be in the order Praepagen WB > Ultramina TA20 > Ultramina TA50. The authors concluded that, when mixed with oil, OPAL can be used as an additive to OBDF due to its enhanced thermal stability and better rheological properties when compared with dispersions prepared with olefin at a high temperature (150 °C). This study shows that the nonionic surfactant can also be used to obtain OCs, which could have important implications for the development of more efficient and cost-effective drilling fluids.

4. APPLICATION OF OTHER ORGANOCLAYS (OCS) IN OIL-BASED DRILLING FLUIDS (OBDFS)

Li et al.[90] developed and evaluated an OBDF for ultradeep well drilling and shale gas well drilling. The authors describe the synthesis and evaluation of an OC and an oil-based filtrate reducer as well as the optimization of the OBDF formulation. Long-carbon-chain quaternary ammonium salt was used as a modifying agent when synthesizing organo-bentonites. The laboratory tests showed that the OC and oil-based filtrate reducer had great compatibility and performance with other additives in the OBDF. The OBDF formula was determined based on optimal additive addition amount tests, and the test results showed that the OBDFs with various densities had great performance. The laboratory tests also showed that the oil-based drilling fluid developed was high temperature resistant and had good inhibition and reservoir protection performance. The field test showed that the developed OBDF had a stable performance with a great ability to maintain wellbore stability and a lower density than WBDF. The drill bits could be used for a longer time, and the average penetration rate was increased. The OBDF was able to satisfy the drilling requirements.

Ratkievicius et al.[91] studied the effect of dispersing organo-bentonite (OBEN) as a viscosity enhancer. The authors performed a surface modification procedure to disperse the clay in the organic phase of a vegetable OBDF. They used soybean oil, lauryl alcohol triethoxylate, brine, bentonite modified by hexadecyl trimethylammonium bromide (CTABr), and barite to prepare the fluids. The study evaluated the influence of the concentration of CTABr in clay modification, viscosity enhancer concentration in the composition of the drilling fluid, and temperature on the rheological properties of the fluid. The results showed that temperature was the most influential factor in the rheological properties of the prepared fluid. The study also found that, as higher amounts of quaternary ammonium cations were adsorbed on clay surfaces, there was a decrease in the contact angle, suggesting an increasing affinity for oil.

Li et al.[92] introduced a modified rectorite clay that can be used as an additive in biodiesel-based drilling fluid to improve its rheological and filtration properties. The modified rectorite was created through a suspension production technique that involved modifying the clay with nonionic surfactants. The authors presented laboratory results that demonstrate the effectiveness of the modified rectorite in improving the yield point, low-end rheology, and suspendability of the fluids. Organo-rectorite (OREC) has better swell performance in a biodiesel emulsion compared to traditional organophilic bentonite. Furthermore, the modified rectorite can be combined with appropriate rheological modifiers to provide formulated fluid with great suspendability, as evidenced by the static barite-sag test. Moreover, the electrical stability of the biodiesel emulsion is enhanced by the addition of the modified rectorite due to the formation of a Pickering emulsion. Therefore, this novel modified rectorite clay can be used as a cost-effective viscosifier for biodiesel-based fluids and other non-aqueous drilling fluids.

Fakoya and Ahmed[93] studied the rheological properties of OBDFs and their continuous phase by adding different concentrations (2.9, 8.6, and 17.1 g/L) of organophilic clay (amine-treated bentonite) at different oil/water ratios (OWRs) (65/35, 75/25, and 85/15) within a temperature range of 24−87 °C. The study focuses on the apparent viscosity of OBFs and how it is affected by various factors such as organophilic clay concentration and OWR. The authors concluded that the apparent viscosity (AV) of the OBDF increased with the OC concentration and OWR, and the influence of the OWR was major (Figure 8). Furthermore, the thermal thinning of the OBDF was reduced by increasing the OWR. The Herschel−Bulkley model was found to be the best fit to describe the rheological behavior of OBDFs. In addition, the rheological parameters of OBDFs showed a higher decrease with temperature than WBDFs; this clarifies the sensitivity of OBDFs to barite-sag challenges. Moreover, a comprehensive rheological model was created to combine the OBDFs' viscosity with the temperature, continuous phase viscosity, and dispersed phase volume fraction. The authors developed empirical models that link the AV of the continuous phase to that of the OBDF, which can be used to predict OBDF rheological parameters based on its formulation and the borehole's condition.

Geng et al.[94] investigated the effects of three different OCs, namely, OSEP, organo-hectorite (OHEC), and OMMT, on the rheological properties of OBDFs at high temperatures. The organoclays were prepared through chemical modification of unmodified clays using dioctadecyldimethylammonium chloride (DODMAC), which is a quaternary ammonium salt. The results of X-ray diffraction (XRD) and scanning electron microscopy (SEM) show that DODMAC is adsorbed on the surface of particles and inserted into the layers of OMMT and OHEC, while it can only be adsorbed on the surface of OSEP particles. The study found that the OHEC particle-stabilized invert emulsion fluid provides better rheological properties than the other two organoclays at high temperatures. This is attributed to the weak flocculation of the OHEC particles, which is maintained by their nonreactive Mg−OH surface groups. On the other hand, on the particle surface of OMMT and OSEP, Al−OH may react with OH under alkaline conditions, which destroys the weak flocculation due to increased repulsion interaction.

Msadok et al.[20] investigated the effect of using modified Tunisian clay with different cationic surfactant concentrations on the rheological properties of diesel OBDFs. The modified clay samples were characterized by using various techniques such as X-ray diffraction, infrared spectroscopy, scanning electron microscopy, and specific surface area analysis. The oil−clay suspensions were investigated by using polarized light optical microscopy and a double cone rheometer. The results showed that the rheological properties of the suspensions were influenced by the concentration of the surfactant used. As the surfactant concentration increased, the yield stress and consistency coefficient also increased. The best behavior was observed for the 3.0 CEC concentration. The organoclay sample at 10 wt % showed the highest Herschel−Bulkley parameters, indicating that it could be used as a viscosity enhancer for OBDFs.

Jiang et al.[95] formulated a low-cost, environmentally friendly biodiesel of soybean oil ethyl ester with low temperature and low viscosity properties as a base oil for OBDFs. The authors optimized the raw materials and selected cheap and environmentally friendly biodiesel of soybean oil ethyl ester as the base oil. They also developed key treatment agents compatible with biodiesel to establish and evaluate the drilling fluid system. The authors selected Span80 with a hydrophile−lipophile balance (HLB) value of 4.3 as the only emulsifier and prepared biodiesel-based emulsions with different OWRs. They optimized the oil/water ratio and formulated a biodiesel-based flat-rheology drilling fluid system with a density of 1.2 g/cm^3. The authors used OC prepared with a cationic modifier of hexadecyl trimethylammonium chloride to improve the rheologic properties, stability, and fluid loss of the drilling fluid while preventing low-temperature thickening. They also synthesized a flat-rheology modifier with the dimer fatty acid and coconut fatty acid diethanolamine, which could form a strong network structure in the biodiesel-based drilling fluid to effectively adjust the rheological properties of the drilling fluid.

5. INTEGRATION OF DIFFERENT ORGANOCLAYS (OCS) IN OIL-BASED DRILLING FLUIDS (OBDFS)

The synergistic use of two clay minerals to enhance the rheological properties of WBDFs has been studied by some researchers. Neaman and Singer[96] studied the rheological properties of MMT and PAL as additives in WBFDs. The authors concluded that the addition of a low concentration of MMT (≤10 wt %) increased the rheological properties in terms of PV and yield value. Later, İşçi and Turutoğlu[97] investigated the effect of a mixture of MMT and SEP as additives in WBDFs. The authors concluded that the mixture is not suitable for WBDFs and recommended the use of stabilizers. Au and Leong[98] used a mixture of MMT and kaolinite in WBFDs. They concluded that, by changing the concentration of these two clay minerals, the optimized pH value can be adjusted. Al-Malki et al.[36] used a mixture of bentonite-based drilling fluids with SEP nanoparticles. The authors revealed enhanced stability in the yield point (YP) and PV over a wide range of temperatures and pressures, particularly under HPHT conditions.

The previous work showed that the combined use of OMMT and OSEP can also improve the rheological properties and thermal stability of OBDFs. Mainye and Teutsch[99] investigated the use of a mixture of OMMT and OPAL (or OSEP) as a rheological additive to enhance the ultralow shear rate viscosity and to improve the carrying capacity of OBDFs. Compared to using the OCs separately, the mixture of OCs yielded stable gels that were nonprogressive. Zhuang et al.[24] evaluated the rheological properties and thermal stability of OBDFs by using a mixture of OMMT and OSEP as the rheological additive. The authors prepared OMMT and OSEP in water and characterized their structures by using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The authors found that OMMT swelled in oil at low temperatures and then exfoliated above 150 °C, while OSEP always maintained its crystal structure. Mixing these two OCs did not significantly influence their structures, but it did promote the gel formation ability, resulting in improved rheological properties and thermal stability of OBDFs. The nanolayers of OMMT and nanofibers of OSEP interwove with each other, reinforcing the network structure and protecting them from collapse at high temperatures. The mixture of OMMT and OSEP with a mass proportion of 50% for each displayed optimal rheological properties and thermal ability.

6. LESSONS LEARNED

For several years, the oil and gas industry has searched for novel ways to enhance the rheological properties of OBDF systems. The recent advancement in nanotechnology has promoted the development of OCs for application in OBDFs. To solve the current problems, new OCs with suitable

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rheological additives for OBDFs must be developed and evaluated. Clay mineralogy, colloidal chemistry, and rheological properties are important in the study of OCs developed for OBDFs. OCs control the rheological behavior of OBDFs by dispersal, swelling, and exfoliation, eventually increasing the fluids' viscosity and thixotropy. OCs exhibit unique characteristics in improving the formulation of OBDFs. This work has reviewed three different OCs, namely, OMMT, OSEP, and OPAL, in terms of the structure, rheological properties, and thermal stability of OBDFs. In general, the following are the key lessons learned from this study.

- The viscous flow behavior of OBDFs at different pressures is greatly influenced by the OC's nature and concentration.
- At low OC concentrations, the yield stress varies linearly; on the other hand, at high OC concentrations, the yield stress varies according to a power law model.
- CN-OMMT presents a novel potential rheological control additive for OBDFs, especially for fluids with high oil/water ratio.
- OPAL forms a network structure in oil easily due to its fibrous morphology. Compared to the house of cards structure of OMMT, OPAL exhibits excellent thermal stability due to the haystack structure in OBDFs.
- OPAL, when mixed with oil, can be used as an additive to OBDF due to its enhanced thermal stability and better rheological properties compared with dispersions prepared with olefin at a high temperature (150 °C).
- The rheological properties of OSEP/oil fluids are improved with temperature. However, at extremely high temperatures (>180 °C) the rheological properties decline due to the desorption of surfactants.
- The combination of high temperatures and high concentrations of OBEN significantly affects the yield strength and thixotropy of OBDFs.
- When compared to OBEN, OREC has better swelling behavior, an improved yield point, and improved rheological properties in a biodiesel emulsion. In addition, OREC enhanced the thermal stability of the inverted biodiesel emulsion.
- OCs prepared using cationic surfactants enhance the rheological properties, stability, and fluid loss of OBDFs.
- Synergistic use of OMMT and fibrous OC enhances the rheological properties and thermal stability of OBDFs.

7. RECOMMENDATIONS

For further studies of the application of OCs in OBDFs, the following recommendations should be investigated in extensive research.

- Aiming to provide greater viscosity, thixotropy, and thermal stability for OBDFs, it is recommended to use surfactants with longer alkyl chains to prepare OMMT.
- OMMT is the most common rheological additive used in OBDFs. More research is needed on the application of OPAL and OSEP in OBDFs.
- OBDFs are complex mixtures that contain several agents, such as emulsifiers and weighting agents; the compatibility between OCs and these agents must be evaluated to develop adequate physicochemical characteristics.
- The Casson rheological model accurately predicts drilling fluid behavior across low and high shear rates. In addition, it is preferred to the Herschel–Bulkley rheological model due to the correction factor that is introduced to the yield stress and PV.
- The effects of temperature and pressure must be studied extensively, as they have a significant effect on the rheological properties of OBDFs.
- The interactions between OCs and organic surfactants and their effect on the structure of OCs in oil need to be deeply investigated.

AUTHOR INFORMATION

Corresponding Author

Rahul Gajbhiye – *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0003-3906-5453; Email: rahulg@kfupm.edu.sa

Authors

Ali Mahmoud – *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-7374-9624

Salaheldin Elkatatny – *Department of Petroleum Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-7209-3715

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c07679

Notes

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NOMENCLATURE

OBDF: Oil-Based Drilling Fluid
WBDF: Water-Based Drilling Fluid
SBDF: Synthetic-Based Drilling Fluid
HPHT: High-Pressure High-Temperature
OC: Organoclay
MMT: Montmorillonite
OMMT: Organo-Montmorillonite
SEP: Sepiolite
OSEP: Organo-Sepiolite
PAL: Palygorskite
OPAL: Organo-Palygorskite
CO-MMT: Cationic-Organo-Montmorillonite
CN-OMMT: Cationic-Nonionic-Organo-Montmorillonite
NO-MMT: Nonionic-Organo-Montmorillonite
MRC: Maximum Reservoir Contact
OWR: Oil/Water Ratio
CTAB: Cetyltrimethyl Ammonium Bromide
CTABr: Hexadecyl Trimethyl Ammonium Bromide
CO-SEP: Cationic-Organo-Sepiolite
CA-OSEP: Cationic-Anionic-Organo-Sepiolite
OREC: Organo-Rectorite
OBEN: Organo-Bentonite
OHEC: Organo-Hectorite
AV: Apparent Viscosity
PV: Plastic Viscosity
YP: Yield Point

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OTMAC: Octadecyl Trimethyl Ammonium Chloride
HDTMAB: Hexadecyl Trimethyl Ammonium Bromide

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