Impact of ZnO and CuO nanoparticles on the rheological and filtration properties of water-based drilling fluid

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Graphical abstract

Abstract

During the past decade, many researchers have reported on various improvements to water-based drilling fluid properties through the addition of different nanoparticles to improve the...
rheological properties, the thermal and electrical conductivity, and fluid loss control. Although various types of nanoparticles have been tested for their ability to improve the rheological and filtration properties of water-based drilling fluids at low pressure and temperature, some of them have not yet been tested at elevated pressure and temperature. In this study, the impact of different concentrations of ZnO and CuO nanoparticle additives on the rheological properties of a water-based drilling fluid at 25°C, 50°C and 80°C, and on the filtration properties at 500 psi and 100°C was studied. A range of ZnO and CuO nanoparticle concentrations, from 0.1 to 1 wt%, were prepared as nanofluids and introduced as additives (1 vol%) into prepared water-based base drilling fluids. The rheological properties for both nanoparticle-based drilling fluids showed a significant improvement over the base drilling fluid, with ZnO providing a better overall performance than CuO. Both nanoparticle-based drilling fluids were also observed to be more stable at elevated temperatures. For the filtration tests conducted under elevated pressure and temperature conditions (500 psi and 100°C), a greater reduction in filtration loss was obtained at 0.8 wt% CuO nanoparticles (30.2%), compared to 0.8 wt% ZnO nanoparticles (18.6%). Mud cake thickness was also reduced, compared to the base fluid, with the CuO (27.6%) and ZnO (24.6%) nanoparticle fluids. These results demonstrate the ability of ZnO and CuO nanoparticles to enhance the properties of water-based drilling fluids, and their potential to be used as a high-efficiency filtration loss additive.

**Keywords:** Water-based drilling fluids; ZnO nanoparticles; CuO nanoparticles; Pressure; Temperature; Rheological properties; Filtration properties.

1. **Introduction**

Drilling fluids, which are viscous fluids that result from the mixture of liquid or gas with a suspended solid, were invented by, and have been used in, oil and gas exploration since the
early 19th century. Since that time, the primary advantages of drilling fluids have been to, for example, cool and lubricate the drill bit and drill pipe, lift the rock cuttings up to the surface, create hydrostatic pressure to overcome the rock formation pressure, and deposit mud cake around the walls of the hole to reduce fluid loss to the formation, etc. Developments in drilling fluids have been the focus of several recent studies, aimed at designing one that can satisfy industry’s needs, including decreasing fluid loss through the rock formations, providing it with excellent rheological properties and, more importantly, making it environmentally friendly.

Currently, several types of drilling fluid are being used, such as oil-based, polymer-based and water-based. Oil-based drilling fluids are widely used in the oil and gas industry due to their outstanding stability (i.e., superior rheological properties and very low fluid loss) in high pressure and high temperature (HPHT) wellbore conditions over long periods of operation. As environmental issues come to the fore, however, the use of oil-based drilling fluid is becoming undesirable because the excess fluid left in the wellbore can disperse and cause freshwater aquifers to become contaminated. On the other hand, despite the fact that polymer-based drilling fluids have a lot of useful properties, in terms of rheology and filtration loss, they tend to decompose over a period of time under extreme wellbore conditions. Water-based drilling fluids are more environmentally friendly and should therefore be further developed to achieve similar performance to oil-based drilling fluids while, at the same time, maintaining their less-harmful environmental credentials.

It has become established that 75% of wells drilled globally are in shale formations and about 90% of wellbore instability problems are caused by shale formations. Although water-based drilling fluids have less of an impact on the environment, they do cause problems with shale hydration, which leads to issues such as wellbore caving, sticking drill pipes, changing pore pressures, loss of well control, etc. In order to prevent these undesirable situations from arising, any modifications to such drilling fluids would require an additive to combine with the
water-based drilling fluid that would decrease the contact between the shale formation and the water and inhibit shale instability. The cost of natural gas has been highly variable in the last several decades and the recent downward trend in prices has been partly due to the rapid development of shale gas deposits in Pennsylvania, Texas and elsewhere, which have drastically redistributed availability of gas supplies in the U.S and the world. The lithological characteristics of the reservoir sections of shale gas, shale oil, and tight sandstone gas formations are very complex and conventional plugging materials are not effective because the size of the holes in the shale formation (probably in nanometer scale) is smaller than that in other formations, hence for better plugging performance during drilling in shale formations, smaller and more effective plugging materials for use in water-based drilling fluids are needed. During the past decade, many researchers have reported on various improvements to water-based drilling fluid properties through the addition of different nanoparticles to improve the rheological properties and thermal and electrical conductivity, and reduce fluid loss. In 2011, Kosynkin et al., reported that a thinner filter cake and less fluid loss from the base drilling fluid system was achieved through the addition of graphene oxide nanoparticles as a fluid loss additive. Next, in 2012, Cai et al., discovered the possibility of reducing shale hydration by using silica (SiO₂) nanoparticles as an additive. Later, in 2013, Abdo and Haneef, optimized the rheological properties and reduced the filtration loss by more than 50% by using in-house-produced ATR (Attenuated total reflection) nanoparticles. Moreover, by mixing nanographite powder with water-based drilling fluid, Nasser et al., in 2013 reported that the rheological stability is enhanced at higher temperatures and pressures. More recently, nanoparticle-based drilling fluid has become more widespread. Ponmani et al., in their study in 2014, reported that the thermal and electrical conductivity properties of nanoparticles-based drilling fluids have been improved by roughly 50% and 25% respectively.
by adding copper oxide (CuO) and zinc oxide (ZnO), respectively. The same nanoparticles were also examined to determine whether they could significantly reduce filtration loss at low pressures and temperatures (LPLT) conditions; the authors reported that these nanoparticles performed better than others, i.e., graphene powder, nanoclay, nanographite and nanosilica. Multi-walled carbon nanotubes, nanosilica and glass beads have also been tried, resulting in the improvement of either rheological properties or thermal conductivity over the water-based drilling fluid. In addition, a reduction in shale swelling rate, imbibition amount and Young’s modulus has been achieved by adding SiO$_2$ nanoparticles to water-based drilling fluid. Those researchers also observed that the nanoparticles could block the fluid flow paths through the pores in the shale, leading to a reduction in shale instability. In 2016, Mahmoud et al., reported that ferric oxide improved the rheological properties of the drilling fluid, but that SiO$_2$ nanoparticles obtained the opposite result and in addition, the drilling fluid still exhibited stable rheological properties under HPHT conditions. Since then, the focus has shifted to studying the effects of adding nanoparticles under more realistic environmental conditions.

Again in 2016, Abdo and Hassan, demonstrated the superior ability of nano-sepiolite in maintaining the filtration loss of water-based drilling fluid at up to 2500 psi and 200°C; however, the aluminium oxide (Al$_2$O$_3$) nanoparticles caused an increasing trend of filtration loss at higher concentrations, due to the agglomeration of the nanoparticles. The rheological properties, nevertheless, were still significantly improved. Poly (sodium p-styrene sulfonate)-modified ferrous oxide (Fe$_3$O$_4$) nanoparticles were found to improve rheological properties at elevated temperatures, while a decrease in fluid loss under HPHT conditions was observed.

Generally, at higher temperatures, the rheological properties of water-based drilling fluids are degraded. Subsequently, this results in a reduction in shear thinning behaviour and rock cuttings carrying ability. In addition, high filtration loss of drilling fluid is a critical problem
in drilling operations, leading to wellbore instability and environmental issues, i.e. chemical spillage to the marine environment\textsuperscript{10}. Although, various types of nanoparticles have been tested for their ability to reduce filtration loss\textsuperscript{23,30} at low pressure and temperature, some of them, e.g. ZnO and CuO nanoparticles, have not yet been tested at elevated temperature and pressure conditions. Moreover, the constraints on using nanoparticles in drilling fluids have not been determined in most studies. Ascertaining such limitations is necessary in order to ensure a positive outcome from nanoparticle-based drilling fluids.

In response to these problems, the performance of ZnO and CuO nanoparticles was tested in water-based drilling fluids, in relation to their rheological properties at low and elevated temperatures, and analysed in order to understand the flow behaviours of the resultant fluids. The ability of the nanoparticles to prevent filtration loss was also investigated at elevated temperature and pressure. Finally, the optimum type and concentration of nanoparticles, in comparison with other nanoparticles, was demonstrated.

2. Materials Used, Experimental Equipment and Experimental Procedures

2.1 Materials Used in Formulating Nanoparticle-based Drilling Fluids

In this study, ZnO and CuO nanopowders, containing particles with a spherical shape, were supplied by Sigma–Aldrich, UK. The drilling fluid samples were prepared in a similar way to typical drilling fluids, according to the industrial application\textsuperscript{31}. The components of the drilling fluid were deionised water as the main fluid, with bentonite clay and xanthan gum (supplied by Schlumberger, M-I SWACO UK) both added to increase the viscosity. To decrease fluid loss, PAC-L was added. KCl was also added to prepare the inhibitive mud that can slow the hydration, swelling and disintegration of shale. NaOH was used to control the pH of the drilling
fluid, keeping it in the range of 9 to 9.5. Formaldehyde was also added to lower degradation caused by bacterial action. A summary of all the properties (i.e. chemical formula, molecular weight, particle size, surface area and purpose of use) of the materials used is shown in Table 1. In Table 2, is a summary of the product specification for the CuO and ZnO nanoparticles used in the experiment.

Table 1: Summary of the materials used in formulating nanoparticle-based drilling fluids and their purposes

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>Molecular weight (g/mol)</th>
<th>Ave. Particle size</th>
<th>Surface area</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>18</td>
<td>N/A</td>
<td>N/A</td>
<td>Main fluid</td>
</tr>
<tr>
<td>Wyoming bentonite</td>
<td>Al₂O₃·4SiO₂·H₂O</td>
<td>422.286</td>
<td>1-100 µm</td>
<td>370-487 m²/g</td>
<td>Viscosifier</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>C₃₅H₄₉O₂₉</td>
<td>933</td>
<td>N/A</td>
<td>N/A</td>
<td>Viscosifier, dispersing agent</td>
</tr>
<tr>
<td>Polyanionic cellulose (PAC)</td>
<td>C₂₃H₂₈N₄O₂</td>
<td>392</td>
<td>1-100 µm</td>
<td>130-161 m²/g</td>
<td>Filtration loss control</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>74.55</td>
<td>63-100 µm</td>
<td>N/A</td>
<td>Inhibitive agent</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>39.997</td>
<td>N/A</td>
<td>N/A</td>
<td>pH adjustment</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH₂O</td>
<td>30.026</td>
<td>N/A</td>
<td>N/A</td>
<td>Biodegradation retardant</td>
</tr>
<tr>
<td>Zinc oxide nanoparticles</td>
<td>ZnO</td>
<td>81.39</td>
<td>50 nm</td>
<td>10.8 m²/g</td>
<td>Viscosifier, filtration loss control</td>
</tr>
<tr>
<td>Copper oxide nanoparticles</td>
<td>CuO</td>
<td>79.55</td>
<td>50 nm</td>
<td>29 m²/g</td>
<td>Viscosifier, filtration loss control</td>
</tr>
</tbody>
</table>

Table 2: Summary of product specification for the CuO and ZnO

<table>
<thead>
<tr>
<th>No</th>
<th>Product Name</th>
<th>Average particle size /method of analysis</th>
<th>Appearance(form &amp; Colour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper(II) Oxide</td>
<td>50nm size measured with Transmission Electron Microscope(TEM)</td>
<td>Powder and black</td>
</tr>
</tbody>
</table>


| 2 | Zinc oxide | 50nm measured with Brunauer-Emmett Teller (BET) | White to yellow and faint green to green and yellow-green |

2.2 Experimental Equipment

A Hamilton beach mixer was used for mixing of additives in the drilling fluids. The rheological properties were tested using two OFITE viscometers model 900. For the filtration loss measurement, a HPHT filter press from OFITE, with a drilling fluid capacity of 175 ml, was used. According to the API (Recommended Practices 13B-1 and 13B-2), the filter papers used in the experiment must have a diameter of 2.5 inches (6.35 cm), with a particle-size retention range of 2 to 5 µm.

2.3 Experimental Procedure

2.3.1 Nanoparticle-based drilling fluid preparation procedure

ZnO and CuO nanoparticles were incorporated into the nanofluid by using a two-step method, in which the nanopowders were first prepared and then mixed with the prepared fluid. This method is the most widely used for preparing nanofluids due to its cost effectiveness. The base drilling fluids were formulated separately from the nanofluid so as to ensure the uniform dispersion of the nanoparticles.

Nanofluid preparation

Firstly, Xanthan gum at a concentration of 0.4 wt% was mixed with deionised water. Then, 0.1, 0.3, 0.5, 0.8 and 1 wt% ZnO or CuO nanopowder was added to the prepared mixture to formulate the nanofluid. In Table 3, the nomenclature N1-N10 represents the nanofluid, and
the compositions of those fluids are given. After preparation, the samples were sonicated in an ultrasonic bath at a frequency of 25 kHz and an input power of 450 W for one hour to increase nanofluid stability and the dispersion of the particles. All the nanofluid samples were prepared and used on the same day to ensure that the properties remained the same for every test.

Table 3: Nanofluid formulations used in this study

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Nanoparticle concentration (wt%)</th>
<th>Xanthan gum concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>ZnO, 0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>N2</td>
<td>ZnO, 0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>N3</td>
<td>ZnO, 0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>N4</td>
<td>ZnO, 0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>N5</td>
<td>ZnO, 1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>N6</td>
<td>CuO, 0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>N7</td>
<td>CuO, 0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>N8</td>
<td>CuO, 0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>N9</td>
<td>CuO, 0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>N10</td>
<td>CuO, 1.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Base drilling fluid preparation

The base drilling fluid formulation started with the preparation of a mixture of 0.0479 g Wyoming Bentonite per milliliter (ML) of deionised water with a viscosity of 5 cp. The drilling fluid additives were then incorporated as detailed below:

- PAC-L (0.5 wt%)
- KCl (5 wt%)
- NaOH (0.01 wt%)
- Formaldehyde (0.1 wt%)

Before each drilling fluid additive was included, the mixture was blended with a Hamilton Beach single spindle mixer for 15 to 30 minutes, to ensure full dispersion of the additives. After
finishing formulating the base fluid, ultrasonification was carried out for 1 hour, the same as for the nanofluids.

Finally, a 1 vol% of nanofluid was added to the base drilling fluid and mixed using a Hamilton Beach single spindle mixer to formulate the nanoparticle-based drilling fluid.

2.3.2 Rheological and filtration testing procedure

The rheological properties of the nanoparticle-based drilling fluid were tested at temperatures of 25°C, 50°C, and 80°C using OFITE viscometer model 900. Each drilling fluid sample was placed in a testing cup and its shear stress measured at 600 rpm, 300 rpm, 200 rpm, 100 rpm, 60 rpm, 30 rpm and 6 rpm rotation speeds. The measured values were used to calculate Plastic Viscosity (PV), Apparent Viscosity (AV) and Yield Point (YP). For measurement of gel strength, the speed selector knob was rotated to 3 rpm to measure the shear stress after the drilling fluid was rested for 10 seconds and 10 minutes to determine gel strength at 10 seconds (Gel 10s) and gel strength at 10 minutes (Gel 10min), respectively.

The filtration properties were measured at 500 psi and 100°C using an OFITE HPHT filter press. The reported values were doubled from the measurement due to the filtration area of the API standard being 7.1 in² (whereas the cell in the HPHT filter press is 3.55 in²). Measurements at each drilling fluid concentration were repeated three times and the average result reported.

2.3.2 Procedure used for characterization of filter cake using Scanning Electron Microscope (SEM)

The filter cakes generated after the filtration process were air dried under ambient temperature for 48 hours. Then the samples were morphologically characterized via SEM analysis. The SEM observation was carried out using varying magnifications (150X, 900X, 350X and 200X) so as to obtain the optimal field of view (FOV) where possible for the different layers.
(youngest, middle and oldest) observed in the samples. The resolution used were 10microns, 20microns and 100microns.

2.3.2.1 Determination of the Permeability of the Filter Cake.

The filtration behavior of a filter cake is measured by two parameters: the permeability of the filter cake (k) and the specific volume (b) (which is filter cake volume divided by filtrate volume and is therefore, dimensionless \(^{35}\)). The permeability of the filter cake was obtained using a method which depends on relationship between the cumulative filtrate volume and time \(^{35,36}\)

\[
k = (Q_t \times l_t \times \mu) \times \frac{1}{2P \times F \times t} \quad \text{equation …………………, (1) }^{35,36}
\]

\(Q_t\) = The quantity of filtrate volume in cm\(^3\) separated after time \(t\)

\(l_t\) = Thickness of filter cake in cm

\(\mu\) = viscosity of filtrate in centipoise

\(P\) = The filtration pressure in Atmosphere

\(t\) = time in seconds

\(F\) = Effective filter surface in cm\(^2\)

3. Presentation of Results

The results are presented in three sections:

- Firstly, the rheological properties of the ZnO and CuO nanoparticle-based drilling fluids, including plots of shear stress versus shear rate, PV, AV, YP and gel strength (Gel 10s and
Gel 10min) at different nanoparticle concentrations and at three different temperatures (25°C, 50°C, and 80°C), are compared and discussed.

- Secondly, the filtration loss properties of the samples at 500 psi and 100°C are compared and discussed.

- Thirdly, the characterization of the filter cakes generated by 0.8% CuO and 0.8% ZnO nanoparticles drilling fluids and the base drilling fluid without nanoparticles using Scanning Electron Microscope (SEM) are compared and discussed in addition to their permeability values.

3.1 The Effect of Nanoparticle Concentration and Temperature on the Rheological Properties of the ZnO and CuO Nanoparticle-based Drilling Fluids

3.1.1 Temperature of 25°C

The shear stress of the various ZnO and CuO nanoparticle-based drilling fluid samples was measured using an OFITE viscometer model 900 at room temperature (25°C). The results are shown in Figure 1.
Figure 1: Shear stress versus shear rate of base drilling fluid (BF), in log-log scale ZnO (0.1% to 1%) and CuO (0.1% to 1%) nanoparticle-based drilling fluids at 25°C

As can be seen, all the drilling fluid samples show shear thinning behaviour, as apparent viscosity decreases with increasing shear rate. By adding ZnO and CuO nanofluid to the base drilling fluid (BF), the shear stress was significantly reduced. In particular, the ZnO nanoparticle-based drilling fluids displayed lower shear stresses than the CuO nanoparticle-based drilling fluids. It was also observed that an increase in nanoparticle concentration (ZnO 0.1% to 1% and CuO 0.1% to 1%) produced an increasing shear stress trend.

Figures 2 and 3 illustrate the following rheological parameters: PV, AV, YP and Gel 10s and Gel 10min at 25°C for ZnO and CuO nanoparticle-based drilling fluids, respectively.
Figure 2: Rheological properties of base drilling fluid (BF) and ZnO nanoparticle-based drilling fluid (ZnO 0.1% to 1%) at 25°C
(PV [cp], AV [cp], YP [lbf/100ft²], Gel 10s [lbf/100ft²], Gel 10min [lbf/100ft²])

Figure 3: Rheological properties of base drilling fluid (BF) and CuO nanoparticle-based drilling fluid (CuO 0.1% to 1%) at 25°C
(PV [cp], AV [cp], YP [lbf/100ft²], Gel 10s [lbf/100ft²], Gel 10min [lbf/100ft²])

Overall, the addition of nanoparticles reduced the magnitude of the rheological properties of the base fluid; however, at greater concentrations of both nanoparticles, all of the rheological
properties showed an increasing trend. In comparing the ZnO and CuO nanoparticle-based drilling fluids, the ZnO ones exhibited lower rheological properties throughout. It was observed that the 10-minute gel strength in the drilling fluid samples ZnO 1% and CuO 1% revealed a significantly reduced value from the ZnO 0.8% and CuO 0.8% fluids, respectively.

### 3.1.2 Temperature of 50°C and 80°C

Rheology tests were performed at higher temperatures to simulate the use of drilling fluids at higher temperature conditions. Plots of shear stress versus shear rate in log scale at 50°C and 80°C, compared to those at 25°C, are shown in Figures 4 and 5 for ZnO and CuO nanoparticle-based drilling fluids, respectively.

**Figure 4:** Shear stress versus shear rate of ZnO nanoparticle-based drilling fluid in log-log scale (ZnO 0.1% to 1%) at 25°C, 50°C and 80°C
Figure 5: Shear stress versus shear rate of CuO nanoparticle-based drilling fluid in log-log scale (CuO 0.1% to 1%) at 25°C, 50°C and 80°C

At elevated temperatures, both drilling fluids still exhibited shear thinning characteristics; however, it can clearly be seen that the shear stress at 80°C and 50°C is significantly lower than at 25°C. Another observation from the results is that the ZnO 0.8% and ZnO 1% drilling fluids showed a sharp increase in their shear stress values with concentration along all shear rates at 80°C and 50°C, while the CuO nanoparticle-based drilling fluids displayed a steady increase in shear stress at higher concentrations.

Figures 6 and 7 show the measured values of PV, AV, YP and Gel 10s and Gel 10min at 50°C for ZnO and CuO nanoparticle-based drilling fluids, respectively.
Figure 6: Rheological properties of base drilling fluid (BF) and ZnO nanoparticle-based drilling fluid (ZnO 0.1% to 1%) at 50°C (PV [cp], AV [cp], YP [lbf/100ft²], Gel 10s [lbf/100ft²], Gel 10min [lbf/100ft²])

Figure 7: Rheological properties of base drilling fluid (BF) and CuO nanoparticle-based drilling fluid (CuO 0.1% to 1%) at 50°C (PV [cp], AV [cp], YP [lbf/100ft²], Gel 10s [lbf/100ft²], Gel 10min [lbf/100ft²])

Figures 8 and 9 show the measured values of PV, AV, YP and Gel 10s and Gel 10min at 80°C for ZnO and CuO nanoparticle-based drilling fluids, respectively
Figure 8: Rheological properties of base drilling fluid (BF) and ZnO nanoparticle-based drilling fluid (ZnO 0.1% to 1%) at 80\(^\circ\)C (PV [cp], AV [cp], YP [lbf/100ft\(^2\)], Gel 10s [lbf/100ft\(^2\)], Gel 10min [lbf/100ft\(^2\)])

Figure 9: Rheological properties of base drilling fluid (BF) and CuO nanoparticle-based drilling fluid (CuO 0.1% to 1%) at 80\(^\circ\)C (PV [cp], AV [cp], YP [lbf/100ft\(^2\)], Gel 10s [lbf/100ft\(^2\)], Gel 10min [lbf/100ft\(^2\)])
Compared to both materials, the base drilling fluid had the highest values for all categories of data. For the ZnO nanoparticles, PV decreased from 0.1 wt% to 0.5 wt% concentrations, and then started to rise again as the concentration is increased to 0.8 wt% and 1 wt%. The other properties (AV, YP and gel strength) showed a gradual increase at higher ZnO nanoparticle concentrations. Overall, all of the parameters exhibited an increasing trend in the CuO nanoparticle-based drilling fluid samples; however, for the gel strength at 10 minutes in both nanoparticle fluids, the measured values suddenly dropped at 1 wt%. This shows the same characteristic as was measured at 25°C, which was predicted to be a result of particle agglomeration.

3.2 The Effect of Nanoparticle Concentration on the Filtration Loss Properties of ZnO and CuO Nanoparticle-based Drilling Fluids

In this study, the filtration loss experiments on ZnO and CuO nanoparticle-based drilling fluids were carried out at 500 psi and 100°C conditions using an OFITE HPHT filter press. Figure 10 shows the cumulative fluid loss of each drilling fluid sample at 30 minutes after the experiment started.
According to the results, the highest filtration loss, at 17.2 ml, was obtained from the base drilling fluid. The lowest loss was recorded from the CuO 0.8% nanoparticle-based drilling fluid, at 12 ml. Both ZnO and CuO nanoparticles exhibited similar trends, with the filtration loss starting to decrease and then increasing when more nanoparticles were added. The CuO nanoparticles, however, showed a better performance in reducing fluid loss. The decrease in filtration loss, compared to the base drilling fluid, obtained from the ZnO 0.8% and CuO 0.8% nanoparticle-based drilling fluids was 18.6% and 30.2%, respectively.

The reduction in filtration volume obtained from the experiment demonstrates the ability of the drilling fluid to form a thin, low-permeability mud cake layer to block the liquid from flowing through the filter paper. In general, any drilling fluid formulation is required to have as low as possible fluid loss to decrease problems of wellbore instability. In particular, in water-sensitive rocks such as shale formations, it is very important to carefully design the drilling fluid system.
so as to prevent formation instability problems resulting from fluid loss \(^ {37} \). In this experiment, the CuO nanoparticle-based drilling fluid exhibited a lower filtration loss than ZnO. This shows the stronger ability of CuO nanoparticles to create bonds between the particles to hold more fluid. The higher filtration loss occurred with 1 wt% ZnO and CuO nanoparticles. Again, this might result from agglomeration, which causes the nanoparticles to behave like larger particles, resulting in higher filtration loss \(^ {27} \).

Figure 11 shows the mud cake thicknesses recorded after the filtration loss experiment was completed.

![Mud cake thicknesses](image)

**Figure 11**: Mud cake thicknesses of base drilling fluid (BF), ZnO (0.1% to 1%) and CuO (0.1% to 1%) nanoparticle-based drilling fluids at 500 psi and 100°C

The results exhibit the same trend as the filtration loss. The thickest mud cake resulted from the base drilling fluid. Gradually decreasing thicknesses were obtained from the ZnO 0.1% to ZnO 0.8% drilling fluids; however, the mud became thicker at 1 wt% ZnO concentration. The CuO nanoparticles showed fluctuating results, but an increase in mud cake thickness after
adding more nanoparticles was still apparent. The thinnest mud cakes acquired from each nanoparticle were 1.53 mm and 1.47 mm for ZnO 0.8% and CuO 0.8%, respectively. These can be represented as 24.6% and 27.6% reductions relative to the base drilling fluid for the ZnO and CuO nanoparticle-based drilling fluids, respectively.

Generally, it is necessary to keep the mud cake as thin as possible. According to Onuh et al. less than 2/32 in, or 1.5875 mm, of mud cake is considered to be an acceptable thickness \(^{38}\), as an inappropriate mud thickness can result in problems such as a stuck pipe in highly-permeable formations \(^{39}\). From Figure 11, it can be seen that the ZnO 0.8%, ZnO 1%, CuO 0.3%, ZnO 0.8% and ZnO 1% drilling fluids resulted in mud cake thickness lower than that of the standard thickness. In order to form a thin mud cake, the drilling fluid must contain small-sized particles that will precipitate and plug the pores in permeable formations. This engineered impermeability allows less fluid loss to occur, resulting in less excess precipitation from the other drilling fluid components flowing through the mud cake \(^{25}\). For the ZnO 1% and CuO 1% drilling fluids, the precipitation of nanoparticles might have been lower due to the larger agglomerated sizes of the nanoparticles that would be unable to plug the tiny pores.

Figure 12 shows a comparison of the filtration losses among ZnO, CuO and other nanoparticles at elevated pressure and temperature.
Figure 12: Comparison of filtration loss from various nanoparticle-based drilling fluids at elevated temperatures and pressures

All the results are the best obtained from each study. The poly (sodium p-styrene sulfonate)-modified Fe$_3$O$_4$ nanoparticles have the highest value among the other nanoparticles, at roughly 37 ml $^{28}$. The Al$_2$O$_3$ and SiO$_2$ nanoparticles and multi-walled carbon nanotubes exhibited the same range of filtration loss at 19.5, 18 and 16 ml, respectively $^{27,40,41}$. The SiO$_2$ nanoparticles $^{27}$ and graphene nanoplatelets $^{41}$ resulted in 12.5 ml and 14 ml, respectively, similar in performance to the ZnO (14 ml) and CuO (12 ml) nanoparticles in this study. Lastly, the ferric oxide nanoparticles exhibited superior filtration loss, at only 6.9 ml – a huge difference compared to the other nanoparticles $^{25}$.

3.3 Characterization of Filter cake Generated by CuO and ZnO nanoparticles Based Drilling Fluids Using Scanning Electron Microscope (SEM).

A detailed investigation was carried on the filter cakes generated from base drilling fluid without nanoparticles (figures 13a & b), Nanoparticle drilling fluid with 0.8% CuO (figures 14a and b), and Nano-based drilling fluid with 0.8% ZnO (figures 15a and b) nanoparticles using SEM. The SEM photomicrographs were taken from cross section of the filter cakes.
Figures 13 a and b are the photomicrographs from the drilling fluid without nanoparticles. The morphology appears to be porous and permeable.

Figure 13a: SEM photomicrograph of filter cake generated from drilling fluid without CuO and ZnO nanoparticles at 900X.

Figure 13b: SEM photomicrograph of filter cake generated from drilling fluid without CuO and ZnO nanoparticles at 200X.
Figures 14 a and b are the photomicrographs for the filter cake with 0.8% CuO. The morphology appears to be less porous and less permeable compared to the filter cake of the base drilling fluid shown in figures 13 a & b. The pores in figures 13 a & b have been plugged effectively plugged by the CuO nanoparticles. The nanoparticles in the filter cake from 0.8% CuO drilling fluid, at first effectively plugged the pores and secondly, the permeability is reduced. Then lastly, the rate of filtration is drastically reduced leading to low volume of fluid loss. Hence, the better performance of 0.8% CuO drilling fluid as an effective fluid loss control agent than the base drilling fluid without nanoparticles and the 0.8% ZnO nanoparticle drilling fluid.

Figure 14a: SEM photomicrograph of filter cake generated from drilling fluid with 0.8% CuO nanoparticles at 900X
Figure 14b: SEM photomicrograph of filter cake generated from drilling fluid with 0.8% CuO nanoparticles at 350X

The figures 15a & b are the photomicrographs of the filter cake for 0.8% ZnO drilling fluid. The ZnO nanoparticles have shown increased agglomeration\textsuperscript{42} and ineffective plugging which have affected filtration profile\textsuperscript{16,43}. However, despite the agglomeration of the nanoparticles in the filter cake of 0.8% ZnO nanoparticle drilling fluid, it has proved to be a better fluid loss control agent than the base drilling fluid without nanoparticles because to a certain degree, plugging of pores occurred and this resulted to low filtration leading to ineffective fluid loss control in the 0.8% ZnO nanoparticle drilling fluid.
Figure 15a: SEM photomicrograph of filter cake generated from drilling fluid with 0.8% ZnO nanoparticles at 900X

Figure 15b: SEM photomicrograph of filter cake generated from drilling fluid with 0.8% ZnO nanoparticles at 350X
3.3.1 Determination of Permeability values for Filter Cakes

The parameters mentioned in equation (1) were determined from experimental data during filtration process for base drilling fluid without nanoparticles and for drilling fluid with 0.8% CuO and 0.8% ZnO nanoparticles. Then the following permeability values $K_{bf}$, $K_{CuO}$ and $K_{ZnO}$ were determined and presented in figure 16. The permeability values $K_{bf} > K_{ZnO} > K_{CuO}$ as shown in figure 16 is an indication that filter cake of 0.8% CuO nanoparticle drilling fluid with $K_{CuO} = 6.3 \times 10^{-6} D$ has proved to be of a better plugging performance and hence a better fluid loss control agent than filter cake of 0.8% ZnO nanoparticle drilling fluid with $K_{ZnO} = 7.60 \times 10^{-6} D$. The filter cake from the base drilling fluid without nanoparticles has the highest permeability value $K_{bf} = 1.2 \times 10^{-5} D$.

![Permeability Data](image)

Figure 16: Permeability Data for $k_{bf} = 1.20 \times 10^{-5} D$, $K_{CuO} = 6.30 \times 10^{-6} D$ and $K_{ZnO} = 7.60 \times 10^{-6} D$. 

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4. Discussion of Results

Based on the shear stress versus shear rate results, it can be speculated that, at low concentrations, the distinctive effect of adding nanoparticles was to disorganize the bonds between the other drilling fluid components resulting in a substantial reduction of the shear stress. In contrast, at higher nanoparticle concentrations, a greater quantity of solid particles dominated and the disrupting effect of the nanoparticles was reduced. A greater reduction in shear stress was exhibited by the ZnO nanoparticle fluid. This was caused by the smaller surface area of ZnO (at 10.8 m$^2$/g) compared to CuO (at 29.7 m$^2$/g), which affects the ability to disperse and disrupt the bonds inside the drilling fluid. In addition, the viscoelastic behaviour of the nanoparticle-based drilling fluids obtained from the experiment indicates their flexibility in changing their rheological properties during drilling operations. Drilling fluids are required to have low stress for ease of pumping while the drill bit is penetrating, but their strength must be high enough to suspend the rock cuttings when the operation is stopped.

The nanoparticle-based drilling fluids cause a decrease in PV. This is believed to be the result of the nanoparticles reducing the mechanical friction between the drilling fluid compositions. This leads to an easier flow of fluid through the drill bit and in the annulus. The lower apparent viscosity (AV) at high-speed shear rates would result in a faster penetration of the drill bit when operations start; however, the lower AV might decrease the cuttings lifting ability of the drilling fluid. A reduction of initial resistance to flow of the drilling fluid was obtained from the nanoparticle-based drilling fluids. The reduction in YP results from a decrease in electrochemical forces between the drilling fluid formulations due to the addition of nanoparticles. A better optimisation of gel strength over base drilling fluid, which reduces the pump power required to recirculate flow after stopping the operation, was obtained using both types of nanoparticles. Finally, a reduction in gel strength at 10 minutes at 1 wt%
concentration was observed. This resulted from a closer distance between nanoparticles in the drilling fluid, so that they started to agglomerate and act similar to larger particles. The improvement of the rheological properties resulting from greater nanoparticle concentrations found in this study is consistent with results from a study by Perween et al., in 2018, during their research on ZnTiO₃ nanoparticles. Referring to the findings herein, that improved rheological properties resulted from the larger surface area of CuO nanoparticles compared to ZnO nanoparticles, Perween et al., in 2018, also obtained similar rheological trend results from higher-surface-area material (ENP ZnTiO₃ – 24.47 m²/g) over lower-surface-area material (SNI ZnTiO₃ – 1.04 m²/g). The authors also noted the trade-off that an increasing trend might increase the capacity of the drilling fluid to hold more rock cuttings.

The shear thinning characteristic of the nanoparticle-based drilling fluids at elevated temperatures showed an ability of the fluids to still work effectively at higher temperatures. Thermal expansion at higher temperatures decreases the stress between the particles. Drilling fluid’s viscosity reduction at higher temperatures also reduces the shear stress. The effects of different concentrations of ZnO and CuO nanoparticles on the shear stress trend at elevated temperatures were the same as at 25°C. This indicates that there is no sign of thermal degradation of the nanoparticle-based drilling fluids. Similar evidence was reported by William et al., in 2014, in which ZnO and CuO nanoparticles as drilling fluid additives were tested and found to give a good indication of thermal stability enhancement, even at temperatures up to 110°C.

There is greater consistency in the results at the higher testing temperature in the CuO nanoparticle-based drilling fluid (i.e. constant increasing shear stress versus shear rate trend with concentration). The thermal conductivity of CuO nanoparticles is higher than that of ZnO nanoparticles, according to the study of Ponmani et al., in 2014. This property of drilling fluids...
determines how quickly heat can be transferred inside the fluid column \(^{22, 23}\). Higher thermal conductivity means that the fluid holds heat for a shorter time, resulting in a greater thermal stability of the drilling fluid \(^{47}\).

According to the rheological property results (50°C and 80°C), it can be inferred that the surface area of the nanoparticles was a dominant factor in the trend of the rheological properties at both low and elevated temperatures. For particles with a greater surface area, the volume or amount of particles that can be added to the drilling fluid is less and there is less of an agglomeration problem, as can be seen in the case of CuO nanoparticles. On the other hand, the smaller surface area nanoparticles have the ability to decrease the interactions among larger molecules, due to their smaller size \(^{33}\). However, at higher concentrations the quantity of particles needed to be added is higher. Then, agglomeration of the particles becomes a dominant effect and enhancement of the shear stress is no longer an issue as a result of the reduction in 10-minute gel strength in the ZnO 0.8% to 1% drilling fluids.

Comparison of various filtration loss property results from different nanoparticle-based drilling fluids shows a successful development of the formulation of ZnO and CuO nanoparticle-based drilling fluids in this study. In general, a filtration loss of 10 ml for the API standard filtration test at low pressure and low temperature (LPLT) condition can be considered a low fluid loss \(^{48}\). Since HPHT conditions always result in greater fluid loss (due to lower fluid viscosity), it can be seen that the results obtained in this study are practically acceptable. Nevertheless, a better drilling fluid formulation to further reduce filtration may need to be studied. The results from this study indicate a better filtration loss compared to most other studies, apart from the ferric oxide nanoparticles. The nanoparticles used in the other studies were directly added to the drilling fluid formulation as a calculated wt%, whilst in this study, nanoparticles were added to a mixture of 0.4 wt% xanthan gum and distillated water, and then 1 vol% of these mixtures, or nanofluids, were added to the prepared base drilling fluid. In real oil and gas industrial
applications, less chemical exposure is always preferable. Consequently, this preparation procedure might be a better alternative in order to reduce exposure levels to the environment, whilst still obtaining a satisfactory enhancement of the drilling fluid properties.

The detailed SEM investigation carried out in this study indicates that the process of filtration as observed from the SEM analysis of the filter cake from base drilling fluid without nanoparticles (figures 13 a & b) appears to be very porous and permeable. While for 0.8% CuO filter cake (figures 14 a & b) and 0.8% ZnO filter cake (figures 15 a & b) cases, the nanoparticles are able to reduce the fluid loss considerably by plugging the pores/holes observed in figures (13 a & b), and this mechanism has resulted in thin and less permeable filter cake with low porosities as the volume of filter cake formed per cubic centimeter of filtrate has become very small. However, the agglomeration of nanoparticles observed with 0.8% ZnO filter cake is because these magnetic particles can aggregate easily in water based fluids which results in bigger particles (figures 15 a & b) and leads to higher fluid losses because pristine inorganic nanoparticles are able to aggregate because of their high surface energy. The 0.8% CuO filter cake showed little or no aggregation (figures 14 a & b) hence the better hole plugging performance giving rise to a low filtration velocity and a small volume of filter cake formed per cubic centimeter of filtrate and ultimately a thinner filter cake thickness. The Permeability values in Darcy presented in figure 16, $K_{bf} > K_{ZnO} > K_{CuO}$ validates the observations in figures 13-15. The agglomeration of the nanoparticles in the filter cake from 0.8% ZnO nanoparticle drilling fluid (figures 15 a & b) led to a permeability value of $K_{ZnO} = 7.60 \times 10^{-6} D$ while the filter cake from 0.8% CuO nanoparticle drilling fluid which have shown little or no agglomeration (figures 14 a & b) have a lower permeability value of $K_{CuO} = 6.30 \times 10^{-6} D$, hence the filter cake from 0.8% CuO nanoparticle drilling fluid was able to show a better performance in the fluid loss control process than the filter cakes from base drilling fluid (figure 13 a & b) without nanoparticles, having the highest permeability value of
\[ K_{bf} = 1.2 \times 10^{-5} D \] and 0.8% ZnO nanoparticle drilling fluid with \[ K_{ZnO} = 7.60 \times 10^{-6} D. \] The permeability values have also affected the effective reduction in the thickness of the filter cakes. The mechanism attributed to the effective reduction in thickness of filter cake is linked to the plugging of the existing pores by the nanoparticles that have reduced the filtration process and the rate at which particulates were deposited.

5. Conclusions

This study aimed to develop a high-performance, water-based drilling fluid by using ZnO and CuO nanoparticles as nanofluid additives. From the rheological testing, a significant reduction in shear stress and improvement in rheological properties were observed after the addition of a small quantity of nanoparticles. With higher concentrations of nanoparticles, the shear stress gradually increased and the rheological properties gradually deteriorated for both nanoparticle types, although the ZnO nanoparticles produced better rheological properties than the CuO nanoparticles. Moreover, at higher temperatures, the drilling fluids still exhibited shear thinning characteristics, decreases in shear stress and improvement in other rheological properties.

For the filtration tests under elevated pressure and temperature conditions (500 psi and 100°C), 18.6% and 30.2% reductions in filtration loss, compared to the base drilling fluid (17.2 ml), resulted from 0.8 wt% ZnO and 0.8 wt% CuO nanoparticle-based drilling fluids, respectively. However, after increasing the concentration of ZnO and CuO nanoparticles to 1 wt%, the nanoparticle-based drilling fluid filtration loss increased due to the agglomeration of nanoparticles. Mud cake thicknesses showed 24.6% and 27.6% reductions, compared to the base drilling fluid, for ZnO and CuO nanoparticles, respectively. The filter cakes for base drilling fluid, 0.8% CuO base drilling fluid and 0.8% ZnO base drilling fluids have been
characterized using SEM. The mechanism for thicker filter cakes has been attributed to a faster/increased velocity of filtration due to a poor plugging performance. The permeabilities of the filter cakes were calculated and the base drilling fluid have a higher permeability followed by 0.8% ZnO based drilling fluid then 0.8% based drilling fluid have the lowest permeability \( (k_{bf} > k_{ZnO} > k_{CuO}) \).

In conclusion, the ZnO nanoparticles exhibited a better ability to improve the rheological properties, while the CuO nanoparticles showed superior filtration loss reduction. However, CuO nanoparticles might be considered a more environmentally-friendly drilling fluid additive. Overall, nanoparticles have the potential to enhance the industry-required properties of drilling fluids.

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