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ORIGINAL PAPER

Enhancement of the heat capacity of water-based drilling fluids for deep drilling applications

Milad Cheraghi[1] · Mastaneh Hajipour[1] · Abolghasem Emamzadeh[1]

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Abstract
Formulation of drilling fluids with appropriate thermal properties is needed for cooling the drill bit, especially under high-pressure high-temperature conditions. Using proper additives for drilling fluid preparation can decrease the drill bit replacement costs in deep drilling operation. Nanoparticles have been extensively investigated as drilling fluid additives for thermal conductivity enhancement. However, studies of drilling nanofluid specific heat capacity are limited in the literature. As increase of thermal conductivity is necessary but not sufficient for achieving high performance heat transfer. This study was carried out to complement existing research by measuring the specific heat capacity of water-based drilling fluids containing nanoparticles. For this purpose, three types of metal oxide nanoparticles were added to an industrial formulated drilling fluid. Transmission electron microscopy was used to investigate nanoparticles morphology and X-ray diffraction was applied to determine nanoparticles purity. A simple device was designed, constructed and calibrated to measure the drilling fluid heat capacity. The experimental data revealed that the heat capacity of the drilling fluid can be enhanced by adding nanoparticles due to increased surface atomic contributions. The highest increase in heat capacity, i.e., 4.8%, was observed in the presence of 0.5 wt% titania nanoparticles. The results obtained from the measurement of rheological properties indicated that viscosity, yield point, and gel strength of the drilling nanofluid are highly dependent on nanoparticle type, size and concentration. Maximum increase obtained in rheological properties was 29% in plastic viscosity by adding titania nanoparticles and 37% in yield point for silica nanoparticles, at a concentration of 0.5 wt%. It was shown that nanoparticles may enhance thermal and rheological properties of drilling fluids and can be used as an efficient additive for deep drilling operation.

Keywords Heat capacity · Rheological properties · Drilling fluid · Nanoparticle additive

Introduction

One of the significant tasks of drilling fluids in oil and gas well drilling is drill string and bit cooling. Proper cooling decreases the drill bit replacement costs, especially under high-pressure high-temperature (HPHT) conditions (Adams 1991; Hossain and Al-Majed 2015). Thus, drilling fluids should have enough thermal stability and efficient performance at great depths. Production of oil and gas needs drilling of a hole to the reservoir located far away from the surface. In the drilling operation, drill string carries the drill bit to the bottom of the well. The drilling fluid is conveyed in the drill string and it continually reaches to the bottom of the well bore. The drilling mud cools the drill bit and assists to transport drill cuttings to the well head (Bourgoyne et al. 1991).

Drilling and exploration is moving towards drilling wells to depths in excess of more than 5000 m due to continuous increasing demand for fossil fuels. These wells are very expensive to drill and completion costs more than $100 million (Kelessidis 2009). The drilling fluid plays a key role in complex conditions found during deep drilling operations. Most critical operational issues and concerns related to the drilling fluid design and application are lost circulation, mud properties, cuttings transport, stuck pipe, wellbore stability, and formation damage. There are several works available in the literature about challenges to deep and ultra-deep oil and gas drilling operations (Zamora et al. 2000; McLean et al. 2010; Leffler et al. 2011).

✉ Mastaneh Hajipour
m.hajipour@srbiau.ac.ir

1 Department of Petroleum Engineering, Faculty of Petroleum and Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

One of the main concerns in designing drilling fluid formulations is the requirement of thermal stability and high heat transfer characteristics at elevated temperatures. Therefore, various chemical additives have been investigated to enhance the drilling fluid thermal and rheological properties. Over the past decades, nanoparticles have been applied as effective additives to adjust the drilling fluid characteristics (Sameni et al. 2015; Movahedi et al. 2021; Akhtarmanesh et al. 2013).

The presence of nanoparticles in a fluid improves the thermal and rheological properties. Dispersing nano-sized solid particles in a base fluid increases fluid stability (Karthikeyan et al. 2008). Designing a smart drilling fluid by adding nanoparticles at low concentration can improve the physico-chemical characteristics of conventional drilling fluids and increase drilling efficiency.

Although several investigations have been conducted on drilling fluid thermal conductivity, research on the effects of adding nanoparticles to drilling fluids on its heat capacity are scarce and little information is available. Drilling fluids with greater heat capacities are needed to increase the heat transfer performance in deep drilling operation.

Published papers in the literature indicate that adding nanoparticles to drilling fluids improves thermal conductivity (Xu et al. 2019; Jabbari et al. 2017; Liu et al. 2005, 2006), but investigation of the effect of nanoparticles on the specific heat capacity of drilling fluids demonstrates different results (Veisi et al. 2020; Vajjha and Das 2009; Movahedi et al. 2017; O'Hanley et al. 2012; Sekhar and Sharma 2015; Zhou et al. 2009; Shin and Banerjee 2010). William et al. explored the influence of copper and zinc based drilling nanofluids. Their experiments showed the maximum improvement of 53% in thermal conductivity of the drilling fluid (William et al. 2014). Hassani et al. investigated the effect of multiwall carbon nanotubes (CNT), silica (SiO_2) and zinc oxide (ZnO) nanoparticles on thermal conductivity of drilling fluid. They observed a maximum enhancement of 22% in thermal conductivity of the drilling fluid by adding 2 vol% of zinc oxide nanoparticles (Sadegh Hassani et al. 2016). Baghebanzadeh et al. (2012) used silica/multiwall carbon nanotube hybrid nanoparticles to explore the nanofluid thermal conductivity. They concluded that nanofluid thermal conductivity is dependent on the nanoparticle concentration and ratio in the hybrid.

As stated, enhancement of drilling fluid thermal conductivity due to adding nanoparticles has been extensively investigated. However, fewer studies of drilling nanofluid specific heat capacity have been reported in the literature. The increase of thermal conductivity is necessary but not sufficient for achieving high performance for heat exchange purposes. The specific heat capacity determines the rate at which the drilling fluid will heat up or cool down. As the specific heat capacity is directly related to the atomic structure of materials, measurement of drilling fluid heat capacity should be carried out for any kind of additive.

The aim of the present study was to complement the existing research by measuring the specific heat capacity of water-based drilling fluids in the presence of nanoparticles. For this purpose, the impact of metal oxide nanoparticles on specific heat capacity of an industrial formulated water-based drilling fluid was experimentally investigated. Since adding any kind of additive to drilling fluids can affect their rheology, the variations of rheological parameters were also investigated. The rheological parameters including plastic viscosity, yield point, and 10 s/10 min gel strength were measured after dispersing nanoparticles in the drilling fluid. For all the samples of drilling nanofluid, variations of specific heat capacity as well as rheological properties were compared and discussed.

Theory

As described in the literature, specific heat capacity (C) for a substance is defined by the following equation (Uzunov 1978; Hajipour and Molaei Dehkordi 2011):

$$C = \frac{Q}{m \cdot \Delta T}, \quad (1)$$

where m is body's mass in kg, Q is rate of heat transfer in J, and ΔT refers to temperature difference in K. This property is an intensive property and does not depend on the body's mass. This thermal property shows the capacity of a body to absorb heat and depends on the temperature at which it is measured.

Specific heat capacity cannot be measured directly. The heat delivered to the body and its temperature should be measured, to calculate specific heat capacity. According to Eq. (1), plotting the data on heat energy supplied to the body against the temperature variations results in a straight line. The specific heat capacity is calculated from the slope of that line.

The rate of convective heat transfer (Q) between a solid body and adjacent fluid is given by Newton–Richman's law (Eq. (2)).

$$Q = hA\left(T - T_{\mathrm{f}}\right), \quad (2)$$

where h is the convective heat transfer coefficient in W/(m^2K), A is the heat transfer surface area in m^2, T and T_{f} are the solid and surrounding fluid temperatures in K, respectively. According to Eq. (2), the heat transfer rate from a drill bit can be enhanced by raising the temperature difference between the bit and drilling fluid. Therefore, designing a drilling fluid with high specific heat capacity leads to efficient cooling of the drill bit.

Materials and methods

Drilling fluid formulation

Nanofluids are defined as a suspension of nano sized solid particles in a base fluid. The analysis of a nanofluid's thermal properties requires proper synthesis procedure that produces stable suspensions of nanoparticles in liquid. There are two processes for nanofluid formulations. In the first process, the synthesis and dispersion of nanoparticles in a base fluid is done simultaneously using chemical techniques (Zhu et al. 2004). In the second procedure, nanoparticle powder is first produced using different methods, and then dispersed in a base fluid (Paul et al. 2011). The second method is economical, but particle agglomeration can occur due to large specific surface area of nanoparticles. Thus, preparing a stable nanofluid requires various techniques such as sonication, pH modification or adding a stabilizer (Experimental and numerical study 2014).

In this study, three types of metal oxide nanoparticles i.e., alumina (Al_2O_3), silica (SiO_2), and titania (TiO_2) were used. The nanoparticle properties are summarized in Table 1. Transmission electron microscopy (TEM) was used to investigate nanoparticle morphology and X-ray diffraction (XRD) was applied to designate nanoparticle purity.

Nanofluids were prepared by dispersing the nanoparticles in distilled water at a certain concentration. Then, the nano suspensions were sonicated using an ultrasonic disruptor (Elmasonic, E 30 H) for 20 min, for obtaining homogeneous nanofluids. To formulate the drilling nanofluid, the nano suspensions were added to the drilling fluid and stirred to produce uniform suspensions.

Water-based drilling fluid is commonly prepared using different minerals, organic substances, and inorganic salts in water. The base drilling fluid was prepared on the basis of a formulation that is currently being used for drilling operations in an oilfield in the south of Iran. The formulation used in preparing the base drilling fluid is presented in Table 2. The chemical additives were slowly stirred into 350 ml of water, then mixed well using a high speed mixer (Fann Multi Mixer, 9B29X).

Table 1 Properties of metal oxide nanoparticles

Nanoparticle	Size (nm)	Purity (%)	Specific heat capacity [J/(kg K)]
Al_2O_3	30	99.9	955
TiO_2	20	99.5	697
SiO_2	30	99.5	730

Table 2 The formulation used in preparing water-based drilling fluid

Component	Weight (g)	Mixing duration (min)
Sodium carbonate	0.18	3
Caustic soda	0.10	3
Calcium chloride	95	10
Potassium chloride	10	8
Starch (C6H10O5)	10	8
Xanthan gum	1	8
PAC LV	1	5
Barite	20	10

Experimental measurements

A device was designed and constructed for measuring the liquid samples' heat capacity. This apparatus, shown in Fig. 1, consists of an insulated container with a stirrer, an internal thermocouple, and a heating element placed in the middle of the container. The following procedure was used to gather the data required for evaluation of the specific heat capacity. The insulated container was put on a digital balance, and after calibration, 200 g of prepared drilling nanofluid was weighed to a precision of 1 mg. The initial temperature of the sample was recorded. The heat generated by the heating element caused the sample to increase in temperature. The stirrer inside the container homogenized the sample thermally. The temperature of the sample was recorded at frequent time intervals.

Specific heat capacities of the prepared drilling fluid and nanofluids were computed according to Eq. (1). For each nanofluid concentration (i.e., 0.01, 0.05, 0.1, and 0.5 wt%),

Fig. 1 The experimental device used for heat capacity measurement

measurements were repeated three times, and calculated specific heat capacities were then averaged to yield the final value. The main objective of this study was to investigate the effect of nano-additives on drilling fluid properties for application in deep drilling operation. As large volume of drilling mud is used in deep drilling operations and a low concentration of additives is economical and preferred. Therefore, in this study, low concentration of nanoparticles i.e., less than 0.5 wt% was explored.

To calibrate the device, a reference sample with a known heat capacity was selected. The calibration ensured that measured data and the reference value coincided. Distilled water was used to calibrate the device. Distilled water sample was heated, temperature versus time data were gathered, and heat capacity was calculated from the slope of the line plotted in Fig. 2. The value of water specific heat capacity was measured as 4.21 J/(g °C), whereas the reference value is 4.18 J/(g °C) (Green and Perry 2007). The relative error was evaluated as 0.7%.

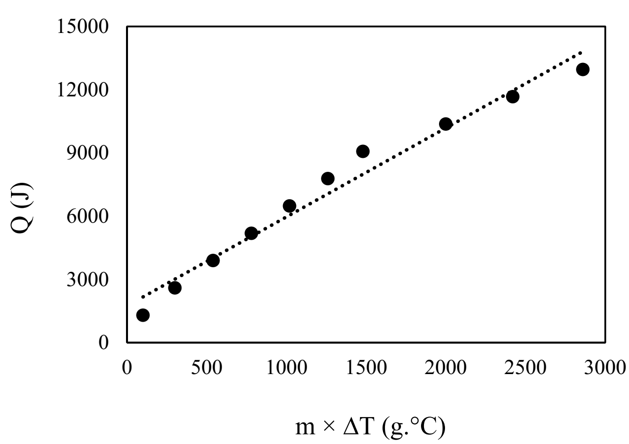

Fig. 2 Measured data and fitted straight line for distilled water used for device calibration

The rheological properties including plastic viscosity, yield point, and 10 s/10 min gel strength were measured based on the API standards (API 2003). To carry out rheological measurements, a Fann rotational viscometer model 35A was used. The shear stress- shear rate relationship for the base drilling fluid and nanofluid samples was explored with an Anton Paar rheometer (MCR 302). Before performing each experiment, the drilling nanofluids were agitated for at least 5 min to homogenize the samples.

Results and discussion

TEM images of the metal oxide nanoparticle powder before dispersion in the base mud are displayed in Fig. 3. It is shown that the nanoparticles used are spherical. It was observed that the average diameters of alumina, titania, and silica nanoparticles are 25, 11, and 36 nm, respectively. The nanoparticle XRD analyses are displayed in Fig. 4. A good consistency was observed between the characteristic peaks and the reference pattern for the nanoparticles.

Drilling fluid heat capacity

The accuracy of the apparatus developed to measure the specific heat capacity was assessed using distillated water. The specific heat capacity of the drilling fluid without nanoparticles was measured to have a baseline for evaluation of the drilling nanofluids' performance. Drilling nanofluids containing a type of nanoparticle i.e., alumina, titania, and silica at concentrations of 0.01, 0.05, 0.1 and 0.5 wt% were tested. Experimental results for three types of drilling nanofluids that included 0.1 wt% nanoparticles are illustrated in

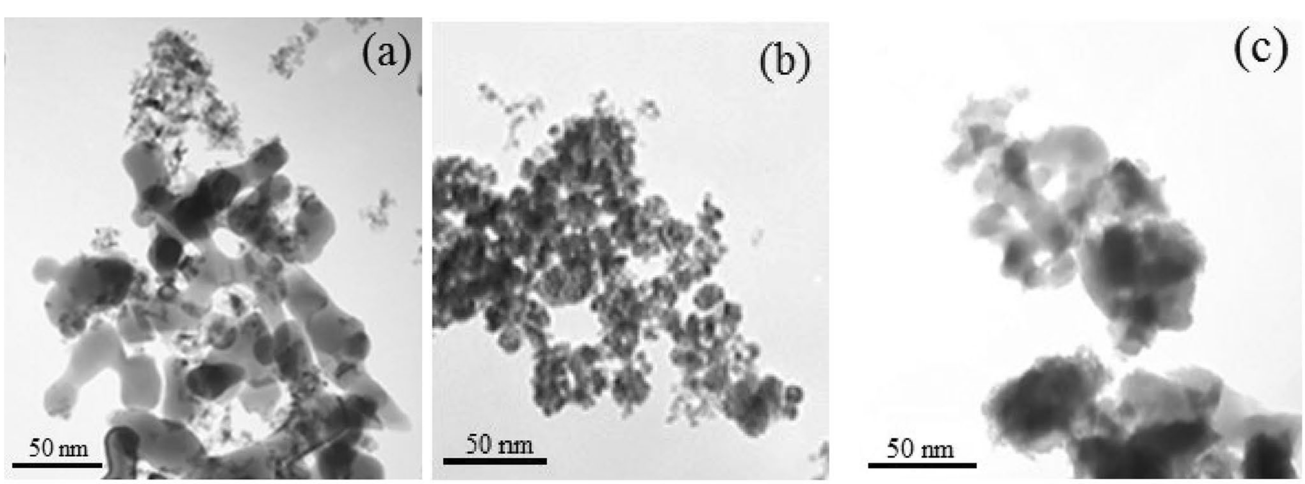

Fig. 3 TEM image of **a** alumina, **b** titania, and **c** silica nanoparticles

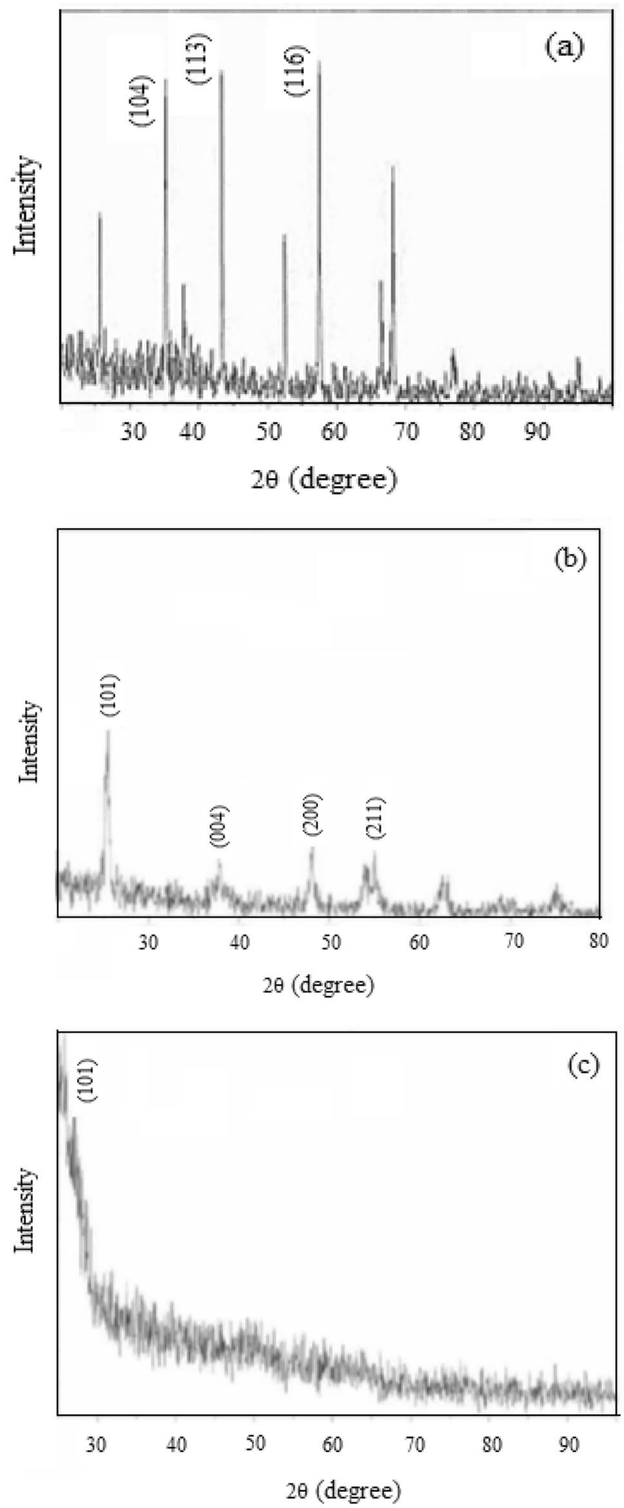

Fig. 4 XRD pattern of **a** alumina, **b** titania, and **c** silica nanoparticles

Fig. 5, with the base drilling fluid for comparison. Specific heat capacity was computed for different samples from the slope of the straight line fitted to measured data and reported in Table 3.

The experimental results revealed that, among the nanoparticles investigated in this study, addition of titania nanoparticles to the base drilling fluid enhances specific heat capacity. The increase of specific heat capacity by adding nanoparticles to the drilling fluid indicates that drilling nanofluids can cool the drill bit more efficiently than base drilling fluids. The maximum enhancement in specific heat capacity was detected by adding 0.5 wt% of titania nanoparticles.

To ensure the repeatability and reliability of the measurements, each test was carried out at least three times and the averages of the obtained values were plotted. Uncertainty analysis performed on experimental data via the propagation of error indicated that the maximum uncertainty in heat capacity measurements is on the order of 10^{-3} J/(g °C). It is worth noting that the observed heat capacity enhancement is much higher than the measurement uncertainty.

Table 3 presents the ratio of the specific heat capacity of drilling nanofluids to the base drilling fluid (C_{p0}) as a function of the nanoparticle weight fraction. It can be seen that for alumina and silica nanoparticles, the specific heat capacity of drilling nanofluids decreases by increasing the nanoparticle concentration up to 0.5 wt%. The obtained data showed that the addition of more than 0.05 wt% of titania nanoparticles to the base drilling fluid leads to the heat capacity increase. This behavior can be attributed to the smaller sized titania nanoparticles. The enhanced heat capacity in nanofluids with smaller nanoparticles is due to larger thermal vibrational energies of the particles' surface atoms. Results show that the ratio of nanoparticle surface to volume significantly affects the nanofluid specific heat capacity. As the ratio of surface to volume for solid particles increases, the number of surface atoms is increased. Thus, more heat is needed to increase the temperature of surface atoms by one degree, and consequently the heat capacity is higher. (Angayarkanni et al. 2015).

Different mechanisms may affect the variations of specific heat capacity due to adding nanoparticles to the drilling fluid. One of these mechanisms that can justify the enhancement of specific heat capacity is higher specific surface energy of nanoparticles in comparison with the base fluid. Moreover, interfacial interactions between the base fluid and nanoparticles with large specific surface area affect the nanofluid thermal storage and heat capacity. Another mechanism is the existence of a nanolayer on the nanoparticle surface, in which intermolecular spacing is smaller in comparison with the base liquid (Shin and Banerjee 2011). The thermal conductivity of nanofluids has been shown to increase due to various reasons including nanoparticle Brownian motion (Evans et al. 2006; Hajipour et al. 2014), nanoparticle aggregation (Evans et al. 2008), and nanolayer existence on the surface of nanoparticles (Li et al. 2010; Lu and Huang

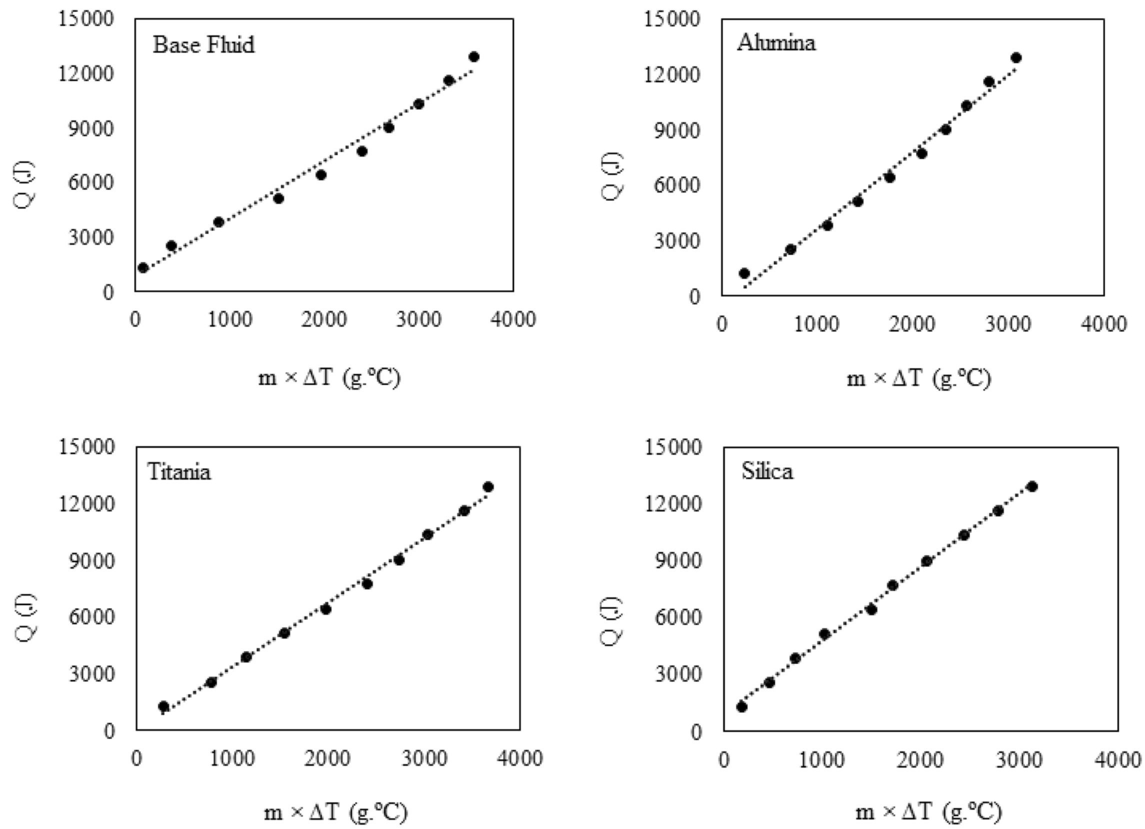

Fig. 5 The measured data and the fitted straight line for drilling fluid samples

Table 3 Ratio of specific heat capacity of drilling nanofluids to the base fluid

Sample	Nanoparticle wt%	C_p/C_{p0}
Base mud + Al_2O_3 nanoparticles	0.01	0.996
	0.05	0.991
	0.1	0.987
	0.5	0.972
Base mud + TiO_2 nanoparticles	0.01	0.999
	0.05	0.998
	0.1	1.002
	0.5	1.048
Base mud + SiO_2 nanoparticles	0.01	0.993
	0.05	0.990
	0.1	0.985
	0.5	0.962

2013). Among various mechanisms which affect nanofluid thermal conductivity, the nanolayer formation has the most significant impact on the nanofluid heat capacity (Kumar Sharma et al. 2016).

Drilling fluid rheology

The objective of the present work was to study the effect of dispersed nanoparticles on the specific heat capacity of water-based drilling fluids for a better understanding of their application in deep drilling operation. Since adding any kind of additive to drilling fluids can affect their rheology, the rheological characteristics of the base drilling fluid were measured and compared in the presence of various nanoparticles. To perform rheological analysis, the drilling fluid's properties including plastic viscosity, yield point, and 10 s/10 min gel strength were measured.

The variations of shear stress versus shear rate indicate the rheological behavior of fluids. Several mathematical models that describe the behavior of non-Newtonian fluids are available (Kumar Sharma et al. 2016). The rheological model which is appropriate for the drilling fluid samples was determined by plotting shear stress values over a range of shear rates. Figure 6 illustrates the results for drilling nanofluid samples including 0.1 wt% nanoparticles.

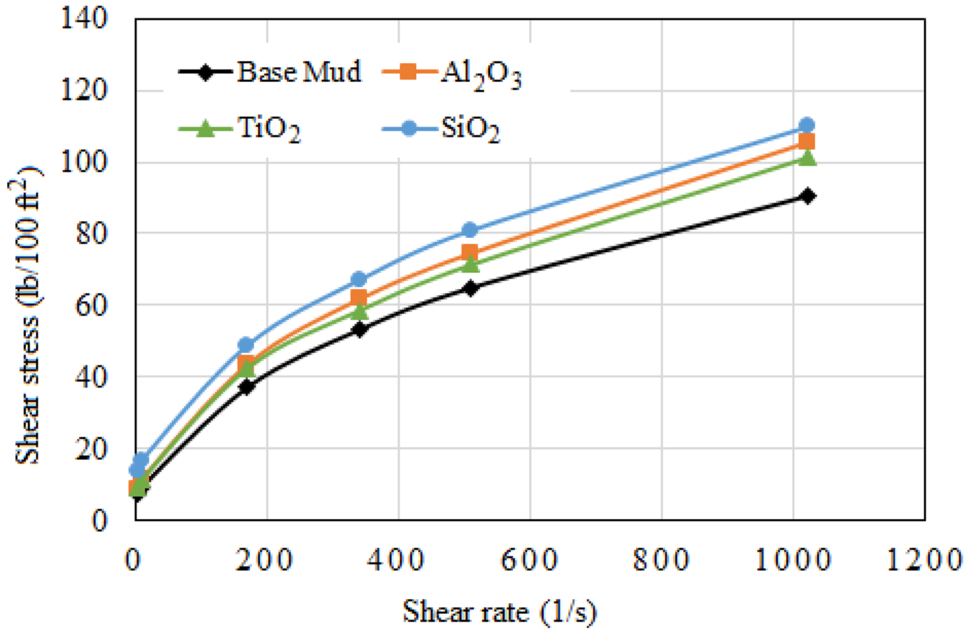

Fig. 6 Shear stress against shear rate for drilling nanofluid samples

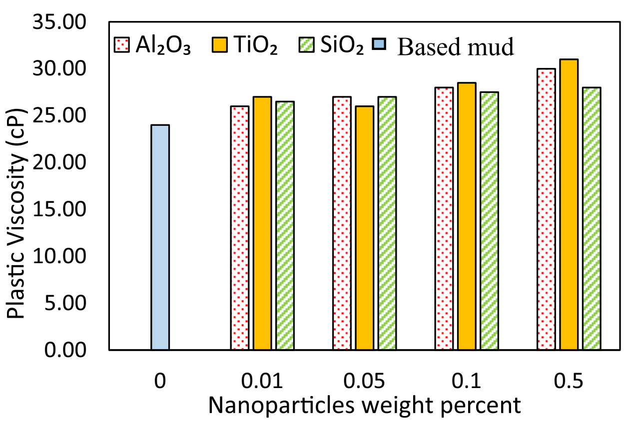

Fig.7 Plastic viscosity for various nanoparticle concentrations

It was observed that the shear stress is increased by adding nanoparticles to the drilling fluid. The variations of shear stress against shear rate indicates that all drilling nanofluid samples exhibit viscoplastic shear thinning behavior.

The experimental values of plastic viscosity for different drilling nanofluid samples are shown in Fig. 7. The plastic viscosity for drilling fluid without nanoparticles was measured to be 24 cP. It can be seen that the addition of nanoparticles to the base drilling fluid increases the plastic viscosity. Moreover, the plastic viscosity of drilling nanofluids rises with an increasing concentration of nanoparticles.

In Fig. 7 an irregular reduction is observed for titania nanoparticles after increasing the concentration from 0.01 to 0.05 wt%. However, a further increase in titania nanoparticles causes the viscosity values to increase. In fact, the increase in friction between fluid layers due to Brownian motion of nanoparticles within the base fluid leads to the increase of drilling fluid viscosity in the presence of nanoparticles (Kumar Sharma et al. 2016). The maximum value of plastic viscosity, i.e., 31 cP was observed with titania nanoparticles at a concentration of 0.5 wt%. Nanoparticle Brownian motion is greatly dependent on the solid particles diameter. The smaller the nanoparticle size, the greater the Brownian motion. This can justify the highest increase in drilling fluid viscosity detected by adding titania nanoparticles.

The yield point of a drilling fluid should be adjusted in order to achieve proper cuttings transport. High values of the yield point which lead to extra pumping energy must be prevented. The value of the yield point for a non-Newtonian fluid depends on its electro-chemical charges under flowing conditions. The higher the attractive forces, the higher the value of the yield point. Whenever particles are charged so that they attract each other, a higher yield point is obtained and when particles repel one another, the fluid yield point is lower. However, by adding proper additives to the drilling fluid the desired value of yield point can be determined (El-Sukkary et al. 2014; Ghassem Alaskari and Nickdel Teymoori 2007).

The impact of adding nanoparticles to the base drilling fluid on the yield point value is demonstrated in Fig. 8. The value of the yield point for the base drilling fluid was recorded as 37 (lb/100 ft^2). It can be seen in Fig. 8 that the yield point value of drilling fluid increases by adding nano sized additives. The increase in nanoparticle concentration increases the yield point value. The highest value of yield point, i.e., 51 (lb/100 ft^2) was observed in the presence of silica nanoparticles at a concentration of 0.5 wt%.

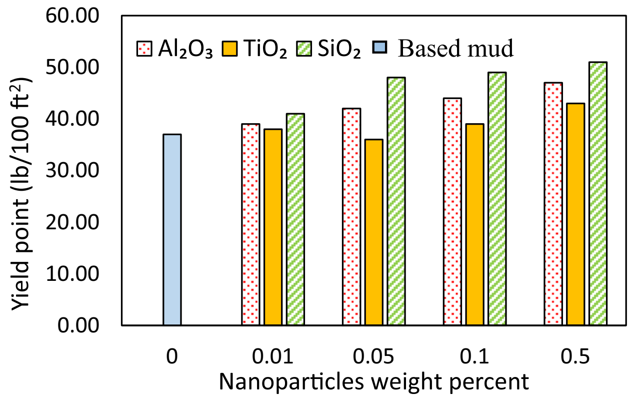

Fig. 8 Yield point for various nanoparticle concentrations

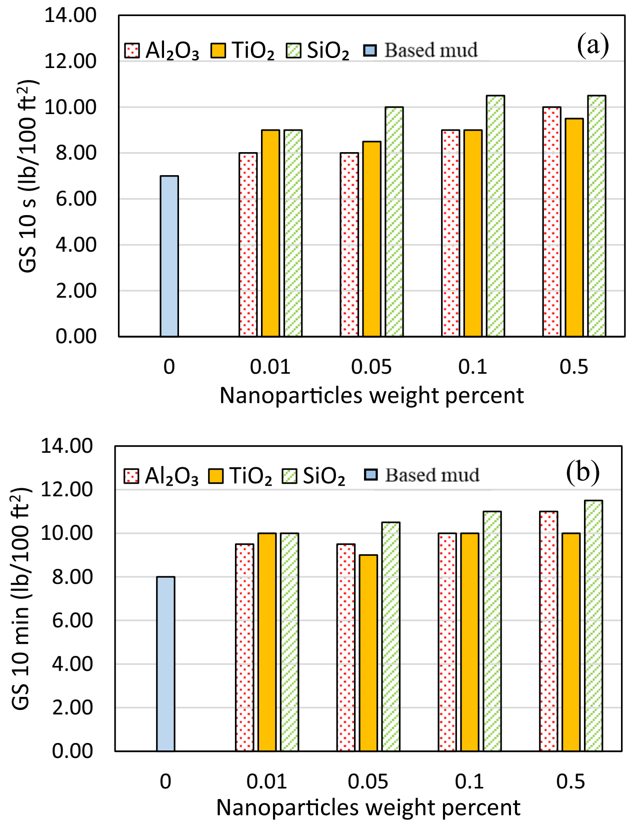

Fig. 9 Gel strength for various nanoparticle concentrations, **a** GS 10 s and **b** GS 10 min

A comparison between rheological properties of the drilling nanofluids and the base drilling fluid reveals that better rheological behavior can be achieved by adding nanoparticles to the drilling fluid (Maxey 2006; Dahlem 2013).

The ability of a fluid to suspend solid particles under static conditions is called gel strength, which is an important property of drilling fluids. Gel strength is measured immediately after preparation of the drilling fluid (10 s GS) and after a rest period of the mud for 10 min (10 min GS) (Dardir et al. 2014; Hafiz and Abdou 2003). Figure 9 displays the gel strength values of drilling nanofluid samples at various nanoparticle concentrations.

The general trend of gel strength variations with nanoparticle concentration is incremental except for titania nanoparticles at a weight percent of 0.05. For some of the nanoparticle concentrations, no change was observed in the values of 10 s GS or even in 10 min GS. The gel strength values do increase when the concentration of both alumina and silica nanoparticles is increased. However, for titania nanoparticles, the gel strength values decline when the concentration increases from 0.01 to 0.05 wt% and then increases with rising nanoparticle concentration. The maximum increase in gel strength value was detected by adding silica nanoparticles at a concentration of 0.5 wt%.

Conclusion

The impact of nanoparticles on the enhancement of drilling fluid thermal conductivity has been widely investigated. However, research works on the effect of adding nanoparticles to drilling fluid on its heat capacity are limited in the literature. This study aimed to cover this gap in the literature. Therefore, a base drilling fluid prepared on the basis of an industrial formulation was augmented with various concentrations of alumina, titania and silica nanoparticles to produce drilling nanofluids. The specific heat capacity and rheological behavior of drilling nanofluids were measured and compared. The main findings are summarized as follows:

- Dispersion of titania nanoparticles with more than 0.05 weight percent in water-based drilling fluid enhances the specific heat capacity.
- Variations of the drilling nanofluid heat capacity are highly dependent on nanoparticle type, size and concentration. The enhancement of heat capacity by adding titania nanoparticles to the base drilling fluid can be attributed to the smaller sized titania nanoparticles.
- Increasing the concentration of nanoparticles increases the viscosity and yield point of the base drilling fluid, except for titania nanoparticles, for which a reduction was observed when the concentration was raised from 0.01 to 0.05 wt%.
- Maximum increase in rheological properties was obtained of 29% in plastic viscosity by adding titania nanoparticles and 37% in yield point for silica nanoparticles, at a concentration of 0.5 wt%.
- The best enhancement in gel strength of 50% was observed for silica nanoparticles and after that 42% and 35% for alumina and titania nanoparticles, respectively.

- Among the nanoparticles investigated in this study, titania nanoparticles are recommended as water-based drilling fluid's additive for deep drilling applications. Adding these nanoparticles to the drilling fluid results in maximum enhancement in heat capacity while providing appropriate rheological properties.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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