Thermal and Rheological Properties Improvement of Oil-based Drilling Fluids Using Multi-walled Carbon Nanotubes (MWCNT)

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ABSTRACT

In this paper, we detail our results for the impact of MWCNT on the thermal and rheological properties of oil-based drilling muds. Our analysis considers the effects of time, temperature, and MWCNT volume fraction. The scanning electron microscopy imaging technique was used to monitor the MWCNTs dispersion quality. The experimental results unveil a considerable enhancement in the thermal conductivity of the MWCNT-oil-based mud by 40.3% (and 43.1% in case of functionalized MWCNT) and 1% vol. MWCNT. The rheological properties results for the MWCNT-oil-based mud exhibit a similar (improvement) trend by reducing annular viscosity and increasing yield point and gel strength. The high-temperature high-pressure filtration tests conducted at 280°F and 500 psi show a reduction of 16.67% for the filtrate amount in case of MWCNT-oil-based mud (with 1% vol. MWCNT). The effect of time on thermal conductivity reduction in both unfunctionalized and functionalized systems was observed to equalize (at 9.7%), after 100 hours of sample preparation. The performance results of MWCNT-oil-based mud are presented for an actual industrial drilling operation case.

Keywords: Multi-walled Carbon Nanotube, Oil-based Drilling Fluid, Thermal Conductivity, Annular Viscosity, Scanning Electron Microscopy (SEM)

INTRODUCTION

Oil-based drilling fluids (drilling muds) are used to meet demanding applications, including those requiring the highest degree of thermal stability. Their application has been extended to such technically challenging issues as unconventional drilling operations. To achieve their utmost performance and to meet the stability require ments under the high-temperature high-pressure (HTHP) conditions require finding ways for enhancing the thermal and rheological properties of the drilling mud.

The literature contains numerous recent reports devoted to the concept of alterations occurring in the thermophysical, electrokinetic, and rheological properties of a base fluid due to the introduction of nanosized entities, including multi-walled carbon nanotubes (MWCNT). The MWCNT results have unveiled improvements in the rheological [1,6] as well as thermal conductivity of the nanofluid systems [6,14]. The mentioned reports served as our motivation to probe the possibility of improving the thermal and rheological properties of oil-based drilling fluids using MWCNT.

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Experimental Procedures and Materials

The MWCNTs were purchased from Neutrino Co. (Tehran, Iran). The MWCNTs was produced by chemical vapor deposition. A typical scanning electronic microscopy (SEM) micrograph of the MWCNTs is shown in Figure 1. The average diameter and length of MWCNTs are about 15 nm and 20 µm respectively. The purity of MWCNTs was (>95%) and the specific surface area was (>200 m^2/gr.), as received. The base formulation considered for the oil-based drilling fluid is presented in Table 1. This specific base formulation is industrially attractive in the sense that it is currently being used for drilling operations in an oilfield in the southwest of Iran.

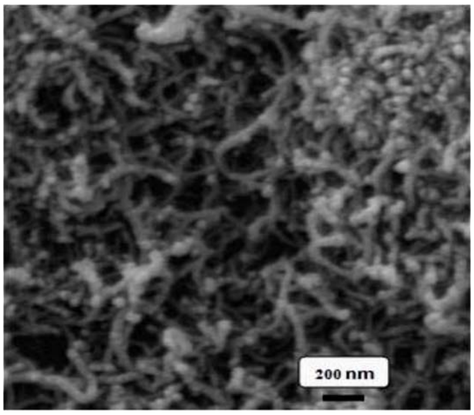

Figure 1: Typical SEM image of the MWCNTs used for the formulation of nano-based muds.

The MWCNTs are usually hydrophobic, so they are not readily dispersed in water. We introduced hydrophilic functional group to the surface of the nanotubes by acid treatment.

Nitric acid (69%) was used to modify the surface of MWCNTs. In a typical treatment in the present work, one gram of MWCNTs and 40 ml of acid were boiled and refluxed for 4 hrs. Then, the sample was diluted by deionized water (DW), filtered, and washed repeatedly until the washings show no acidity. The cleaned MWCNTs were collected and dried at oven for 12 hrs. to remove the attached water.

The MWCNT forms a more uniform dispersion in non-polar environments (such as oil-based systems), compared to the polar environments (such as water-based systems). Hence, the ball-milling process was not implemented for sample preparation in the oil-based systems analysis (for both unfunctionalized and functionalized MWCNT cases) as it does not seem to significantly improve the MWCNTs dispersion quality. Figure 2 depicts a SEM image of the MWCNT-oil-based sample (with 1 vol. % of MWCNT).

Table 1: The base formulation considered for the oil-based drilling fluid.

Mud Properties †	Value
Mud Weight (pcf)	75
Oil/Water Ratio	73/27
Fluid Lost (cc)	3
Alkalinity	4.5
Chloride (ppm)	345000
Solid (%)	16
Yield Point (lb./100ft^2)	10
Viscosity (cP)	49
Thermal conductivity (W/mK)	0.275
Diesel Oil (bbl)	0.73
Calcium Chloride Water (bbl)	0.27
Primary Emulsifier (gal)	1
Fluid Lost Controller (lb)	14

† Components per barrel

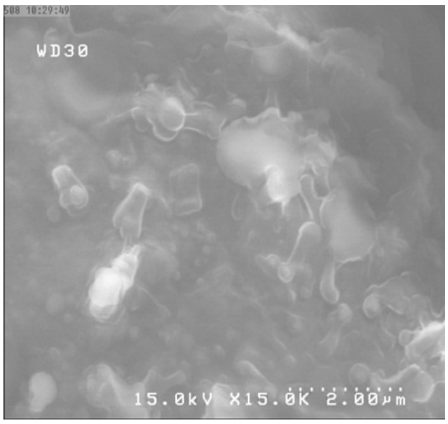

Figure 2: SEM image of the MWCNT-oil-based sample (with 1 vol.% MWCNT).

The thermal conductivities of these MWCNT-formulated samples was measured by transient hot-wire (THW), which is one of the most accurate techniques for determining thermal conductivity of materials. The uncertainty concomitant with the measurements is estimated to be better than 2%. The detailed underlying principles as well as the apparatus setup are described elsewhere [12].

RESULTS AND DISCUSSIONS

Scopes in this article are focus on two major and three sub major divisions. The effect of MWCNTs on thermal conductivity and rheological properties of oil-based drilling fluid are two major goals in this research. In this regard, ten different oil-based drilling fluids are selected based on various MWCNTs volume fraction.

We initiated the experiments by adding 0.1 vol. % of the nanoparticle to the mentioned oil-based drilling mud and investigated increasing nanoparticles volume fraction in 0.1 stepwise.

Effect of MWCNTs on Thermal Conductivity of Oil-based Mud

With respect to thermal conductivity investigation, the volume fraction of MWCNTs, time duration rule after preparing drilling mud, and temperature disturbance effect on thermal conductivity for ten different oil-based drilling fluid samples are investigated.

Volume Fraction

The results for the thermal conductivity change in the oil-based mud against MWCNT volume fraction are shown in Figure 3. Both unfunctionalized and functionalized MWCNT systems seem to have a similar impact on thermal conductivity alteration in the region (with MWCNT volume fraction < 0.4%). The functionalized system, however, enhances the thermal conductivity further as the MWCNTs volume fraction is increased. This may be credited towards the better dispersion quality of functionalized MWCNTs in oil-based systems (with 27% water presence). Improvements as much as 40.3% and 43.05% in thermal conductivity were measured (with 1 vol.% MWCNT) for unfunctionalized and functionalized systems respectively.

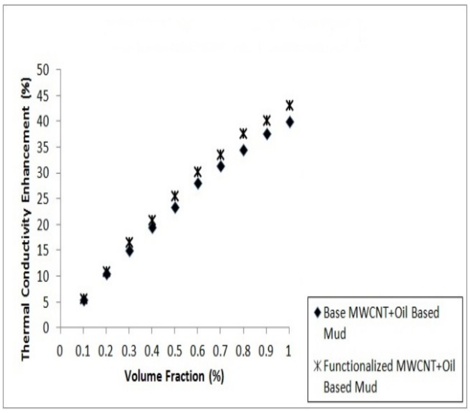

Figure 3: Thermal conductivity enhancement in OBM vs. MWCNT volume fraction

Time Effect

The variation in the thermal conductivity of samples with time was investigated for different types of MWCNT-oil-based drilling muds formulated and the results are presented in Figure 4. The tests were conducted on unfunctionalized as well as functionalized samples (with 1 vol.% MWCNT) at ambient temperature (25°C) and at time intervals of 1, 10, 25, 50, 75, and 100 hrs. after sample preparation.

It can be seen that the thermal conductivity of all suspensions decreases with time; however, the various dispersion scenarios show different reduction rates. The thermal conductivity reduction with time indicates that the MWCNTs are agglomerated and precipitated gradually by time. The profile clearly shows that the reduction rate for the MWCNT unfunctionalized system surpasses the functionalized case, within the first 10 hrs of sample preparation. Such declining trend seems to level-off and a roughly similar limit is reached (in both cases) as the time elapses. The converged limit of thermal conductivity reduction, after 100 hours of sample preparation, was measured at 9.79% and 9.73% for the unfunctionalized and functionalized systems respectively.

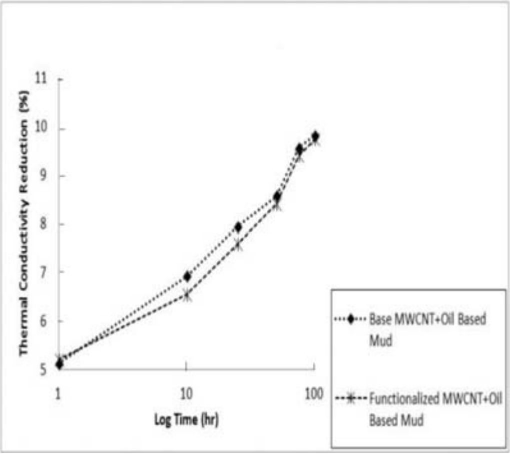

Figure 4: Thermal conductivity reduction vs. logarithm of time for MWCNT-oil-based mud.

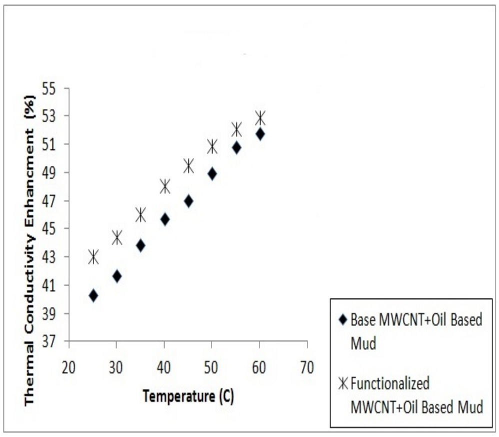

Figure 5: Thermal conductivity enhancement of MWCNT-oil-based mud (with 1 vol. % MWCNT) versus temperature.

Temperature Effect

Figure 5 presents the experimental results for the thermal conductivity enhancement of MWCNT-oil-based muds (with 1 vol.% MWCNT) versus temperature. Generally, the thermal conductivity of all MWCNT-formulated oil-based drilling muds increases with temperature, irrespective of the MWCNT condition in the sample (i.e. unfunctionalized/functionalized).

The temperature region over which the experiments were conducted was between 25-60°C. A nearly linear dependency of thermal conductivity enhancement on temperature was observed in the case of unfunctionalized MWCNT sample. The analysis unveils a reduction in the rate of thermal conductivity enhancement for the functionalized MWCNT case as the temperature is increased above 50°C. This may be interpreted in terms of the dissociation of the functional groups attached to the functionalized MWCNT due to temperature increase and the resultant system instability, which should reasonably cause deterioration in the MWCNT dispersion quality. For the MWCNT-oil-based samples formulated, and at a temperature of 60°C, the percentages of increase in the thermal conductivity were measured at 51.8% and 52.9% for unfunctionalized and functionalized MWCNT samples respectively.

Effect of MWCNTs on the Rheological Properties of Oil-based Mud

For the sake of rheological analysis, major mud properties which are used prevalently as base for designing proper drilling fluid in industry, including mud viscosity, yield point, high pressure high temperature filtration, and spurt loss are investigated. The results are obtained as follows:

Viscosity and Yield Point Effect

The mud properties tests were conducted in accordance with the API standards (American Petroleum Institute, 2003). Figure 6 shows Fann VG meter data on the base of Bingham plastic model for the conventional oil-based mud and those of MWCNT-formulated oil-based drilling fluids (with 1 vol.% unfunctionalized MWCNTs). Table 2 lists our experimental results for the oil-based mud rheological properties.

It is obvious that adding functionalized MWCNTs to oil-based mud increases the shear stress and this enhancement is promoted by increasing shear rate. This phenomenon could be explained in terms of increased dispersion of MWCNTs at high shear rates (i.e. 600 rpm). The yield point (Y.P.) comparison between the conventional and the MWCNT-formulated oil-based muds shows a significant increase.

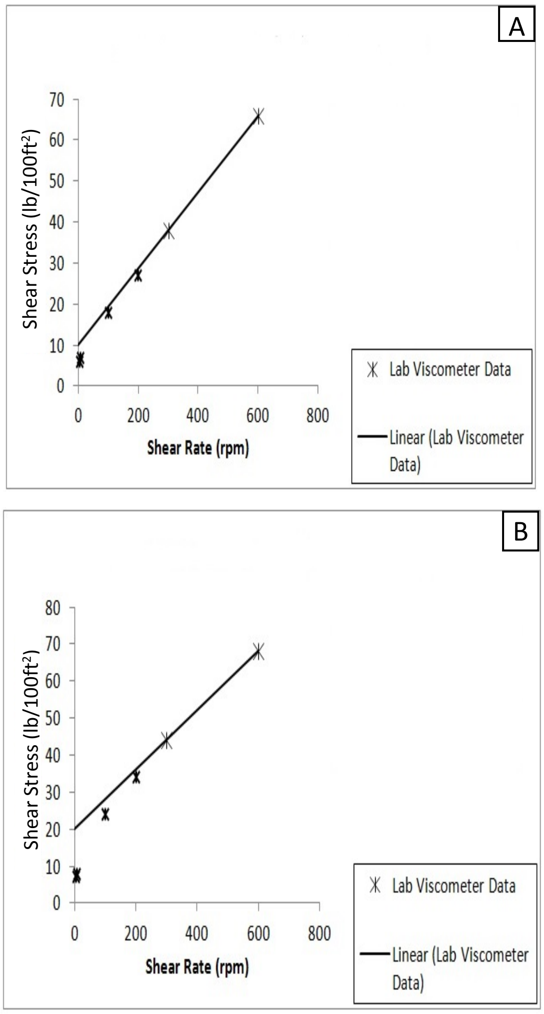

Figure 6: Shear stress versus shear rate for conventional oil-based mud (A), and MWCNT-oil-based mud (B).

Table 2: Rheological properties results for oil-based drilling fluids.

Rheological Factor	Conventional (Base) Oil-based Mud	MWCNT oil-based Mud
Plastic Viscosity (cP)	28	24
Yield Point ($lb_f/100ft^2$)	10	20
Gel Strength 10 Sec ($lb_f/100ft^2$)	7	8
Gel Strength 10 min ($lb_f/100ft^2$)	8	12

The MWCNT-oil-based sample also has increased gel strength (compared to the base fluid), which should enhance its capability for sedimentation inhibition in case of circulation lost.

Nevertheless, such increased value of gel strength should be carefully engineered (by choosing the proper MWCNT volume fraction) to avoid damaging the pumping system during drilling operations.

API Filtration Test

Owing to high viscosity value of the oil-based mud considered (49 cP), and to further mimic the actual wellbore conditions, the filtration properties of the samples were determined using HTHP apparatus. The filtration experiments were conducted at 280°C and 500 psi.

Figure 7 illustrates the HTHP filtration test results. Moreover, the HTHP filtration test parameters for the oil-based muds are listed in Table 3.

Table 3: HTHP filtration test parameters for the oil-based muds.

Parameters	Base Oil-based Mud	MWCNT Oil-based Mud	Reduction (%)
$V_{30\ min}$ (cc)	3.6	3	16.67
Spurt Loss (cc)	0.62	0.62	0

The amount of filtrate for base oil-based mud after 30 min, which is in accordance with the API filtration test, was 3.6 (cc), while this parameter was 3 (cc) for MWCNT-oil-based mud (with 1 vol.% MWCNT). In other words, the addition of 1 vol.% of MWCNT reduces the filtrate volume by as much as 16.67%. This reduction should cause further ease during the drilling operation.

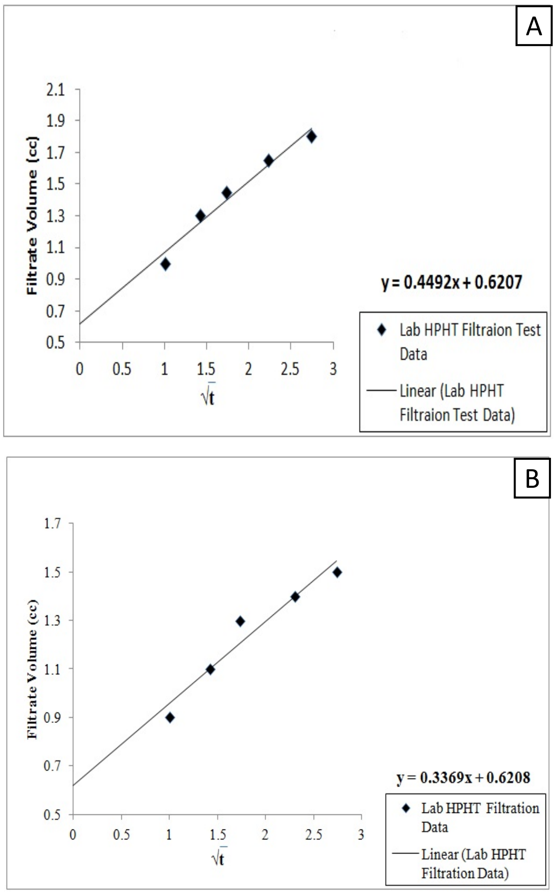

Figure 7: Filtrate volume versus square-root of time for base oil-based mud (A) and MWCNT-oil-based mud (B) in HTHP conditions.

Annular Viscosity for a Case Study

In order to extend our investigation to an industrial case study, we tested the performance of MWCNT-oil-based mud during the actual drilling operations in an oilfield in the southwest of Iran. The profile of the well and casing depth are shown in Figure 8. Our aim was to analyze the performance of the MWCNT-oil-based mud for cutting removal from the annular portion of the well by investigating annular viscosity for an industrial case.

In general, lifting capacity of the mud will increase when the annular viscosity increases. Therefore, we examined such an increment by adding 1 vol.% of unfunctionalized MWCNTs to the base oil-based mud, which was used for drilling the well and determined annular viscosity for each section of the wellbore.

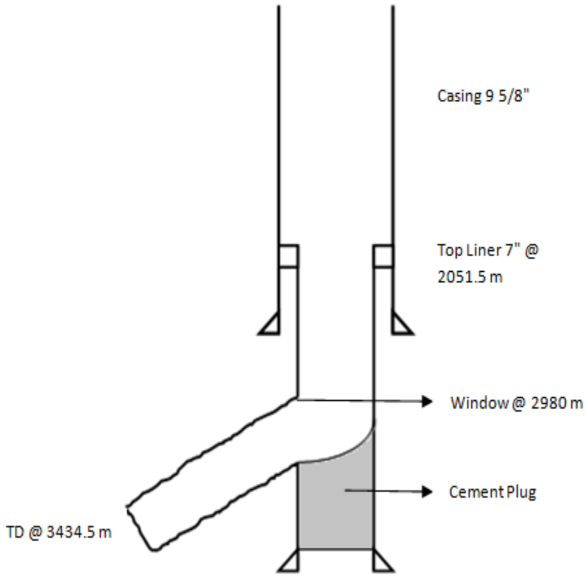

Figure 8: The profile of the well and casing depth for the well in the case study in an Iranian oilfield.

The results of annular viscosity in the presence and absence of unfunctionalized MWCNT's in the mud are presented in Figure 9. The results indicate that the annular viscosity slightly increases by the addition of unfunctionalized MWCNTs. The percentage of the increase in annular viscosity for each section of the well bore was determined against depth. The annular viscosity enhancement generally increases by depth. Moreover, it can be inferred that the maximum percentage increase in the annular viscosity (by applying MWCNT-oil-based mud) has occurred near the drilling bit. Such induced properties may improve the mud`s cutting-lifting capacity and hole cleaning where the load of cutting is high. This feature may reduce the risk of pipe sticking and decrease torque and drag during drilling operations. In this case study, the pressure drop in the annular section of the wellbore was determined to increase from 86.2 (psi) (for the case of base oil-based mud) to 99.1 (psi) (for the case of unfunctionalized MWCNT-oil-based mud) with 1 vol.% MWCNT.

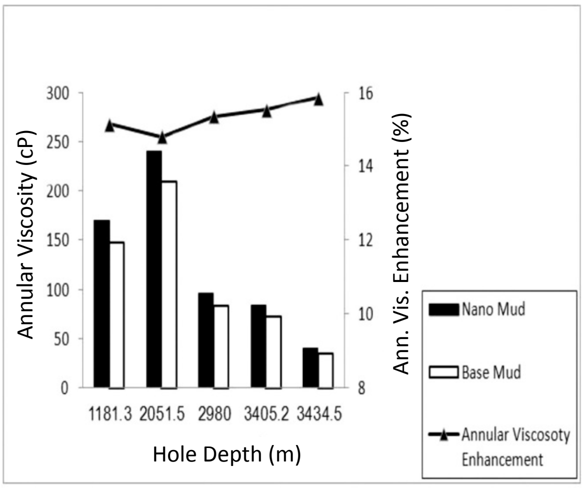

Figure 9: The percentage increase in annular velocity and the annular viscosity results for the base oil-based mud and MWCNT-oil-based mud (with 1 vol.% of unfunctionalized MWCNT) versus depth in the well considered in our case study.

CONCLUSIONS

The introduction of MWCNTs to a (base) oil-based system results in favorable changes in the rheological as well as thermal properties of the system and should pose great industrial promise.

The thermal conductivity of MWCNT-formulated water-based drilling fluid increases nonlinearly with the volume fraction of MWCNTs. The increase rate of the functionalized-MWCNT system seems to surpass the unfunctionalized counterpart, especially in MWCNT volume fractions above 0.4%. Improvements as much as 40.3% and 43.05% in thermal conductivity were measured (with 1 vol.% MWCNT) for unfunctionalized and functionalized systems respectively.

The rate of reduction in thermal conductivity in the unfunctionalized-MWCNT system was higher than the functionalized system within the first few hours of sample preparation, but eventually an identical rate limit (~9.7%) was detected, as the time elapses to 100 hrs. The impact of temperature increase on the thermal conductivity enhancement of MWCNT-oil-based mud experiences a reduction in rate as the temperature reaches 50°C. This phenomenon can be interpreted in terms of the dissociation of the functional groups attached to the functionalized MWCNT due to temperature increase, and the resultant system instability, which should reasonably cause deterioration in the MWCNT dispersion quality. For the MWCNT-oil-based samples formulated, and at a temperature of 60°C, the percentages of increase in the thermal conductivity were measured at 51.8% and 52.9% for unfunctionalized and functionalized MWCNT samples respectively.

The rheological properties results for the MWCNT-oil-based mud exhibit a similar (improvement) trend by reducing annular viscosity and increasing yield point and gel strength. The high-temperature high-pressure (HTHP) filtration tests conducted at 280°F and 500 psi show a 16.67% reduction for the filtrate amount in case of MWCNT-oil-based mud (with 1 vol.% MWCNT). This feature may reduce the risk of pipe sticking and decrease torque and drag during drilling operation.

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