

An Improvement in Thermal and Rheological Properties of Water-based Drilling Fluids Using Multiwall Carbon Nanotube (MWCNT)

M. Sedaghatzadeh¹, A. A. Khodadadi^{2*}, and M. R. Tahmasebi Birgani³

¹Petroleum University of Technology, Ahwaz, Iran

²Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

³National Iranian Drilling Company, Ahwaz, Khuzestan, Iran

Abstract

Designing drilling fluids for drilling in deep gas reservoirs and geothermal wells is a major challenge. Cooling drilling fluids and preparing stable mud with high thermal conductivity are of great concern. Drilling nanofluids, i.e. a low fraction of carbon nanotube (CNT) well dispersed in mud, may enhance the mixture thermal conductivity compared to the base fluids. Thus, they are potentially useful for advanced designing high temperature and high pressure (HTHP) drilling fluids. In the present study, the impacts of CNT volume fraction, ball milling time, functionalization, temperature, and dispersion quality (by means of scanning electron microscopy, SEM) on the thermal and rheological properties of water-based mud are experimentally investigated. The thermal conductivities of the nano-based drilling fluid are measured with a transient hot wire method. The experimental results show that the thermal conductivity of the water-based drilling fluid is enhanced by 23.2% in the presence of 1 vol% functionalized CNT at room temperature; it increases by 31.8% by raising the mud temperature to 50 °C. Furthermore, significant improvements are seen in the rheological properties—such as yield point, filtration properties, and annular viscosity—of the CNT-modified drilling fluid compared to the base mud, which pushes forward their future development.

Keywords: Carbon Nanotube, Thermal Conductivity, Water-based Fluid, Mud Viscosity

1. Introduction

Drilling fluids, commonly referred to as drilling mud, are an integral part of drilling oil and gas and geothermal wells. A drilling fluid is typically pumped through the drill string and is subsequently introduced to the bottom of the bore hole as it squirts out from the drill bit nozzles. This action cools and lubricates the drill bit and helps to convey rock debris and drill cuttings from the drilling area to the surface (Bourgoyne A. T. et al., 1991).

A drilling fluid must have the correct heat transfer and fluid flow characteristics to function in an effective manner. Furthermore, it must be environmentally benign. These requirements have been satisfied by both water-based and oil-based fluids. Both contain some forms of bentonite clay as well as a number of other additives. For deep hole and geothermal drilling, the temperature and pressure can be prohibitively high, and the heat transfer demands on the drilling fluid may seem impossible to be met. It is essential that the fluid thermal properties are significantly enhanced.

* Corresponding Author:
Email: khodadad@ut.ac.ir

Recent improvements in nanotechnology made it possible to produce solid particles with diameters smaller than 100 nm. As a result, an innovative idea of preparing liquid suspensions by dispersing these nanoparticles instead of millimeter- or micrometer-sized particles in a base fluid and utilizing them for heat transfer enhancement was proposed (Liu M. S. et al, 2005; Kleinstreuer C. et al., 2011; Choi S. U. S. et al., 2001).

The addition of nanoparticles improves the rheological, mechanical, and thermal properties of the fluid. The suspension of nanosized particles may also enhance the fluid stability and lessen the sedimentation and clogging of small passages (Karthikeyan N. R. et al., 2008). It is also shown that by using a proper dispersion method, it is possible to obtain stable suspensions.

This study is concerned with preparing nanofluids by dispersing MWCNT's in water-based mud and studies their potential use as heat transfer fluids. The motivations behind the current study are as follows. Firstly, there is limited information about the effect of preparation conditions on the thermal performance of MWCNT's used in water-based fluids. Secondly, limited experimental data are currently available for using MWCNT's in drilling mud, particularly on the viscosity of drilling fluids.

In this study, an effort has been made to consider the influence of volume fraction, ball milling, temperature, and time on conventional water-based mud and its rheological properties so as to adopt an approach to the study of drilling nanofluids.

2. Experimental procedures and materials

2.1. Materials

Deionized water (DW) and bentonite, which is also called conventional water-based mud, as the base fluid along with four kinds of MWCNT's were used to prepare water-based mud. The MWCNT's were purchased from Neutrino Co. (Tehran, Iran). The MWCNT's were produced by a chemical vapor deposition method. A typical scanning electronic microscopy (SEM) micrograph of the MWCNT's is shown in Figure 1.

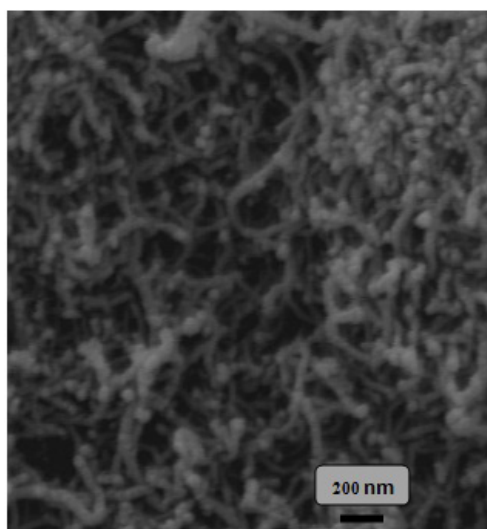


Figure 1

A typical SEM micrograph of MWCNT's

The average diameter and length of these MWCNT's are about 15 nm and 20 μm respectively. The purity and specific surface area of the MWCNT's are higher than 95% 200 $\text{m}^2.\text{gr}^{-1}$ respectively.

2.2. Preparation procedure

1. Adding 17 gr. bentonite to an equivalent bbl of a mud (350 cc) to prepare a 17 lb/bbl water-based fluid;
2. Mixing the mud at least for 15 min to prepare a unique fluid;
3. Adding various amounts of pure (without any treatment), ball milled, functionalized, and functionalized and ball milled MWCNT's as an additive to the fluid prepared to make Sample 1, Sample 2, Sample 3 and Sample 4 respectively;
4. Mixing all the samples produced at 6000 rpm for 5 min.

MWCNT's are usually hydrophobic, thus they are not readily dispersed in water. We introduced hydrophilic functional groups to the surface of the nanotubes by acid treatment. Nitric acid (69%) was used to modify the surface of the MWCNT's. In a typical treatment of the present work, one gram of the MWCNT's and 40 ml nitric acid were boiled and refluxed together for 4 hrs. Then, the sample was diluted by deionized water, filtered, and rinsed repeatedly until the sample showed no acidity. The cleaned MWCNT's were collected and dried in an oven for 12 hrs to remove the attached water. We also milled the MWCNT's for 12 hrs in those samples which required ball milling as a mechanical dispersion method in order to investigate the effect of ball milling on the thermal properties of the drilling nanofluid.

The thermal conductivities of these MWCNT-based drilling fluids were measured by the transient hot-wire (THW) method which is one of the most accurate procedures for determining the thermal conductivity of materials. The uncertainty of this measurement is about 2%. The detailed principles and the apparatus setup were described elsewhere (Xie H. et al., 2002).

3. Results and discussion

3.1. Effect of MWCNT's on the thermal conductivity of the water-based mud

a. Volume fraction

Aggregation and precipitation take place for the MWCNT's/DW pair if the MWCNT's are not functionalized. The pure hydrophobic MWCNT's cannot be dispersed into a polar liquid like deionized water. However, because of the existence of bentonite and the gel strength properties of the base fluid, the precipitation of MWCNT's occurs very slowly and the nanofluid is stabler in this regard.

Figure 2 shows the enhancement of thermal conductivity in percentage as a function of volume fraction for the 17 lb/bbl water-based mud at room temperature. It is apparent that the thermal conductivity of the MWCNT-based drilling mud increases nonlinearly by increasing the volume fraction of the MWCNT's. The maximum thermal conductivity enhancement equal to 23.2% at 1 vol% of the MWCNT's belongs to the functionalized and ball milled MWCNT's.

In the case of the functionalized MWCNT's, the thermal conductivity enhancement is significantly more than the pure (simple) and ball milled MWCNT's. This phenomenon is due to introducing hydrophilic functional groups to the surface of the multiwall carbon, which causes the nanotubes to disperse more efficiently in the water-based mud.

This figure also shows that the thermal conductivity enhancement for a typical water-based fluid is linear to some extent for volume fractions lower than 0.4% and ball milling is not very influential in increasing thermal conductivity for these samples. The comparison of the experimental data suggests

that the thermal conductivity of the base fluid, the volume fraction of the MWCNT's, and the dispersion method play a dominant role in the thermal conductivity enhancement in a water-based fluid.

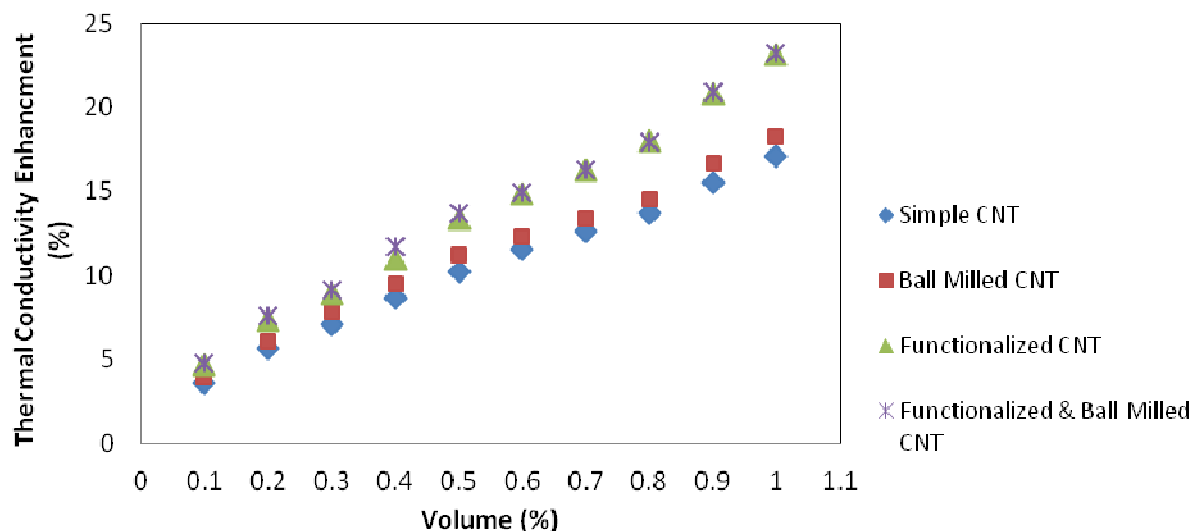


Figure 2

Thermal conductivity enhancement against the volume fraction of the MWCNT's

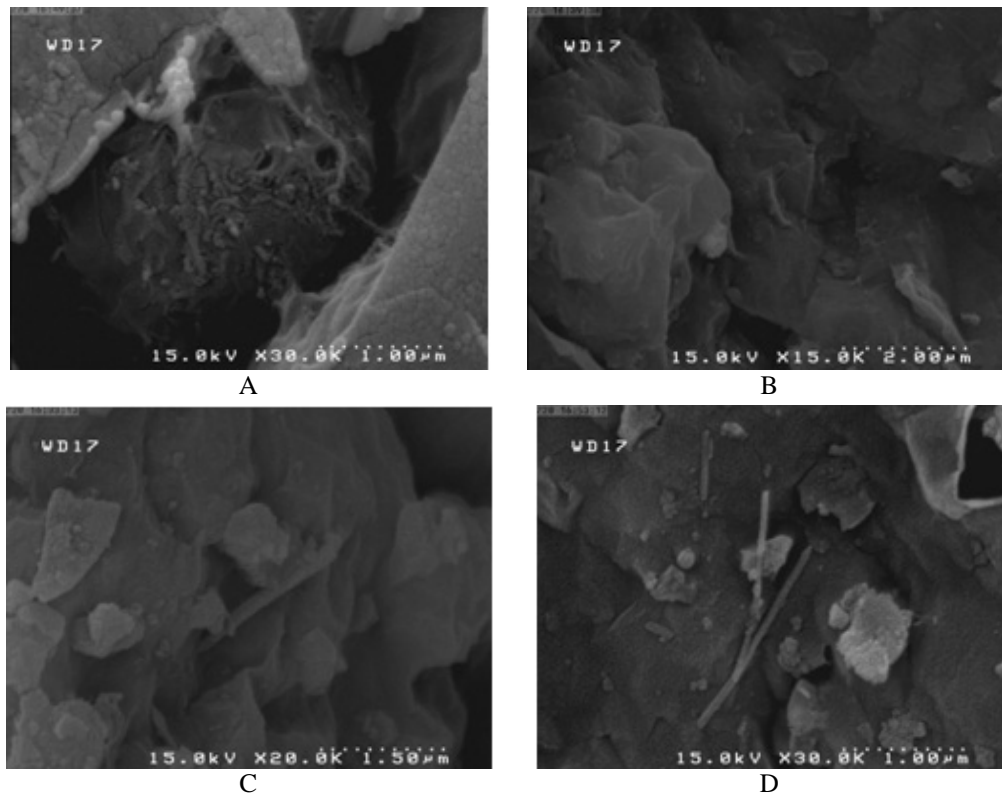
Figure 3 shows the different SEM micrographs of the samples with 1 vol% of the multiwall carbon nanotubes in order to compare the quality of the MWCNT's dispersion in water-based mud.

Due to strong van der Waals attractive forces, nearly all the MWCNT's are in the form of agglomerates with dimensions much larger than the primary particles. According to double-layer theory, this force rises by increasing the ratio of surface area to volume, because the magnitudes of surface charge density increase and as a result promote this attractive force. As shown in Figures 3A and 3B, the degree of agglomeration changes for the ball milled MWCNT's; however, they are not effectively dispersed. By introducing hydrophilic functional groups to the surface of the MWCNT's, they are dispersed more effectively in the water-based mud and it seems that the MWCNT's conduct heat more efficiently by passing through the bentonite layers as it is shown in Figures 3C and 3D.

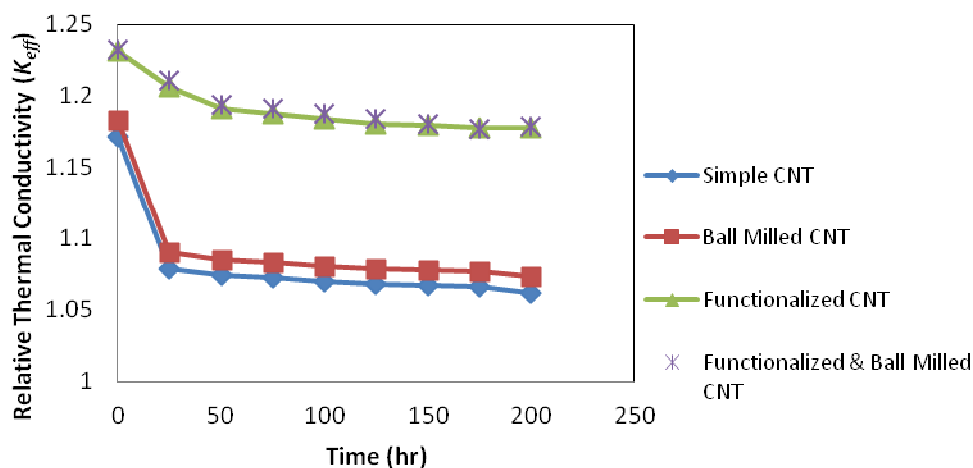
b. Time effect

The variations of the effective (relative) thermal conductivity (K_{eff} , the ratio of the thermal conductivity of the drilling nanofluid to that of the base fluid) of the MWCNT-based drilling mud against time are investigated for the different types of water-based drilling nanofluid and the results are shown in Figure 4. It can be seen that the thermal conductivity of all the suspensions decreases with time; however, the various dispersion methods show different reduction rates.

The thermal conductivity reduction with time indicates that the MWCNT's are agglomerated and precipitated gradually by time. The profile clearly shows that the reduction rate of the water-based drilling nanofluids prepared by the pure and ball milled MWCNT's is faster than that of the samples produced by functionalized MWCNT's. Due to the gel strength properties of the water-based fluid, the reduction in the effective thermal conductivity starts to level off after a while and the declining trend does not continue for a long time.

**Figure 3**

SEM micrographs of different water-based drilling nanofluids with 1 vol% of MWCNT's; A: pure (simple) MWCNT's; B: ball milled MWCNT's; C: functionalized MWCNT's; D: functionalized and ball milled MWCNT's.

**Figure 4**

Effect of time on the effective (relative) thermal conductivity of different water-based drilling nanofluids with 1 vol% of MWCNT's at room temperature

c. Temperature effect

The thermal conductivity enhancement of the nanofluids with 1 vol% of MWCNT's as a function of temperature is also investigated and the results are presented in Figure 5. In general, the thermal

conductivity of all the water-based drilling nanofluids increases as the temperature rises regardless of the dispersion method; but, the variation trends vary for the different cases. For the cases of the pure and ball milled MWCNT's, a nearly linear dependence of thermal conductivity enhancement on temperature is observed and the paths have the least deviation. But, the trends begin to level off in the case of the functionalized MWCNT's. This behavior can be attributed to the destruction and deterioration of the functional groups at high temperatures.

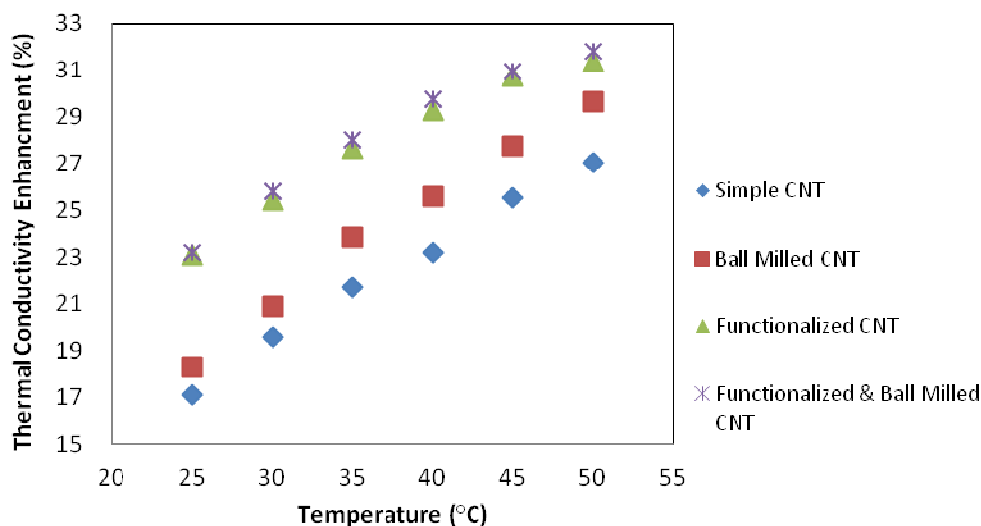


Figure 5

Effect of temperature on the thermal conductivity enhancement of different water-based drilling nanofluids with 1 vol% of MWCNT's

Thermal conductivity enhancement increases to 31.8% for 1 vol% of the functionalized and ball milled MWCNT's at 50 °C. It can be also seen that ball milling has a less significant effect on increasing thermal conductivity; however, it is clear that this effect is amplified by increasing temperature.

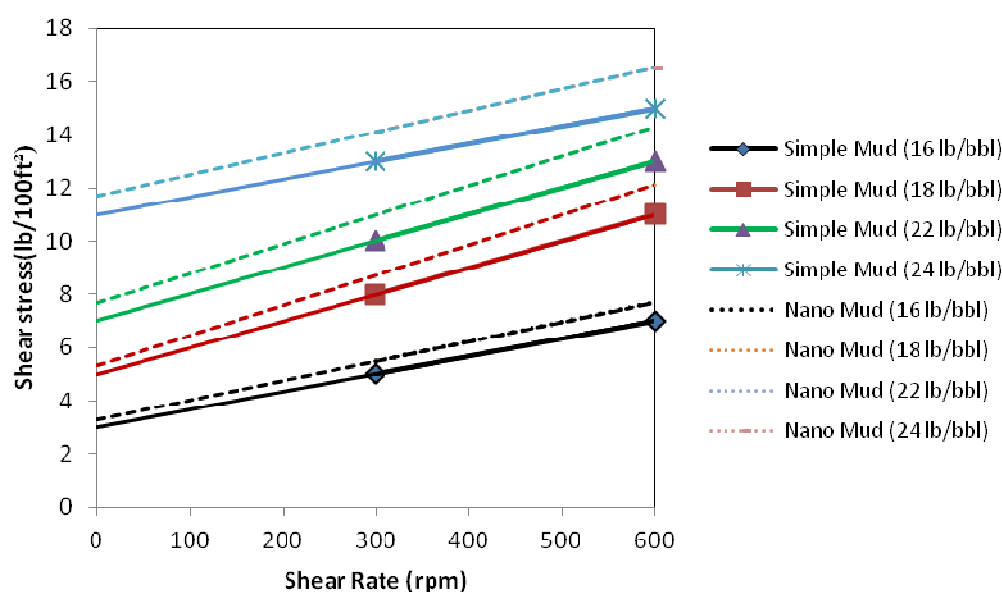
3.2. Effect of MWCNT's on the rheological properties of the water-based mud

a. Viscosity and yield point

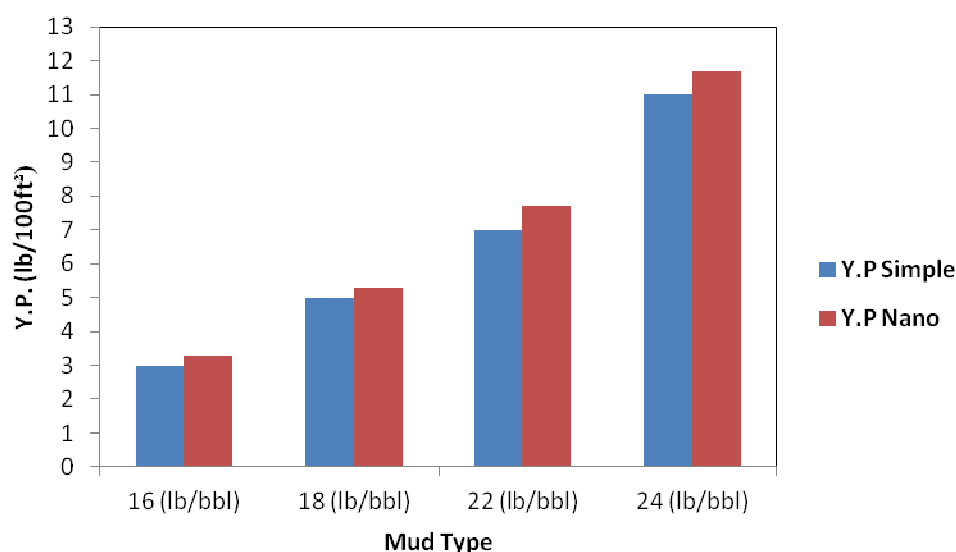
The mud properties were tested in accordance with the American Petroleum Institute (API) standards (American Petroleum Institute). Figure 6 depicts viscosity data (obtained by Fann VG viscosity meter) on the base of Bingham plastic model for different conventional water-based fluids having various amounts of bentonite as well as for those with 1 vol% of the functionalized MWCNT's.

It is obvious that adding the functionalized MWCNT's to the water-based mud increases shear stress; also, shear stress is linearly proportional to shear rate. This phenomenon could be ascribed to the better dispersion of the MWCNT's at high shear rates (i.e. 600 rpm).

The comparison of yield point (Y.P.) of the conventional water-based mud and the MWCNT-modified mud is investigated for (16, 18, 22, and 24) lb/bbl fluids and the results are shown in Figure 7. Generally, the yield points of MWCNT-based drilling fluids are slightly higher than those of the conventional water-based fluids. So, by adding the functionalized MWCNT's to the water-based mud, pressure lost slightly increases, especially in those portions of the well bore and drill string where the flow regime is laminar.

**Figure 6**

Viscometer data of different pure (simple) and MWCNT-modified water-based drilling fluids

**Figure 7**

Comparison of the yield point of the conventional and MWCNT-modified water-based drilling mud

b. API filtration test

The filtration properties of the drilling mud are determined by means of a standard filter press. A filter press consists of a cylindrical mud cell having an inside diameter of 3.0 in and a height of at least 2.5 in. The filtration area is then 45 cm². Below the support is a drain tube for discharging the filtrate into a graduated cylinder.

The effect of the functionalized MWCNT's in amounts of filtrate is also studied. The results of this study are shown in Figure 8. The conventional water-based mud (simple mud)—prepared by adding 24 gr. bentonite to 350 cc deionized water to form a 24 lb/bbl drilling fluid—is used as the reference.

The amount of the filtrate of the conventional mud after 30 min (as defined by API filtration test method) was 28.4 cc; however, this value changed to 26.3 cc after adding 1 vol% of the functionalized MWCNT's to the mud. This means that the amount of the filtrate decreases by 7.4% after adding MWCNT's.

It should also be mentioned that the amount of spurt lost when initiating the test decreases from 0.57 cc to 0.44 cc, which emphasizes that the mud cake created by MWCNT-based drilling mud is partly more uniform than that of the conventional mud.

c. Annular viscosity for a real case

Herein, an effort has been made to investigate the annular viscosity of a well (called Well A) of Ragsefid oil field located in the southwest of Iran. The profile of the well and casing depth are shown in Figure A in Appendix A.

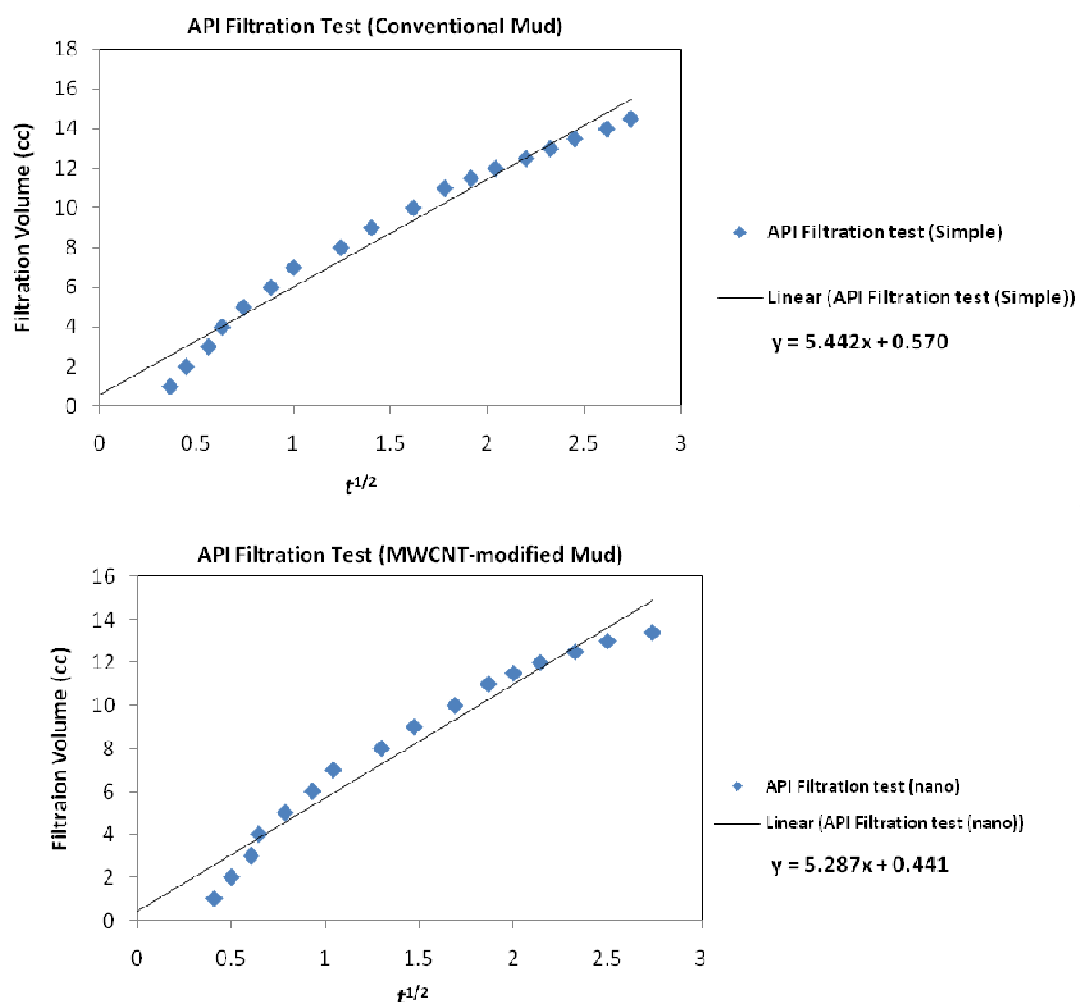


Figure 8

API filtration test results of the conventional (Simple) and MWCNT-modified (Nano, containing 1 vol% of the functionalized MWCNT's) water-based drilling mud

It is the aim of this section to analyze the performance of the MWCNT-modified water-based drilling mud in cutting the removal from the annular portion of a real well (Well A) by investigating the

annular viscosity. In general, the lifting capacity of the mud increases when the annular viscosity rises. Hence, this increment was examined by adding 1 vol% of the functionalized MWCNT's to the water-based mud used for drilling Well A and the annular viscosity was measured for each section of the well bore. The mud specifications are as follows:

Table 1
Specifications of the mud used for drilling Well A in Ragsefid oil field

Mud Specification	Quantity
Mud Type	Water-based mud
Mud Weight (pcf)	66
Viscosity (cP)	44
PV/YP [cP/(100lb/ft ²)]	17/9
Solid (%)	14
GPM	200

Figure 9 shows the results of annular viscosity, for the conventional mud and functionalized MWCNT-modified one. It is clear that annular viscosity slightly increases by adding the functionalized MWCNT's. The percentage the increase in annular viscosity for each section of the well bore is given on the figure.

It is important to mention that annular viscosity enhancement increases by depth. For example, the enhancement of annular viscosity at the top hole is 6%, while it rises to 12.2% at the bottom of the well. This may improve the cutting lifting capacity of the mud and hole cleaning where the load of the cutting is high.

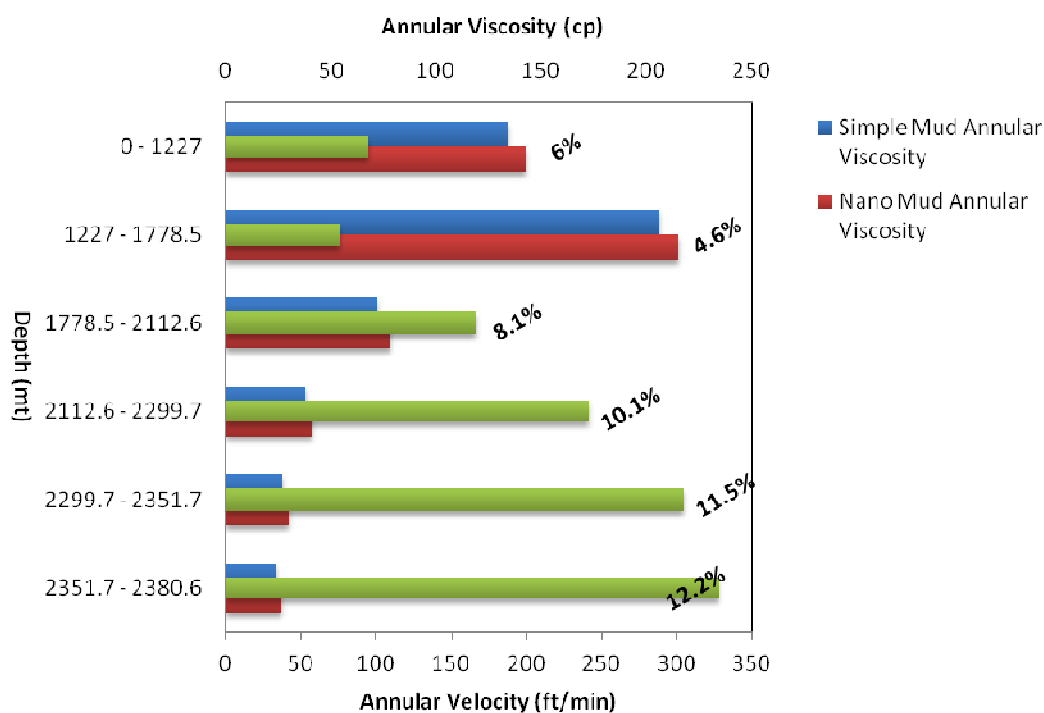


Figure 9

Comparison of the annular viscosity and velocity of the conventional and functionalized MWCNT-modified mud used in Well A

4. Conclusions

The addition of MWCNT's to a water-based drilling fluid and the parameters influencing the thermal conductivity of the mud were investigated. In addition, the effect of MWCNT's on the rheological properties of the water-based drilling mud was studied and the modified mud was used in a real case (Well A). On the whole, the following conclusions can be drawn:

1. The thermal conductivity of the water-based drilling fluid increases nonlinearly with the volume fraction of MWCNT's;
2. Among four types of water-based drilling fluids, the functionalized ball milled MWCNT's shows the best results in terms of thermal conductivity enhancement;
3. Ball milling, as a mechanical dispersion method, has the least effect on the enhancement of thermal conductivity;
4. The thermal conductivity of all the samples as a function of time decreases initially and then, due to the gel strength of the water-based drilling fluid, levels off. However, this reduction varies for different dispersion methods. Pure (simple) and ball milled MWCNT's show the highest reduction in thermal conductivity due to agglomeration;
5. Increasing temperature also enhances thermal conductivity. The thermal conductivity of the MWCNT-modified water-based drilling mud enhances linearly with temperature for the samples containing pure (simple) and ball milled MWCNT's; nevertheless, this enhancement levels off at high temperatures for the samples having the functionalized MWCNT's;
6. Adding the functionalized MWCNT's increases the plastic viscosity and yield point of the water-based drilling mud. Nonetheless, it reduces the amount of filtrate and spurt lost. Therefore, the mud cake created is more uniform when MWCNT's are used. This feature may reduce the risk of pipe sticking and decrease torque and drag during drilling operations;
7. This study confirms that using MWCNT's could enhance annular viscosity and that the annular viscosity enhancement increases by increasing depth along the well bore; also, this could improve hole cleaning and lifting capacity in comparison with conventional water-based drilling fluids.

Acknowledgment

The authors would like to thank National Iranian Drilling Company (NIDC) for supporting this work.

Nomenclature

MWCNT's	: Multi wall carbon nano tubes
CNT	: Carbon Nano Tube
GPM	: Gallon per minute
PV	: Plastic viscosity
YP	: Yield point
DW	: Deionizer water
SEM	: Scanning electronic microscope

References

American Petroleum Institute, Recommended Practice for Field Testing Water-Based Drilling Fluids, 2009.

- Bourgoyne, A. T., Millheim, K., Chenevert, M. E., Young, F. S., Applied Drilling Engineering, SPE textbook, Chapter 2, 1991.
- Choi, S. U. S., Zhang, Z. G., Yu, W., Lockwood, F. E., Grulke, E. A., Anomalous Thermal Conductivity Enhancement in Nanotube Suspensions, J. Applied Physics Letter, V. 79, No. 14, p. 2252-2254, 2001.
- Karthikeyan, N. R., Philip, J., Raj, B., Effect of Clustering on the Thermal Conductivity of Nanofluids, J. Materials Chemistry and Physics, V. 109, p. 50-55, 2008.
- Kleinstreuer, C., Feng, Y., Experimental and Theoretical Studies of Nanofluid Thermal Conductivity Enhancement: A Review, J. Nanoscale Research Letters, V. 6, p. 229-241, 2011.
- Liu, M. S., Lin, M.C., Huong, I. T., Wang, C. C., Enhancement of Thermal Conductivity with Carbon Nanotubes for Nanofluids, J. Heat and Mass Transfer, V. 32, p. 1202-1210, 2005.
- Xie, H., Wang, J., Xi, T., Liu, Y., Int. J. Thermophys, V. 23, p. 571-580, 2002.

Appendix A

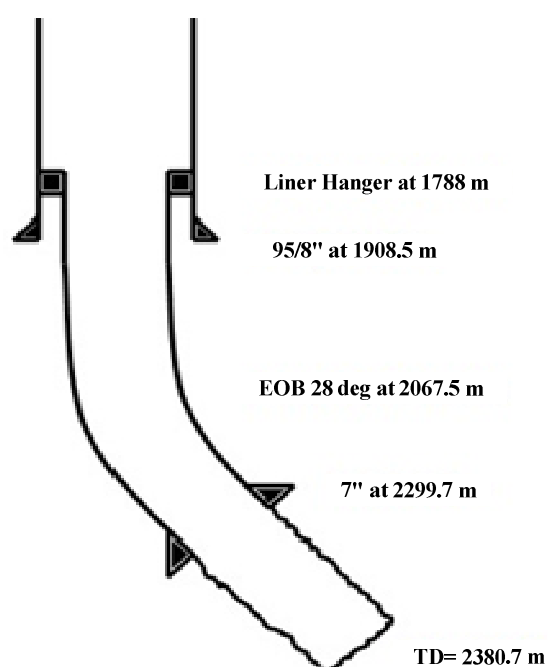


Figure A

Well A profile located in Ragsefid oil field in the southwest of Iran