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Graphene nanoplatelets as high-performance filtration control material in water-based drilling fluids

Syahrir Ridha[1], Arif Ibrahim[1], Radzi Shahari[1], Syarizal Fonna[2]
[1] Petroleum Engineering Department,
Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610,
Perak Darul Ridzuan, Malaysia.
[2] Mechanical Engineering Department, Universitas Syiah Kuala,
Banda Aceh, 23111, Indonesia.

E-mail: mohamad.arif_g03640@utp.edu.my

Abstract. The main objective of this work is to evaluate the effectiveness of graphene nanoplatelets (GNP) as filtration control materials in water based drilling fluids. Three (3) general samples of water based drilling fluids were prepared including basic potassium chloride (KCl) drilling fluids, nanosilica (NS) drilling fluids and GNP drilling fluids. Several concentrations of NS and GNP were dispersed in controlled formulations of water based drilling fluids. Standard API filtration tests were carried out for comparison purposes as well as High Temperature High Pressure (HTHP) filtration tests at 150 °F (~66 °C), 250 °F (~121 °C) and 350 °F (~177 °C) at a fixed 500 (~3.45MPa) psi to study the filtration trend as a function of temperature. Mud cake samples from several tests were selectively chosen and analyzed under Field Emission Scanning Electron Microscope (FESEM) for its morphology. Results from this work show that nanoparticle concentrations play a factor in filtration ability of colloid materials in water based drilling fluids when studied at elevated temperature. Low temperature filtration, however, shows only small differences in volume in all the drilling fluid samples. 0.1 ppb concentrations of GNP reduced the fluid loss of 350 °F by 4.6 mL as compared to the similar concentration of NS drilling fluids.

1. Introduction

Drilling fluids are a mixture of solids, liquids and chemicals with the liquid being the continuous phase. During conventional overbalance drilling, hydrostatic pressure applied by drilling fluid is higher than the formation pore pressure as a primary well control mechanism. Thus, there is a flow of liquid from the wellbore into the formation leaving solid particles suspended in the fluid initially, on the wall of the wellbore forming a layer of the impermeable zone known as filter cake [1]. At the early stage of filtration also known as spurt loss, both large and small particles will be deposited on the face of the wellbore; because the drag force is driving the particles to the cake surface is high. Afterwards, only smaller and smaller particles are deposited [2]. The amount of fluid loss which is directly proportional to the cake growth rate gradually decreases until the cake becomes very impermeable at which no particles small enough to be deposited on the smallest pores on the cake are available in the suspension. Thus, theoretically having a smaller size of particles in drilling fluid is desirable to form a more impermeable filter cake.

The applications of nanomaterials in the petroleum industry have always been thought since the emergence of nanotechnology with the invention of scanning tunneling microscope in 1981 [3] and the discovery of fullerene in 1985 [4]. The beginning of the research on nanomaterials in drilling fluids however is largely unknown in literature. The interest is mainly due to its size, these materials have access to the smallest pores and act as sealing agent in any lithology types [5]. Up to now, several laboratory applications of nanomaterials in drilling fluids have been reported in literature such as the applications in filtration control [6-11], mitigation of pipe sticking [10], torque and drag [9] and shale stabilization [11, 12].

Sensoy et al. [11] studied the potential of using nanoparticles to plug the pore throat of shales and reduce its permeability. The idea of this study come from the result of their previous works about the average pore throat sizes of shales in which they found it to be around 10 to 30 nanometers and is smaller than the conventional colloid materials in drilling fluids. Sensoy et al. [11] used 20nm silicon dioxide (NS) and found that with the use of silicon dioxide in water based drilling fluids, the permeability of shales was reduced by a factor of 5 to 50 [11]. In 2011, Javeri et al. [10] also used NS in the water based drilling fluid and tested for its filtration properties at 80°F and 100 psi differential pressure though the amount of the NS used was reported. The results show that with the addition of NS in the drilling fluid, the filter cake thickness was reduced by 34%. However, no filtrate volume was reported from this study [10]. In 2015, Taraghikhah et al. [12] and Wahid et al. [13], further the study of NS in drilling fluids. Though Taraghikhah et al. continue to test it on water based fluids with a slightly different modification for shale stabilization property, the latter tested the filtration properties of NS in the synthetic based drilling fluid. The results of both researches show that the conventional drilling fluids system are improved with the addition of NS.

Although discovered in 2004 by Andre K. Geim and Konstantin Novoselov [14], application or invention research on graphene have only started recently after its fundamental properties studies have been proven to exceed most materials in the world in every aspect. Graphene is the world's first two-dimensional (2D) crystalline material has a theoretical thickness of 0.34 nm [15, 16]. Graphene consists of a single layer of carbon atoms in the sp^2 hybridization state with each atom being covalently bonded to three other carbon atoms in a hexagonal lattice with a carbon to carbon distance of 0.142nm [14, 17].

Two reports from early 2016 by Aftab et al. [18] and Ismail et al. [19], presented the comparison in rheological properties, lubricity, and filtration properties of several nanomaterials at Low Temperature Low Pressure (LTLP) conditions. Aftab et al. used the same concentration on multiwalled carbon nanotubes (MWCNT), NS and GNP in water based drilling fluids while Ismail et al. studies the effect of different concentration of MWCNT, NS and Glass Beads (GB) in water based drilling fluids as well. While both kinds of literature show improvement in the performance of drilling fluids with nanomaterials, the highlight here is the performance of GNP which is significantly better than both MWCNT and NS in every aspect [18, 19]. Both studies however were carried out under LTLP conditions which would yield unrealistic scenarios to be extrapolated to field conditions.

In this study, experimental works have been conducted to study the effectiveness of GNP as filtration control materials under different temperatures, compared with NS and conventional KCl drilling fluid systems. Filter cake produced from filtration tests were analyzed under FESEM for its morphology.

2. Materials and Method

2.1. Materials

Conventional drilling fluid additives such as viscosifiers, alkalinity control and weighting materials were all procured from Scomi Oiltools Sdn. Bhd. Nanosilica (7 – 24 nm, purity >99.8 wt. %) was procured from PlasmaChem GmbH. Graphene Nanoplatelets-SigmaAldrich (diameter 40 – 70 nm, length 2 – 5 nm, purity > 95 wt. %) procured from Advance Altimas (M) Sdn. Bhd. was used as received. Surfactants used to functionalize GNP were procured from Avantis Laboratory Sdn. Bhd. and was used as received.

2.2. *Functionalization of GNP*

500 ppm surfactants were prepared in 500 mL of distilled water in an Erlenmeyer flask. A fixed amount of GNP was then dispersed in the solutions at a concentration of 0.1 mg / mL. The resultant solution was then ultrasonicated in an ultrasonic bath for 30 minutes to get surfactant-coated GNP.

2.3. *Water based drilling fluids formulations and preparations*

350 mL of water based drilling fluids were prepared by mixing distilled water, potassium chloride, xanthan gum, polyanionic cellulose, caustic soda and barite. Each formulation was designed to achieve 11.5 pounds per gallon (ppg). Table 1 shows the approximate drilling fluid formulation with mixing time and order of each additive. Each formulation may have small differences in the amount of distilled water and barite to achieve a consistent 11.5 ppg due to the difference in nanomaterials concentrations.

Table 1. Formulations of drilling fluids

Materials	Basic WBM	WBM + NS	WBM + GNP	Mixing time	Mixing order
Distilled water, (ml)	300	300	300	-	1
Potassium Chloride, (ppb)[a]	20.0	20.0	20.0	2	2
Xanthan gum, (ppb)	1.0	1.0	1.0	5	3
Polyanionic cellulose, (ppb)	3.0	3.0	3.0	5	4
Caustic soda, (ppb)	0.1	0.1	0.1	5	5
Barite, (ppb)	160	160	160	30	6
NS, (ppb)		0.01,0.05,0.1, 0.2,0.3		15	7
GNP, (ppb)			0.01,0.05,0.1, 0.2,0.3	15	7

[a] ppb – pounds per barrel

2.4. *Filtration Tests*

2.4.1. Standard API filtration test. Standard API filtration tests followed API RP 13B-1 Recommended Practice for Field Testing Water-Based Drilling Fluids. Tests were conducted using a OFITE standard LPLT API Filter Press and Whatman quantitative filter paper, hardened low-ash grade 50 (estimated pore size 2.7 µm). All filtration loss tests were conducted at 25 °C. In a standard run, 100 mL of drilling fluids were placed in the apparatus with 100 ± 1.0 psi differential pressure supplied across a filter paper. Filtrate volume was then measured every one minute for 30 minutes. The filter paper was then removed, lightly washed, and set out at room temperature for 24 hours to allow for the water to evaporate from the filter cake. After the filter cake has dried up, its thickness was determined using a Vernier caliper to the nearest millimeter.

2.4.2. HTHP filtration tests. HTHP filtration tests followed API RP 13B-1 Recommended Practice for Field Testing Water-Based Drilling Fluids. Tests were conducted using OFITE 4-unit HTHP Filter Press with Regulators and Temperature Controller with Whatman quantitative filter paper, hardened low-ash grade 50 (estimated pore size 2.7 µm). Three (3) different temperatures were studied; 150 °F (~66 °C), 250 °F (~121 °C) and 350 °F (~177 °C) for each formulation of drilling fluids to study the filtration trend as a function of temperature. In a standard run, 100 mL of drilling fluids were placed in the apparatus with 500 ± 1.0 psi differential pressure between top and minimum recommended back pressure supplied using nitrogen gas across a filter paper. Filtrate volume was then measured every one minute for 30 minutes. After the tests, the cell was allowed to cool a minimum of one hour before releasing the pressure inside the cell. The filter paper was then removed, lightly washed, and set out at room temperature for 24 hours to allow for the water to evaporate from the filter cake. After the filter cake has dried up, its thickness was determined using a Vernier caliper to the nearest millimeter.

2.5. Microstructure analysis

Several cakes were chosen and the top solids were removed for the plugged particles to be studied under Field Emission Scanning Electron Microscope (FESEM). The microstructures were observed using Zeiss Supra 55VP in Universiti Teknologi PETRONAS' Centralized Analytical Laboratory (CAL). After the samples have been dried, a small part of the filter cakes was cut and coated with a thin layer of gold prior to vacuum and observation at an accelerated voltage of 5.00 keV.

3. Results and Discussion

3.1. Fluid Loss

Table 2. Filtration test results of different drilling fluid formulation

Drilling Fluids	API (ml)	HPHT @ 150 °F (ml)	HPHT @ 250 °F (ml)	HPHT @ 350 °F (ml)
WBM	5.1	9.6	15.8	70.0
WBM + 0.01 ppb NS	5.0	9.0	14.8	70.0
WBM + 0.05 ppb NS	4.8	8.6	14.6	70.0
WBM + 0.1 ppb NS	4.7	8.5	14.5	26.6
WBM + 0.2 ppb NS	4.7	8.7	13.4	26.4
WBM + 0.3 ppb NS	4.6	7.6	13.0	22.4
WBM + 0.01 ppb GNP	5.1	8.8	14.6	70.0
WBM + 0.05 ppb GNP	4.8	8.5	12.5	70.0
WBM + 0.1 ppb GNP	4.6	8.4	12.2	22.0
WBM + 0.2 ppb GNP	4.5	7.6	12.0	21.4
WBM + 0.3 ppb GNP	4.4	6.9	11.2	21

Table 2 summarizes the total drilling fluid filtration tests results for (a) API, (b) HTHP, 150 °F, (c) HTHP, 250 °F and (d) 350 °F for each formulation. At 250 °F, similar trends were observed by Aftab et al. [18] for 0.1 ppb concentration of NS and GNP although using a different surfactant and surfactant concentrations.

Looking at the trend, generally fluid loss decreases with increasing amount of both nanomaterials even on the highest concentration used in this study. As can be seen fluid loss deteriorated with increasing temperatures. This deterioration becomes significant especially at HTHP conditions (350 °F). Although there was not much difference in fluid loss between 0.05 ppb and 0.1 ppb of both NS and GNP at 250 °F, the difference is significant at 350 °F suggesting the minimum concentrations of both nanomaterials needed for high temperature conditions is between 0.05 and 0.1 ppb.

The effect of the addition of nanomaterials on the decreasing trend of fluid loss can simply be explained by plugging the small pores on the filter cake created after larger particles have deposited on the surface of the filter paper during spurt loss making the filter cake less permeable after some time. Thus, decreasing the overall total fluid loss.

In addition, the stability of fluid loss at high temperature is also affected by the addition of nanomaterials. This could be explained by understanding colloidal dispersion. The properties of colloidal dispersions are closely related to its surface area to mass ratio. Large colloids are mainly affected by gravitational forces while other forces affect smaller colloids such as van der Waals forces and electrostatic forces. The enormous difference between its surface area and mass is the reason the properties of the surface including the shape is very important for the colloidal solution. The greater the degree of subdivision of a solid body, the greater will be its surface area per unit mass and therefore the greater the influence of the surface are on properties of colloidal dispersions [20]. At static high temperature filtration, nanomaterials may have help in the suspensions of other colloids materials preventing it from sagging thus reducing the overall fluid loss. However, to confirm this, high temperature dynamic filtration need to be carried out to study the cross flow of colloids in the fluid. Although factors such as thermal stability of the nanomaterials itself may also play a factor as seen by the difference in fluid loss volume between NS and GNP. This phenomenon was also observed by Aftab et al. [18].

Although the decreasing trend of fluid loss with increasing nanomaterials may seem beneficial, having excessive nanomaterials may impose detrimental effect; not only on its cost effectiveness but also on drilling induced formation damage. It was observed during filtration tests, the spurt loss fluid is different in color, suggesting that some nanomaterials which is much smaller than the filter cake pore size (~2.7 μm) may have invaded through the filter papers. It is believed at some point, increasing the concentrations of nanomaterials any further will no longer reduce the fluid loss suggesting its optimum concentrations. In this study, the optimum concentrations of nanomaterials have yet to be found.

3.2. Mud Cake Thickness and Sample Characterization

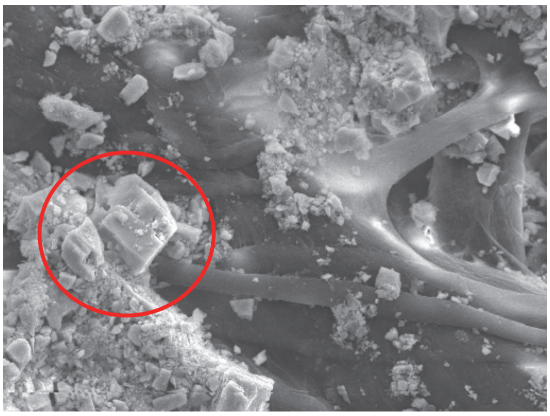

Figure 1. SEM image of NS filter paper after top solids have been removed

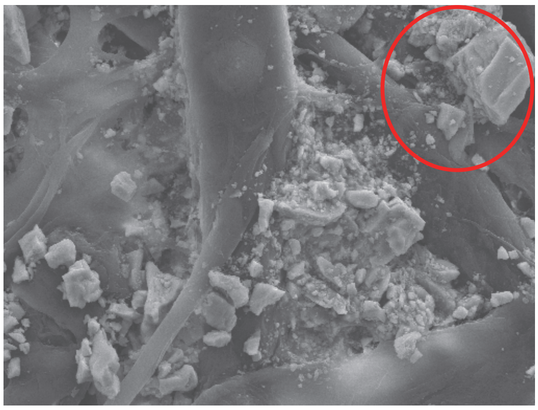

Figure 2. SEM image of GNP filter paper after top solids have been removed

For every test temperatures, the thickness of filter cake remains consistent among all drilling fluid formulations; < 2 mm for API, 4 mm for 150 °F, 6 mm for 250 °F and 9 mm for most 350 °F test temperatures. Figure 1 and Figure 2 shows the SEM image of NS and GNP filter paper after top solids have been removed to study the particles that have been plugged into the filter paper at 5,000 magnification size. From the raw observation and mapping, it was difficult to discern which particle is the nanomaterials itself especially GNP which is made of the same material as the filter paper; carbon. Thus, spectrum processing which studies the concentration of fundamental elements were employed at different pore throats. On average basic WBM filter paper shows 36.27 wt. % of carbon, 0.37 wt. % of silicon while NS filter paper shows only 31.07 wt. % of carbon due to the increase of 0.84 wt. % of silicon. In contrast, GNP filter paper shows a carbon content of 37.93 wt. % and only 0.43 wt. % of silicon. From this, it is evident that nanomaterials do in fact plug the small pore throats of the filter papers.

4. Conclusion

This work was devoted to evaluating the effectiveness of GNP as a filtration control material in water based drilling fluid with NS which has been extensively studied as a benchmark. The results from all sets of tests and concentrations indicate that GNP is an effective filtration control material in water based drilling fluids. This is especially evident at the higher temperature as compared to NS. By adding a small 0.3 ppb of GNP in a similar formulation of basic WBM, the 70 mL spurt loss was slowed down to 21 mL which is 1.4 mL less than similar concentrations of NS for 30 minutes period interval at 350 °F. Even though the minimum concentration of nanomaterials has been discovered for high temperature applications, the optimum concentration in term of cost effectiveness and formation damage due to its small sizes is still under investigation. Therefore, further research with the aim to study its cost effectiveness and formation damage effect should be considered to get a broader understanding of the effectiveness of GNP as a filtration control material.

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