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EFFECT OF NANOPARTICLES ON CLAY STABILITY IN WATER: IMPLICATION FOR WATER BASED DRILLING MUD

Naomi Amoni Ogolo [1]

Mike O. Onyekonwu [1]

[1] Institute of Petroleum Studies, University of Port Harcourt, Rivers State, **Nigeria**
e-mail: amoniogolo@yahoo.com

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ABSTRACT

Clay stability in water is essential in chemical and manufacturing processes. In water based drilling fluids, montmorillonite dispersed in water is commonly used to maintain fluid density that counter-balances pressure effects from formation layers. However, due to gravity, clay particles settlement at the bottom of holes is inevitable especially if operations in holes are suspended for technical reasons such as during fishing operations and dislodging of stuck pipes. This necessitates the introduction of additives that can enhance dispersion of clay particles in water columns. It has been reported that some nanoparticles can enhance clay stability in water; hence the primary objective in this work is to identify nanoparticles that have potentials to enhance clay stability and nanoparticles that promote clay instability in distilled water and brine of 30 g/l. In the experimental work, clays and different kinds of nanoparticles were dispersed in columns of water and the volumes of settled particles were plotted against time. Experimental results show that nanoparticles of silicon, zirconium, iron, tin, nickel and magnesium oxides all have the capacity to improve clay stability in water, while the presence of Al_2O_3 and ZnO nanoparticles promote clays instability in water. It is therefore recommended that further research on desirable drilling fluid properties be conducted with nanoparticle oxides that promote clay stability in water to investigate their suitability as additives in water based drilling muds.

Keywords: Brine, settling, unstable, particles, oxide, volume, distilled water.

INTRODUCTION

Clays are a class of earth materials that are extensively used in various industries and they are encountered during oil and gas production operations. The four main types of clays are Montmorillonite, Kaolinite, Illite and Chlorite. In the drilling industry, Montmorillonite clay dispersed in water based drilling fluids is commonly used to maintain fluid density that counter-balances pressure effects from different formation layers. In fact, Montmorillonite, also called bentonite is the main component of water based drilling mud. However, due to gravity effect, clay particles settle at the bottom of the hole especially when drilling operations are suspended for technical reasons such as during fishing operations, dislodging of stuck pipes and pulling out of drill strings to change drill bits. Thus, the settling velocity of clay particles becomes critical in order not to undermine the functions of drilling fluids, and especially to prevent the occurrence of a blowout. It is therefore imperative that additives be added to drilling fluids to promote clay stability and nanoparticles have been proposed as good agents that can enhance clay stability in water. Stability in this context means maintaining a uniform dispersion of clay particle suspension along the vertical column; hence preventing or slowing down the rate of particle settlement at the bottom of drilled holes.

Nanoparticles have wide applications especially in the manufacturing, chemical, construction and pharmaceutical industries. In the oil and gas industry, the potential uses of nanoparticles are numerous; it ranges from enhanced oil recovery to production operations, quality improvement of equipment, drilling engineering and crude oil refining. Nanoparticles that have been mostly recommended for various uses in the petroleum industry include aluminum oxide and silicon oxide. It is however worthwhile to investigate the potential of these and other kinds of nanoparticles in addressing the problems of the petroleum industry such as improving the stability of clay in water based drilling fluids. In this work which is experimental, Montmorillonite clay dispersed in distilled water and brine in the presence of eight kinds of nanoparticles were allowed to settle down under gravity while the volume of settled particles are studied. The aim of the study is to identify metal oxide nanoparticles that can militate against clay settlement and enhance particle dispersion in water such as in wellbores during downtime in drilling operations.

Several kinds of nanoparticles have been reported to positively modify water based drilling fluid properties but most recommendations have been on silica (SiO_2) nanoparticles. It has been shown that SiO_2 nanoparticles and graphene oxide nanoparticles can enhance the inhibition capacity of water based mud for unconventional shale [1]. It is reported that the presence of silica nanoparticles in water stabilizes clay particles [2], while another study shows that in combination with dissolved NaCl, it strongly influences the stability of Montmorillonite as indicated by increased turbidity [3]. Addition of graphite and SiO_2 nanoparticles to water based mud improves gel structure, viscoelasticity and thixotropic properties of water-based mud, and concentration of the nanoparticles is an important factor to consider [4]. Though silica nanoparticle has been recommended to improve the stability of Montmorillonite in water based mud [1], [2], [5], there seems to be other types of nanoparticles that can improve other rheological properties of water based drilling fluids.

Zinc oxide (ZnO) nanoparticle has also been noted to improve the rheological properties of water based drilling fluids. It has been noted that adding carbon nanoparticles and ZnO nanowire to water based drilling fluid has significantly controlled drilling fluid rheological properties and has improved stability [6]. ZnO has also been observed to remove hydrogen sulphide from drilling fluids while CuO and ZnO improve thermal properties at high pressure and temperature conditions. A study on the use of ZnO nanoparticles in water based drilling fluids shows that the rheological properties of water based mud improved significantly by 40 – 65% and it was noted that larger sizes of ZnO nanoparticles (30 – 45nm) formed a more stable fluid at all conditions [7].

Other kinds of nanoparticles that have been studied in relation to water based drilling fluid include carbon, iron oxide, aluminum oxide (Al_2O_3) and tin oxide (TiO_2). Experiments have shown that Al_2O_3 nanoparticles can form a thin and impermeable cake that reduces drilling fluid loss [8]. Multi-walled carbon nanotube controls viscosity at high pressure and temperature conditions while carbon improves thermal conductivity. Research has proved that Fe_2O_3 nanoparticles can improve rheological properties of drilling fluids and can control fluid loss. It is also reported that graphene alumina reduces fluid loss while Al_2O_3 nanoparticles improve thermal properties in water based drilling mud. TiO_2 has been observed to increase rheological and filtration properties, and graphene controls fluid loss and improves rheology. All of these studies have been conducted and reported in various literatures [9], [10], [11], [12], [13]. Aside from silica that has been noted to improve stability of water based drilling fluids, few reports have been made with regard to enhancement of clay stability in water based mud using nanoparticles. Hence, it is part of the objective in this work to find out if other kinds of nanoparticles have potentials to stabilize clay in water based drilling fluids.

Settling of Clay Particles under Gravity

When a colloid is poured into a vertical column, there is uniformity all through the height of the column as shown in Figure 1 (t_o) at time zero. The ability of colloids to remain in this uniformly dispersed state for a considerable duration of time without settling is described as a stable colloid. On the other hand, when colloids settle down within a short time after being dispersed in a medium, it is described as unstable. However, after a period of particle dispersal in a medium, suspended particles begin to settle down under gravity as depicted in Figure 1 (t_1), and the column is divided into three regions. The top region becomes clearer as dispersed particles fall down either into the middle region or the lowest region of the column as shown in t_2 of Figure 1 [14]. In fact at this stage, the top part of the column contains fewer particles than the other two parts and the height of the top region continues to increase until it becomes constant at the maximum height. As for the middle part of the vertical column, the maximum height is attained at the minimum height of the top region (clear liquid) of the column. As time increases, the height of the middle part decreases until it disappears into the lowest region of the column as shown in t_f of Figure 1. At this stage, only two regions will exist in the column; the top and low regions because all the particles in the middle region have fallen into the lowest region.

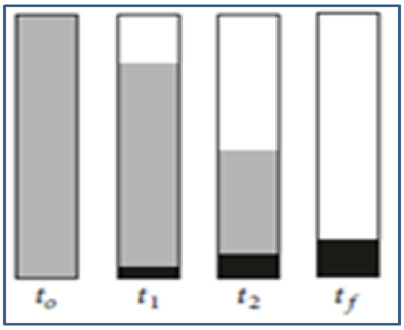

Figure 1: Illustration of the particle settling process [14].

An interesting part of this work that constitutes an area for further research is plotting graphs of the increasing volume of the top region and decreasing volume of the middle region against time for about one hour. The results will give a wider and more complete picture of clay sedimentation in a quiescent column of water containing nanoparticles and under gravitational force. Obtained linear graphs can be used to determine the falling rate of clay particles in a water column influenced by the presence of nanoparticles.

MATERIALS AND METHODS

This research work is focused on studying the volume of clay particles that settle in the lowest region of vertical water columns. The volume of settled particles increases with time to a maximum and then starts decreasing (compacting) to the lowest possible volume. In Figure 2, the graphical results of the volume of clay in the third region under different scenarios are illustrated. A typical particle settling graph (blue), a graph for an unstable case (red) and for a stable case (green) are presented. In all the cases, the particle settling volume forms a graphic shape of a parabola which consists of a rising slope, a peak, a descending slope and a constant volume part. For a stable scenario, it takes a lot of time for the graph to attain its peak (green) while for an unstable scenario (red), the peak is attained very quickly and the descending slope and constant volume part closely follow which shifts the graph to the left. However, in this work, the experiments were studies only for twenty minutes.

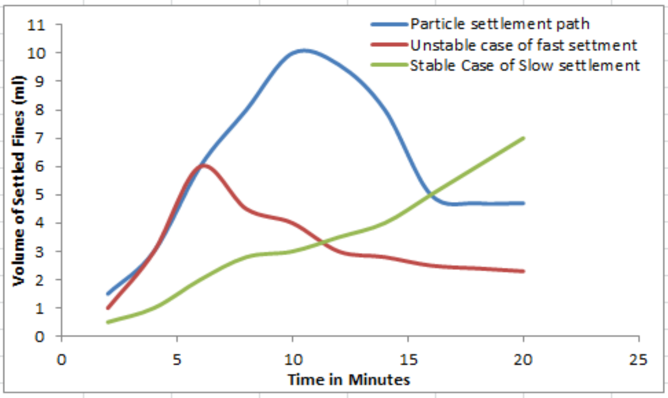

Figure 2: Graphical illustrations of stable and unstable particle settlement volume in the lowest region

Materials

The primary aim in this work is to identify nanoparticles that can improve Montmorillonite clay stability and those that promote clay instability in water both in the absence and presence of crude oil. The eight kinds of nanoparticles experimented with are Aluminum oxide (Al_2O_3), Magnesium oxide (MgO), Zinc oxide (ZnO), Iron oxide (Fe_2O_3), Nickel oxide (Ni_2O_3), Tin oxide (SnO_2), Zirconium oxide (ZrO_2) and Silane treated Silicon oxide (SiO_2). The nanoparticles were procured from Skyspring Nanomaterials, Inc., Houston, Texas, USA and their particle sizes and surface areas are presented on Table 1. Each type of these nanoparticles was dispersed in distilled water, and brine of 30g/l salinity at a concentration of 3g/l. The crude oil used in the experiments has a density of 0.9114g/cc at 27^{o}C, a viscosity of 53.27735cp and an API gravity of 22.44^{o}.

***Table 1**: Particle size and surface area of nanoparticles*

S\No.	Type of Nanoparticles	Particle Size (m)	Surface Area (m^2/g)
1.	Aluminium Oxide	40	~ 60
2.	Magnesium Oxide	20	~ 50
3.	Iron Oxide	20-40	40-60
4.	Nickel Oxide	100	6
5.	Tin Oxide	50-70	10-30
6.	Zinc Oxide	10-30	90
7.	Zirconium Oxide	20-30	35
8.	Silane Treated Silicon Oxide	10-30	> 400

Experimental Procedure

The experiment was conducted using a calibrated glass cylinder. 10g of Montmorillonite was separately dispersed in distilled water and brine of 30g/l salinity. 4ml of nano-fluid (at a concentration of 3g/l) land 4ml of crude oil (when the presence of crude oil was required) were poured into the beaker already containing the clay. The mixture was thoroughly stirred and poured into a calibrated glass cylinder. The time it takes for the particles of clay and nanoparticles in the mixture to start settling down at the bottom of the cylinder was noted. The volume of settled clay particles was read off and recorded at 2 minute, 4 minutes, 6 minutes, etc. to 20 minutes. It should be noted that in all the cases, the volume of particles in the lowest region of the colloid kept increasing up to a maximum height before compacting which shrinks the volume of settled particles with increasing time. This leaves a clear transparent liquid above the settled particles as illustrated in Figure 1.

The experimental results are graphs of volume of settled particles plotted against time. Within the short duration of the experiment, a relative parabolic graphical shape with a constant end for unstable cases and a relatively linear graph for stable cases are obtained as illustrated in Figure 2. As particle settlement commences, only two layers can be observed but as the process progresses, three layers become visible. The top layer is clear and transparent; the second layer is cloudy while the third layer is mainly composed of settled particle and this is the layer considered in this work.

RESULTS AND DISCUSSIONS

The graphical presentations of the results are given in Figures 3 to 6. It can be observed that the graphical shape of Al_2O_3 and ZnO nanoparticles are similar in all the cases but it is noted that Al_2O_3 nanoparticle settles down clay particles in water faster than ZnO nanoparticles. In other words, ZnO nanoparticles keeps clays dispersed in water longer than Al_2O_3 which implies that ZnO nanoparticles stabilizes clay in water better than Al_2O_3 nanoparticles. In fact one of the challenges of Al_2O_3 nanoparticles is that it is very unstable in water [15], [16], [17] which also keeps clays in water unstable as confirmed from experimental results in this work. The results however, do not show if clay in the control cases requires stabilization, only further studies in terms of extending the time of the experiments to about forty minutes or more will indicate that, but the results of Al_2O_3 and ZnO nanoparticles are noteworthy.

In Figures 3 and 4 are presented the results of clay settlement in distilled water and brine respectively in the presence of nanoparticles but in the absence of crude oil. In both sets of results, it can be observed that the results of silicon oxide and tin oxide nanoparticles are close while the results of nickel oxide, zirconium oxide and magnesium oxide nanoparticles are close.

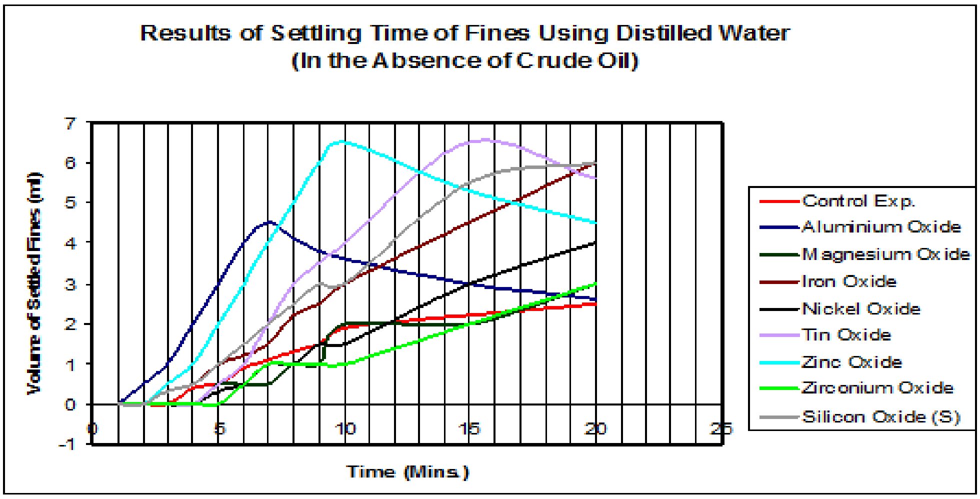

Figure 3: Results of settling time of clay in distilled water in the absence of crude oil

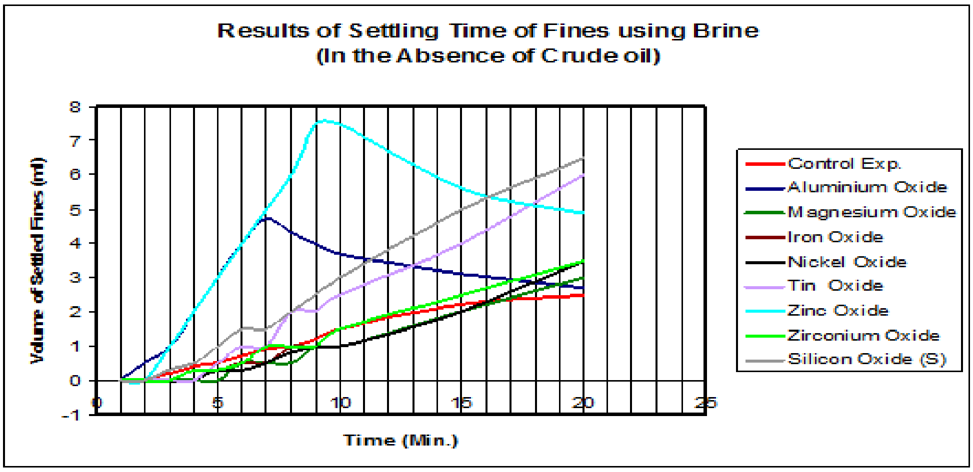

Figure 4: Results of settling time of clay in brine in the absence of crude oil

In Figure 4 (where brine is used), the results of zirconium oxide nanoparticles is almost exactly like the results of iron oxide nanoparticles, thus the results of zirconium oxide obscures the results of iron oxide, making it invisible. However, the situation is quite different in Figure 3 with distilled water because iron oxide results are closer to results of silicon and tin oxides.

The results of Figures 5 and 6 are cases where the experiments were conducted in the presence of crude oil. Once again it can be observed that the pattern of clay settlement with Al_2O_3 and ZnO nanoparticles are similar but Al_2O_3 nanoparticles settle particles of clays at a faster rate than ZnO nanoparticles.

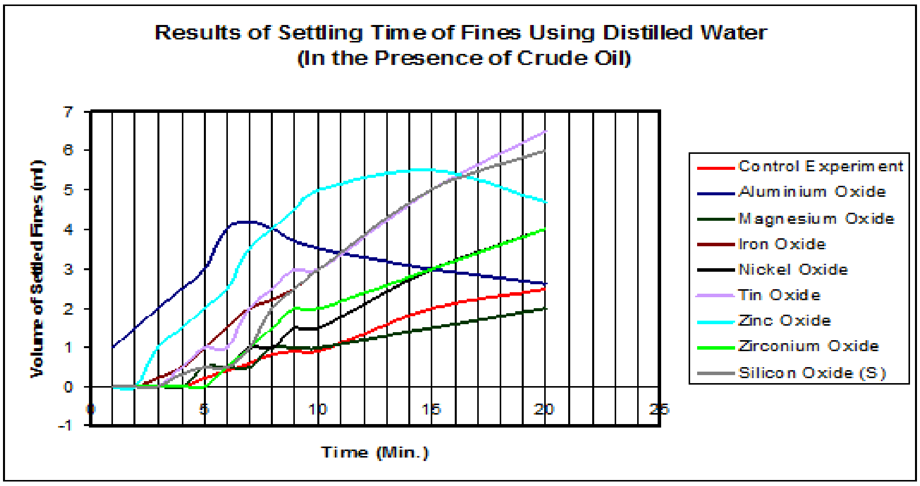

Figure 5: Results of settling time of clay in distilled water in the presence of crude oil

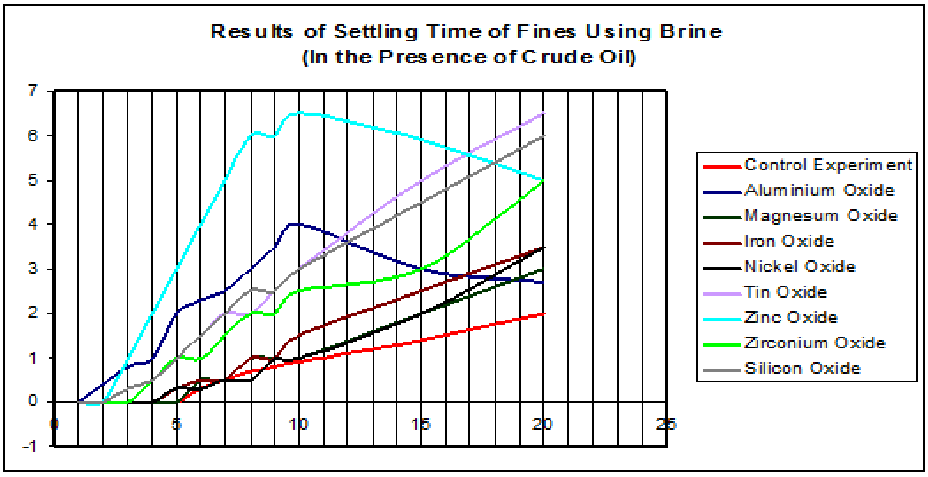

Figure 6: Results of settling time of clay in brine in the presence of crude oil

It is also observed again that the results of silicon and tin oxides are close while the results of zirconium, nickel and magnesium oxides are close. It is worthy of note that just like in Figures 3 and 4, iron oxide result is closer to silicon oxide and tin oxide in distilled water (Figure 5), in fact, some part of silicon oxide results lie exactly on iron oxide results, making it invisible. On the other hand, in brine (Figure 6) iron oxide results are closer to results from magnesium, zirconium and nickel oxides. What these imply is that salinity significantly affects iron oxide stability in water and this has been confirmed in previous literatures [18], [19], [20]. The stability of nanoparticles in water affects its ability to stabilize clays in water. An unstable nanoparticle in water such as Al_2O_3 nanoparticles cannot effectively stabilize clay in water, while stable nanoparticles in water can stabilize clay particles in water.

Apart from Al_2O_3 and ZnO nanoparticles, the rest of the nanoparticles used in this work namely nickel oxide, zirconium oxide, magnesium oxide, tin oxide, iron oxide and silane treated silicon oxide all have potentials to stabilize clay in water. Nevertheless, further research work in this study is required in extending the duration of time to about one hour. This will paint a better picture of clay stabilization in water using different kinds of nanoparticles; in fact the study will reveal the best clay stabilizer in water among the eight kinds of nanoparticles used in this work.

CONCLUSIONS

Al_2O_3 and ZnO nanoparticles promote clay instability in water compared to other nanoparticles used in this paper. However, Al_2O_3 nanoparticles cause clay instability more than ZnO nanoparticles, meaning that ZnO nanoparticles stabilize clay in water better than Al_2O_3 nanoparticles. Al_2O_3 and ZnO tend to behave alike from the shape of their graphs, implying that the pattern of clay particles settlement in the presence of Al_2O_3 and ZnO nanoparticles are similar. The performance of silane treated silicon oxide and tin oxide nanoparticles are close and the results of magnesium, zirconium and nickel oxides in stabilizing clay in water are also close. Nanoparticles of magnesium, nickel, tin, zirconium, iron and silane treated silicon oxides all have potentials to stabilize clay in water. Salinity affects iron oxide stability in water; in distilled water, the results are close to the results of tin and silicon oxides but in brine, the results fall within the result range of magnesium, nickel and zirconium oxides.

RECOMMENDATION

To achieve clay stability in water based drilling fluids, Al_2O_3 and ZnO nanoparticles should be avoided. To enhance clay stability in water based drilling fluids, nanoparticles of silicon, zirconium, iron, tin, nickel and magnesium oxides can be used as additives but further research work is required to ensure that other desirable properties of drilling fluids are not compromised.

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