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Communication

Settling velocity of clay with zinc oxide and aluminum oxide nanoparticles

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Abstract
Clays are ubiquitous earth minerals that are used globally in various fields such as in the ceramic, pharmaceutical, construction, chemical and drilling industries. Various industrial processes involve clay dispersal in liquids that form colloids of which the settling velocity is critical, necessitating enhanced or delayed sedimentation. It has been reported that the presence of some nanoparticles such as aluminum oxide (Al_2O_3) and zinc oxide (ZnO) can speed up clay sedimentation. It is therefore the primary objective in this study to determine and compare the settling velocities of a clay composition of Montmorillonite, Kaolinite and Illite in the presence of Al_2O_3 and ZnO nanoparticles, and to find out the effect of crude oil on the rate of deposition. The experiments were conducted using distilled water, brine of 30g/L salinity and ethanol as dispersing mediums for the clay particles and nanoparticles. Experimental results show that Al_2O_3 nanoparticles settle particles of clay at a faster velocity of about $2.80x10^{-4}$m/s and $3.08x10^{-4}$m/s in the absence and presence of crude oil respectively. ZnO nanoparticles settle clayey particles at about $2.65x10^{-4}$m/s and $2.91x10^{-4}$m/s in the absence and presence of crude oil respectively. It is speculated that Al_2O_3 nanoparticles which initiated a higher settling velocity occurred as a result of a strong attractive force between the nanoparticles and clay minerals. It was also observed that the presence of crude oil in the liquid columns increased the settling velocities of the clays.

Keywords: *montmorillonite, kaolinite, brine, ethanol, distilled water*

INTRODUCTION

Clays are very fine natural particles less than two microns, mainly composed of hydrous layers of silicates and aluminosilicates with plastic properties in the presence of water. There are different classes of clay minerals with peculiar characteristics and these include Kaolinite, Illite, Smectite, Vermiculite and Chlorite. These different types of clay sometimes exist together, not in isolation but in different percentages [1]. In any case, the settling velocities of these clays have been studied in isolation. In a particular research work, it was reported that the settling velocities of Kaolinite and Montmorillonite are 0.16mm/s ($1.6x10^{-4}$m/s) and 0.022mm/s ($2.2x10^{-5}$m/s) respectively [2]. Another experimental work reported that the settling velocities of Illite, Kaolinite and Montmorillonite are 0.95cm/s ($9.5x10^{-3}$m/s), 0.71cm/s ($7.1x10^{-3}$m/s) and 0.2cm/s ($2x10^{-3}$m/s) respectively [3]. The variations in these results could have emanated from different factors such as the type and accuracy of the pieces of equipment used, chemical compositions of the minerals and method of study, hence prompting that further work on the subject be conducted. Clay and its rate of sedimentation are important in disciplines of earth science; thus, they are studied by geologists, petroleum, agricultural, environmental and civil engineers.

Nanoparticles are a class of particles in the range of 1÷100 nanometers with significantly different physical and chemical properties compared to their larger material sizes. They also have the capacity to better alter various processes than larger sizes of the same material; some of these nanoparticles have been deployed to achieve various objectives in process engineering, material science, medicine and the energy industry. It has been reported that aluminum oxide (Al_2O_3) and zinc oxide (ZnO) nanoparticles can control fine particles of clay from detachment and migration in porous media [4, 5]. It is therefore necessary to also compare their performances and find out how they affect clay sedimentation in a column of fluid. Hence in this work, the effect of Al_2O_3 and ZnO nanoparticles on the settling velocity of clay composed of Montmorillonite, Kaolinite and Illite is investigated. In the presence of crude oil, these effects are further studied and compared against each other. Studies on the effect of nanoparticles in clay sedimentation are very scanty, making this an interesting research area to explore since clay minerals have wide application in the manufacturing industry.

In the petroleum industry, different types of clay minerals are encountered. During drilling operations, the presence of Montmorillonite, a swelling type of clay causes permeability impairment, and Kaolinite, a migratory type of clay also undermines permeability. Montmorillonite which is sometimes referred to as Bentonite is extensively used in preparing drilling fluids that counter formation pressure during drilling. Clays also constitute sealing rocks in oil and gas reservoirs. Clay minerals are studied by geologists and are of interest when studying drill cuttings and reservoir rock core samples. No doubt, the study of clay minerals especially their importance during drilling to counter formation pressures is very relevant in petroleum engineering. In an era when the effects of nanoparticles on various materials and processes are studied and deployed, it is also necessary to investigate the effect of nanoparticles on various properties of clays.

Factors that affect settling velocity of clays in fluids

There are several factors that affect the sedimentation rate of clay particles [6]. Temperature is one of such factors in which settling velocity increases with drop in temperature [7]. It has also been reported that increase in temperature decreases clay sedimentation time [8]. Clay settling rate also depends on particle concentration and water salinity; high particle concentration decreases rate of settling while increase in salinity increases settling velocity [8÷12]. Other factors include size and shape of particles [13], fluid viscosity [14] and pH value of the medium [15, 16].

The presence of organic matter in a medium is another factor that affects settling velocity in clays but reports on this are not consistent. A study indicated that the presence of organic matter in a colloid of clay in water increased settling velocity [17] while other researchers reported otherwise. It seems that the effect of organic matter on settling velocity of clays depends on the percentage of organic matter present. A study showed that a coastal clayey sediment with low percentage of organic content resulted in a high settling characteristic while the zone with high percentage of organic content gave low settling velocity [18]. The type of clay mineral involved could also be another factor that affects settling velocity in the presence of organic matter. A study that compared the settling velocity of kaolinite and Bentonite in the presence of mineral oil showed that Bentonite has a higher settling velocity than Kaolinite. However, in a Kaolinite-Bentonite mix of 1:1, it was reported that the settling velocity of the mixture increased [19].

This is an area for further research; nevertheless, the effect of the presence of crude oil on the settling velocity of the combined clay composition in this work is investigated.

MATERIALS AND METHODS

The main materials used in this experimental work are clays, crude oil, nanoparticles and three kinds of liquid. The clay is comprised of Montmorillonite, Kaolinite and Illite procured from Clay Minerals Society, USA. The crude oil used was obtained from the Niger Delta region of Nigeria and it has a density of 0.9114 g/cc at 27^oC, a viscosity of 53.28 cp and API gravity of 22.44^o. The two kinds of nanoparticles used are Al_2O_3 and ZnO purchased from Skyspring Nanomaterials, Inc., Houston, Texas, USA. The sizes of the nanoparticles and surface areas are presented on Table 1. The three kinds of dispersing fluids used are distilled water, brine of 30g/L salinity and ethanol of 98% concentration. The densities of the nano fluids were determined using a pycnometer, while the pH values of the nano fluids were determined using a calibrated pH meter. The densities and pH values of the nano fluids are presented on Tables 2 and 3 respectively. The nanoparticles and clay minerals were dispersed in these fluids and thoroughly stirred before the settling velocity tests commenced.

Table 1. Particles sizes and surface area of nanoparticles used

Type of Nanoparticle	Particle Size (nm)	Surface Area (m^2/g)
Al_2O_3	40	60
ZnO	10÷30	90

Table 2. Density of nano fluids (g/L)

Type of Nanoparticles	Distilled water	Brine	Ethanol
Al_2O_3	1.0245	1.0449	0.8293
ZnO	1.0252	1.0448	0.8291

Table 3. pH values of the nano fluids

Type of Nanoparticles	Distilled water	Brine	Ethanol
Al_2O_3	3.6	3.5	2.5
ZnO	7.2	7.1	6.7

Experiments were conducted using calibrated cylinders and colloids made from clay minerals and nanoparticles. 20 mL of colloids were prepared from clays at 10g/L concentration in a ratio of 2:2:1 of Montmorillonite, Kaolinite and Illite respectively and these colloids were made using distilled water, brine and ethanol separately. Al_2O_3 and ZnO nanoparticles were dispersed in each of these fluids at a concentration of 5g/L and 4 mL of the liquids containing nanoparticles were poured into beakers containing clay colloids. When the presence of crude oil was required, 4 mL of crude oil was also poured into beakers containing clays and nano-fluids. The mixtures were well stirred and poured into empty calibrated cylinders of 50 mL. A stop watch was used from the onset of sedimentation and after a specified duration of time, the volumes of settled particles were read off from the calibrated cylinders.

Figure 1 depicts different divisions of the colloids during the process of sedimentation but the area of interest in this process is the volume of settled clays. Stokes' law of particle settlement in fluids was not deployed in this work because several assumptions on which the law is based were defied, [20] hence the settling velocity of particles in the colloids were determined by calculation. The method of calculating the settling velocity involves plotting graphs of clear fluids above the settling materials against time and following other processes as discussed in referred literature [21].

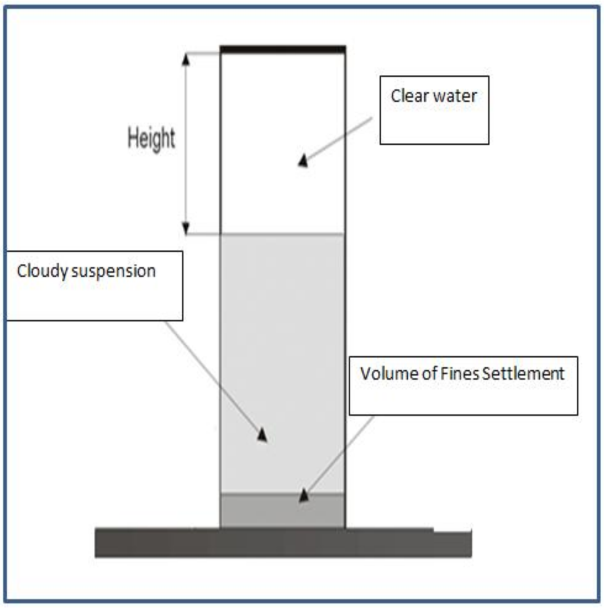

Fig. 1. Settling of Clay in a Liquid Column

RESULTS AND DISCUSSION

Three sets of results were obtained from the conducted experiments and they are presented in Figures 2 to 4. These include the effect of Al_2O_3 and ZnO nanoparticles on the settling velocity of clays, the effect of crude oil on the settling velocity of the clays and the influence of the dispersing medium on the settling process. Results of the effect of Al_2O_3 and ZnO nanoparticles on the settling velocity of clays are presented in Figure 2. Al_2O_3 nanoparticles settled particles of clay at about $2.80\text{x}10^{-4}$m/s and $3.08\text{x}10^{-4}$m/s in the absence and presence of crude oil respectively while ZnO nanoparticles settled clayey particles at about $2.65\text{x}10^{-4}$m/s and $2.91\text{x}10^{-4}$m/s in the absence and presence of crude oil respectively. It is observed that for all the dispersing mediums used, Al_2O_3 nanoparticles recorded a higher settling velocity of the clays than ZnO nanoparticles in the absence of crude oil (ACO) and in the presence of crude oil (PCO). This can be attributed to the attractive forces that exist between the clay particles and Al_2O_3 nanoparticles. Particles of clay minerals are mostly negatively charged and Al_2O_3 nanoparticles are positively charged which results in attraction, flocculation, forming of larger particle aggregates, heavier weights of the aggregation and subsequent higher falling velocity of the flocculated particles.

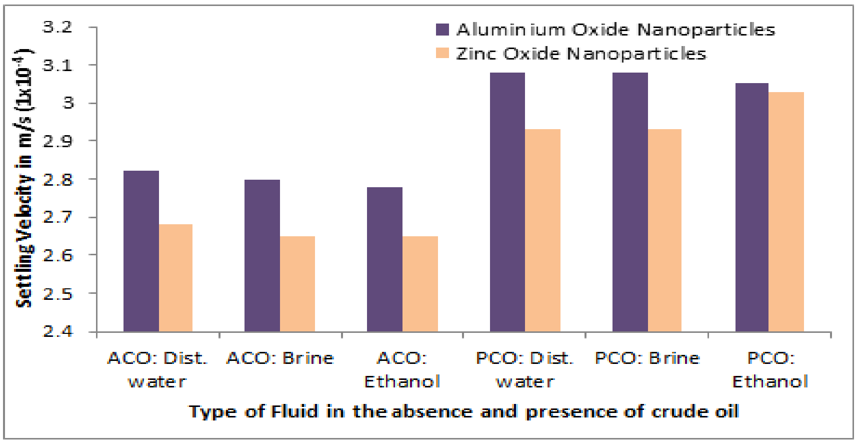

Fig. 2. Effect of Al_2O_3 and ZnO nanoparticles on the settling velocity of clays

Figure 3 shows the result of crude oil on the settling velocity of the clay minerals and it is evident that the presence of crude oil increased the deposition rate of the clays. The results in this work agree with the observation reported by Ye et al. [19] that the settling velocity increased for a combination mix of Kaolinite-Bentonite in the presence of mineral oil. This shows that the presence of hydrocarbons in a medium containing clay minerals can enhance the rate of clay deposition on collector surfaces just as Chase [17] pointed out. However, further investigation in this area is required to determine if for some reasons the opposite can occur as suggested by Ghose-Hajra and Roberts [18].

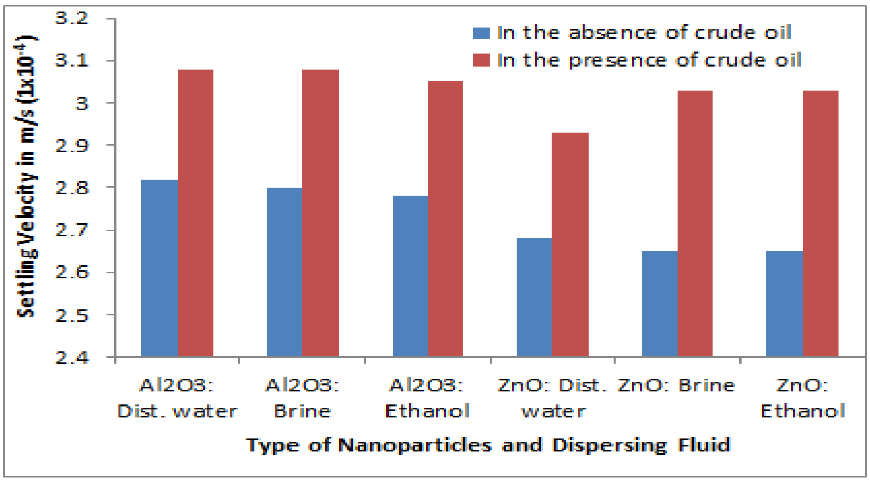

Fig. 3. Effect of crude oil on the settling velocity of clays

Results of the effect of dispersing fluid type on the settling velocity of clays are presented in Figure 4. It can be observed that the dispersing fluid type does not have a significant effect on the settling velocity of the clays. This is probably because there is no significant difference in the density and viscosity values of the dispersing mediums used in this work. It is expected that with more viscous fluids, the settling velocity of the clays will decrease.

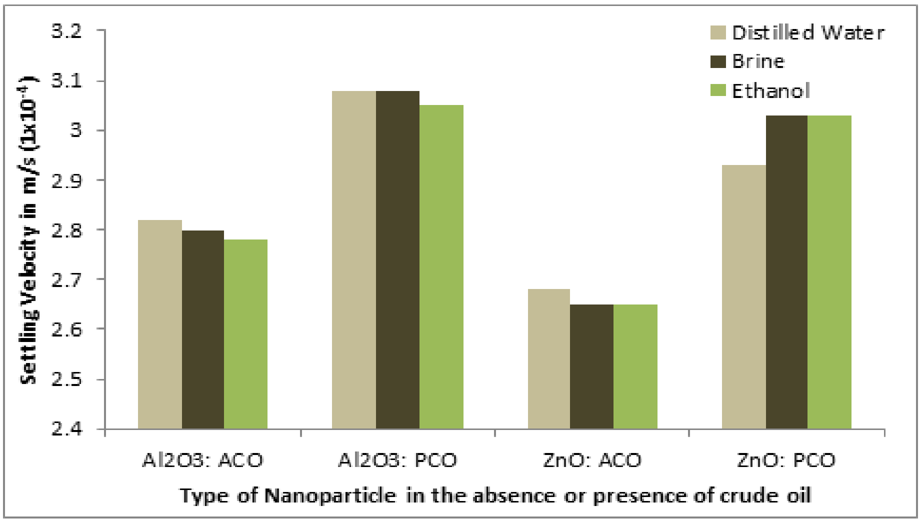

Fig. 4. Effect of Al_2O_3 and ZnO nanoparticles on the settling velocity of clays

The application of nanoparticles in the petroleum industry is growing, necessitating that its effect on various substances be studied. Clay is one of the common substances used in the upstream and downstream sector of the petroleum industry for various purposes. In the upstream sector, Montmorillonite clay is used in drilling and the modification of this clay using nanoparticles in order to improve its rheological properties has been recommended. In crude oil refineries, clay is used in the purification process of some petroleum products and nanoparticles too have been recommended at various stages to improve the quality of products. In the treatment of oilfield produced water before discharge, sometimes clay is used for the adsorption of pollutants and some nanoparticles have been recommended for water purification. In the petrochemical industry, clays are used as catalysts, for color cleansing and for purification, nanoparticles too have been incorporated into different products for various reasons. It is therefore imperative that the effect of these nanoparticles on the settling velocity of clays be studied and considered before application.

CONCLUSIONS

The presence of Al_2O_3 nanoparticles in a liquid column settles clayey particles at a faster velocity than ZnO nanoparticles. The settling velocity of clay composed of Kaolinite, Montmorillonite and Illite in the ratio of 2:2:1 respectively is about 2.8×10^{-4} m/s and 3.08×10^{-4} m/s in the absence and presence of crude oil respectively using Al_2O_3 nanoparticles. The settling velocity of clay composed of Kaolinite, Montmorillonite and Illite in the ratio of 2:2:1 respectively is about 2.65×10^{-4} m/s and 2.91×10^{-4} m/s in the absence and presence of crude oil respectively using ZnO nanoparticles. The presence of crude oil in a colloidal mixture of liquid and clays increases the settling velocity of the colloidal particles. It is recommended that Al_2O_3 nanoparticles be added to liquid mediums containing clay minerals if quick settling velocity is desired. Addition of a hydrocarbon fluid in a liquid can also improve the rate of clay sedimentation. On the other hand, if slow sedimentation is desired like in drilling fluids, then Al_2O_3 and ZnO nanoparticles and organic materials should be avoided. But if Al_2O_3 and ZnO nanoparticles must be used because they improve some rheological properties in drilling fluids, then they must be used cautiously.

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