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Clay stability with nanoparticles in a polar and non-polar liquid

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Abstract. Clay dispersed in polar or non-polar liquids has various industrial uses. In the petroleum industry, clay suspended in oil-based mud is used in drilling sensitive formations. In crude oil refining, clay serves as catalysts in dehydrating ethanol and for other purposes. Clay stability in fluids is critical, necessitating deployment of additives to maintain stability. It is speculated that some nanoparticles have the potential to stabilize clays in fluids. This work therefore focuses on identifying types of nanoparticles that can promote clay stability in polar and non-polar liquids. Nine kinds of nanoparticles were investigated in vertical columns of ethanol and diesel containing Montmorillonite clay, and settled volumes of clay were plotted against time. Results show that oxides of aluminum and zinc nanoparticles promote clay instability in organic fluids while oxides of magnesium, iron, nickel, tin, zirconium and silicon have the tendency to enhance clay stability in polar and non-polar liquids.

Key words: Montmorillonite, ethanol, diesel, dipole moment, sedimentation.

1. Introduction

Clay is a ubiquitous earth material that has wide application in the construction, ceramic, pharmaceutical, chemical and petroleum industries. In the petroleum industry, the settling velocity of clay is important in drilling engineering because clay is the major constituent of water and oil-based drilling fluids that counter formation pressures. In crude oil refining, clays are used as catalysts in the production of biodiesel from oils derived from plants [1]-[2] and as catalysts for dehydration of methanol and ethanol [3]-[4]. It has also been observed that clay

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modified with metals has a high potential as a catalyst for oxidation of ethanol [5]. Clay has been recommended for use in cleanup of soil contaminated with diesel [6].

Experimental results have shown that activated Bentonite which is a type of clay can be used to eliminate sulphur compounds from diesel fuel through oxidative desulfurization and adsorption. A high initial sulphur content of about 1109.3ppm in a petroleum product was reduced to about 10ppm with the use of clay [7]. It is reported that in a certain typical batch operation procedure, 1g of Montmorillonite clay impregnated with zinc added to 20ml of diesel and kerosene separately was able to desulphurize diesel and kerosene by adsorption [8]. Hence the usefulness of clay in the petroleum refining industry and in drilling operations is crucial, but one challenge in using clays dispersed in liquids is its instability. This means the inability of clays to remain suspended in a quiescent liquid after a considerable amount of time due to gravitational pull. Thus to enhance clay stability in fluids, chemical additives are deployed and some additives that have been proposed includes nanoparticles. In this work therefore which is experimental, the aim is to find out types of nanoparticles that can promote clay stability in organic polar and non-polar liquids, hence retarding the rate of clay particle settlement in a liquid column.

Nanoparticles are particles of elements and compounds in the nano scale which is around 10^{-9}m in size. Due to the very tiny sizes of these particles, they tend to be very reactive more than same materials in the bulk sizes. Different kinds of nanoparticles have been deployed in various industries to enhance desired properties in different materials such as in polymers, fuels, cosmetics, chemicals and textiles. In process engineering, nanoparticles have been explored to study how the properties of mixtures can be enhanced for example, the use of nanoparticles to improve drilling fluid rheology has been reported [9]-[15]. Nanoparticles have also been deployed in hydraulic fracturing fluids [16].

To function effectively, nanoparticles require a dispersing medium or carrier fluids because they are in powder form. However, liquid mediums are often used and they can be acidic, basic, amphoteric, solvents, hydrocarbons, polar or non-polar liquids. In this work, the focus is on organic liquids that are polar and non-polar; the polar liquid is a solvent, ethanol while the non-polar liquid is diesel, a hydrocarbon and a petroleum product. Organic solvents are carbon-based compounds that can dissolve other substances to become a solution such as hexane and toluene. Generally, organic solvents are volatile, they contain carbon atoms in their structure and most times also contain hydrogen atoms, and they have various uses in the petroleum industry [17]. Ethanol and diesel are organic compounds that have carbon atoms that are linked to hydrogen.

Ethanol is a polar organic solvent, an alcohol also called ethyl alcohol and a compound with the chemical formula C_2H_6O, which can also be expressed as C_2H_5OH or CH_3-CH_2-OH. It has an ethyl group that is linked to a hydroxyl group and is an important industrial chemical. It is colorless, volatile, flammable, soluble in water and boils at 78°C. Ethanol has a dipole moment of 1.69D and a density and viscosity of 0.78945g/cm^3 and 1.2 mPa.s respectively at 20ºC. It is a chemical solvent that is used in the synthesis of organic compounds and has medical applications. Ethanol is extensively used in the petroleum industry; in fact, it can be hydrated into ethylene, a very important chemical feedstock. It is used as an engine fuel and fuel additive especially in gasoline.

Diesel is a non-polar liquid and a mixture of hydrocarbons obtained by crude oil distillation within the range of 150 – 380ºC and has the chemical formula $C_{12}H_{23}$. The major uses of diesel include road transportation, rail transportation, sea transportation for marine diesel engines, electric power generation and it also powers farm and construction equipment. Diesel has a minimum cetane number of 40, a cloud point of 34ºC, density of 0.832kg/l, a heating value of 45.5MJ/kg and a minimum flash point of 40ºC. It has a viscosity of 2.5 – 3.5mm^2/s at 40ºC, an oxidation stability of 0.025 mg/ml, maximum ash content of 0.01% and a maximum carbon residue mass of 0.1% [18].

1.1 Clay particle settlement under gravitational pull

When clay is dispersed in a column of fluid, it gradually settles down at the bottom of the column with time. For a stable colloid, solid particles will remain in suspension for a longer time, but when a colloid is unstable, particle sedimentation occurs quickly within a short time. When Montmorillonite is dispersed in a medium, three parts can be observed from the quiescent colloid after about ten minutes as illustrated in Fig. 1. Initially, the colloid column is uniform (t_o) but with time, a clear liquid phase without particles can be observed at the top of the fluid (t_1). At the bottom of the column, a denser phase with settled particles appears (t_1) while the middle phase is lighter than the bottom phase, but denser than the topmost phase. As time increases, the volume of the topmost phase also increases; the volume of the middle phase decreases while the volume of the third phase increases (t_2). Given more time, the middle phase disappears and only two phases can be observed from the column (t_f). Plotting graphs for reduction of the middle phase with increasing time as the phase gradually disappears is an interesting area for further research which is not considered in this work.

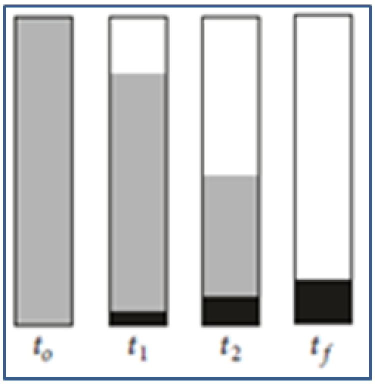

Fig. 1. Illustration of the particle settling process [19].

The three parts of a clay colloid column illustrated in Fig. 1 have been extensively discussed [19], but the area of interest in this work is the volume of the bottom phase which increases to a maximum before decreasing due to compaction. When this volume is plotted against time, the shape of the graph resembles a parabola and the end points become constant. For a colloid that is unstable, this graph appears early in time and shifts to the left, but for a stable colloid, this parabolic graph appears later in time and shifts to the right as illustrated in Fig. 2.

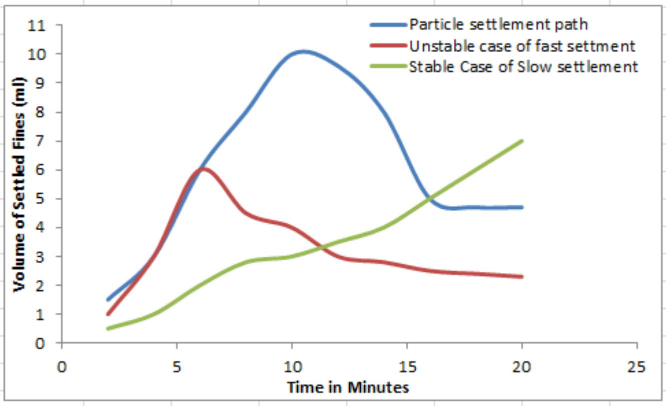

Fig. 2. Illustrations of stable and unstable particle settlement volume in the lowest phase.

2. Materials and Methods

This work studies the volume of settled clay particles at the bottom phase of organic fluid columns. The objective is to identify nanoparticles that initiate clay stability and clay instability in organic liquids. The study was conducted for twenty minutes only and the obtained graphical results are presented. Same experiments are conducted in the absence and presence of crude oil to find out the effect of crude on clay stability especially in the presence of nanoparticles.

Materials that constitute a major part of the experimental study are Montmorillonite clay, nine kinds of nanoparticles and two organic fluids, ethanol, a polar solvent and diesel, a non-polar hydrocarbon liquid. The 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), hydrophobic Silicon oxide (H-SiO_2) and Silane treated Silicon oxide (S-SiO_2). The nanoparticles were purchased from Skyspring Nanomaterials, Inc., Houston, Texas, USA and their surface areas and particle sizes are presented on Table 1. Each type of these nanoparticles was dispersed in ethanol (98%) and diesel. Half of the experimental work was conducted in the presence of a crude oil sample with 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. Some properties of the nanoparticles used

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
9.	Hydrophobic Silicon Oxide	10-20	100-140

Experiments were conducted using Montmorillonite clay with nanoparticles and organic fluids in calibrated cylinders. 20ml of 10g/l of clay in ethanol and diesel with 4ml of nano-fluid at a concentration of 3g/l were mixed together and thoroughly stirred. 4ml of crude oil was added when required and also thoroughly stirred. The mixture was then poured into a calibrated cylinder and allowed to settle down. The volume of settled clay particles at the bottom of the cylinder was plotted against time for each case. Control experiments where nanoparticles were not added served as references cases.

3. Results and discussions

Experimental results are presented in Fig. 3 to 6; Figs. 3 and 4 are the cases of clay dispersal in ethanol in the absence and presence of crude oil respectively while Figs. 5 and 6 are the cases of clay dispersal in diesel in the absence and presence of crude oil respectively. It can be observed from all four sets of results that Al_2O_3 and ZnO nanoparticles exhibit the same pattern of clay particle sedimentation in organic liquids, in fact, both kinds of nanoparticles promote clay instability than the rest seven. Interestingly, Al_2O_3 and ZnO are amphoteric oxides and on the Periodic Table, Aluminum belongs to group 13, period 3 while Zinc belongs to group 12, period 4, so both elements are close to each other. Al_2O_3 nanoparticles in particular have been reported to be very unstable in fluids [20]-[28]. It is evident from the experimental results that Al_2O_3 nanoparticles enhance clay instability more than ZnO nanoparticles. Note that the presence of hydrocarbon tends to slightly distort the graphical shapes of clay settlement in liquids and this is clearly observed in cases containing Al_2O_3 and ZnO nanoparticles.

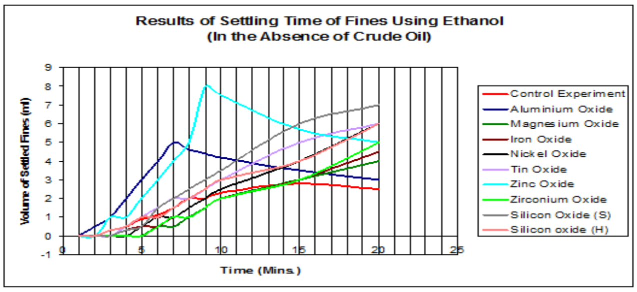

Fig. 3. Results of clay stability in ethanol in the absence of crude oil.

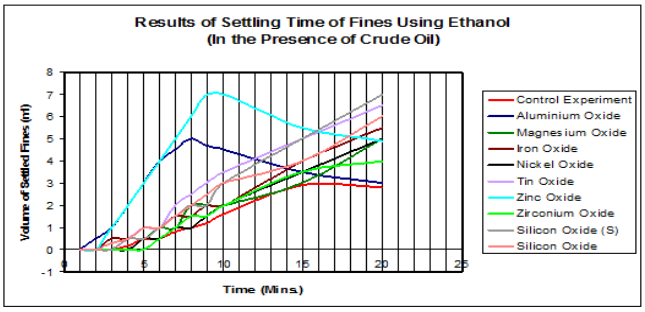

Fig. 4. Results of clay stability in ethanol in the presence of crude oil.

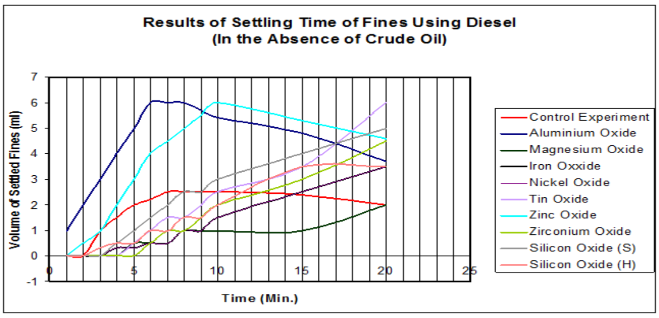

Fig. 5. Results of clay stability in diesel in the absence of crude oil.

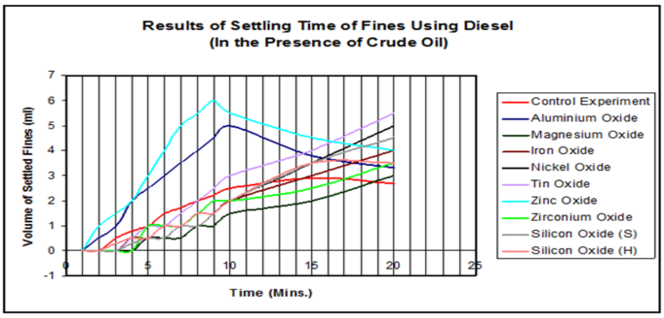

Fig. 6. Results of clay stability in diesel in the presence of crude oil.

Experimental results show that the control experiments which do not contain nanoparticles in all the four sets of results are unstable. Results have also shown that nanoparticles of MgO, Fe_2O_3, Ni_2O_3, SnO_2, ZrO_2, hydrophobic and Silane treated SiO_2 all have the tendency to stabilize clay particles in polar and non-polar organic liquids. The performances of SnO_2 and silane treated silicon oxide are close, but further studies in extending the particle settling time will show which of the two nanoparticles is a better clay stabilizer in organic fluids. Further research is also required to determine the best performing nanoparticles amongst the seven good clay stabilizers in polar and non-polar liquids. Extending the experimental time to one hour will give a clearer and more complete picture of the performances of these nanoparticles in clay stabilization in organic fluids.

4. Conclusions

Montmorillonite clay in the absence of nanoparticles is unstable in organic liquids such as ethanol and diesel. Al_2O_3 and ZnO nanoparticles render Montmorillonite clay unstable in ethanol and diesel which are polar and non- polar liquids respectively, but Al_2O_3 nanoparticles promote clay instability more than ZnO nanoparticles. The pattern of clay particles settlement in the presence of Al_2O_3 and ZnO nanoparticles are similar. The performances of silane treated silicon oxide and tin oxide nanoparticles in stabilizing clay in organic liquids are close. Oxides of magnesium, nickel, tin, zirconium, iron, hydrophobic and silane treated silicon nanoparticles all have potentials to enhance clay stability in organic polar and non-polar liquids.

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