



## Clay Stability in Liquids: Effect of Aluminum Oxide and Zinc Oxide Nanoparticles

N.A. Ogolo<sup>1\*</sup>, K. Amachree<sup>2</sup>, M.O. Onyekonwu<sup>1</sup>

<sup>1</sup>*Institute of Petroleum Studies, University of Port Harcourt, Rivers State, Nigeria.*

<sup>2</sup>*Department of Chemical Engineering, University of Huddersfield, Queensgate, Huddersfield, England.*

\*Corresponding author: [amoniogolo@yahoo.com](mailto:amoniogolo@yahoo.com)

Received. December 21, 2023. Accepted. March 15, 2024. Published May 15, 2024.

DOI: <https://doi.org/10.58681/ajrt.24080103>

**Abstract.** In the petroleum industry, clay is a major composition of water and oil based drilling fluids, but other additives are introduced to enhance rheological properties. One of such additives includes aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and zinc oxide ( $\text{ZnO}$ ) nanoparticles which have been reported to improve drilling fluid characteristics. However, the effect of these nanoparticles on the stability of clays in different liquid mediums needs to be investigated.

In this work, the effect of  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  nanoparticles on the stability of clays in distilled water, brine of 30g/l salinity, ethanol and diesel is studied in quiescent column of liquids in the absence and presence of crude oil. Results show that  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  nanoparticles enhance clay instability in liquids; in fact, clays are more stable in liquids in the absence of these two kinds of nanoparticles than in their presence.

In order not to enhance clay instability in liquids, it is suggested that  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  nanoparticles be used cautiously and possibly with other kinds of nanoparticles that promote particle stability in fluids. Further studies in determining the effect of organic matters on clay stability is encouraged since observations are inconsistent especially in the references cases where nanoparticles are absent.

**Keywords.** Particles, instability, Drilling fluid, Volume, Crude oil, Organic matter.

### INTRODUCTION

Clay is an important material in geology, construction, agriculture, pottery, ceramics, chemicals, and pharmaceuticals. In the petroleum industry, clay plays a key role during drilling operations; it is the main constituent of water based and oil based drilling fluids that counter-balances pressure effects from different formation layers. But to enhance various rheological properties of drilling fluids, several additives are usually introduced and this has

recently included nanoparticles. Studies have shown that several kinds of nanoparticles can improve drilling fluids characteristics (Cheraghian, 2020; Rafati et al., 2017; Talukdar et al., 2021; Vryzas et al., 2017).

Two types of nanoparticles among others that have been reported to significantly modify the properties of drilling fluids are aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and zinc oxide (ZnO) nanoparticles. Effects of  $\text{Al}_2\text{O}_3$  nanoparticles on the properties of water based drilling fluids have been studied experimentally.  $\text{Al}_2\text{O}_3$  nanoparticles have the ability to improve the rheological properties of drilling fluids and there is an optimum concentration that can improve filtration properties (Smith et al., 2018; Amarfio et al., 2016; Al-Yasiri et al., 2019; Khaled et al., 2017; Medhi et al., 2019). Addition of 1% of  $\text{Al}_2\text{O}_3$  nanoparticles to drilling fluids increases friction, and decreases effective and dynamic viscosity values (Hosseini et al., 2016).

Adding 1g of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  nanoparticles improves swelling, filtration and lubrication properties of drilling muds (Abbood et al., 2022; Al-Yasiri and Wen, 2019).  $\text{Al}_2\text{O}_3$  nanoparticles can stabilize ethyl octanoate ester as a low-molecular weight synthetic oil for formulating an ester-based drilling fluid (Ahmed et al., 2021).

The presence of ZnO nanoparticles in drilling fluids has also impacted positively on rheological properties (Albajalan et al., 2021). Using a low concentration of about 0.05wt% of ZnO nanoparticles at high temperatures improves the rheology of water based drilling muds (Ahasan et al., 2021). 1wt% of ZnO nanoparticles in drilling fluids enhances thermal stability, induces viscoelastic solid properties and reduces fluid loss (Medhi et al., 2021). ZnO nanoparticles in drilling fluids also have the ability to eliminate hydrogen sulfide.

A study has shown that addition of synthesized ZnO nanoparticles can eliminate hydrogen sulfide from water based drilling muds in 15minutes whereas the bulk ZnO can perform the same function in about 90minutes under the same conditions (Sayyadnejad et al., 2008).

It is evident that  $\text{Al}_2\text{O}_3$  and ZnO nanoparticles can enhance the performances of drilling fluids in several ways, but the stability of clay in drilling fluids in the presence of  $\text{Al}_2\text{O}_3$  and ZnO nanoparticles has not been studied. In this work therefore, the stability of clay in water, ethanol and diesel in the presence of  $\text{Al}_2\text{O}_3$  and ZnO nanoparticles is investigated. Stability in this context means the ability of clay particles to remain suspended in liquids without settling at the bottom of the well.

Clay stability in drilling fluids is important because segregation of the particles from the fluid undermines the functions of drilling muds and renders drilling fluids ineffective especially along top zones where most of the particles have settled down. Clay particle settlement during drilling mostly occurs during down time such as during fishing operations and when dislodging stuck pipes from the bottom of holes.

## **MATERIALS AND METHOD OF STUDY**

The clay used in this work comprises of Montmorillonite, Kaolinite and Illite in the ratio of 2:2:1 respectively (though in drilling fluids, only Montmorillonite is used) and these clays were purchased from Clay Mineral Society in USA.  $\text{Al}_2\text{O}_3$  and ZnO nanoparticles were obtained from Skyspring Nanomaterials, Inc., Houston. Texas in USA and the nanoparticles sizes and surface areas are presented in Table 1. The crude oil which was obtained from the Niger Delta region of Nigeria has a viscosity of 53.28cp, API gravity of 22.44° and density of

0.9114g/cc at 27°C. The liquid mediums used in dispersing the clays are distilled water, brine of 30g/l salinity, ethanol (98%) and diesel.

Table 1. Some Properties of the Nanoparticles used.

S\No.	Type of Nanoparticles	Particle Size (m)	Surface Area (m <sup>2</sup> /g)
1.	Aluminium Oxide	40	~ 60
2.	Zinc Oxide	10-30	90

The concentration of clays and nanoparticles in the liquid dispersants are 10g/l and 3g/l respectively. 20ml of the clay colloid was poured into a beaker and 4ml of nano-fluid was also poured into the same beaker. When the presence of crude is required, 4ml of it was also poured into the same beaker and thoroughly stirred.

The mixtures were then poured into a calibrated cylinder and allowed to settle down. The settling process moved from one phase of homogeneous fluid of uniformly dispersed particles to two distinct phases which lasted for a short time before the appearance of a third phase at the bottom of the cylinder.

Gradually with the passage of time, the first phase at the top becomes a clear fluid without particles while the middle phase becomes lightly cloudy as the last bottom phase becomes densely clouded as particles from the middle phase fall into the bottom phase. The three volume phases are illustrated in Figure 1, but this work is focused on the volume of the bottom region which is plotted against time. This region gradually increases to a maximum volume as the middle phase disappears into the bottom phase, and then decreases with time due to compaction. Finally, only two phases can be observed in the liquid column; the volume of bottom settled particles and a clear liquid volume free of particles on top of the volume of settled particles.

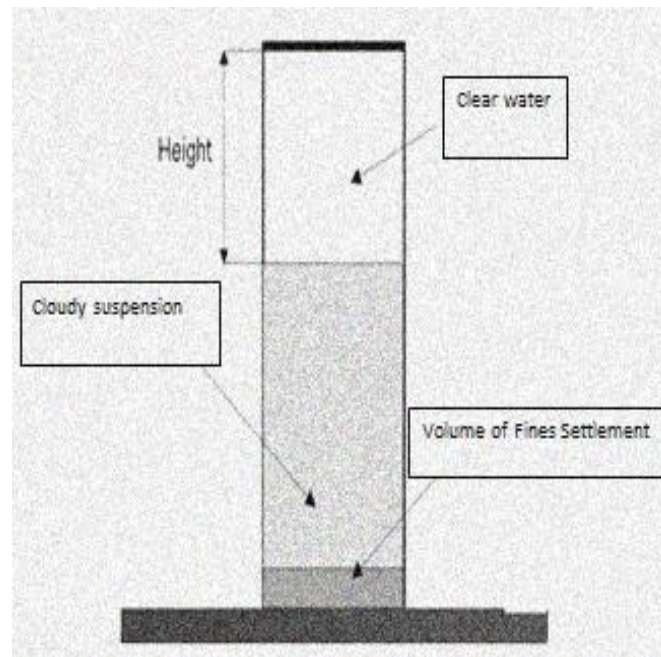


Fig.1. Illustration of Three Phases in the Particle Settling Process .

## RESULTS AND DISCUSSIONS

Three sets of results are presented in figures 2 to 7. Each set shows two experimental results conducted in the absence and presence of crude oil, and in each result, four graphs are presented for each of the four fluids (distilled water, brine, ethanol and water) used in the experiments. Figures 2 and 3 are the reference cases where there are no nanoparticles in the colloids, only clays are present. These two experimental results show that clays are more stable in water than in organic liquids such as ethanol and diesel. It is observed that the particle fall rates in ethanol and diesel are higher; in fact, at 15 minutes, the particles have already attained their maximum height and are already compacting which results in volume reduction. But for distilled water and brine, the volumes of particles are yet to attain their maximum height at 15 minutes because a lot of the particles are still in the middle region, not the bottom region.

The results also indicate that the presence of crude oil slightly distorts the trend of clay deposition. In figure 2, the particles settled faster in diesel than in Figure 3 when crude oil was present. This observation agrees with a similar study that was previously reported which noted that more organic matter slows down the particle settling rate, thereby promoting stability (Ghose-Hajra et al., 2020).

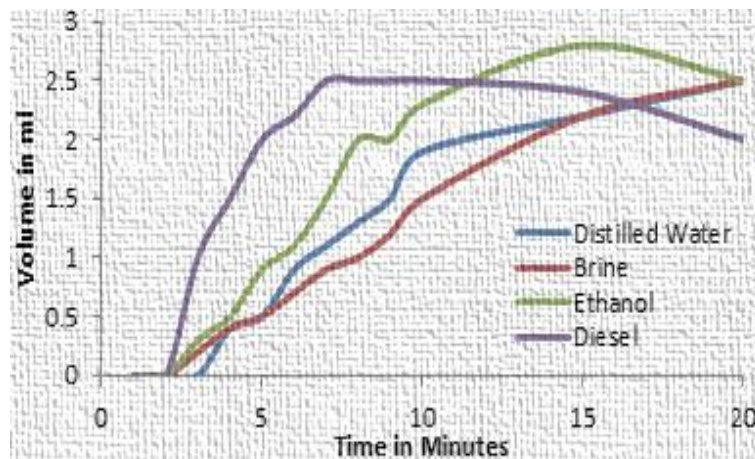


Fig.2. Reference Case in the Absence of Crude.

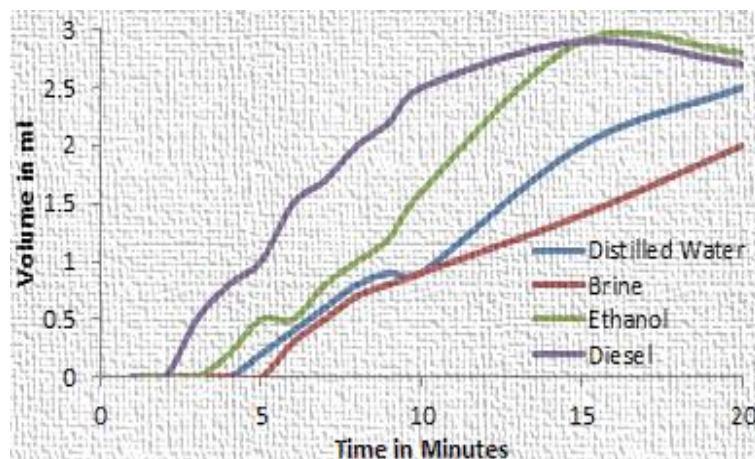


Fig.3. Reference Case in the Presence of Crude.

Figures 4 to 7 show that  $\text{Al}_2\text{O}_3$  and ZnO nanoparticles in a colloid of clay particles promote clay instability; in fact, both kinds of nanoparticles exhibit the same trend in clay instability. Figures 4 and 5 are sets of results with the use of  $\text{Al}_2\text{O}_3$  nanoparticles while figures 6 and 7 are results with the use of ZnO nanoparticles. In the presence of  $\text{Al}_2\text{O}_3$  nanoparticles, the falling rates of particles in the polar liquids (distilled water, brine and ethanol) are very close and similar in the absence of crude oil except for the non-polar liquid diesel which is slower. But in the presence of crude oil, the falling rates are in close ranges for all the mediums. In Figure 4, the clay particles settled in diesel very slowly than in the polar liquids (water and ethanol), but in the presence of more organic matter (crude oil in figure 5), the particles settling pattern falls in the range of other liquids which is faster.

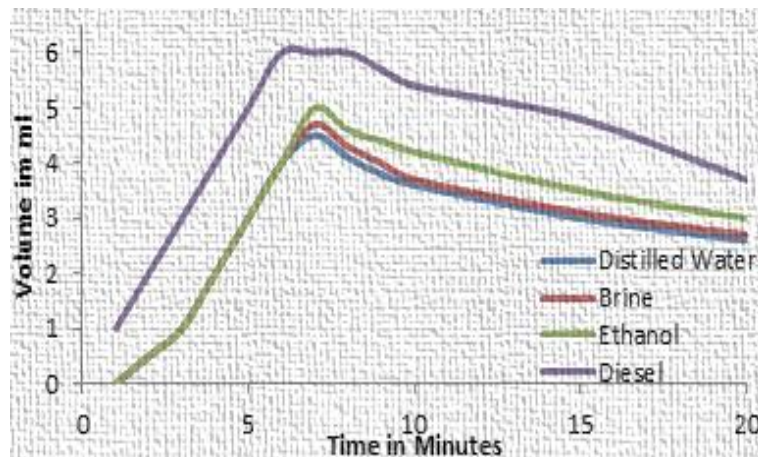


Fig.4.  $\text{Al}_2\text{O}_3$  in the Absence of Crude Oil.

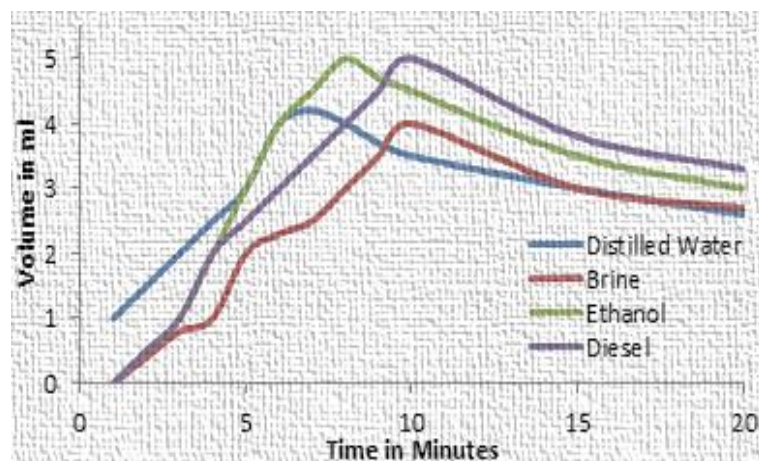


Fig.5.  $\text{Al}_2\text{O}_3$  in the Presence of Crude Oil.

In the presence of ZnO nanoparticles and in the absence and presence of crude oil (Figures 6 and 7 respectively), the falling rate of particles are approximately within the same range in all the fluids but especially in the absence of crude oil.

In the absence of crude oil, the fall pattern of particles in diesel is similar to other mediums, but in the presence of crude oil, it is faster. In terms of viscosity of which most oils have higher viscosity than water, it is expected that the rate of particle settlement will be slow,

enhancing stability. But in the presence of ZnO nanoparticles and in the reference cases, an opposite result is observed which requires explanations and further research.

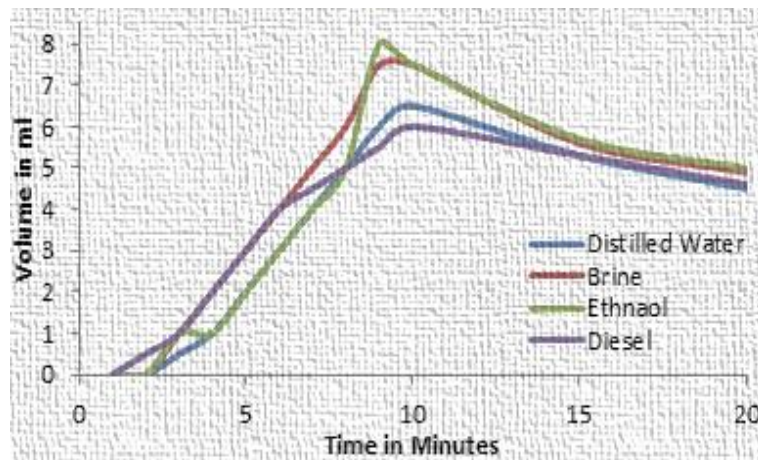


Figure 6: ZnO in the Absence of Crude Oil.

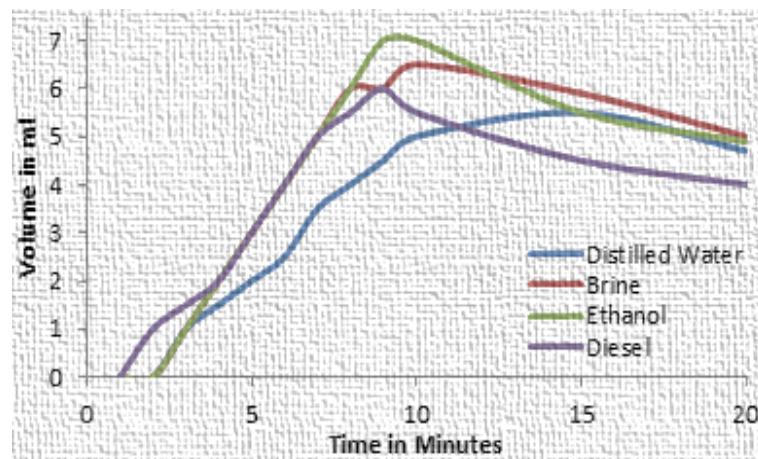


Figure 7: ZnO in the Presence of Crude Oil.

Reports have shown that the presence of organic matter in a medium affects the settling rate of particles which invariably affect the stability of particles in the medium. But unfortunately, the results have not been consistent because while some researchers report that the presence of organic matters in fluids enhances instability or particle settlement (Chase 1978), others report that it enhances stability which implies slowing down particle settlement.

However, a study pointed out that the rate of particle settlement depends on the percentage of organic matter present; low percentage promotes high settling characteristics (high instability) while high percentages slow down the rate of settling which promotes stability (Ghose-Hajra et al., 2020). This is an area that requires further investigations perhaps testing with different percentages of different organic matters.

The inconsistency of the reference case results with the nanoparticles results with regard to determining if the presence of crude oil enhances or slows down particle stability in a column of fluid deserves further investigations.

Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles have positive impacts on drilling fluid properties but at the same time, they promote particle instability which is not desirable in drilling fluids especially during down time. There are several other nanoparticles that promote particle stability in fluids such as silica (Mirzaasadi et al., 2021; Yang et al., 2015; Agarwal et al., 2011).

It is therefore suggested that Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles be used cautiously in drilling fluids in order not to jeopardize stability of clay particles. In fact, other types of nanoparticles that can enhance clay particle stability in liquids can be used in combination with Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles in drilling fluids.

## CONCLUSION

The conclusions drawn from this work are as follows:

1. Clays are more stable in distilled water and saline water (brine) than in organic liquids such as ethanol and diesel.
2. Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles enhance clay instability in liquids and they exhibit almost the same trend in clay instability.
3. The effect of liquid type on clay stability in the presence of Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles is not significant.
4. The presence organic materials such as crude oil in a colloid containing particles of clay can distorts the pattern of particle sedimentation and can promote clay instability.

## RECOMMENDATION

Al<sub>2</sub>O<sub>3</sub> and ZnO nanoparticles promote clay instability in liquids, hence they should be used cautiously in drilling fluids, and if possible they should be used along with other kinds of nanoparticles that promote particle stability in liquids.

## ACKNOWLEDGEMENT

We thank the Petroleum Technology Development Fund (PTDF) for sponsorship of this work through a research grant.

## REFERENCES

- Abbood, H. A., & Shakir, I. K. (2022). Improved Water-Based Mud Rheological Properties and Shale-Inhibition Behavior by Using Aluminum Oxide and Iron Oxide Nanoparticles. *Engineering and Technology Journal*, 40(09), 1171-1178.
- Agarwal, S., Trans, P., Soong, Y., Martello, D., Gupta, R., (2011), "Flow Behavior of Nanoparticle Stabilized Drilling Fluids and Effect on High Temperature Aging," *Material Science Journal*, Corpus ID: 73687051.
- Ahasan, M. H., Alvi, M. F. A., Ahmed, N., & Alam, M. S. (2022). An investigation of the effects of synthesized zinc oxide nanoparticles on the properties of water-based drilling fluid. *Petroleum Research*, 7(1), 131-137.
- Ahmed, A., Haddad, A. S., Rafati, R. and Bashir, A., Alsabagh, A. M. and Aboulrous, A. A., (2021), "Developing a

- Thermally Stable Ester-Based Drilling Fluid for Offshore Drilling Operations by Using Aluminum Oxide Nanorods”, MDPI, Volume 13, Issue 6, pp. 1 – 18.
- AlBajalan, A. R., & Haias, H. K. (2021). Evaluation of the performance of conventional water-based mud characteristics by applying zinc oxide and silica dioxide nanoparticle materials for a selected well in the Kurdistan/Iraq oil field. *Advances in Materials Science and Engineering*, 2021, 1-10.
- Al-Yasiri, M., & Wen, D. (2019). Gr-Al<sub>2</sub>O<sub>3</sub> Nanoparticles-based multifunctional drilling fluid. *Industrial & Engineering Chemistry Research*, 58(23), 10084-10091.
- Amarfio, E. M., & Abdulkadir, M. (2016). Effect of Al<sub>2</sub>O<sub>3</sub> nanoparticles on the rheological properties of water based mud. *Int. J. Sci. Eng. Appl*, 5, 7-11.
- Chase, R. R. (1979). Settling behavior of natural aquatic particulates 1. *Limnology and Oceanography*, 24(3), 417-426.
- Ogolo, N. A., & Onyekonwu, M. O. (2023). EFFECT OF NANOPARTICLES ON CLAY STABILIT Y IN WATER: IMPLICATION FOR WATER BASED DRILLING MUD. *Romanian Journal of Petroleum & Gas Technology*, (1).
- Ghose-Hajra, M., & Roberts, B. M. (2020, February). Effects of Organic Matter on Settling Characteristics of Fine Grained Coastal Sediments Used in Marsh Creation Projects. In *Geo-Congress 2020* (pp. 722-731). Reston, VA: American Society of Civil Engineers.
- Hosseini, S., Farahbod, F., & Zargar, G. (2016). The study of effective of added aluminum oxide nano particles to the drilling fluid: the evaluation of two synthesis methods. *J Pet Environ Biotechnol*, 7(283), 2.
- Khaled, S. (2017). Improving the drilling fluid performance by alumina oxide nanoparticles.
- Medhi, S., Chowdhury, S., Sangwai, J. S., & Gupta, D. K. (2023). Effect of Al<sub>2</sub>O<sub>3</sub> nanoparticle on viscoelastic and filtration properties of a salt-polymer-based drilling fluid. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 45(1), 2385-2397.
- Medhi, S., Gupta, D. K., & Sangwai, J. S. (2021). Impact of zinc oxide nanoparticles on the rheological and fluid-loss properties, and the hydraulic performance of non-damaging drilling fluid. *Journal of Natural Gas Science and Engineering*, 88, 103834.
- Mirzaasadi, M., Zarei, V., Elveny, M., Alizadeh, S. M., Alizadeh, V., & Khan, A. (2021). Improving the rheological properties and thermal stability of water-based drilling fluid using biogenic silica nanoparticles. *Energy Reports*, 7, 6162-6171.
- Rafati, R., Smith, S. R., Haddad, A. S., Novara, R., & Hamidi, H. (2018). Effect of nanoparticles on the modifications of drilling fluids properties: A review of recent advances. *Journal of Petroleum Science and Engineering*, 161, 61-76.
- Sayyadnejad, M. A., Ghaffarian, H. R., & Saeidi, M. (2008). Removal of hydrogen sulfide by zinc oxide nanoparticles in drilling fluid. *International Journal of Environmental Science & Technology*, 5, 565-569.
- Smith, S. R., Rafati, R., Haddad, A. S., Cooper, A., & Hamidi, H. (2018). Application of aluminium oxide nanoparticles to enhance rheological and filtration properties of water based muds at HPHT conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 537, 361-371.



Talukdar, P., Barman, D., Borah, A., Dihingia, M., & Chakravarty, T. A REVIEW ON APPLICATIONS OF NANOPARTICLES TO ENHANCE THE PROPERTIES OF WATER BASED DRILLING FLUID.

Vryzas, Z., & Kelessidis, V. C. (2017). Nano-based drilling fluids: A review. *Energies*, *10*(4), 540.

Yang, X. Y., Yue, Y., Cai, J. H., Liu, Y., & Wu, X. M. (2016). Experimental study and stabilization mechanisms of silica nanoparticles based brine mud with high temperature resistance for horizontal shale gas wells. *Journal of Nanomaterials*, *2015*, 2-2.