

Analysis of the Effect of Fresh Zeolite on the Rheological Properties and Thermal Stability of Water Based Mud at High Temperature Conditions

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Abstract: Drilling operations in High Pressure and High Temperature (HPHT) environments are usually conducted with Oil Based Muds (OBMs) due to their superior stability at such conditions to Water Based Muds (WBMs). However, OBMs are not eco-friendly, and are more expensive to prepare and manage than WBMs. There is therefore, the need to develop a WBM system that would be as stable as OBMs at HPHT conditions. This study therefore looked at the performance of WBM systems formulated with nano particles (nano-WBM system) at elevated temperatures, and their potential as substitutes for OBMs. In this study, WBMs were enhanced with Fresh Zeolite Catalysts. The study was conducted by preparing and aging mud samples with the nanoparticles in mass concentrations of 0.0 g, 0.5 g, 1.0 g and 1.5 g. The rheological properties, filtration and pH tests were conducted over a temperature range from 120 °F to 360 °F. The behaviours of the fluids under each of the tests were then compared to the performance of a control sample (0.0 g aged). Results indicated that the aged samples that had been treated with nanoparticles showed improved thermal stability potential. Fresh zeolite provided good thermal stability with an optimum concentration of 1.5 g. The nanoparticles also reduced the shear stresses, yield points, plastic viscosities and gel strengths of the samples, leading to the inference that they acted as dispersants. It was therefore concluded that aged fresh zeolite, in its optimum concentration, can serve as a thermal stability additive for WBMs.

Keywords: Water Based Muds System, Nanoparticles, Thermal stability, High Temperature High Pressure, Rheological Properties, Fresh Zeolite

1. INTRODUCTION

Drilling operations are advancing into HTHP zones as the frontiers of the world's oil fields have shifted to deeper depths. These operations have placed myriad requirements on drilling fluids in order to achieve a successful drilling programme. These include but are not limited to carry cuttings from beneath the bit to the surface, reduce friction between the drill string and the side of the hole, and maintain the stability of uncased sections of the hole (Hossain and Al-Majeed, 2012). The thermal stability of WBMs in HTHP zones tends to be problematic because of their degradation at elevated temperatures as opposed to OBMs (Amanullah *et al.*, 2009). OBMs are therefore preferable at such hostile zones even though comparably, they are environmental unfriendly and more expensive to build, maintain, treat and dispose.

The advancement of drilling operations into HTHP formations demands the usage of drilling fluid systems with good thermal stability to preserve the rheology of the drilling fluids under such conditions. Most of the OBMs and other Synthetic Based Muds (SBMs) systems have the intrinsic disposition to withstand the high temperature conditions, but have environmental pollution limitations. Therefore, there is the need to develop a WBM system with better thermal stability. Studies have recommended different kinds of additives to improve the thermal stability of WBM systems; some of which are chemicals, polymers and zeolite nanoparticles (Dahab, 1991; Amanullah *et al.*, 2009). To this end, different types of chemicals and polymers are being used in designing various drilling mud systems to meet some functional requirements such as the appropriate mud rheology, density and fluid loss control property (Anon., 2000). According to Amanullah *et al.* 2009, at extreme HTHP conditions, mud systems formulated with macro and micro based materials (chemicals and polymers) become drastically altered

due to possible breakage or disassociation of polymer chains and branches by vibration, increase in Brownian motion and thermal stress, causing drastic reduction in gelling and viscous properties. While these chemicals and polymers have received quite considerable research attention, nano-zeolites are yet to be given same attention in drilling fluid formulation programmes. Meanwhile, nano-materials have shown unique abilities in their functionalities in the areas of thermal conductivity, electrical conductivity and optical features (Chai *et al.*, 2014).

In light of the above, this study seeks to investigate the thermal stabilisation performance of fresh zeolite in WBM systems at elevated temperature conditions. It is being considered because of its ability to withstand high temperatures without considerable degradation and because of its metal element composition.

2. METHODOLOGY

A series of experiments were conducted to determine the following fluid properties:

- The rheological properties of the formulated water-based systems treated with fresh nano-zeolite (temperature range of experiments: 120 °F to 360 °F); and
- The fluid loss control ability and pH of the same sample systems in (i) above.

These tests were done to simulate the behaviour of water-based fluid systems at down hole conditions during drilling operations.

2.1. Formulation of the Water Based Systems

Series of tests were performed to evaluate the performance of the rheological properties of the formulated mud systems with varying mass fractions of the nanoparticle as shown in Table 1.

The recommended API standard procedures for field testing water-based fluids were followed in the formulation of the mud systems.

Table 1. Mud Formulation Additives for a 10.4 ppg Water Based Mud System Including Fresh Zeolite (F-Z)

Materials	Quantity
1. Fresh water	0.91 bbl
2. Soda Ash	0.1 ppb
3. Bentonite	12.5 ppb
4. Caustic Soda	0.3 ppb
5. Barazan D	0.8 ppb
6. PAC L	21 ppb
7. Barite	101.8 ppb
8. F-Z (average particle size of 100 nm)	0.5, 1, 1.5 ppb

2.1.1. Mud Mixing Orders

In the formulation of the mud system for this study, a API standard procedure was followed to maximise the performance of each component. The addition of each component in their proper sequence during initial mixing optimises the performance of each product. The procedure followed for mixing the water-based mud is as follows:

- Addition of required volume of water into the mixing container;
- Addition of a water purification additive, which in this study was Soda Ash.
- Addition of viscosifying material, which in this case was bentonite
- Addition of caustic soda to control the pH of the medium
- Addition of viscosity extenders (Barazan D)
- Addition of filtration control additives (PAC L)
- Addition of weighting material

2.1.2. Equipment Used

Mud Mixing

To ensure a homogeneous mixture of the fluid, the mud was mixed between 15 and 20 minutes using a mud mixer.

Mud Density Measurement

To make sure the formulated mud for the study was within the API standards, a conventional mud balance was employed to ascertain the density as a quality assurance guide. The mud balance was checked for accuracy by calibrating it with fresh water to give a reading of 1 000 kg/m³ (8.345 lb/gal or 62.4 lb/ft³) at 70° F ± 5°F (21 °C).

Mud Viscosity Measurement

The Model 1100 HPHT viscometer was used in this study to measure the rheological properties of the prepared mud samples. Basically, the shear rate/shear stress parameters were determined from this equipment at varying temperatures between 120 °F (49 °C) and 360 °F (182 °C) at an interval of 80 °F (27 °C). This was to ascertain any thermal changes within the fluid rheology.

Static Filtration Test

An HPHT Filter Press was used to measure the amount of fluid loss from the mud samples after 7.5 and 30 minutes.

pH Measurement

The pH meter, equipped with a glass electrode was used to measure the pH of the test fluids.

Mud Aging Measurement

The high temperature mud aging chamber was used to simulate and investigate the heating and agitation which the water-based mud may be subjected to at higher temperature conditions while being circulated down hole and back to the surface. The mud samples were aged at a temperature of 250 °C (482 °F) for sixteen hours (16:00) before testing.

2.2. Properties of the Fresh Zeolite Used

The properties of the nanoparticles used in this study were determined with the help of thermogravimetric analysis, energy-dispersive X-ray spectroscopy (EDS) and a scanning electron microscope. These measurements were conducted to help provide an explanation for the presence or absence of thermal stability in the nano-WBM samples.

2.2.1. Thermogravimetric Analysis (TGA) Plot

Fig. 1 shows the TGA plot for the fresh zeolite particles used in this study. From the plot, it can be seen that the nanoparticles have the potential to withstand extreme temperatures, until degradation occurs. F-Z decomposed between 500 °C and 600 °C, signifying that it is thermally stable up until those temperatures; a quality required for a thermal stability additive since the over all material/ mass loss was about 5%.

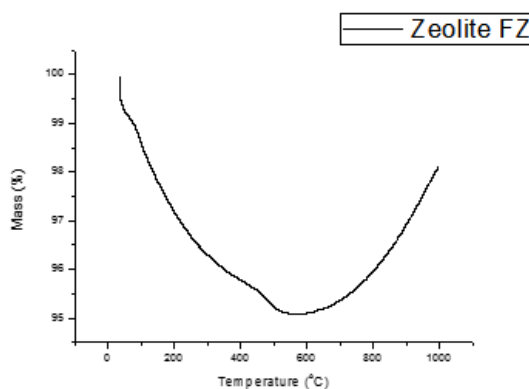


Fig1. Thermogravimetric Analysis Plot for Fresh Zeolite

2.2.2. Energy-Dispersive X-Ray Spectroscopy (EDS) Plot

Fig. 2 shows the elements present in the samples under investigation. This is relevant because certain elements are good conductors of heat, while others are not. Conductors will have an effect on the thermal stability potential of the nanoparticles (R).

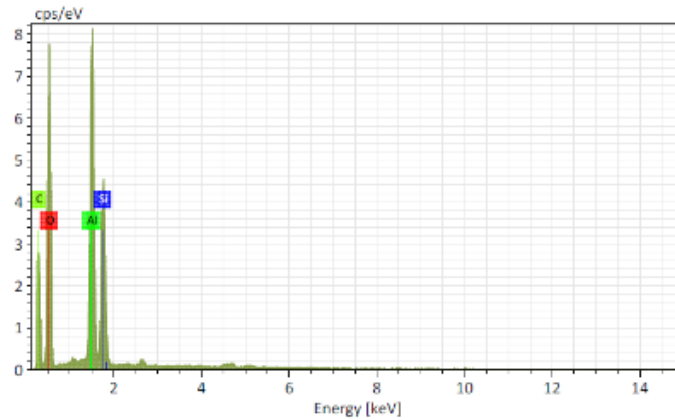


Fig2. Energy-Dispersive X-Ray Spectroscopy Plot for Fresh Zeolite

2.2.3. Scanning Electron Microscope Images

Fig. 3 shows a detailed image obtained from a scanning electron microscope. This image depicts the size and shape of the nanoparticles under investigation.

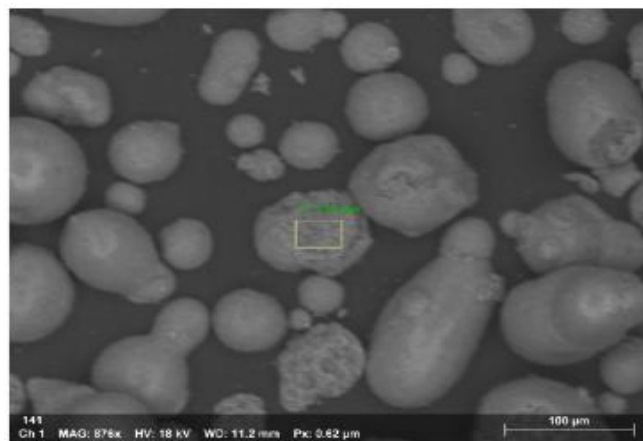


Fig3. Fresh Zeolite Scanning Electron Microscope Image

3. RESULTS AND DISCUSSIONS

3.1. Effects of F-Z on Fluid Model

The fluid model describes a fluid and its flow behaviour. The rheograms of all the fluid samples throughout all the temperature ranges had yield points other than zero as observed with their index factors or n values < 1 in Figs. 4 to 7. This means that they are non – Newtonian fluids. The shape of the curves (and lack of curves) assume the Herschel Buckley and Bingham Plastic models. The addition of fresh zeolite significantly reduced the shear stresses of the fluids. At 360 °F however, the 0.5 g and 1 g samples had higher shear stress values than the control sample.

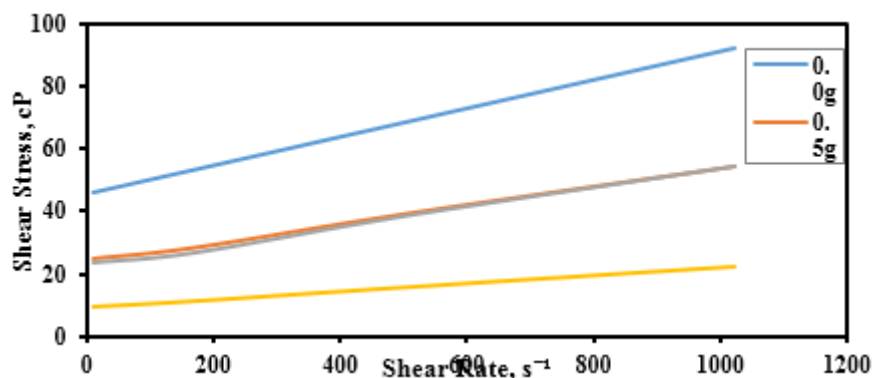


Fig4. Rheogram of Fresh Zeolite Water Based Mud at 120 °F

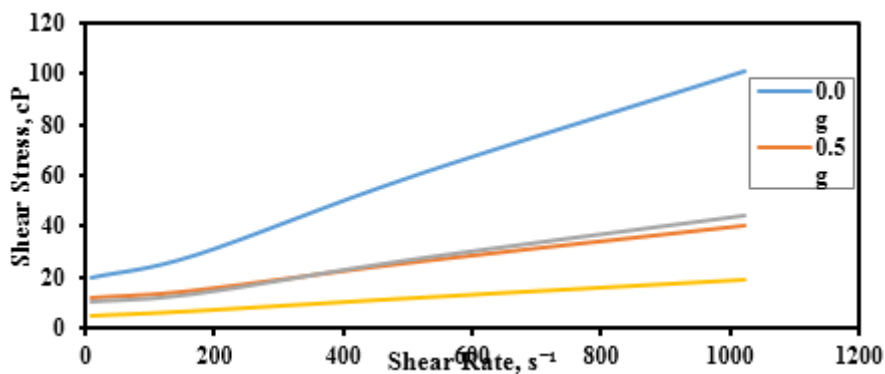


Fig5. Rheogram of Fresh Zeolite Water Based Mud at 200 °F

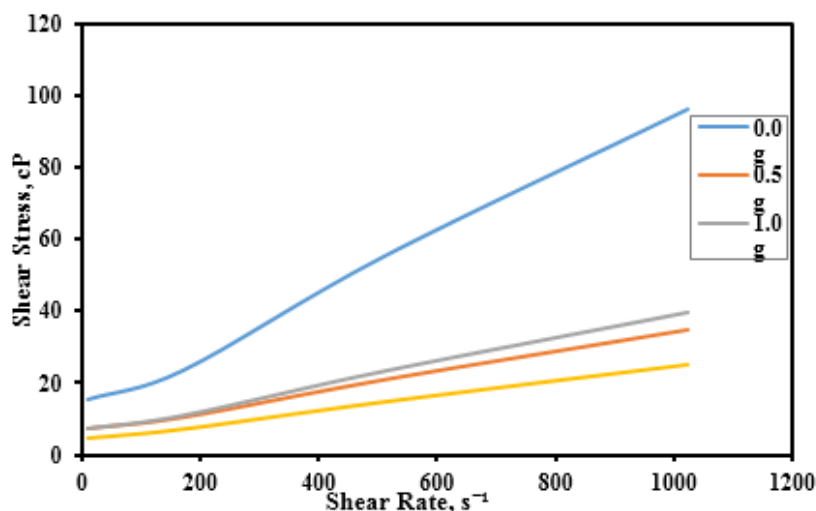


Fig6. Rheogram of Fresh Zeolite Water Based Mud at 280 °F

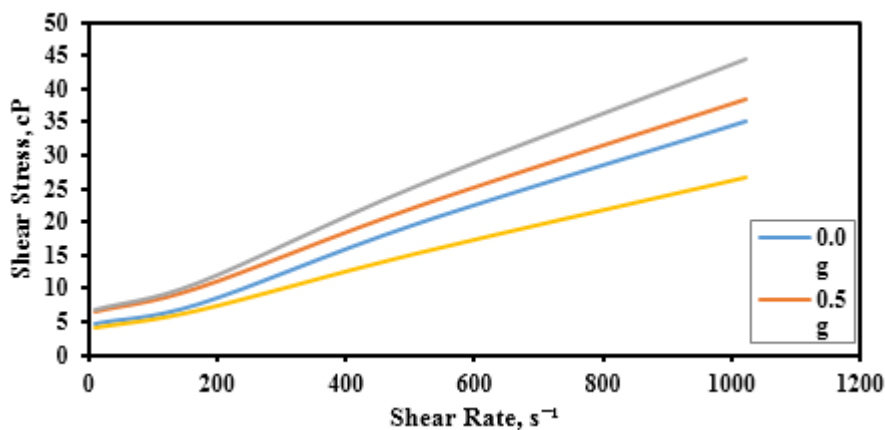


Fig7. Rheogram of Fresh Zeolite Water Based Mud at 360 °F

3.2. Effects on Rheological Properties

3.2.1. Plastic Viscosity (PV)

The PV of a drilling fluid is expected to decrease as temperature increases due to the breakdown (degradation) of the additives in the fluid, and the breakdown of the molecules of the base fluid. The control sample exhibits a decline in PV values with increasing temperature from 200 °F to 360 °F, as expected. With the addition of fresh zeolite in increasing quantities, the PV of the samples seem to stabilise as temperature changes. All three concentrations of the nanoparticle give relatively good thermal stability. The nanoparticles however significantly reduced the PV of the fluid at constant temperature, which was not expected. This could be because the nanoparticles acted as thinners. A study

by Medhi *et al.* (2020), where the effects of silica and copper oxide nanoparticles on the rheological properties of drilling fluids were investigated, produced similar results. The PVs and YPs of their samples reduced when nanoparticle concentrations increased, leading to the inference that the nanoparticles acted as thinners. They proposed that the nanoparticles united on the bentonite plates in the formulation, preventing the maintenance of attractive forces between the plates. This eventually led to deflocculation of the bentonite. The 0.5 g sample generally had the best stability, and compared to the 1.0 g sample, it had less PV values which makes it require less pump pressure during operations. It also met the API standard at all temperatures. As a result of these, 0.5 g is the optimum amount of F-Z to be used in the thermal stability of the PV of this WBM.

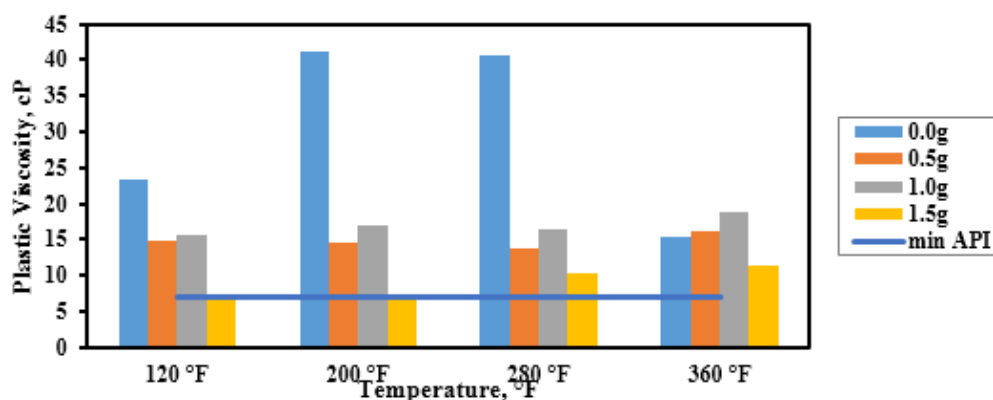


Fig8. Plastic Viscosity of Fresh Zeolite Water Based Mud at Varying Temperatures

3.2.2. Yield Point (YP)

YP values for the control sample decreased as the temperatures of the samples increased. This is explained by the increase in inter-molecular distances of the base fluid with temperature, leading to a reduced resistance to flow. Stabilisation is almost achieved rather early on by the addition of 0.5 g of F-Z to the drilling fluid. YP values of the 0.5 g and 1 g samples decrease as expected from 120 °F to 280 °F. In contrast, there is a rise in YP values for the 1.5 g sample from 200 °F to 360 °F. All but the YP values of the control sample from 120 °F to 280 °F meet the API standard. The 1.5 g concentration gives the least variation of YP values with changes in temperature. It could thus be said that it is the optimum amount of the nanoparticle to be used in this situation. The ability of F-Z to act as a dispersant is again noticed in Fig. 9, primarily at 120 °F and partially at 200 °F and 280 °F. This behaviour could be explained by the reason cited by Medhi *et al.* (2020).

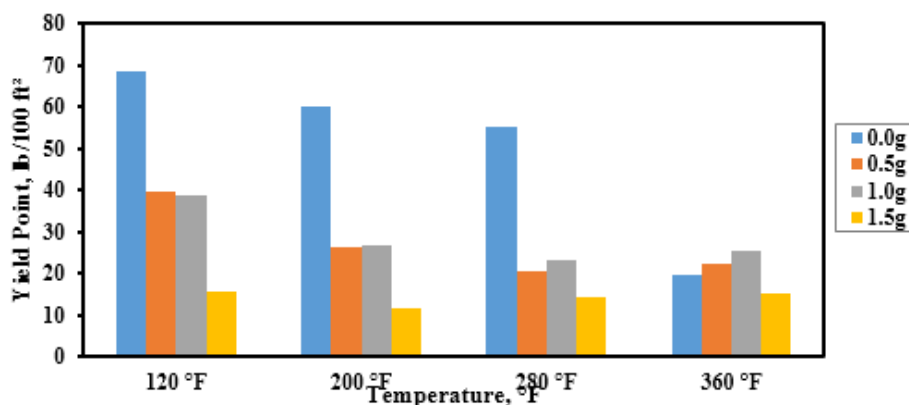


Fig9. Yield Point of Fresh Zeolite Water Based Mud at Varying Temperatures

3.2.3. Yield Point on Plastic Viscosity (YP/PV) Ratio

The YP/PV ratio gives an indication of the thickness of the drilling fluid. The higher the ratio, the thicker the mud is. The YP/PV ratio also gives some valuable information if the drilling fluid is being recycled. All the fresh zeolite nanoparticles base mud samples were below the API standard 3 as seen in Fig. 10. There was a general decrease in the YP/PV ratios for all the samples as temperature increased. This means that the bulk of the samples became thinner as temperature increased. The general decline

in the ratios was as a result of the reduction in YP values of the samples as temperature increased. The YP values of all the samples containing the nanoparticles from 280 °F to 360 °F however are balanced by the corresponding PV values of those samples at the same temperatures. Stabilisation was almost achieved, so for a decline in YP/PV values to be observed here, however small, the PV values must have risen up to extents greater than the YP values did. At 120 °F, the samples become thinner with the addition of the nanoparticles. At higher temperatures, the effect of the nanoparticles is not clearly defined and is almost negligible. Also, with an increase in temperature, the ratios of the samples with nanoparticles dropped just as that of the control did.

The only trend here is the general reduction in the thickness of all the samples, control inclusive, with temperature. The fresh zeolite does not seem to have much of an effect on the ratio with temperature. However, isothermally, a trend is observed at 120 °F, 280 °F and 360 °F, where there is a reduction in the ratio with an increase in the concentration of the nanoparticle. This again is not 100% concrete since there is an initial rise in the ratio from control to 0.5 g at 280 °F and 360 °F.

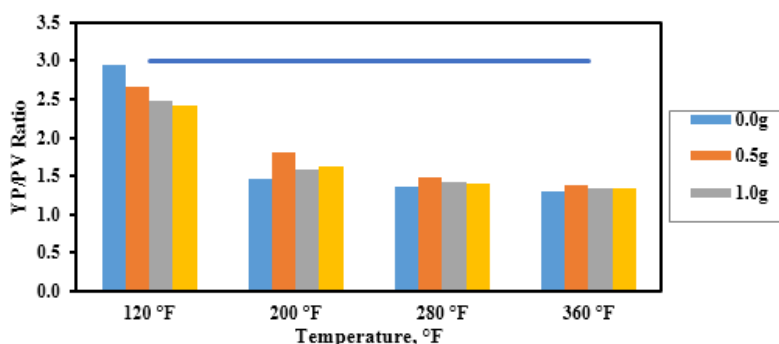


Fig10. YP/PV Ratio of Fresh Zeolite Water Based Mud at varying Temperatures

3.2.4. Gel Strength

Gel strength values of the control sample decreased significantly as the temperature of the sample was increased. This is not ideal, since during operations we would like to keep the value near-constant. In a study on the effect of high temperatures on WBM, Amani and Al-Jubouri (2012) concluded from their results that their drilling fluid samples had reductions in gel strength values as the temperature was increased, just as it occurred with the control sample in this study. They further explained that this was because of the increase in molecular distances due to high temperatures, which lowered the resistance of the fluid to flow. The increase in intermolecular distances occurred because the bonds between the molecules of the fluid were weakened and broken at high temperatures. Upon addition of F-Z, the gel strength values stabilised over the range of temperatures used in the experiment. The 0.5 g and 1 g samples had similar levels of stability, and both fell within the range given by API (3 – 20 lb /100 ft²). As a result, both can be used to keep the gel strength of the mud stable as temperatures vary with depth. One may however decide to go with the 1.0 g concentration because it provides slightly higher gel strength values than the 0.5 g concentration at 200 °F and 280 °F, thus improving upon the solids-suspension properties of the mud. It is also further away from the API lower limit. At 120 °F, 200 °F and 360 °F, the gel strength of the 1.5 g sample falls below the lower limit, making it unsuitable for use.

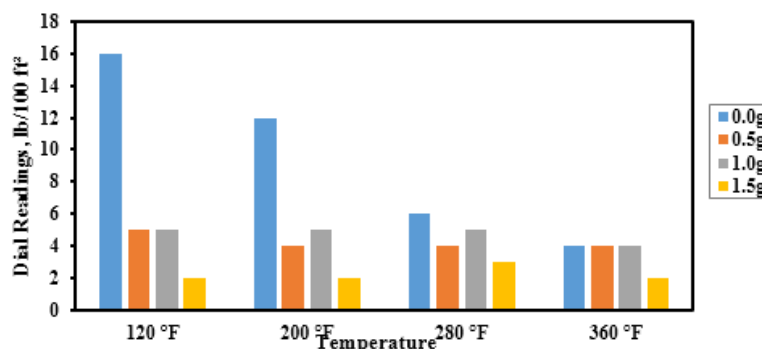


Fig11. Ten Seconds Gel Strength of Fresh Zeolite Water Based Mud at varying Temperatures

Similar to the 10 s experiment, the gel strength of the control sample in Fig. 12 decreased with an increase in temperature as expected. Stabilisation occurs upon addition of the F-Z particles to the mud samples, and the best stabilisation is attained with the 0.5 g sample. At 120 °F and 200 °F, the 1.5 g sample has its values below the lower limit of 3 lb /100 ft², just as in the 10 s test. Another thing to note is how the results of this experiment support the idea that the F-Z particles act as thinners (dispersants). Thinners are added to a mud to reduce its viscosity, gel strength and yield point. The gel strength values of the samples are reduced at 120, 200 °F and 280 °F with the addition of F-Z nanoparticles and at 360 °F, they are reduced with the increase of F-Z concentration from 0.5 g to 1.5 g. The gel strength of a mud is expected to increase with the increase of its solids concentration, which is the opposite case here.

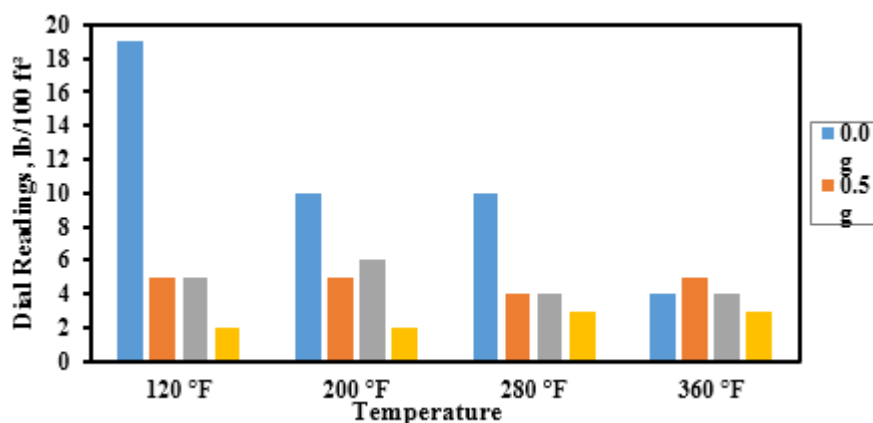


Fig12. Ten Minutes Gel Strength of Fresh Zeolite Water Based Mud at Varying Temperatures

3.2.5. Fluid Loss

Fig. 13 presents the filtration loss of mud samples containing fresh zeolite nanoparticles. As shown, none of the samples meet the API specification of less than 12 ml after 30 minutes. The volume of filtrate obtained after the test also depends on the viscosity of the fluid being tested. A fluid with a higher viscosity, especially one with a higher solids content, will tend to have a thicker mud cake being formed faster (from the residue of the fluid, which is its solids concentration), thereby preventing the continuous loss of fluid. The viscosity of the samples, especially the control sample, could also be a factor. It has also been seen that the fresh zeolite particles have the potential to act as dispersants, which lower the viscosity of the drilling fluid. With the addition of the nanoparticles, the fluid viscosity could have been reduced, leading to the formation of a less effective filter cake. As a result of this, greater amounts of water were lost during the test. This is evident both after 7.5 and 30 minutes. A possible trend could also be extrapolated from the graphs, seeing as gradual increments in F-Z concentration led to corresponding increments in filtrate volumes. This does not hold for the 1.5 g sample though. However, studies by Majid *et al.* (2018) inferred an indirect correlation between pH and filtration loss of WBMs. It was observed from their work that reducing the pH of the base fluid leads to an increase in filtration losses. If this was the cause, then the high filtration loss could be caused by the filter cake depletion by the acidic medium.

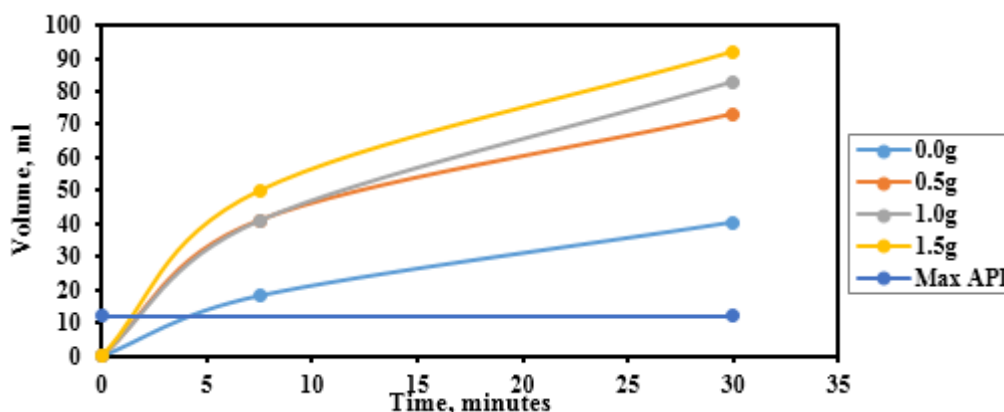


Fig13. Filtration Loss of Fresh Zeolite Water Based Mud after 7.5 and 30 Minutes

3.2.6. Hydrogen Ion Concentration (pH)

In Fig. 14, the pH of the mud samples decreases with an increase in fresh zeolite concentration. Al^{3+} is known to be a very acidic ion. It partially reacts with water to form H^+ ions. In water, the Al^{3+} ion forms $[Al(H_2O)_6]^{3+}$, which is a Brønsted–Lowry acid, and can donate a proton (H^+) to water in a second chemical reaction. The result of all the reactions is a $[Al(H_2O)_5OH]^{2+}$ ion and H^+ ions. From the EDS analysis for F-Z (Fig. 2), F-Z has a significant amount of aluminium ions. Zeolites are aluminosilicates as well. The zeolite's Al^{3+} component could have reacted with the base water used for the mud formulation and acted as a Brønsted–Lowry acid, reducing the pH of the entire formulation. It is also known that the acidity of a zeolite is dependent on its Silicon-Aluminium (Si/Al) ratio. A lower ratio means the zeolite will act acidic. The ratio can be lowered by an increase in aluminium content or a decrease in silicon content. From Fig. 2, it is seen that aluminium occurs in much greater quantities than silicon does. This may also have helped in increasing the acidity of the formulation.

Kang *et al.* (2016) conducted a study where they attempted to improve wellbore stability using silica nanoparticle WBMs. They recorded similar results; the pH of their WBMs decreased with increasing nanoparticle concentrations. Most of the samples in this study were basic, with the 1.5 g sample being acidic with a pH value of 6.53. Problems such as corrosion and hydrogen embrittlement, which arise due to the acidity of the fluid, may be encountered with the 1.5 g concentration of F-Z, though they may not be severe. Nevertheless, pH control additives like caustic soda could be employed to keep the 1.5 g sample's pH above 7, the neutral value. The other samples also became less basic with increasing nanoparticle concentrations. 1 g could therefore be a threshold beyond which the drilling mud becomes acidic.

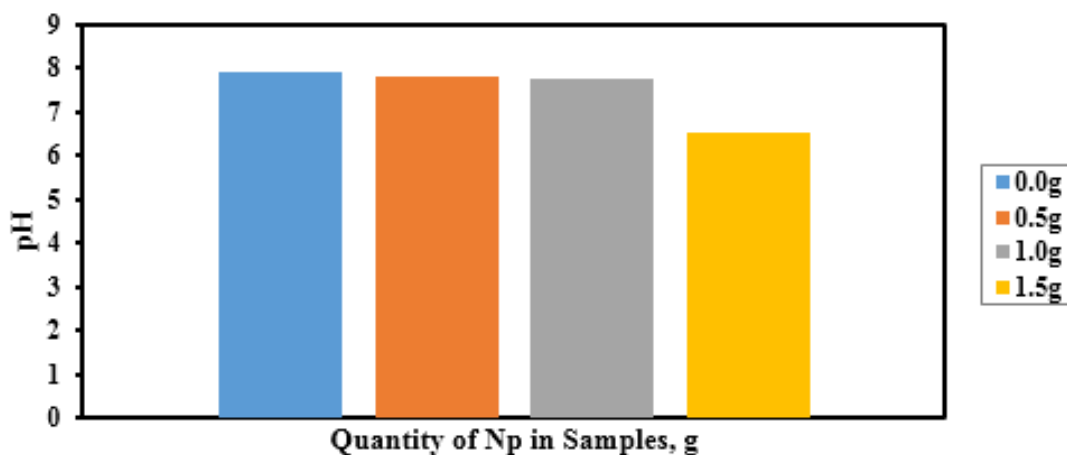


Fig14. pH of Varying Quantities of Fresh Zeolite in Water Based Mud Samples

3.3. Thermal Stability

The thermal stability being sought after by the addition of nanoparticles is simply the maintenance of the shear stress values of a fluid as its temperature increases. The shear stress of a fluid affects a lot of its rheological properties, including its PV and YP. Once the shear stress of a fluid remains as close to constant as possible, its rheological properties will not change much with temperature. Shear stress values of the samples decreased with temperature at all four shear rates. This was expected because at higher temperatures, the drilling fluid becomes thinner and viscosity reduces accordingly. The viscosity of a fluid is directly proportional to its shear stress. Also, the shear stress of the fluid increases with increments in the shear rates. This is expected because at higher shear rates, a greater shearing force is applied to the fluid. This creates a directly proportional internal reaction, the shear stress.

In Fig. 16, stability is almost achieved from 200 °F to 360 °F after introducing 0.5 g of F-Z into the sample. At 1 g (Fig. 17), stability is much better than it was with the 0.5 g sample. At 1.5 g, the sample is much more stable than it was with the other concentrations. At 6 and 100 rpm, the stresses from 200 °F to 360 °F are almost equal. At 300 rpm, the shear stress at 360 °F is almost equal to that at 120 °F, which is a very good indicator of thermal stability. At 600 rpm, the shear stress values at higher temperatures begin to exceed that at 120 °F. 1.5 g could be chosen as the optimum amount of F-Z to be used for thermal stability.

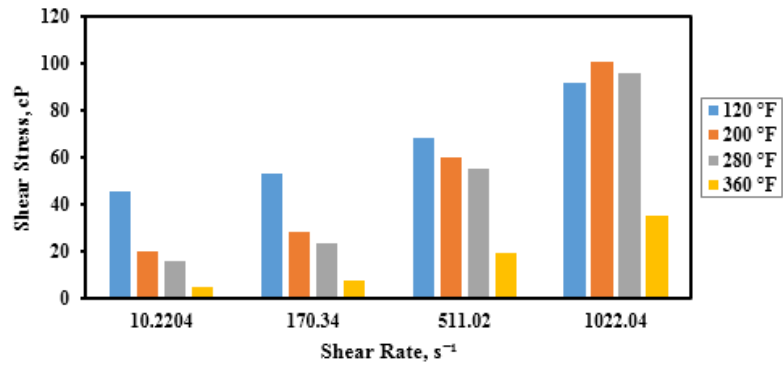


Fig15. Rheogram of 0 g of Fresh Zeolite Water Based Mud

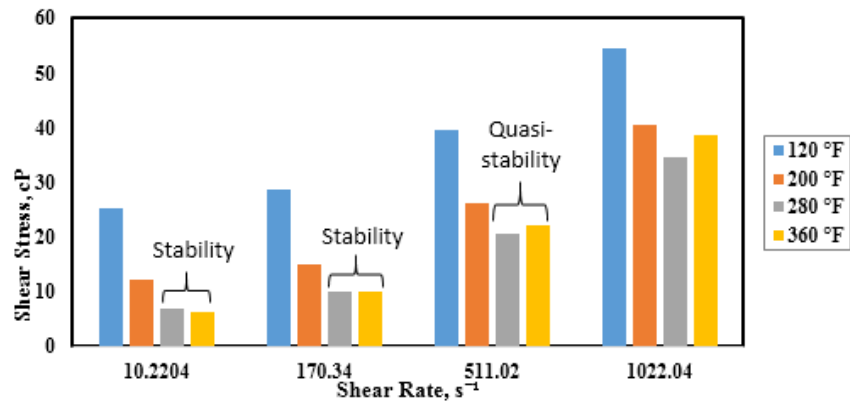


Fig16. Rheogram of 0.5 g of Fresh Zeolite Water Based Mud

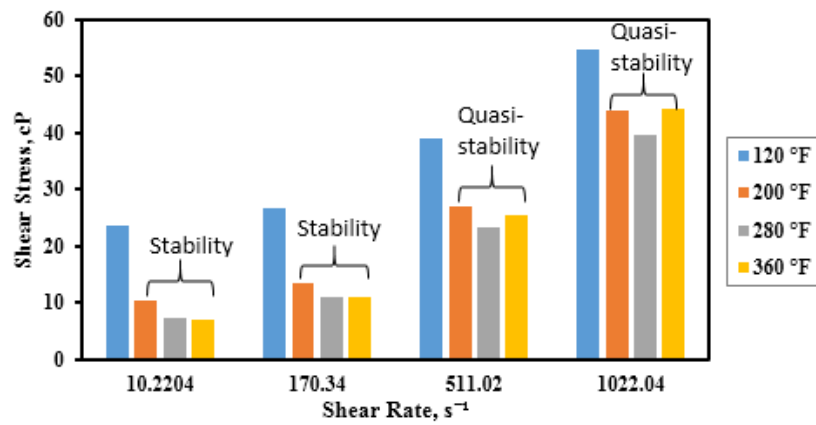


Fig17. Rheogram of 1.0 g of Fresh Zeolite Water Based Mud

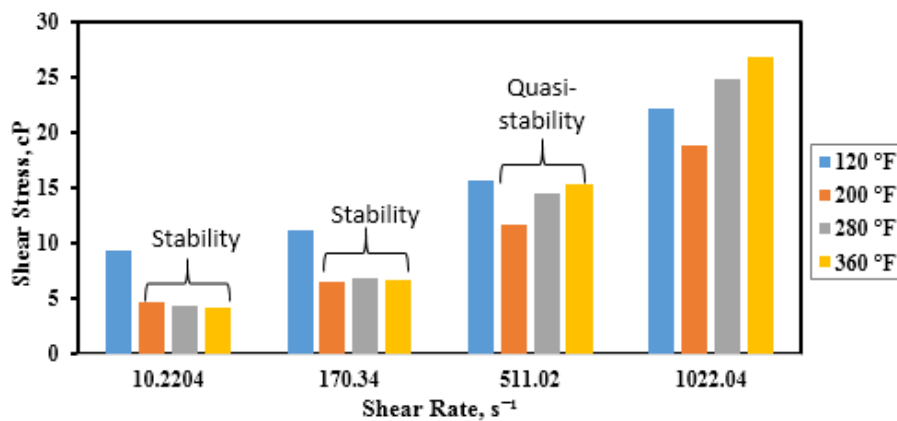


Fig18. Rheogram of 1.5 g of Fresh Zeolite Water Based Mud

3.4. Thermal Stability

The thermal stability provided by the fresh zeolite catalysts may have resulted from one or more of the following:

- Presence of metals that conduct and dissipate heat
- Surface area of the nanoparticles and nanoparticle size

Heat dissipation is assisted by the presence of metal elements in the nanoparticle sample. The fresh zeolite used contained aluminium in significant quantities, which is a conductor of heat. It also contained semiconductors such as carbon and silicon (Fig. 2, EDS). These elements promoted heat dissipation, reducing the overall impact of heat on the fluid sample.

It is also known that the surface area to volume ratio of a substance made of nanoparticles has a significant effect on the properties of the material. Materials made up of nanoparticles have a relatively larger surface area when compared to the same volume of material made up of bigger particles. Larger surface areas facilitate heat conduction and subsequent dissipation. Also, as particle sizes decrease, a greater proportion of the particles are found at the surface of the material. This makes plenty of electrons available for heat transfer. In order to take advantage of this, it is imperative to reduce the individual sizes of the nanoparticles, thereby creating a larger surface area. The small size of the particles also allows for free movement and hence micro-convection, which promotes heat transfer (Das, Choi and Patel, 2006). Water based muds will maintain their rheological properties if their shear stresses do not vary much with temperature. The key to stability is to get rid of the effect of heat on the fluid, maintain the shear stress and ultimately the fluid's rheology. The effect of temperature is countered by the presence of nanoparticles, and this is done through the conduction and dissipation of heat by the metal elements and the large surface areas of the nanoparticles.

4. CONCLUSIONS

This study set out to investigate the thermal stability potential of fresh zeolite on water-based mud. After experimentation and analyses, the following conclusions were drawn:

- F-Z mostly reduced the fluids' plastic viscosities, yield points and gel strengths, while increasing the amount of fluid loss during filtration control experiments.
- F-Z was able to thermally stabilise the WBM samples over the range of temperatures, with the 1.5 g concentration giving the best results.
- F-Z may have the potential to act as a fluid dispersant. This was seen from the persistent reduction of the PVs, YPs and gel strengths of the fluids, which was not expected.
- Aged F-Z reduced the pH of the drilling fluids, thus, making them more acidic.
- The fluid behaviours depicted both the Herschel Buckley and Bingham Plastic models.

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