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Study of the Potential of Calcium Hydroxide Synthesized from Periwinkle Shell as a pH Enhancer in Water Based Drilling Mud

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ABSTRACT

Reservoirs that contain acidic gases can lead to the corrosion of the drilling string and casing which could result in incessant down time and also increase the cost of drilling operation. This research work aimed at investigating the potential of using locally sourced materials such as Periwinkle Shell Ash (PSA) that can serve as substitutes to imported chemicals used in the industry, to help raise the mud pH to the API standard (9.5-12.5) whilst reducing the cost of drilling operation. Calcium hydroxide, $\text{Ca}(\text{OH})_2$ was extracted from Periwinkle Shell using two different process routes via the calcination of the PSA and without it. Characterization tools were used to assess the functional groups present and the elemental composition of the periwinkle shell. Various laboratory equipment was used to observe the impact the additives would have on the mud properties (pH, mud weight, filtration characteristics and rheological properties) of the new drilling fluid. Results showed that as the mass of the synthesized $\text{Ca}(\text{OH})_2$ from the calcined PSA, the uncalcined PSA and the commercial $\text{Ca}(\text{OH})_2$ was increased; the pH of the mud samples was observed to have increased the pH of the base mud by 20.9%, 15.1% and 10%. Therefore, this research showed that the extracted $\text{Ca}(\text{OH})_2$ acted primarily as a pH enhancer. However, the addition of $\text{Ca}(\text{OH})_2$ from all sources exhibited poor filtration characteristics as there was high filtrate loss as the filtration time and the additive concentration increased which could affect the formulation and the performance of the drilling mud.

KEYWORDS: Drilling fluids, Periwinkle shell Ash, Calcium hydroxide, eggshells, pH

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1 | INTRODUCTION

Drilling fluid, often known as "drilling mud," in drilling engineering literature, is frequently referred to as the "blood" of all drilling related work in the oil sector. Drilling a successful hole is a crucial step in the hydrocarbon exploration process, and it depends on how well the drilling fluid performs. The drilling process involves drilling through the earth's crust to a depth of several thousand feet, where the hydrocarbons are stored in a reservoir ^[1]. The formulated drilling fluid must perform its fundamental functions for a drilling operation to reach this key goal. Basic drilling fluid functions include clearing drill cuttings from the bottom of the hole, keeping the wellbore stable, maintaining high-pressure areas etc^[2]. Water- or oil-based drilling fluids are used during the drilling process to move mud from the surface to the bottom of the hole, keeping the wellbore stable, maintaining high-pressure areas etc.

The environment is typically impacted in some way by all of the hydrocarbon exploration and production activities. The release of wastes into the environment in concentrations that are not typically present in such environments, however, has the greatest impact. Wastes created during the extraction of petroleum can be broadly divided into two categories: liquid (produced water and drilling mud) and solid (cuttings). Wastes are a growing global problem in contemporary civilization because they can have a variety of unintended effects that can harm both the environment and human health ^[2]. In order to minimize these problems, it is essential to develop a novel strategy for resolving these problems. Instead of being disposed of in the environment, these wastes might be put to a number of applications in petroleum activities. For example, food byproducts may be added to mud or utilised in various ways. Numerous literatures have conducted studies and tests

regarding how to utilize food waste as substitute additives for drilling fluid.

The use of environmentally friendly drilling mud and its additives is suggested for the exploration and exploitation of hydrocarbons in offshore and onshore environments to prevent any harm to the aquatic life and the terrestrial environment. However, the majority of them have significant environmental issues, degradability problems, and post-treatment challenges, which create a conflict between clean drilling and drilling operating needs ^[3]. The usage of these drilling fluids is restricted by the high toxicity of the majority of effective drilling fluids. In this situation, the petroleum sector needs what is known as environmentally friendly drilling fluid, but before creating it, two factors must be taken into account: the drilling fluid's effectiveness and its cost. Most of the time, one or two of these three factors—ecologically friendly, economically sound, or efficient—must be sacrificed ^[4].

Larger amounts of seashells have been accumulated as waste along disposal sites, markets, or coastal regions in Nigeria due to the scale of fishing activity in riverine areas ^[5]. Environmental damage results from the hard shells being thrown at open areas while the species' flesh is prepared and consumed. The quantity of shell wastes dumped into the environment can be decreased by turning these wastes into useful products ^[1]. Additionally, the risk to the public's health from the careless disposal of the shells will be greatly diminished. The availability, affordability, and high content of calcium carbonate and chitin in these shells makes them useful since these materials may be removed and used to make a variety of goods ^[3].

Therefore, investigation on the use of local products to produce pH additives that are environmentally friendly and will lead to no substantial negative effects on subsurface formation would be necessary in order to

complement conventional chemicals. Suitable shell waste may be a viable option for drilling fluid additives due to its calcium content. As a result, waste can be turned into riches, generating income and employment opportunities. The Nigerian economy and environment would benefit from this, especially in light of the Nigerian National Petroleum Corporation's (NNPC) local content strategy, which encourages the creation and utilization of local resources in the oil and gas industry.

2 | MATERIALS AND METHODS

2.1 Equipment and Materials

The equipment utilized for this experimental investigation includes Speed Mud Mixer, Oven, weighing balance, Mud balance, Viscometer, Digital pH meter, Filter press, Dry blender and Beakers. The reagents and chemicals used for this study include Bentonite clay, Periwinkle shell, Water, Sodium hydroxide, Calcium hydroxide, Hydrochloric acid and Sodium Chloride.

2.2 Raw material collection and Preparation of Periwinkle shell powder

The periwinkle shell, also known as *Tympanotonus fuscatus*, served as an alternative supply of calcium hydroxide for this investigation. The periwinkles were bought from Lugbe Market, Abuja. The periwinkle shells were given a thorough water wash and scraped with a brush to get rid of any dirt or contaminants. After that, they were boiled for 15 minutes in 100°C boiling water to sanitize the sample and get rid of any impurities then sun dried for 12 hours.

Using a 2000W electrical powder grinder, the treated periwinkle shell samples were processed in this stage until shell powder was obtained. The material was ground up using a sieve with a 250mm opening before being placed to a clean container for storage. The yield that was obtained was 200g.



Figure 1: Periwinkle shell before and after the grinding process

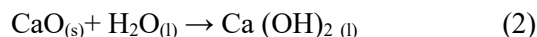
2.3 Synthesizing $\text{Ca}(\text{OH})_2$ from periwinkle shell (calcined)

Using a measuring scale, a sample of produced shell powder weighing about 30 grams was placed in a ceramic crucible and subjected to four hours of calcination at 900°C, followed by another sample at 1000°C. The sample was calcined in an electric furnace and then allowed to cool. The periwinkle shell powder will thereafter transform into pure CaO and release carbon dioxide. This process involves the thermal decomposition of calcium carbonate in the periwinkle shell to produce calcium oxide and

carbon dioxide as a by-product in the absence of air [6]. The chemical equation is shown below.



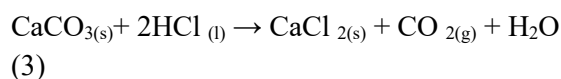
To extract calcium hydroxide from this, the CaO would undergo lime slaking, which refers to the reaction between calcium oxide and water [7]. This would produce calcium hydroxide also referred to as slaked lime.



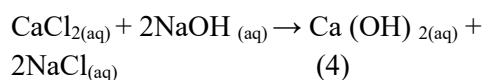
The resulting calcium oxide extracted from the PSA was mixed with 350 mL of distilled water. The solution was then decanted and filtered which yielded the calcium hydroxide needed for the experiment. The Ca (OH)₂ was then dried in an oven for about 4 hours. The dried powder gotten which is now Ca (OH)₂ extracted from calcined periwinkle shell ash was stored in an airtight container.

2.4 Synthesizing Ca(OH)₂ from periwinkle shell (Uncalcined)

First, 50 g of the sample was placed in HCl solution. The mixture was stirred continuously. This yielded a solution of calcium chloride and carbon dioxide.



125 ml of distilled water were used to dissolve 70g of NaOH, which was then gently added to the first reaction yield in order to extract the calcium carbonate. Equation for the reaction is provided in eq 4.



The resulting Ca (OH)₂ was decanted and dried in an oven at 100°C for 5 hours. The dried Ca (OH)₂ was also stored in an airtight container.

2.5 Characterization studies

Identification of molecular components is done via FTIR analysis. It works by assessing a sample's capacity to absorb infrared light [8]. Energy-dispersive X-ray spectroscopy, often known as EDS, EDX, or EDXA, is an effective technique for determining and characterizing the elemental structure of a sample [9].

2.6 Bentonite Clay Preparation

The bentonite clay was obtained from Nile University of Nigeria. 22 g of fine bentonite clay was used for each of the experiment performed. Four (4) different mud samples—A, B, C, and D—were prepared using various additives in variable amounts. 350 ml of water and 22 g of bentonite clay were combined in a variable-speed mud mixer to form the mud samples.

i.e.- The mass of Ca (OH)₂ added to several samples of the fresh mud was 2 g, 4 g, and 6 g respectively for sample B, C and D.



Figure 2: Bentonite clay preparation

2.7 Drilling Mud Properties Determination

pH test

The pH meter was first calibrated using distilled water to condition it for at least 30 minutes. The mud sample was poured into the glass beaker. The electrode was dipped about 2 cm to 3 cm into the formulated muds. The mud was then stirred with the tester. When the pH value displayed on the screen stabilized, it was recorded as the formulated mud pH value. The testing was done at room temperature.

2.8 Mud weight

The equipment was thoroughly cleaned and dried. The sample was poured into the cup with intermittent tapping to remove any entrapped air bubbles in the sample inside cup. After that, the rider was adjusted, and the balance arm was levelled horizontally; The calibrated arm of the mud balance was used to measure the density of the mud sample.

2.9 Rheological and flow properties tests

Using an OFITE Model 900 viscometer with eight (8) precisely controlled speeds and a wide range of shear rates from 3 (Gel), 6, 30, 60, 100, 200, 300, and 600 RPM, the rheological characteristics of the drilling mud samples were examined. With a regulator knob, the viscometer's speed was changed in RPMs, and the deflection readings were taken as displayed on the dial panel with lighting. Following that, the deflection readings and RPM values were used as inputs for the estimation of the drilling muds' rheological parameters, including apparent viscosity (AV), plastic viscosity (PV), yield point (YP) and gelling characteristics of the mud.

2.10 Filtration test

For samples A, B, C, and D, a static filtration test was performed using an API filter press. Throughout the experiment, Under the recommended API setting of 100 psi, the filtration test was carried out for thirty (30) minutes. The filtrate volume as well as the thickness and consistency of the filter cake deposited on the filter paper after 30 minutes of filtration were used to illustrate the mud samples' filtration control characteristics. Each of the examined samples had its filtrate volume and filter cake properties measured and recorded. The thickness of the mud filter cake is determined to the nearest centimeter.

3 | RESULT AND DISCUSSION

3.1 Calcination of Periwinkle Shell (Physical Observation)

After the Periwinkle shell ash was calcined for 4 hours. The appearance of the PSA compound is one of the first qualitative analysis that was analyzed. The physical observation of the sample is shown in the figure 3. The calcined sample at 900°C has a deeper color and appears grayish based on the figure 3a. The sample that was calcined at 1000°C, however, was whiter. It is established that solid white color is formed at high temperatures whereas dark or grey color is produced at low temperatures ^[10]. More metal oxide was formed at higher calcination temperatures ^[11]. The change in crystalline phase and structure is what caused the color transition.



Figure 3: Calcined PSA @900°C & 1000°C

Mass Loss

After being calcined at various temperatures, the mass loss for the calcium hydroxide recovered from calcined PSA was noted and compared. To examine the impact of calcination temperature on sample mass loss, the temperature for calcination was changed from 900°C to 1000°C. The results of the samples' mass loss are displayed in Table 1.

The data displayed in table 1 shows that when the temperature increases, the samples will lose more mass. According to the Table 1, the PSA had the most decrease in mass when calcined at 1000°C, which is 43.5% (16.95 g) and 40% (18 g) at 900°C. This is due to the fact that most samples

had been reduced to CaO when they were calcined at higher temperatures. This led to a significant loss of mass. The lower percentage of mass loss for PSA when calcined at 900°C is due to the partial conversion of CaCO₃ to CaO, which causes less mass loss.

Table 1: Mass loss for the calcined PSA at different temperatures

Calcination temperature	Mass before calcination (g)	Mass after calcination (g)	Mass loss (g)
900°C	30	16.95	13.05
1000°C	30	18	12

3.2 Characterization Studies

FTIR analysis

FTIR analysis was conducted on the periwinkle shell sample to provide insights on the functional groups present in these materials as shown in fig. 4.

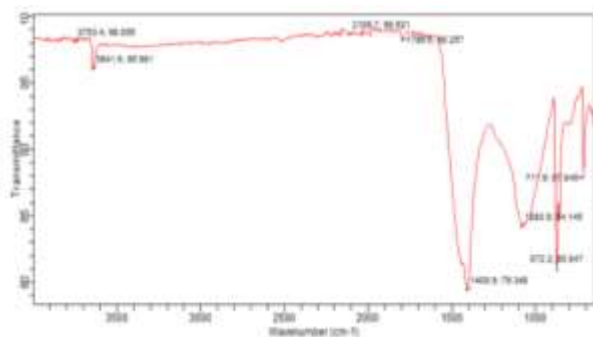


Figure 4: FTIR Analysis of Periwinkle Shell

Fig 4. depicts the Periwinkle shell ash's FTIR spectroscopy. The IR spectra displayed an O-H bond fitting of relatively low intensity band at 3641.6 cm⁻¹ and 3763.4 cm⁻¹. The bands at 2109.7 cm⁻¹ and 1796.6 cm⁻¹ represent harmonic vibrations of the elongation modes of C-O bonds, the bands at 1408.9 cm⁻¹, 872.2 cm⁻¹, and 711.9

cm⁻¹ may be associated to the three different elongation forms of C-O bonds. The features of the calcium carbonate's C-O stretching and bending modes are connected to the very strong band at 1408.9 cm⁻¹. This strongly implies that the majority of light is absorbed at this wavelength; as a result, carbonate makes up the majority of the periwinkle shell sample [12]. The additional trace elements found in the periwinkle shell sample are shown by the other peaks. These include aliphatic hydrocarbons, inorganic carbonate, and furans.

EDX analysis

Figure 5 shows the results of the microstructure and elemental composition of the periwinkle shell sample using scanning electron microscopy with attached energy dispersive spectroscopy (SEM/EDS).

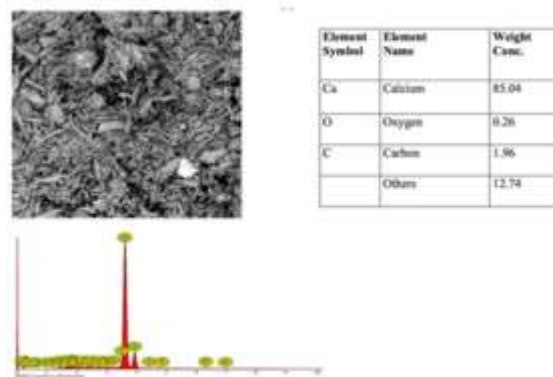


Figure 5: (SEM/EDS) image of periwinkle shell powder

The sample revealed a relatively fibrous appearance. There may be carbon strands present, which would explain the dark surface characteristics as shown in figure 5.

It is clear from the Figure 5 that the periwinkle shell is primarily composed of calcium (about 78%) and thus calcium is the periwinkle shell's primary elemental composition. However, the ED spectrum reveals trace levels of other elements

such carbon, potassium, oxygen, magnesium, sulfur, sodium, aluminum, and silicon.

3.3 Effect of Extracted $\text{Ca}(\text{OH})_2$ and Imported $\text{Ca}(\text{OH})_2$ on the mud properties

Mud parameters like pH, weight, and rheology were assessed in the prepared mud samples.

3.4 The effect of the local additives on the pH

The pH of an aqueous solution is defined as the negative log of the activity of the hydrogen ion. Acidic solutions are those with a pH under 7, and basic or alkaline solutions are those with a pH over 7.

Figure 6 demonstrates how the pH value increased together with the additive mass. The control mud sample's original pH level was 8.5. According to Figure 6, the addition of 2 g to 6 g of periwinkle shell ash resulted in a pH increase of 0.65% to 2.45%. Significant pH enhancement was observed when the $\text{Ca}(\text{OH})_2$ extracted from the calcined PSA (Sample B) was added to the control mud with 6 g of the additive increasing the pH by 2.45% while the pH of the $\text{Ca}(\text{OH})_2$ extracted from uncalcined periwinkle shell ash (Sample C) increased by 1.9% on the addition of 6 g of the periwinkle shell to the control mud and the commercial $\text{Ca}(\text{OH})_2$ (Sample A) had the least effect on the pH of the mud but still within the API standard.

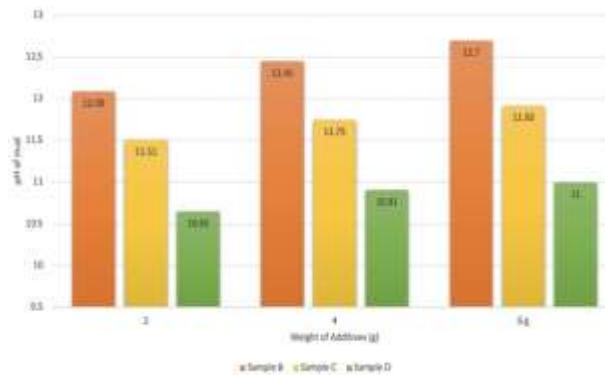


Figure 6: Effects of additives on pH of mud samples.

The calcined periwinkle samples had a pH that is greater than the uncalcined sample. Because CaO is more soluble in distilled water than CaCO_3 , more CaOH was produced, which suggests the existence of CaO in the calcined sample [13]. Overall, the findings support the effectiveness of periwinkle shell ash as a pH enhancer.

3.5 Effect of the local additives on mud weight

The mud weight of the control mud sample before the addition of the periwinkle shell sample was 8.50 ppg. Figure 7 depicts how the local additives affect mud weight. When 2 g of each local additive were added to different samples of control mud, the weight of the calcined PSA increased by approximately 2.32%, that of the uncalcined PSA increased by 1.18%, and that of the commercial $\text{Ca}(\text{OH})_2$ increased by 0.58%. The uncalcined PSA had more significant impact on the weight of the drilling fluid. The mud weight of calcined PSA gave 8.8 ppg, which is an increase of 3.5%, and that of uncalcined PSA gave 8.7 ppg, which is an increase of 2.35% when 6 g of each local additive were added to various samples of the control mud.

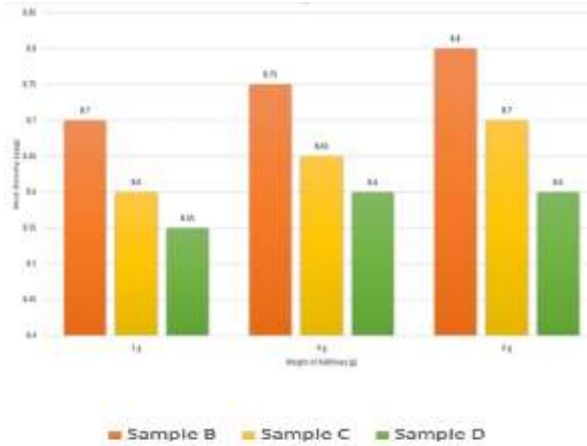


Figure 7: Effects of additives on mud density

According to this experimental finding, the formulation's mud weight increases as the amount of additives added increases. The most significant mud attribute influencing penetration rate is density [14]. The higher the density, the bigger the differential pressure will be for any given formation pressure. The mud may be too thick, and the added weight could result in decreased circulation [15]. Hence, the weight of the mud must be just right to contain the formation fluid without degrading it. The recommended amount of mud weight in the field is approximately 8 to 11 ppg. As a result, the mud weight for the calcined and uncalcined periwinkle shell ash is within the standard specification, and it can be seen from Figure 7 that adding the PSA to the drilling fluid at different concentrations has no noticeable impact on the density value, indicating that using the PSA as lost circulation material is a good option.

3.6 Effect of additives on Rheological Properties

Drilling fluids must have certain rheological characteristics in order to carry drilling cuttings, increase penetration, ensure downhole safety, and minimize formation damage [16]. For the experiment, the samples were prepared by adding $\text{Ca}(\text{OH})_2$ extracted from calcined, uncalcined periwinkle shell ash and the commercial Ca

$(\text{OH})_2$ to bentonite clay. The concentrations which were used here are 2 g, 4 g and 6 g.

3.7 Shear stress vs Shear rate

According to Figure 8 a- 8c, an increase in PSA concentration resulted in an increase in shear stress required to circulate the drilling fluid in the annulus. Several PSA additive concentrations have been added to the bentonite content to create various samples. The graphs below demonstrate that the shear stress increases as the additive concentrations increase. This indicates that shear stress is high at higher concentrations.

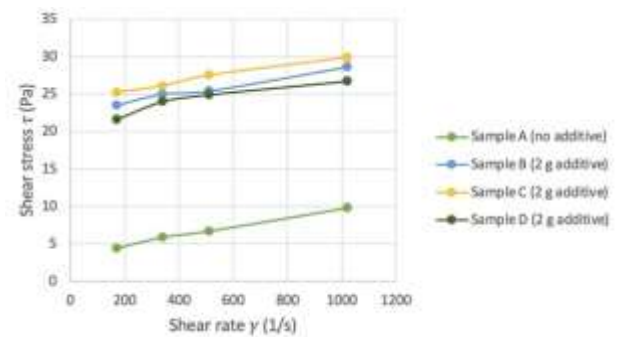


Figure 8a: Shear stress vs shear rate graph for 2g additive

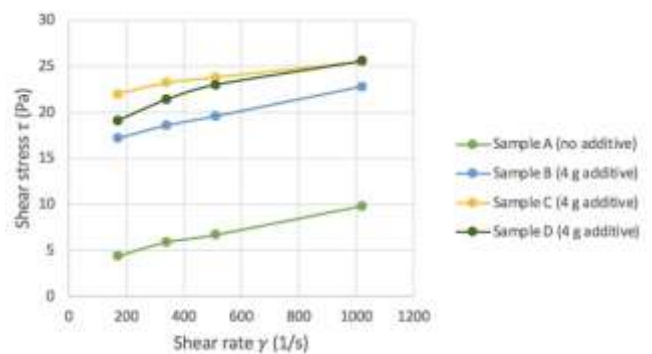


Figure 8b: Shear stress vs shear rate graph for 4 g additive

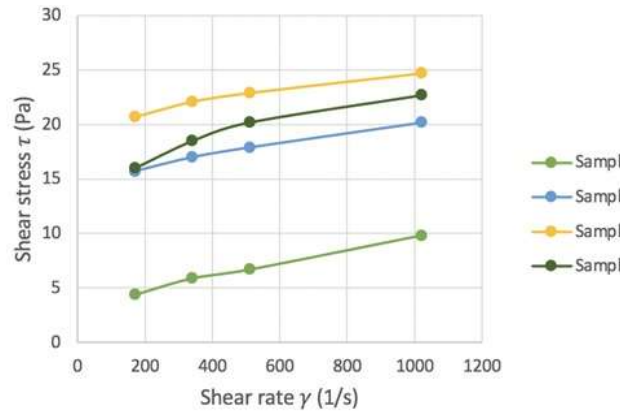


Figure 8c: Shear stress vs shear rate graph for 6 g additive

Plastic Viscosity

The concentration of the additives used to estimate the viscosity of the mud samples is shown in the figure 9. All viscosity measurements were made at 25°C room temperature. The initial test mud sample with no additives has a viscosity of 3.0 cp, but the other samples' plastic viscosities increased as the mass of additives increased and ranged from 4.1 cp to 5.6 cp. The plastic viscosity of the conventional calcium hydroxide was higher than the PSA additives used. The calcined PSA additive also had a higher plastic viscosity than the uncalcined PSA additive. Moreover, the values gotten were not within the API recommended values for plastic viscosity. A high plastic viscosity can lead to issues like differential sticking due to increase in solid content, the rate of penetration would also be affected as thicker mud will have bigger hold down effect than thinner mud, hence leading to a reduced rate of penetration [17].

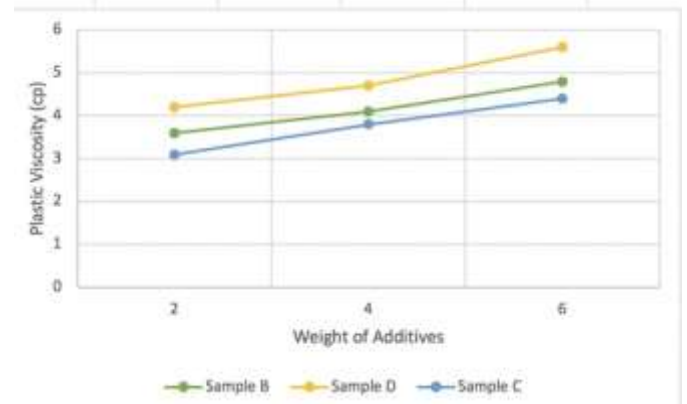


Figure 9: Influence of additive on plastic viscosity

Yield Point

The results in fig 10 indicate that the yield point increases for all samples as the additive increased. The conventional calcium hydroxide had a slightly higher yield point value than the PSA additive. however, all the yield point values are within the API recommended range for yield point values. Having a high yield point indicates that the drilling fluid would carry cuttings better than that with a low yield point. However, having a very high yield point could result in large frictional pressure losses which could hinder the ability of the drilling mud to carry cuttings to the surface. The results show that the PSA additive could be used in place of the conventional calcium hydroxide as this will not cause any negative impact on the yield point during drilling operations.

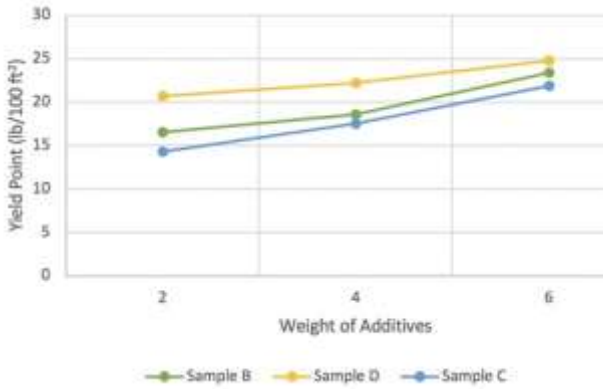


Figure 10: Influence of additive on yield point

Apparent viscosity

The apparent viscosity is very important in preventing various drilling problems and improving well cleaning. It was observed from Fig.11 that apparent viscosity was increased as the amount of additive increased for all samples. The result gave reasonable apparent viscosity values.

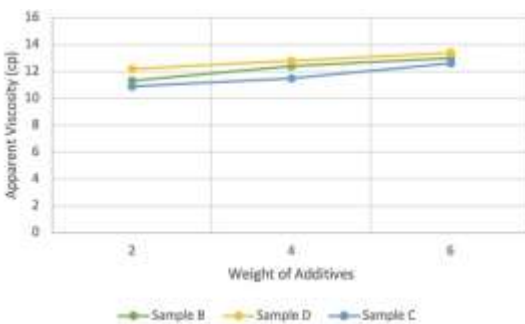


Figure 11: Influence of additive on apparent viscosity

Gel Strength

The gel strength reading was taken after the 10 seconds and the other after 10 minutes which was calculated directly from the rotational viscometer. The readings in fig. 12 show that an increase in concentration of the additives increased the gel strength at 10 secs and 10 minutes, however, the PSA additive does not have enough gel strength as recommended by the API standard which will enable suspend drill cuttings and weighting materials during circulation. Unfavourably, low

and high gel strength can lead to sticking of the drill string due to the accumulation of drilled cuttings in the formation [18].

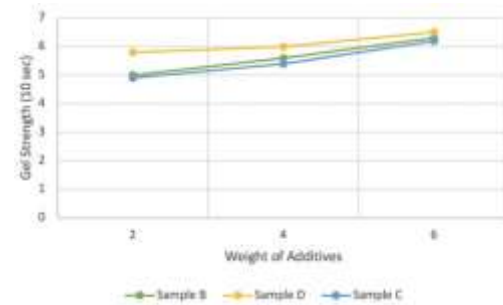


Figure 12: Influence of additive on Gel Strength (10 sec)

3.8 Effect of additives on Filtration Properties

Based on the Figures 13, 14, and 15, it is seen that the solid from the mud produced a layer of solid termed "mud cake" on the filter paper. The result has shown to have very thick mud cakes formed and a high amount of fluid being lost. With increasing additive concentration, filtrate loss increases for all samples with physical examination of the filter cakes showed that filter cake formed by sample B, prepared with 2.0 g of PSA, was thinner (0.75 mm thick) and the filter cake formed by sample C with 6g of PSA was the thickest (1.2 mm thick). After 30 minutes of filtration, mud samples A which is the base mud had a filtrate volume of 18ml while mud sample B, C, and D with 2g of PSA produced the least amount of filtration volume (90ml, 36 ml, and 143 ml filtrate volumes, respectively) as shown in figures 16 a,b and c . Mud samples B, C, and D with 6g of PSA produced the highest amount of filtration volume (142.2 ml, 84.4 ml, and 180 ml filtrate volumes, respectively). Sample D showed the highest amount of filtrate loss volume gotten.

The filtrate volume grows as the additive concentration rises. Which shows the poor mud filtration characteristics for all the samples. Hence, periwinkle shell ash has shown to have

poor filtration control characteristics with thick mud cake. A thick mud cake is usually not recommended in drilling operations as this could affect wellbore operations such as differential sticking, well completion and wellbore clean-up operations.

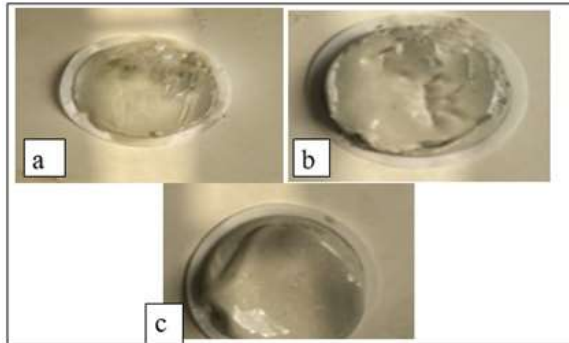


Figure 13 a,b &c: Mud cake outcome for Sample B at 2g, 4g and 6g.

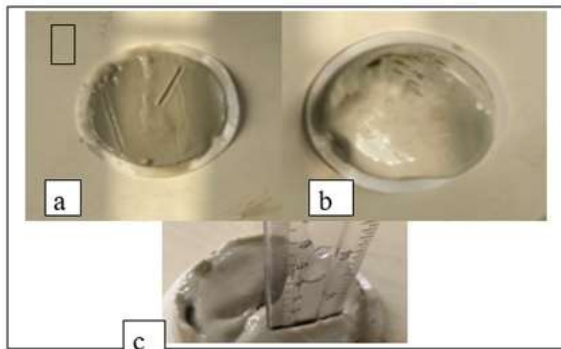


Figure 14 a,b &c: Mud cake outcome for Sample C at 2g, 4g and 6g.

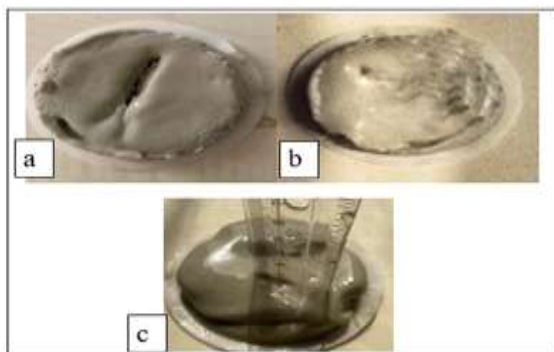


Figure 15 a,b &c: Mud cake outcome for Sample B at 2g, 4g and 6g.

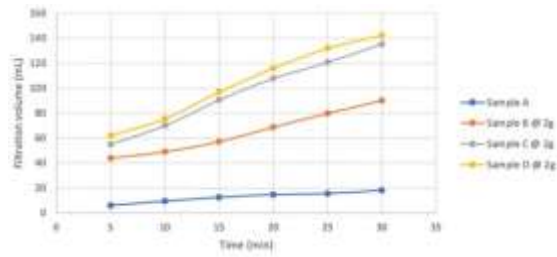


Figure 16a: Filtrate loss volume against time for 2 g additive

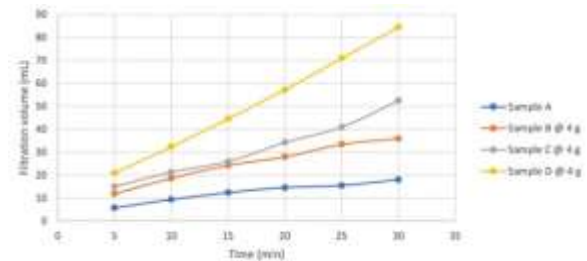


Figure 16b: Filtrate loss volume against time for 4 g additive

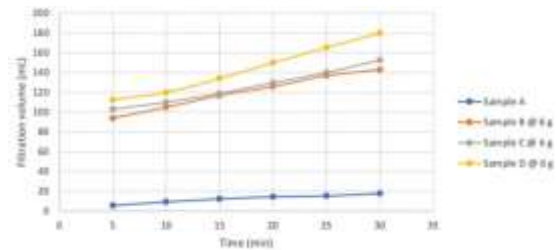


Figure 16c: Filtrate loss volume against time for 6 g additive

4 | CONCLUSION

The pH of the mud is improved as the additives are gradually added, measuring up to the traditional calcium hydroxide in terms of pH enhancement. However, the addition of $\text{Ca}(\text{OH})_2$ from both sources exhibited poor filtration characteristics as there was high filtrate loss as the filtration time and the additive concentration increased which could affect the formulation and the performance of the drilling mud.

Investigating the Potential of using PSA with another local additive that has good filtration and rheological properties can be further investigated. Additionally, the scope of this research is limited to water-based mud (WBM). It is suggested that this research project be expanded to include other drilling fluids with laboratory tests to mimic the real conditions during drilling operations, particularly with regard to the temperature and pressure of a particular selected reservoir.

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