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Evaluation of the Potential of Calcium Hydroxide Synthesized from Eggshells as a Drilling Fluid Additive

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Abstract

This research work studied the suitability of $Ca(OH)_2$ synthesized from eggshell as a drilling fluid additive. $Ca(OH)_2$ was synthesized from calcined eggshells (CES) and uncalcined eggshells (UCES) and characterized using FTIR and EDX. Samples of one laboratory barrel of water-based mud were prepared using bentonite clay from Afuze, Edo State, Nigeria, and the synthesized $Ca(OH)_2$ produced from CES and UCES and commercial $Ca(OH)_2$ were added to different mud samples prepared, and its effect on the mud properties were tested for. The results obtained from the experiment conducted showed that the synthesized $Ca(OH)_2$ gave comparable pH values as the commercial $Ca(OH)_2$. Hence it served primarily as a pH enhancer. However, the addition of $Ca(OH)_2$ from both sources increased the filtrate volume and mud cake thickness far beyond API standard which might create wellbore problems due to the high filtrate loss and mud cake thickness that were observed.

***Keywords**: Drilling fluids; Eggshells; Calcium hydroxide; Calcined eggshells; Uncalcined eggshells; pH.*

1. Introduction

Drilling fluids used in the drilling of wells provide a host of numerous functions during drilling operations. It is one of the most important components of any drilling process, and the success of a drilling operation depends on the type and properties of drilling fluids used. It is a complex mixture of compounds which, based on its continuous phase can either be water based, oil based or gas based [1]. Some of its functions include the cooling and lubrication of the drill bit and string, cleaning of the drill bit face and bottom of the hole, the suspension of solids and transportation of cuttings to the surface. In most operations, it is also relevant in the stabilization of the wellbore, controlling subsurface pressures and gathering of subsurface geological, and formation evaluation data when the cuttings are brought to the surface [2-10].

The effectiveness of the drilling fluid depends on how well its properties such as; pH, viscosity, mud weight/density, filtration properties and gel strength, etc. are maintained. Failure to meet the desired function of the mud can be costly and can result in the loss of hole and other resources. Hence, careful selection of the drilling fluids, as well as its formulation, is imperative for a successful drilling process. Beyond these, continuous research is encouraged to ensure appropriate management of the running cost and associated environmental impact necessary to keep the drilling fluid properties in good condition during drilling operation [11].

Drilling through reservoirs that contain acidic gases poses a threat to the bottom hole assembly and the circulatory system. These gases expose drilling equipment to corrosion which might result in incessant down time and increase the cost of the drilling operation. To mitigate this problem, API standards recommend that the drilling fluid pH range should be 9.5-12.5, which is in the alkaline region [12]. Achieving this requires the use of chemicals (pH enhancers) which are added to the mud to raise the mud pH to the API standard. Some examples of pH enhancers used in the industry include calcium hydroxide ($Ca(OH)_2$), caustic soda (NaOH), soda ash (Na_2CO_3) etc.

In recent times, especially in the Nigerian oil and gas industry, there is an urgent need to examine suitable locally sourced materials that can serve as substitutes to imported chemicals used in the industry [13]. According to [14] that not until the civil war in Nigeria, some of the wells were actually drilled using local additives and the usage of these local additives reduced especially after the civil war. Some of the reasons for the reduction of the use of local additives were due to the civil war and this gave room for the importation of chemicals and to date, the industry still depends on these imported chemicals.

This research work tends to provide an alternative substitute for conventional chemicals (pH enhancers). This was achieved through an appropriate investigation of the potential of eggshells as a pH enhancer in water-based drilling fluid by first processing the egg shell to produce the active compound ($Ca(OH)_2$) necessary for pH enhancement using two different process route. The production process involves the calcination of eggshells, which contain calcium carbonate ($CaCO_3$) to extract calcium oxide (CaO) which was used to produce calcium hydroxide ($Ca(OH)_2$) [15]. Calcium hydroxide was also synthesized directly from the eggshells without calcination. The $Ca(OH)_2$ produced from both process route were then added to a prepared laboratory barrel of mud to study how the additive will have an impact on the mud properties.

2. Methodology

2.1. Materials and equipment

2.1.1. Equipment

The equipment used for this study includes variable speed mud mixer (single spindle Hamilton Beach commercial mixer); weighing balance (Dikomsan weighing balance; Model JS 06 BH); compact mould and rammer (UTEST); UTEST laboratory Test sieve; mud balance (OFITE Atmospheric Mud balance); viscometer (OFITE Viscometer, 900V.G Model); digital pH meter (METTLER TOLEDO pH/MV meter, Model FiveEasy LE438); API standard filter press; drying oven (UTEST Material Testing Equipment); dry blender (Century Electronic Blender, Model CB-8231-D); OFITE compactor; furnace (Lindberg Cole Parmer Box Furnace, Model CBFM516C); EDX (Model EVO LS 10); Fourier transform infrared spectroscopy (FTIR) (ThermoFisher Scientific FTIR, Model Nicolet iS5).

2.1.2. Materials

The reagents and chemicals used for this study include distilled water, sodium hydroxide (NaOH), hydrochloric acid (HCl), eggshells, calcium hydroxide ($Ca(OH)_2$) and bentonite clay.

2.2. Preparation of eggshells

Eggshells were collected from the cafeteria as domestic waste, at Nile University of Nigeria, Abuja. There were washed, boiled, dried in an oven at 100°C for 30 mins, pulverized using a dry blender, and sieved using a mesh size of 106 μm. The processed eggshell was tagged as an uncalcined egg shell (UCES) and stored in an airtight container prior to the synthesis.

2.3. Synthesis of calcium hydroxide

2.3.1. Synthesis of calcium hydroxide from calcined eggshells (CES)

Calcination of eggshells involves the thermal decomposition of the calcium carbonate ($CaCO_3$) present in the eggshells in the absence of air to produce calcium oxide (CaO) and carbon dioxide (CO_2) as a by-product [15]. The chemical equation of the reaction is shown in equation 1 [16].

$$CaCO_{3(s)} \overset{\Delta}{\rightarrow} CaO_{(s)} + CO_{2(g)} \tag{1}$$

Slaking, on the other hand, is the reaction between calcium oxide and water or moisture to form calcium hydroxide. The chemical equation of the reaction is shown in equation 2.

$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(l)}$ (2)

65.5 g of processed eggshells were weighed and heated in a furnace at a temperature of 1000°C for 3 hours [15,17]. Calcined eggshells are referred to as CES. This was left to cool for 2 hours and stored in an airtight container. 15 g of the of the calcined eggshell was weighed and mixed with 125 mL of distilled water. This process is referred to as the slaking of lime, as described in equation 2. The resulting $Ca(OH)_2$ was decanted and dried in an oven at 100°C for 5 hours. The dried $Ca(OH)_2$ was then stored in an airtight container.

2.3.2. Synthesis of $Ca(OH)_2$ from uncalcined eggshells (UCES)

126 mL of HCl was diluted with 175 mL of distilled water. 70 g of the UCES was weighed and added to the prepared diluted HCl and stirred continuously. Similarly, 63 g of NaOH was dissolved in 125 ml of distilled water. The NaOH solution was slowly added to the product of the first reaction to yield a precipitate of $Ca(OH)_2$. Equations for the reactions are given below.

$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow CaCl_{2(s)} + CO_{2(g)} + H_2O_{(l)}$ (3)

$CaCl_{2(aq)} + 2NaOH_{(aq)} \rightarrow Ca(OH)_{2(aq)} + 2NaCl_{(aq)}$ (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.

2.4. Characterization studies

Characterization studies of UCES, CES and the $Ca(OH)_2$ synthesized from the UCES and CES were done using Fourier transform infrared spectroscope (FTIR) [18] and Energy Dispersive X-ray Analyzer (EDX) to determine the functional groups and elemental composition of the UCES, CES and the synthesized $Ca(OH)_2$ respectively.

2.5. Formulation of drilling mud

2.5.1. Bentonite clay preparation

The bentonite clay used in this research work was sourced from Afuze, Edo State, Nigeria. It was dried in a drying oven at 60°C for 24 hours, and it was crushed using a compact mould and rammer. The pulverized clay was sieved using a mesh size of 74 µm. 350 ml of distilled water was mixed with 17.5 g of bentonite clay in a variable speed mud mixer to prepare the mud. The mass of $Ca(OH)_2$ added to several samples of the fresh mud was 0.4 g, 0.8 g, and 1.2 g respectively. The mud was beneficiated using the following design to ascertain the effect of the synthesized and commercial $Ca(OH)_2$ on the mud properties.

- Sample A – Control sample, i.e. mud without additive.
- Sample B – Drilling mud with $Ca(OH)_2$ from CES
- Sample C – Drilling mud with $Ca(OH)_2$ from UCES
- Sample D - Drilling mud with Conventional $Ca(OH)_2$

2.6. Drilling mud properties determination

2.6.1. pH Test

The test was conducted using a digital pH meter to determine the pH of the prepared drilling mud samples (A, B, C, and D).

2.6.2. Mud weight test

The test was conducted using a mud balance. It was also conducted for all the mud samples (A, B, C, and D).

2.6.3. Filtration test

The filtration test was conducted for a total time of 30 mins using an API standard filter press. The filtrate volume was measured at 5 mins intervals, and at the end of the test period, the thickness of the mud cake was measured using a millimetric rule. This process was carried out for samples A, B, C and D when 0 g and 1.2 g of both the synthesized and commercial $Ca(OH)_2$ was added to the mud samples.

2.6.4. Rheology test

An OFITE viscometer was used to measure the viscosity of the mud. The plastic viscosity and gel strength at 10 sec and 10 mins were determined. The reading of the viscosity, shear stress and shear rate were obtained at 6 rpm, 30 rpm, 60 rpm, 100 rpm, 200 rpm, 300 rpm and 600 rpm. This test was conducted for samples A B, C, and D respectively.

3. Discussion

3.1. Effect of calcination on the eggshell

Table 1 shows the mass of UCES and CES. It was observed that the percentage change in mass from the UCES to CES was about 50%. The mass change is half of the initial mass of the UCES prior to calcination. This reduction in mass was as a result of the loss of CO_2 from the eggshells during calcination as a by-product. The loss of CO_2 results in the formation of cavities or pores (holes) in the CaO and consequently, reducing its weight. Moreover, colour change from whitish grey to pure white was observed and identified to be in consonance with the literature [15,17]. Figure 1 shows both UCES and the CES.

Table 1. Mass of UCES and CES

S/N	Sample	Mass (g)
1	Uncalcined eggshells (UCES)	65.5
2	Calcined eggshells (CES)	32.74

Figure. 1. Eggshell before and after calcination: a) UCES; b) CES

3.2. Characterization studies of the synthesized $Ca(OH)_2$ from UCES and CES

3.2.1. FTIR analysis

The FTIR analysis of synthesized $Ca(OH)_2$**,** UCES, and CES samples are shown in Figure 2. Some absorption bands (peaks) within the range of 1500 and 875 cm^{-1} indicate the presence of carbonate groups in UCES in Figure 2(a). The highest peak obtained was at 1420.09 cm^{-1} with an absorbance of approximately 2.4. This convincingly suggests that most of the light is absorbed in this wavelength; hence, carbonate is the major component in the eggshell sample. This is in agreement with the work done by [15]. Also, the absorption band between 1800-1600 cm^{-1} shows the presence of C=O which is seen by the peak at the wavenumber of 1799.46 cm^{-1}. The other peaks seen represent additional trace elements present in eggshells. These include inorganic carbonate, furans and aliphatic hydrocarbons.

In Figure 2(b), the absorption band and concentration of peaks between 518.54-422.12 cm^{-1} show the presence of CaO in the calcined eggshell (CES). From the concentration of the wave numbers within this absorption band, it can be deduced that most of the sample is made up of CaO. On the other hand, the sharp peak with a wave number of 3640.93 cm^{-1} indicates the presence of O-H in $Ca(OH)_2$. This means that the cavities formed in CaO as a result of the calcination have been filled with H_2O as a result of the absorption of moisture from the atmosphere [15,17].

In Figure 2(c), the absorption band for the $Ca(OH)_2$ produced from UCES occurred between 3697.32 cm^{-1} and 433.47 cm^{-1}. The wavenumber 3642.33 cm^{-1} indicates the presence of $Ca(OH)_2$ in the sample, having the highest peak and absorbance of 3.0. Therefore, it can be inferred that the sample is made up mostly of $Ca(OH)_2$ Other materials observed to be present in the prepared samples are impurities, such as inorganic carbonate.

In Figure. 2(d), the absorption band was between 3904.08 cm^{-1}-666.54 $cm^{-1,}$ and wave numbers of 1410.76 cm^{-1} and 873.94 cm^{-1} were observed. These indicate the presence of carbonate with an absorbance intensity of 1.75 which is greater than that of CES but less than that of UCES. The wavenumber at 1793.05 cm^{-1} identifies C=O bonds which is a characteristic of $CaCO_3$. The wavenumber at 3642.17 cm^{-1} and an absorbance intensity of 1.7 indicate the presence of strong O-H bond which confirms the presence of $Ca(OH)_2$.

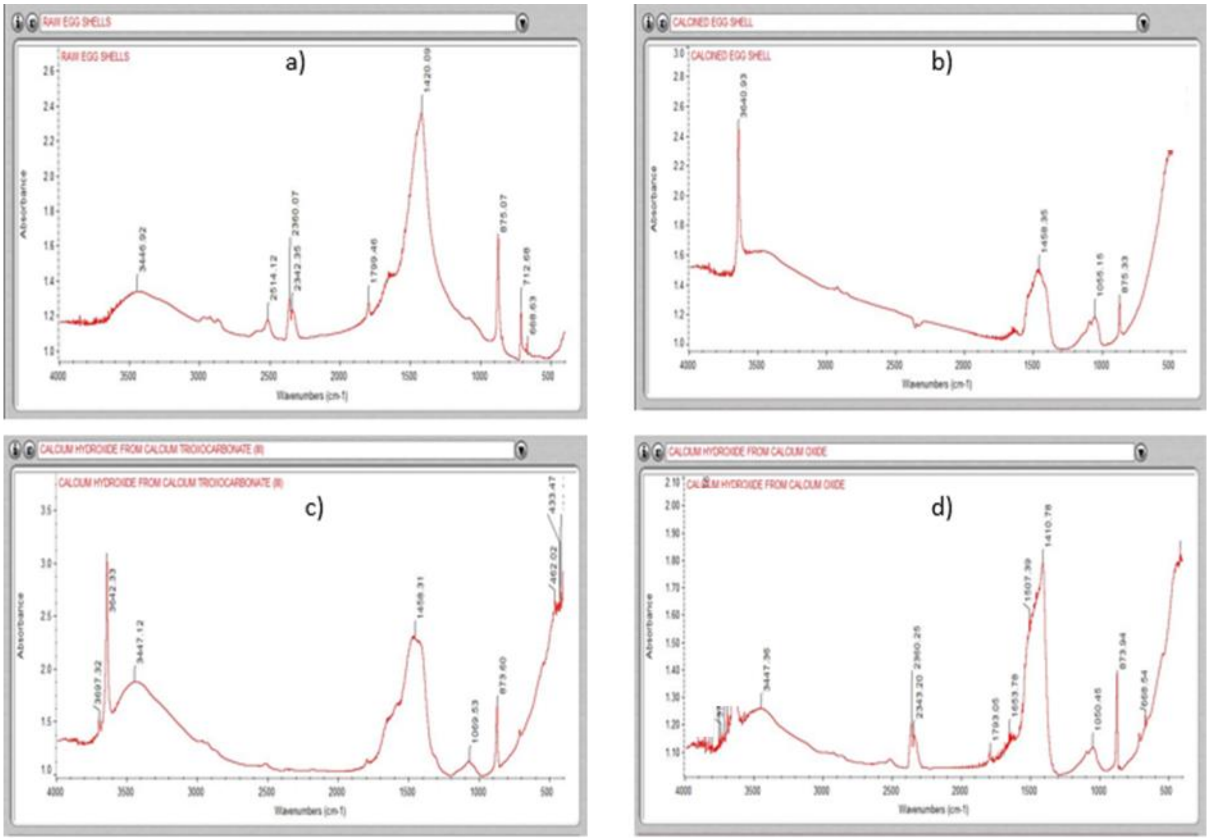
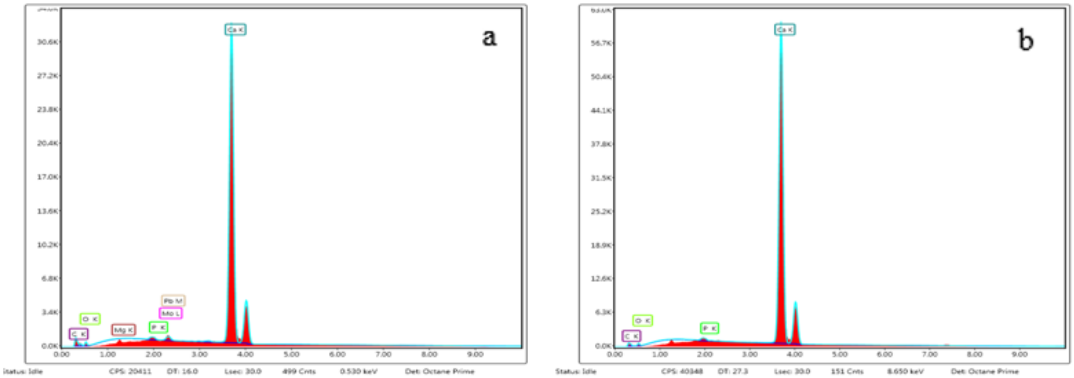


Figure 2. FTIR Results: a) UCES; b) CES; c) $Ca(OH)_2$ from UCES; d) $Ca(OH)_2$ from CES

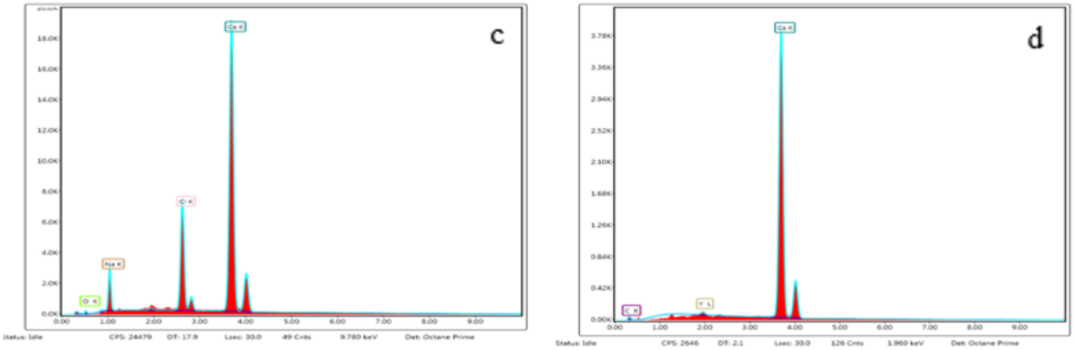
3.2.2. EDX analysis

The EDX analysis of the synthesized $Ca(OH)_2$ and processed UCES and CES samples are shown in Figure 3. In the elemental composition of each sample, it was very clear that calcium (Ca) had the highest percentage concentration, among other components. The formation of calcium hydroxide leads to the removal of some of the elements that were present in the UCES. This was more evident with the EDX analysis of the synthesized $Ca(OH)_2$ from CES.



UCES

CES



Ca(OH)2 from UCES

Ca(OH)2 from CES

Figure 3. EDX Analysis; a) UCES; b) CES; c) $Ca(OH)_2$ from UCES; d) $Ca(OH)_2$ from CES

3.3. Effect of the synthesized and commercial $Ca(OH)_2$ on mud properties

3.3.1. Mud pH

The effect of the two synthesized $Ca(OH)_2$ and commercial $Ca(OH)_2$ on the mud pH was fully expressed in Figure 4. These three additives increase the mud pH as their mass is increased. The addition of synthesized $Ca(OH)_2$ from CES into the blank mud, the mud pH increased from 7.21 to 9.52 for sample B. Here, we have sample B with a higher mud pH. Cumulative addition of 1.2 g of the synthesized $Ca(OH)_2$ from CES increased the mud pH further to 10.68. The pH of the mud at this point met with the API standard [12]. In sample C, the addition of synthesized $Ca(OH)_2$ from UCES increases the mud pH from 7.21 to 9.21.

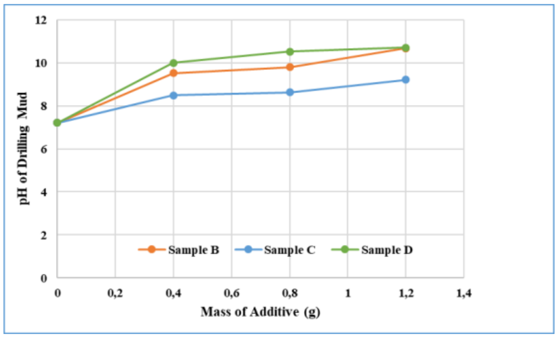


Figure 4. Plot of pH against mass of calcium hydroxide

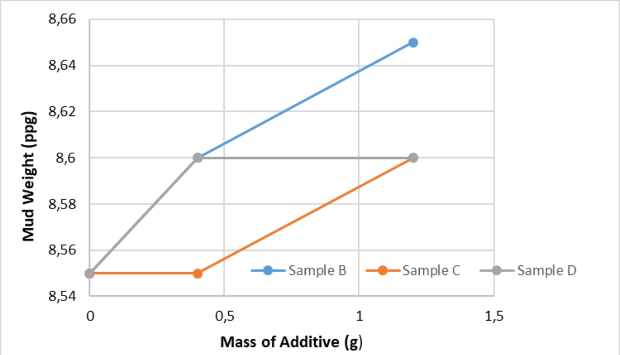


Figure. 5. Plot of mud weight against mass of additive

For sample D, the pH of the drilling mud increases with an increase in the mass of the additive used. The pH obtained due to the addition of the additives was up to the API standard. The pH of sample D increased from 7.21 to 10.7 and recorded an increase of 48.4 %.

3.3.2. Mud weight

The addition of the three additives had a slight effect on the mud weight, as shown in Figure 5. The mud weight increases with increasing mass of the additive. The highest mud weight obtained was gotten at the mass of 1.2 g for sample B which reached the minimum API specification for mud weight. Sample C and D did not reach the recommended API specification for mud weight even at the highest concentration used for this work.

3.3.3. Filtration properties

Results were describing filtration properties in Figures 6 and 7 clearly shown total filtrate losses of 218.8 mL, 81.6 ml and 231 mL, and mud cake thickness of 5 mm, 2 mm and 6 mm for samples B, C and D (Table 2) respectively. The total filtration loss in sample A was quite small when compared to samples B, C and D. These results obtained when the additive was used caused a significantly increase in filtrate loss when compared to the filtrate loss obtained from sample A which was 21.2 mL. This shows that the total filtration losses in samples B, C and D and the thickness of the filter cakes produced were not within the recommended API standards.

The increase in the filtrate volume is quite challenging to the realistic usage of these additives as they can lead to more mud invasion and drilling problems, which translates into an increase in the drilling operations cost. While comparing the effect of the three additives, sample C had the least effect compared to sample D which contains the conventional $Ca(OH)_2$ giving sample C more preference in situations where $Ca(OH)_2$ needs to be used during drilling operations. Another notable observation was identified in Figure 7 which shows the mud cake obtained from all samples under analysis. It was also observed that the mud cake from sample B and sample D have cracks within their matrixes. This was due to the extent of filtrate loss that occurred during the filtration test. Sample C was smooth and moisturized, just like sample A indicating the extent of the filtrate loss.

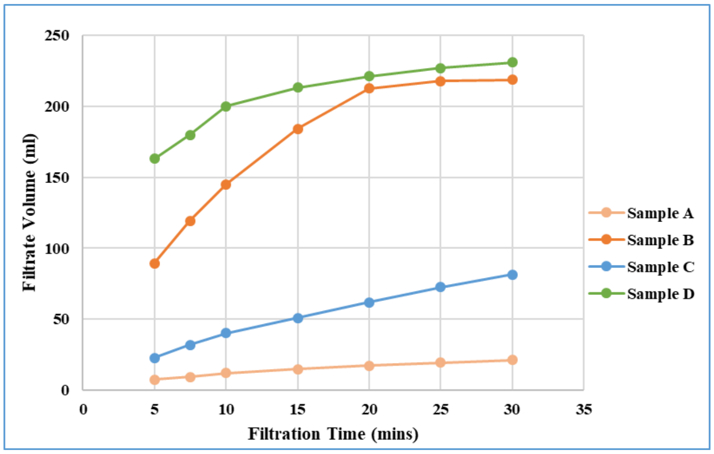


Figure 6. Plot of filtrate volume against filtration time

Table 2. Mud cake thickness

S/N	Additive type	Mud cake thickness (mm)
1	Sample A	1
2	Sample B	5
3	Sample C	2
4	Sample D	6

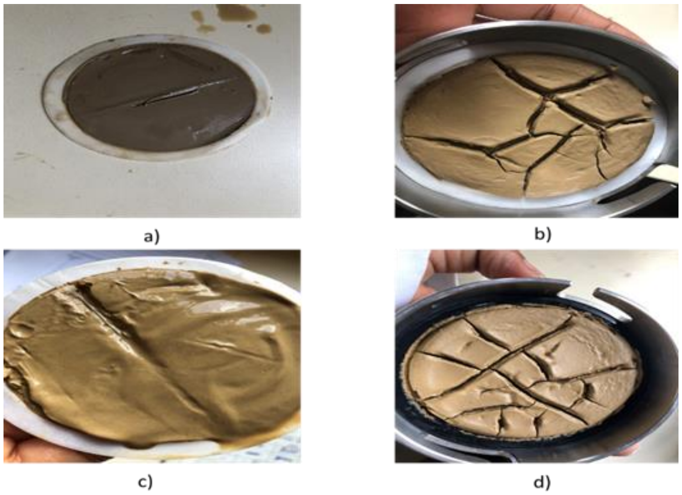


Figure. 7. Mud cake: a) Control sample; b) $Ca(OH)_2$ from CES; c) $Ca(OH)_2$ from UCES; d) Commercial $Ca(OH)_2$

3.3.4. Mud rheology

3.3.4.1. Shear stress vs. shear rate

It was very clear, as shown in Figures 8 and 9 that even at different concentrations the shear stress and shear rate for all samples have a direct relationship. This confirms the behaviour of the drilling fluid. When 0.4 g of the additives were added, sample C had the highest effect on the relationship. However, a diminishing return ensues and the least effect was observed when the quantity of additive in the mud reaches 1.2 g.

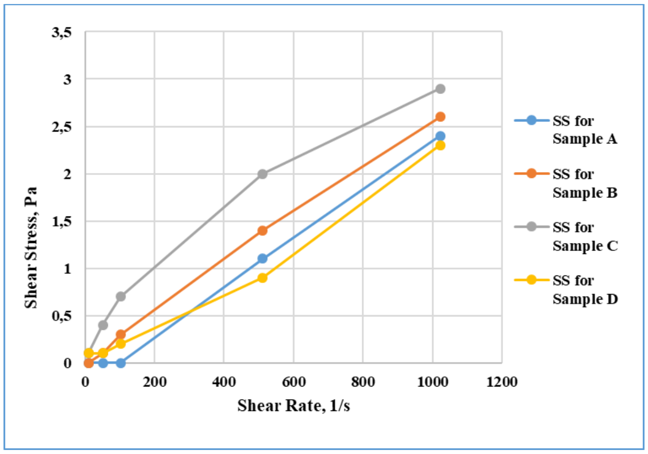


Figure 8. Plot of shear stress against shear rate at 0.4 g of $Ca(OH)_2$

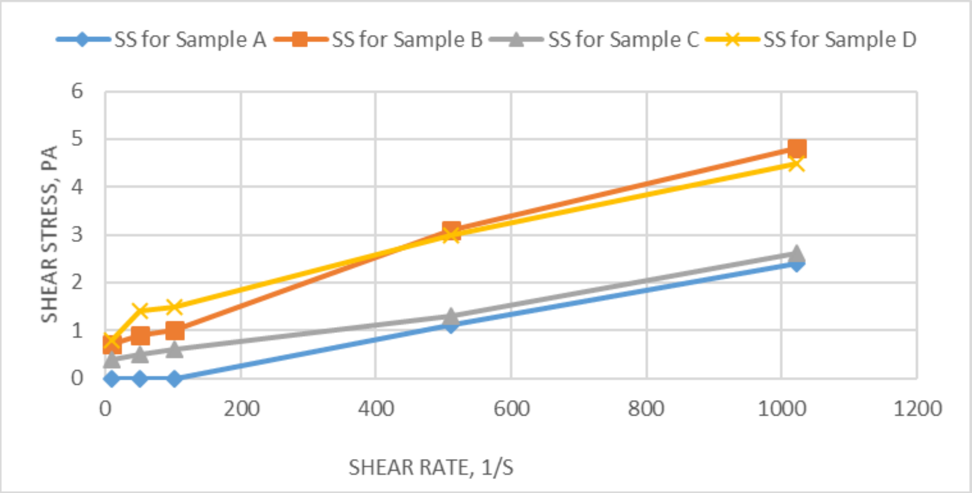


Figure 9. Plot of shear stress against shear rate at after 1.2 g $Ca(OH)_2$

3.3.4.2. Viscosity vs. Shear Rate

The shear thinning behaviour became very obvious on the addition of 1.2 g of all the three additives, as shown in Figure 10. This observation is desirable because, at a low shear rate, the viscosity will be high enough to suspend drilling cuttings while at a high shear rate, the viscosity will be low and thus, low pump energy will be required to start fluid circulation.

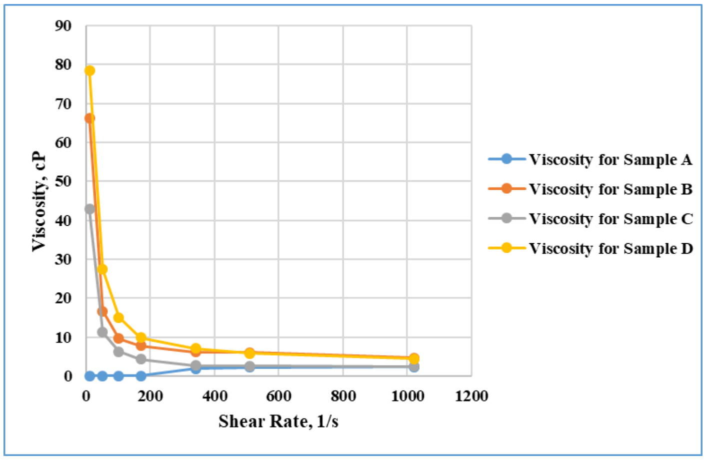


Fig. 10. Plot of viscosity against the shear rate at 1.2 g

4. Conclusion

$Ca(OH)_2$ was synthesized from UCES and CES, and the $Ca(OH)_2$ synthesized from CES had the highest material yield. It gave the most promising pH enhancement and has the potential to replace conventional $Ca(OH)_2$ when compared to $Ca(OH)_2$ synthesized from UCES. The synthesized $Ca(OH)_2$ served primarily as a pH enhancer. Similarly, the addition of 1.2 g of commercial $Ca(OH)_2$ increased the filtrate volume from 21.2 mL to 218.8 ml while the addition of 1.2 g of $Ca(OH)_2$ synthesized from UCES increased it to 81.6 ml. The values obtained gave a cause of concern in a situation that necessitates the use of $Ca(OH)_2$ and Afuze clay. Though the filtrate loss when Ca(OH), $_2$ synthesized from UCES was used had the least value compared to other sources of $Ca(OH)_2$.

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