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POTENTIAL OF LOCAL pH CONTROL ADDITIVES FOR CORROSION INHIBITION IN WATER BASE DRILLING FLUIDS

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Abstract

Corrosion of metals during drilling operation poses serious technical and economic challenges. Consequently, corrosion scavengers are commonly used in drilling fluids. However, Magnetite, the most HSE compliant scavenger is characterized by low reaction rates. Hence the best practice is to maintain the muds pH between 8.0 and 10.5. The objective of this study is to evaluate four pH control additives for corrosion inhibition and rheology in simulated hydrogen sulfide environment. Five (5) sulfurized mud samples were formulated with alkali obtained from cocoa pod husk, rice husk, groundnut shell, plantain peel, and potassium hydroxide. Oil-well steel coupon (N-80 Steel) was used for the corrosion tests by the weight loss method. The test temperatures were 27, 47, 67 and 87°C for pressures of 3000, 4000 and 5000 psi. The result shows that cocoa pod extract exhibited high corrosion inhibition potential when compared to the synthetic KOH. Also, cocoa pod extract is more stable thermally and is very effective reducers of filtration loss at high temperatures. However, it shows a thinning tendency and mud may require additional viscosifier to improve its rheology.

Keywords: Corrosion; Water base mud; Rheology; Scavenger; filtrate loss; local additives.

1. Introduction

Many industries all over the world have suffered significant losses due to corrosion. According to the 2002 U.S. corrosion study, the direct cost of metallic corrosion is $276 billion on an annual basis [1]. Corrosion remains a major concern to oil and gas industries because it causes excessive sand production, emulsion formation, surface equipment failure and site accidents [2]. Protective coatings are commonly used for corrosion inhibition during the drilling operation. However, the unprotected portion of the drill strings are always susceptible to corrosion attack. The harsh, acidic and hazardous environment in underground drilling operations had facilitated research in the area of designing of new compounds and mixtures with both local and foreign materials to meet specific needs of drilling operations.

Drilling fluids perform better in a pH range between 8.0 and 10.5 for water-base mud [3]. If the pH of the mud is below 7.0, it becomes acidic and can corrode the drilling equipment and also pollute the environment. Imported chemicals such as sodium carbonate [Na_2CO_3], sodium hydroxide [NaOH] and calcium hydroxide [$Ca(OH_2)$] are usually added to the mud to raise the mud pH to 8.0 or 10.5. When drilling across formations, the presence of contaminants such as salt [chlorides] water, calcium carbonates, and sulfides will affect the properties of the drilling fluid, which is noticeable in the Rheological properties of the mud [3-4].

Carbon dioxide and hydrogen sulfide are often some of the constituents of natural gas that are often encountered during drilling operations. They form acids in water solution, affecting mud pH, thus causing mud problems such as flocculation, thickening, dispersion and clay separation in mud systems. If other parameters such as formation pressures are known and a good mud weight is maintained at a comfortable overbalance, formations that contain H_2S, O_2 and CO_2 can be drilled safely with Water-Base Mud [WBM] by rough maintenance of high mud pH

in the order of 10.50 to 11.50 to neutralize gases which are entrained in the mud systems. Local materials have been used to produce drilling fluids. Using local clay and additives alone yielded low gel strength, high fluid loss [5].

This research introduced four alternative local sources of pH control additives which are cheap, readily available, non-hazardous and environmentally friendly, and evaluates their potentials for corrosion inhibition and rheology performance in simulated hydrogen sulfide environment.

According to Corbin and Willson [6], most corrosion in the oil and gas industry occurs when steel comes in contact with an aqueous environment and rusts. When metal is exposed to a corrosive solution (the electrolyte), the metal atoms at the anode site lose electrons. These electrons are then absorbed by other metal atoms at the cathode site. The cathode, in contact with the anode, conducts this exchange in an attempt to balance their positive and negative charges via the electrolyte. Positively charged ions are released into the electrolyte capable of bonding with other groups of atoms that are negatively charged. This anodic reaction for iron and steel is:

$$Fe = Fe^{2+} 2e^{-} \tag{1}$$

After the metal atoms at the anode site release electrons, there are four common cathode reactions [7]:
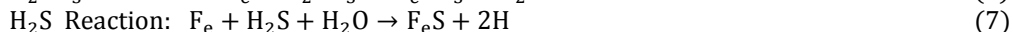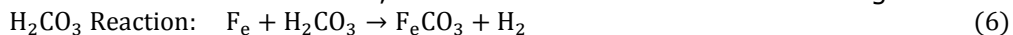
(a) Oxygen reduction in acidic solution

$$O_2 + 4H^+ \rightarrow 2H_2O \tag{2}$$
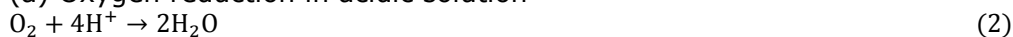
(b) Oxygen reduction in basic solution

$$^1/_2\,O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{3}$$

(c) Hydrogen evolution from acidic solution

$$2H^+ + 2e^{-} \rightarrow H_2 \tag{4}$$

(d) Hydrogen evolution from neutral water

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{5}$$

Gases like carbon dioxide (CO_2) and hydrogen sulphide (H_2S) are commonly present in the sub-surface harbouring oil and gas, and water is their catalyst for corrosion. When water combines with CO_2 and H_2S, the environments form the following reactions [8]:

$$H_2CO_3 \text{ Reaction:} \quad F_e + H_2CO_3 \rightarrow F_eCO_3 + H_2 \tag{6}$$
$$H_2S \text{ Reaction:} \quad F_e + H_2S + H_2O \rightarrow F_eS + 2H \tag{7}$$

There may be a combination of the above two reactions if both gasses are present. These resulting molecules either attach themselves to the cathode or are released into the electrolyte and the corrosion process continues.

As contained in KMC Oiltools manual [9], the most HSE compliant scavenger used in drilling fluids so far is the magnetite, but it is characterized by low reaction rates in high pH muds which are not desirable. Muds' pH is not usually allowed to go below 9.5. The pH is normally maintained between 10 and 11.5 so as to serve as the first prophylactic measure in case H_2S is contacted downhole.

2. Experimental

2.1. Materials and instruments

Cocoa pods, plantain peels, rice husks, groundnut shells and KOH were used as corrosion inhibitors in the mud. The water-based mud used is saturated brine mud (mud's composition shown in Table 1). Analar grade reagents of HCl, sodium sulphide pellets were used. Instruments such as pH meter (model OMEGA PHH-3X), precision weighing balance (model GD-503), corrosion autoclave (model CORTEST 12.45) were used. Oil-well steel coupon (N-80 steel) specimens of specification 50x12x2 mm were used for the corrosion tests. The composition of the coupon is shown in Table 2.

Table 1. Composition of the weighted mud with Barite

Constituents	Concentration	
Fresh water	350	mL
Potassium chloride	10	g
Polypac	6.0	g
API Bentonite	24.5	g
XCD polymer	1	g
Barite	75.4	g

Table 2 Chemical composition of the N80 steel coupon

Elements	Fe	C	Mn	P	S	Si	Cr	Ni	Mo
Wt %	97.237	0.44	1.74	0.019	0.014	0.24	0.12	0.02	0.20

2.2. Procedure

Rice husk (RH), groundnut shells (GRS), plantain peels (PP) and cocoa pods (CPH) were collected from Arowomole, Ogbomoso-South Local Government area of Oyo State Nigeria. These agricultural products were clean of dirt, dried to constant weight and milled to less than 2 µm particle size. The materials were pulverized by measuring 3kg of milled materials into six ashing pans and then placed in a furnace for four hours at 415°C [10]. 2 g each of ashed rice husk, groundnut shells, plantain peels and cocoa pods was weighed into four 100 mL beakers and were digested using concentrated HCl and HNO_3. The quantity of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in each of the sample was determined using Atomic Absorption Spectroscopy (AAS).

2.3 Drilling mud preparation

Pilot plot concept was adopted for drilling mud preparation [11]. In this method, 24.5 g of bentonite clay was added to 350 mL distilled water to produce laboratory barrels of spud mud. The clay-water mixture was mixed rigorously for 10 minutes using a high-speed mixer to produce a homogeneous mixture. The mixture (spud mud) was allowed to age for 24 hours and tested for pH. To all the mud slurries 0.41 g of sulphur was added, and initial pH recorded accordingly. Additives used include viscosifiers (xanthan gum, PAC), fluid loss additives (chrome lignosulfonates, pregelatinized starch), weighing agent (barite) and alcoholic based defoamer. The detail chemical composition of the mud is given in Table 1.

Five (5) drilling mud samples were prepared using the base mud fortified with all the additives except the pH control additives. The different muds contained the pH control agents obtained from cocoa pod husk (CPH), rice husk (RH), groundnut shell (GRS), plantain peel (PP), and commercial potassium hydroxide (KOH). The KOH laden mud served as a control experiment.

2.4 Corrosion experiment

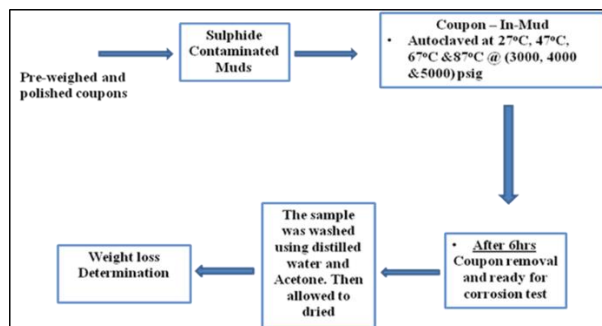A step-by-step procedure for the corrosion test is shown in Figure 1.

Figure 1. Schematic representation for corrosion inhibition process

The pH before and after sulfurization of different mud fortified with RH, PP, CPH, GRS and KOH additives were (9.30; 8.21), (9.10; 8.26), (9.22; 9.04), (9.07; 8.42) and (9.34; 8.92) respectively. It is obvious that the acidity of the mud increased in all cases after sulfurization and was regarded corrosive. Oil-well steel coupon (N-80 Steel) specimens of specification 50x12x2 mm of which the composition is shown in Table 2 were used for the corrosion tests using the weight loss method. The weight of each coupon was

determined before it was subjected to the weight loss test. This test was carried out in a small, high-temperature corrosion autoclave (CORTEST Model 12.45) containing the sulphurized mud. Then an oil-well steel coupon (N-80 Steel of size 50x12x2 mm) which had been treated according to the API specifications (API RP-13 B-1) was hung in the mud. The high-temperature weight-loss tests were conducted using a standard corrosion autoclave. This device is capable of holding 12 eight-ounce bottles in a carbon steel rack and is rated at 10 000 psi (68.9 MPa) to 393°F (200°C). The corrosion coupons were hung from glass hooks in eight-ounce bottles that contained 50 mL saturated brine mud, 1 g/L of sodium sulphide and different pH control additives. The autoclave was closed and heated to the test temperature at 10°C/min until the temperature reached the desired temperature of 27ºC. Once the temperature was stabilized, the vessel was pressurized to 3 000 psig for the selected temperature for six hours. The test rack was agitated at 60 rpm. The autoclave was then cooled at about 10°C/min to room temperature, and the samples were removed from the autoclave. Before the analysis, the coupons were scrubbed with a bristle brush to remove the corrosion products; the corrosion products were carefully observed and then tested in acid arsenic solution. The weight of the coupons was measured and recorded. The above procedure was repeated at 47ºC, 67ºC, and 87ºC for 4,000 psig for, 5 000 psig respectively. A set of the tests was done with the application of KOH to serve as a control for measuring the performance of tested indigenous additives at different conditions of temperatures and pressures.

The corrosion rates in (mm/y) were calculated for each weight loss using the relation shown in the equation below [12]:

$$CPR = \frac{87.6\,W}{\rho\,A\,t} \qquad\qquad (8)$$

where: CPR = corrosion penetration rate (mm/yr); W = weight loss after the test (g); ρ = density of the specimen (g/cm^3); t = time of exposure (hr); A = area of exposure (cm^2).

3. Results and discussion

As one of the primary requirement for drilling mud design is to maintain high corrosion resistance under high salinity and high temperature.
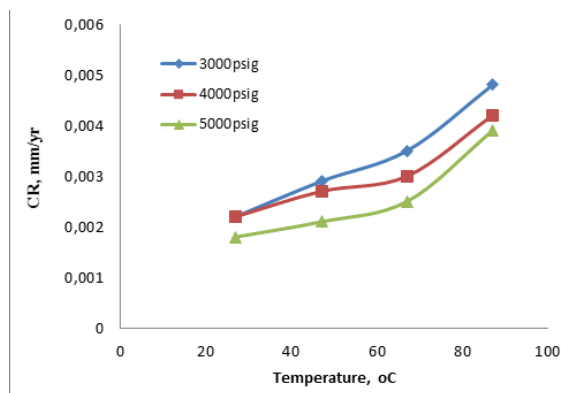

Fig 2 Dependency of corrosion rate on temperature and pressure

Figure 2 shows results of the control experiment. There was an obvious variation of corrosion rate with temperature for KOH fortified mud at pressures of 3000, 4000 and 5000 psig respectively. It can be seen that at a given pressure, the corrosion rate increases with temperature over the entire range of temperatures studied. However, the corrosion rate was inversely proportional to pressure at a given temperature. For example, at about 70ºC, lowest corrosion rate 0.0025 mm/yr was obtained at 5000 psig and highest of 0.0035 mm/yr at 3000 psig.

Similar trends were observed for muds fortified with alkali obtained using RH, PP, CPH and GRS (Figure 3). For instance, Figure 4 shows the corrosion results at a pressure of 5000 psig. The corrosion rate remains fairly constant at 0.00109, 0.0062 and 0.0134 mm/yr for CP, PP and GS as the temperature is increased from 27 to 47ºC.

Within this range of temperature, both KOH and RH corrosion rate increases from 0.0018 to 0.0021 and 0.0197 to 0.0204 mm/yr respectively. As the temperature increases from 47 to 67ºC, the rate of corrosion increases at a lower rate from 0.0021 to 0.0025, 0.006 to 0.0071 and 0.0204 to 0.0209mm/year for KOH, PP and RH respectively. However, a sharp increase in corrosion rate from 0.0132 to 0.0188 mm/yr was observed for GRS mud while a fairly

constant rate of corrosion was still recorded for CPH between 47 and 67ºC. The corrosion rate then generally increases from 0.0025 to 0.0039 (35.89 %), 0.00088 to 0.0015 (41.3 %), 0.0071 to 0.0101 (29.7%), 0.0188 to 0.0229 (17.9%) and 0.0209 to 0.0217 (3.7%) mm/yr for KOH, CPH, PP, GRS and RH muds with increase in temperature from 67 to 87ºC. The lowest CR, mm/yr, observed for RH, PP, CPH, GRS and KOH fortified mud slurries obtained were (0.0186 at 27ºC/ 5000 psig), (0.0060 at 47ºC/5000 psig), (0.00088 at 67ºC/5000 psig), (0.0122 at 47ºC/5000 psig) and (0.0018 at 27ºC/5000 psig) respectively. Thus it is clear that CPH exhibited the lowest rate of corrosion at highest temperature and pressure. On stability test, Figure 5 shows the performance curves for thermal stability of RH, PP, CPH, GRS and KOH alkali as corrosion additives. The test revealed the following order of increasing corrosion rate: GRS > RH > PP > KOH > CPH at 95ºC and at 3000, 4000 and 5000 psig. This shows that the CPH fortified drilling mud is more stable than the commercial KOH at a test temperature of 95ºC for all test pressures.
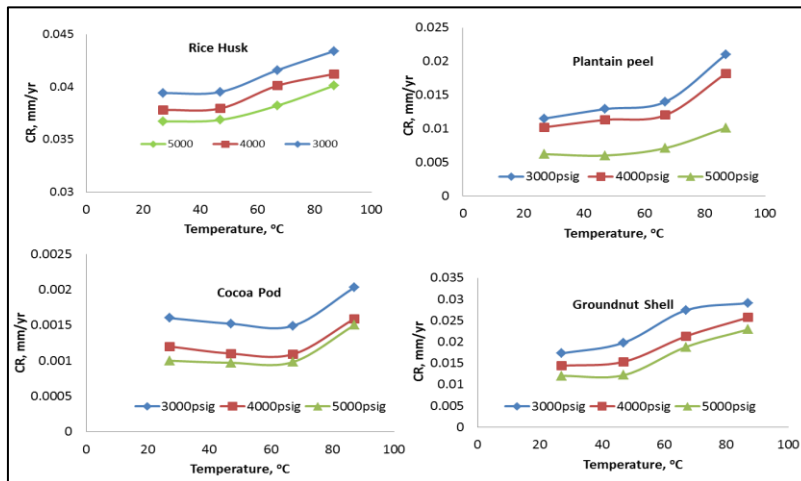

Fig 3. Effects of temperature and pressure on corrosion rate using rice husk, pineapple peel, cocoa pod husk and groundnut shell alkali
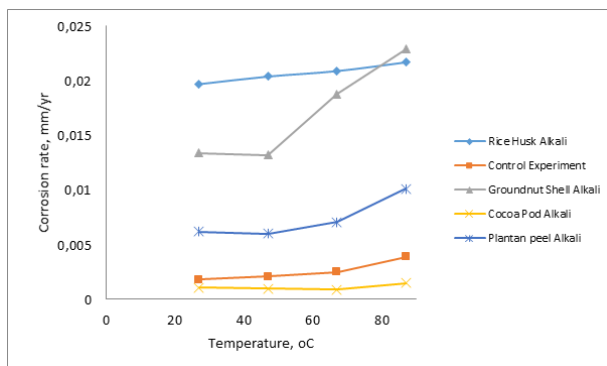

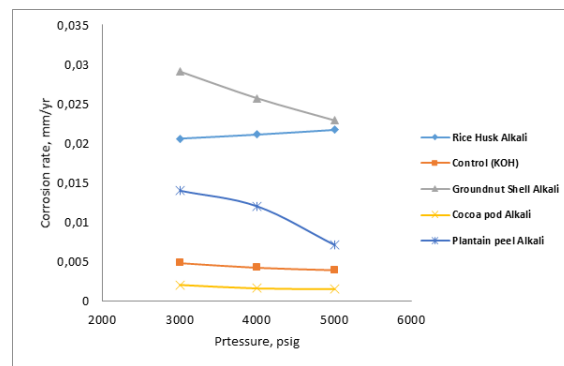Fig 4. Corrosion rate at different temperature and at 5000 psig pressure

Fig 5 Corrosion rate at 90ºC and at different pressures

3.1. Effects of additives on rheology of the muds

The addition of the selected local pH additives was primarily to inhibit corrosion. However, the rheological properties and filtration loss of the mud slurries must equally be maintained. Table 3-6 are the results of the rheological properties of the WBDMs prepared with the selected indigenous pH control additives and KOH at 27ºC, 47ºC, 67ºC and 87ºC. With the equal concentration of the additives in different mud slurries, it was noticed that the different mud slurries

exhibited a different plastic viscosity at room temperature. The KOH additive shows clearly highest PV (12 cP) while rice husk shows the lowest (5 cP). What that suggests is that different additives have different potential in terms of plastic viscosity. Above the room temperature, it was observed that the viscosity was generally degraded with temperature. The control additive was found to be much more stable in plastic viscosity when compared with others at high temperature.

Table 3. Rheological properties at 27ºC

Sample ID	YP_{avg} (lb/100ft^2)	AV_{avg} (cP)	PV_{avg} (cP)	MW (g)	API FL (mL)	pH	CT (mm)
GRS	61.5	35.75	10	8.77	22	9.07	0.1
PP	26	17	8	8.76	22.2	9.1	0.3
CPH	22	14.5	7	8.75	26.7	9.1	0.2
RH	19	12	5	8.75	25.8	9.3	0.1
KOH	26	19	12	8.75	14	9.34	0.2

Table 4. Rheological properties at 47ºC

Sample ID	YP_{avg} lb/100ft^2)	AV_{avg} (cP)	PV_{avg} (cP)	MW (g)	WL (mL)	pH	CT (mm)
GRS	66	37	8	8.77	18	9.1	0.25
PP	35	20	6	8.76	18.4	9.14	0.6
CPH	34.5	19.75	5	8.75	24.3	9.15	0.3
RH	22.5	13.25	4	8.75	22.5	9.34	0.15
KOH	34	22.5	11	8.75	11.5	9.3	0.35

Table 5. Rheological properties at 67ºC

Sample ID	YP_{avg} lb/100ft^2)	AV_{avg} (cP)	PV_{avg} (cP)	MW (g)	WL (mL)	pH	CT (mm)
GRS	80	43.5	7	8.77	15.2	9.11	0.5
PP	27	16.5	6	8.76	15.6	9.16	0.6
CPH	29	16.5	4	8.75	18.4	9.17	0.5
RH	22	13.5	5	8.75	16.6	9.4	0.3
KOH	39	24	9	8.75	12.5	9.36	0.4

Table 6. Rheological properties at 87ºC

Sample ID	YP_{avg} lb/100ft^2)	AV_{avg} (cP)	PV_{avg} (cP)	MW (g)	WL (mL)	pH	CT (mm)
GRS	81	43.5	6	8.77	11	9.1	0.7
PP	41.5	23.75	5	8.76	19.5	9.1	0.65
CPH	32	18	4	8.75	22.5	9.1	0.3
RH	25	14.75	5	8.75	19	9.26	0.5
KOH	42	24.5	7	8.75	12.5	9.22	0.45

The performance of the groundnut shell alkali was found comparable to KOH as shown in Figure 6. At the onset, rice husk was characterized by relatively low viscosity, but as temperature increases, the PV of the mud dosed with rice husk alkali increases slightly which is an indication of high stability at high temperature.

Filtration result of the mud systems reported in Table 3-6 are high and will raise many issues regarding hole stability especially at a higher temperature. The fluid loss for GRS is decreased with the increase in temperature, and further decrease may be expected with an increase in concentrations of carboxy methyl cellulose and polyanionic cellulose which are fluid

loss additives. Both the rice husk (RH) and plantain peel (PP) exhibited an increase in filtrate loss at a temperature beyond 67ºC. Above 67ºC, there is a further decrease in filtrate loss
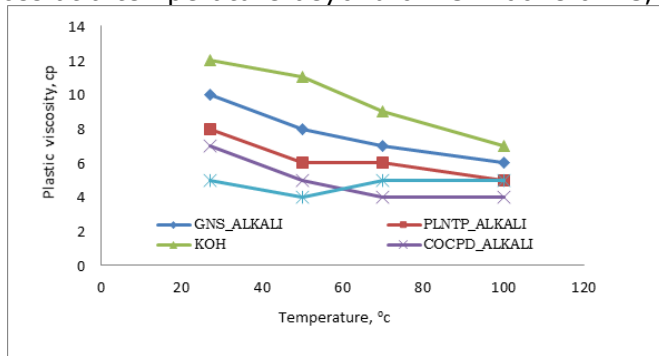

using groundnut alkali (GRS) an indication of superiority in thermal stability when compared with other pH control agents including the KOH. Both cocoa pod and KOH exhibit a fairly constant water loss up to the maximum test temperature of 87ºC. The cumulative filtrate volume at the test temperature for different pH control agents was 19.1 cm^3, 17.8 cm^3, 13.5 cm^3, 12.5 cm^3 and 11.1 cm^3 for rice husk, plantain peel, cocoa pod, KOH and groundnut shell alkali respectively.

Fig 6. Plastic Viscosity observed from mud slurries using different local additives and control experiment at different temperature

Cake thickness is also high at 87ºC which is not desirable. Sometimes removal of higher cake thickness needs extra operations like back flushing, but this operation too has certain limitations and will increase drilling costs & time [13]. Also, high cake thickness may result in decrease production and may demand work over jobs. The quality of the filter cake was observed to be poor especially for plantain peel. This observation is in consistence with the results from Elkatatny et al. [14].
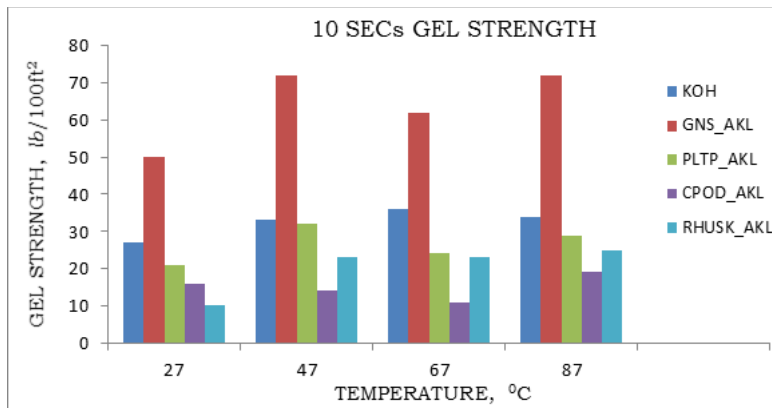

The gel strength of drilling mud is associated with the ability of the mud to suspend the cuttings under static conditions. Figure 7 and 8 show the 10 seconds and 10 minutes gel strength at different temperatures. There was an increase in gel strength at all temperatures for measurements at 10 seconds and 10 minutes for all the mud slurries. However, GRS mud exhibited excessively high gel strength.
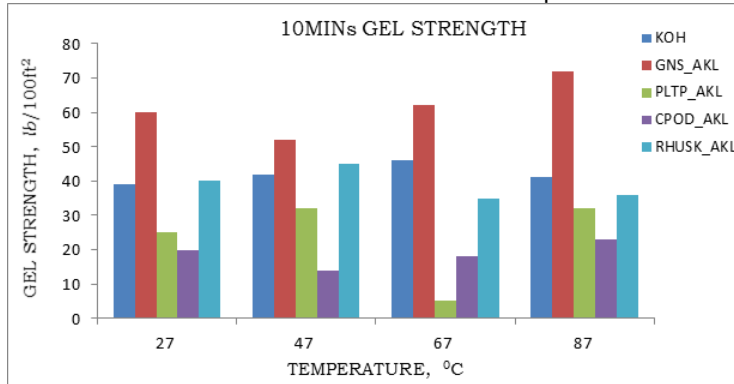
Fig. 7. Variation of gel strength at 10 seconds with temperature for different mud slurries treated with different pH control additives

This is undesirable, and it is responsible for extremely high yield point value as presented in Table 3 through 6 when compared with the value gotten from standard API mud slurry. Some of the other mud slurries showed low yield point and gel strengths. Under this condition, such formulation could not be used for field application. It is therefore recommended that the rheology modifier is used to enhance mud performance during field application.

Fig. 8. Variation of gel strength at 10 minutes with temperature for different mud slurries treated with different pH control additives

4. Conclusions and recommendations

4.1 Conclusions

From the results obtained in this research, it was concluded that:

1. All the selected additives evaluated in this study have different potentials for use as pH control additives at the tested temperature and pressure. Groundnut husk alkali exhibited the least performance followed by plantain peel. Cocoa pod additive, however, competes closely to the commercial additive tested in this study.

2. Laboratory tests indicated that the Cocoa pod additives is more stable thermally and is very effecttive reducers of filtration loss at high temperatures.

3. The performance of the groundnut shell alkali was excellent on the slurry rheological property (PV). However, very high viscosity, yield point, and gel strength are not desirable due to excessive pressure and energy losses.

4. Cocoa pod additive has moderate PV at all temperatures it, however, require additional viscosifier to improve its rheology since it has good filtration loss and corrosion inhibition properties.

4.2. Recommendations

Based on the research conducted, analyses and conclusions of this work, the following are recommended:

1. One of the limitations of this study is the use of small test time of 6 hours and constant additive concentrations throughout the test. The use of equal initial additives concentration may limit the activities of different alkali. Detailed optimization study is therefore recommended to determine optimum concentrations and combination of additives for optimum drilling mud design.

2. More research should be conducted on other agricultural products to identify their true corrosion inhibition capabilities under realistic wellbore drilling conditions.

Conflict of interest

The authors declare no conflict of interest.

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