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Original Article

Improvement of Rheological Properties of Bentonitic Clays Using Sodium Carbonate and a Synthetic Viscosifier

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ABSTRACT
The importation of Bentonite for oil and gas well drilling operation has continued to divert some large amount of foreign exchange that would have impacted on the socioeconomic wellbeing of Nigeria. Large reserves of Bentonitic clay occurrence are found in almost all the parts of the country. These reserves occur as thick deposit of clays with wide lateral extent and with some level of beneficiation these clay deposits can attain the qualities of those used in oil and gas well drilling. In this work, samples of Bentonitic clays in three different sites/locations from Fika formation in north-eastern Nigeria were collected for the purpose of evaluating their chemical, rheological and other physical properties which are critical for their use as drilling mud. The samples collected were found to be Ca-based which require some beneficiation while other properties such as Al_2O_3/Si_2O ratio, sand content, moisture content and fineness of the clay met the required standard even before beneficiation. After beneficiating the samples by ion exchange using Na_2CO_3 as the beneficiating agent, the rheological properties of the samples improved considerably and when a poly-ionic polymer, Trade Name Drispac, was added in the range of 0.2g to 1g, the rheological properties improved dramatically to a level that is typical of the standardBentonite. This study found that Bentonitic clays from north-eastern Nigeria can attain the rheological and other physical properties of a standard commercial grade Bentonite used in oil and gas well drilling with some beneficiation using Na_2CO_3as the beneficiating agent.
KEYWORDS: *rheological properties; beneficiation; Bentonitic clays; physical properties, montmorillonite*

INTRODUCTION

Bentonite is used as drilling mud which is circulated through the drill rod into the hole to cool the bit and to float drill cuttings to the surface during drilling operations. It is also used as binding agent for moulding sands used in foundries. The importance of bentonite as a mud in drilling operations in water, oil and gas well construction cannot be overemphasized. The cost of drilling is reduced by about 15% when drilling mud is used and this is not small given the overall cost of drilling an oil or gas well.In these occurrences, it is found as a rock composed essentially of clay minerals formed as a result of devitrification and chemical alteration of some igneous material. Notable among these occurrences isbentonitic clay enriched in montmorillonitein the Fika shale in north-eastern Nigeria, the Dukamaje and Kalambaina formations in the northwest and Awgu shale in south-eastern Nigeria [1]. Mineralogical compositions of these formations are more than 80% montmorillonite; however, most are enriched in calcium and mixed montmorillonite [2].

The properties of Bentoniteare controlled by the proportion of montmorillonite, but it may also contain some proportions of feldspar, mica and quartz. Impurities such as calcite, gypsum and crystoballite which affect the performance of Bentonitic clays can also be present [4]. In oil and gas industry, Bentonite usefulness is based on its swelling and gel forming capacity when mixed with water and this swelling capacity is dependent on the relative Ca-Na content [5].

Bentonite consumption in drilling operations in the oil and gas industry in Nigeria is very significant; therefore any measure that will reduce dependence on its importation by the oil companies/operators in the industry will go a long way in reducing foreign reserve consumption and thus assist in boosting thecountry's economy. The work reported here was a study aimed at improving the quality of Bentonitic clay occurrences fromFika Formation in north-eastern part of Nigeria to meet standards for application as a drilling mud in the oil and gas industry. Three (3) representative samples each from this Formation at three different locations within the study area (Fig. 1) were collected for evaluation of their physical, chemical and rheological properties. The samples collected were subjected to various samples preparation and beneficiation procedures, and the various samples generated from these procedures were subjected to both physical and chemical analysis. About 33 samples were thus generated for analysis and determinations of elemental, rheological and other physical parameters. Results of these analyses and determinations were compared with API standard commercial grade Bentoniteto ascertain the worth of the beneficiated samples as regard its use in the oil and gas industries.

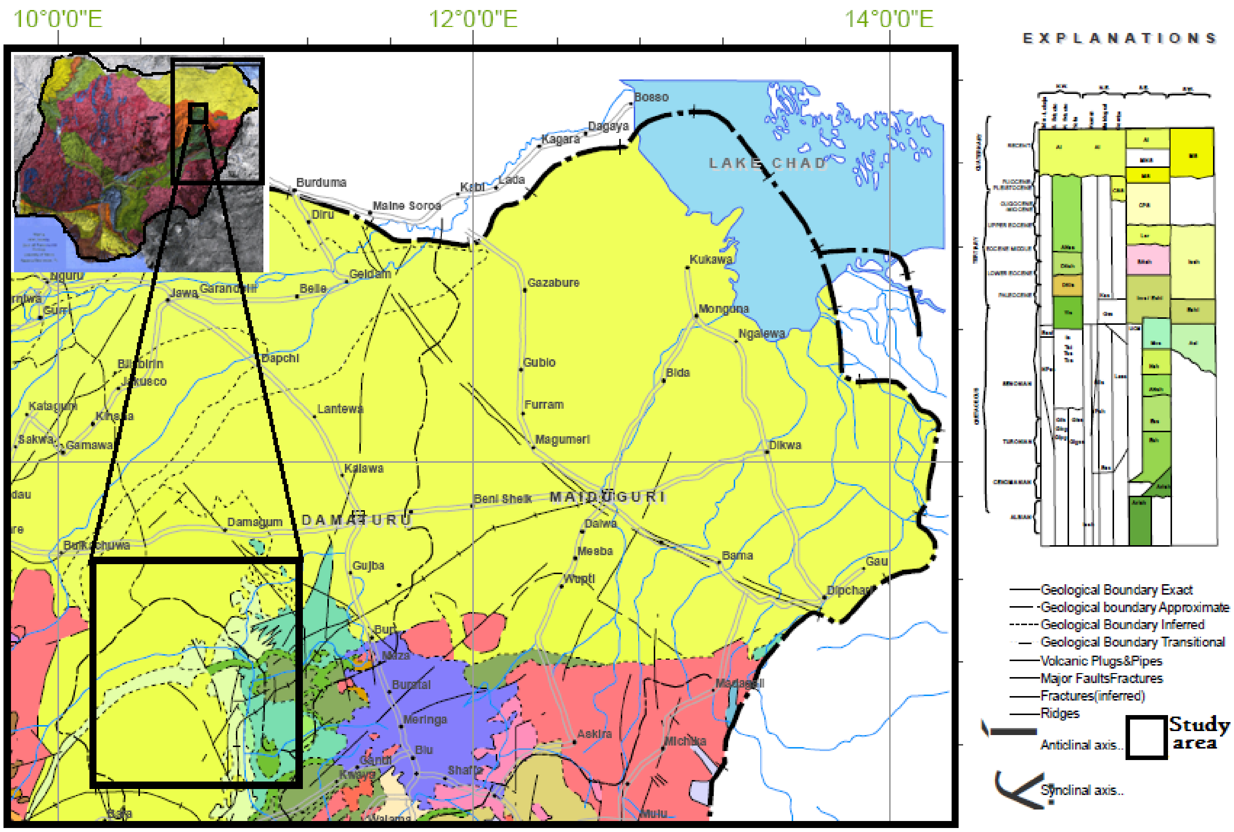

Figure 1: Geologic map of north-eastern Nigeria showing the study area [5]

MATERIALS AND METHODS

Sample Preparation

Bentonitic clay samples from the field were open dried at room temperature. Two sets of samples totaling six (3 raw as brought from the field and 3 raw but sieved) were prepared for the beneficiation process. The sieving process involved grinding using agate mortal and pestle, of some quantity of each of the samples using motorized grinding machine. To avoid cross contamination, the grinding machine was thoroughly cleaned with acetonebefore loading each sample. The ground samples were sieved to obtain the 63µ fractions for beneficiation. A sieve shaker, an ENDECOTTS OCTAGON 200 system, provided with various sieve sizes was used in this exercise. After grinding all the samples to be beneficiated, the sieve shaker on which a sieve of the 63µ mesh was mounted was used to obtain the required quantity of sieved sample. More than 100g of each sample from both sets of samples were obtained for the beneficiation process.

Elemental and Mineralogical Phases Analysis
Elemental analysis of raw Bentonitic clays was carried out using Instrumental Neutron Activation Analysis (INAA) utilizing the Nigerian Research Reactor 1 (NIRR-1) for the elemental analysis. It is a miniature Neutron Source Reactor that is capable of determining a wide range of elements, with limits in the parts per billion (ppb) regions. The elemental analysis was complemented by Atomic Absorption Spectroscopy (AAS), X-Ray fluorescence (XRF) to determine the elemental composition, especially the Ca and Na content; and an X-Ray Diffractometry) (XRD) machine was used to determine the mineralogical contentof the clay samples before beneficiation was carried out. All the samples collected were found to be Ca-based; therefore beneficiation procedure was followed as detailed in the flowchart in Figure 2.

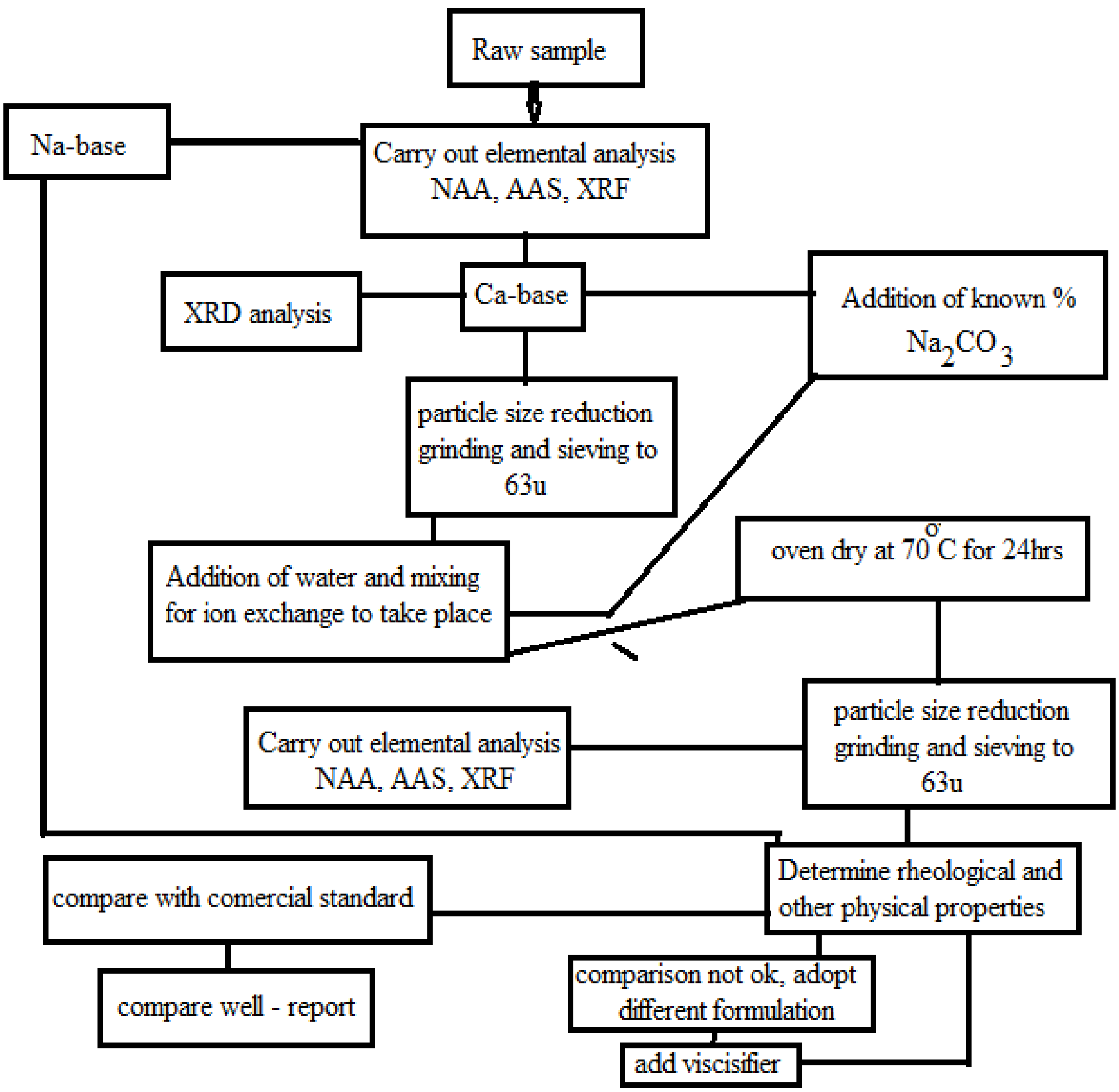

Figure 2: Flowchart of the Beneficiation Procedure Developed for the Work

Beneficiation
From each of the sample, three sets of ten 100g of samples were set aside for addition of the beneficiating agent (Na_2CO_3) as shown in Table 1 below.

Table 1: Quantity of Sample and Beneficiating Agent Added

Quantity of samples (g)	Quantity of Na_2CO_3added (g)	Total weight of sample (g)
100	2	102
100	3	103
100	4	104
100	5	105
100	6	106
100	7	107
100	8	108
100	9	109
100	10	110
100	11	111

From this process, a total of 33 samples were generated and further steps of the beneficiation procedure which included kneading, drying of kneaded samples, re-grinding and sieving of beneficiated samples were followed. Typical crushed samples are shown in Figure 3 below.

Fig 3: A Sample of CrushedBentonitic Clay Sample

Initial elemental analyses were carried out on the samples in order to determine the degree of beneficiation to be used. A sample will require no, little or intense beneficiation. For example, if a sample was found to be a Na-based type, rheological property determination will proceed directly to determine whether its properties has met that of a standard that is required in the oil and gas industry. If a sample was found otherwise, elemental analysis was carried out to determine the extent of addition of beneficiating agent for ion exchange procedure.

RESULTS

The results of elemental, mineralogical, rheological and other physical properties determined are presented in Tables and charts. Elemental analyses were carried out using Instrumental Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS), X-Ray Fluorescence (XRF) and Flame photometer. The essence of using multi analytical techniques was to determine wide range of elements that make up the clay samples in order to prepare an appropriate procedure for the ion exchange and determine impurities in the clay. X-Ray Diffractometry (XRD analysis) was carried out on the samples to determine their mineralogical composition. The XRD diffractometer, a PHILIPS PW 3710 system fitted with software, XPERT PDF-2, was used. Samples were also subjected to rheological and other physical properties determination. The results obtained were used to compare with the API standard. Results of the elemental (both raw and beneficiated samples) and XRD determinations are given in Table 2, Table 3and Table 4 below, respectively.

Table 2: Results of Elemental Analysis of Raw Bentonite Clays

Sample ID	Na,%	Mg, %	Al, %	Ca, %	Ti,%	K, %	Fe, %	V
NGALDA (FKF)	0.153	3.57	7.79	3.35	0.45	1.18	4.34	200
MAIDUWA-I (FKF)	0.14	4.47	7.15	3.91	0.38	1.11	5.16	142
MAIDUWA-II (FKF)	0.134	3.42	7.66	2.33	0.43	1.34	4.71	166

Results are in ppm ($\mu g g^{-1}$) unless otherwise stated.
BDL means Below the Detection Limit.

For viscosity and gel strength determinations, a direct indicating OFITE, MODEL 900 viscometer equipped with a flask was used.In addition, the Loss on Ignition, LOI, moisture content and Yield Point were also determined. Results for the moisture content and the LOI; and those for Yield Point, fineness and pH are displayed in Tables 5 and 6, respectively. Viscosity and gel strength results are shown in Figures 4-9, while XRD spectra for Wyoming and Locally beneficiated clay (Maiduwa) Clay are presented in Fig. 10 and 11.

Table 3: Results of Elemental Analysis of Beneficiated

Sample ID	Na_2CO_3(%)	Na, %	Mg, %	Al, %	Ca, %	Ti, %	V%
NGALDA (CRUDE)	2	0.81	4.13	6.49	4.56	0.33	127
MAIDUWA-1 (CRUDE)	2	1.01	4.22	6.23	6.22	0.32	129
MAIDUWA-2 (CRUDE)	3	1.21	4.26	7.27	6.02	BDL	561
MAIDUWA-1 (SIEVED)	3	1.32	3.73	4.57	4.96	0.30	102
NGALDA (SIEVED)	3	1.69	1.29	8.14	0.8	0.56	81.8
MAIDUWA-1 (SIEVED)	5	1.62	3.81	6.18	5.05	0.27	0108
MAIDUWA (SIEVED	5	0.13	3.81	6.66	5.07	BDL	141
MAIDUWA-2 (CRUDE)	5	1.75	4.17	6.46	4.76	0.28	129
MAIDUWA-1 (CRUDE	9	4.02	4.87	5.69	6.10	0.19	117
MAIDUWA-1 (SIEVED	9	2.94	4.16	5.79	5.58	0.31	111
MAIDUWA-1 (SIEVED)	10	3.66	BDL	1.19	5.60	BDL	106
MAIDUWA-2 (SEIVED	10	3.15	4.13	5.80	4.42	BDL	111

Table 4: Results of X- Ray Diffractometry on the Bentonitic Clay Samples and Standard Wyoming Bentonite

S/N	MINERAL NAME	CHEMICAL FORMULA	WYOMING	MAIDUWA I	MAIDUWA II	NGALDA	AVERAGE
1	MONTMORILLONITE	$NaO. 3Al_2(Si,Al)_4 O_{10} (OH)_2. {}_2H_2O$	8.99	9.11	5.86	7.81	7.59
2	DOLOMITE			4.97		3.67	4.32
3	HALLOYSITE	$Al_2Si_2O_5(OH)_4$	4.49	7.45		5.97	6.71
4	PYROPHYLLITE			8.56		6.89	7.72

5	RUTILE	TiO_2		7.73			7.734
6	QUARTZ	SiO_2		4.97	2.84	3.90	3.90
7	TIN	Sn			5.50		5.50
8	ROALDITE	Fe_4N	6.61		4.26	5.74	5.00
9	RANKINITE	$Ca_3Si_2O_7$			15.98		15.98
10	KAOLINITE	$Al_2Si_2O_5(OH)_4$	11.6		7.63	9.65	8.64
11	ANTIGORITE	$Mg_3Si_2O_5(OH)_4$			15.27		15.27
12	BARITE	$BaSO_4$	22.22				
15	TANTALUM	TaO_2			4.79	7.58	6.19
16	ILLITE	$(K,H_3O)\ Al_2Si_3AlO_{10}(OH)_2$				8.73	8.73
17	PYROLUSITE	MnO_2	7.40		4.79	18.16	11.4
18	CALCITE	$CaCO_3$	6.08				
19	GRAPHITE	C			4.97	2.98	3.98
20	LIME	CaO		5.24	3.37		4.31
21	IRON TIN	Fe_4S		17.67			17.67
	Total		**99.999**	**99.997**	**99.997**	**99.999**	

Table 5: Results of Moisture Contents and Loss On Ignition of the Benthonic Clay Samples and Standard Wyoming Bentonite

S/N	Samples	Moisture content	Loss On Ignition (LOI)
1	Ngalda	11.92	9.73
2	Maiduwa II	11.75	9.24
3	Maiduwa I	13.48	8.77
10	Wyoming	27	10.64

Table 6: Comparison of Some Properties of the Studied Bentonitic clays with API Standard

Parameter	API	Maiduwa 1 (clay sample)	Maiduwa II (clay sample)	Ngalda (clay sample)
Yield	3	1.8	2	1.9
Fineness	4	4	2	3
Moisture cont	13%	13.48%	11.75%	8.65
pH	8	14	14	14

DISCUSSIONS

In terms of fineness, a quality which determines the sand content of the clays, the clays under study showed good qualities. The percentage samples under study that passed through the 63μ mesh range from 95 to 98% compared to 96% for the commercial grade Wyomingbentonite.

The results of elemental analysis of the raw bentonitic clay samples using techniques as enumerated above and presented in Table 2above shows that the bentonitedeposits studied are Ca-rich. Samples had Ca values ranging from 2.33 to 3.91%. After beneficiation, the Na and Ca contents changed, ranging from0.13% to 4.02% and 0.08% to 6.22%, respectively, Table 3. This result indicates that the ion exchange method of beneficiations has drastically improved the Na content. The high Ca values may not be unconnected to the additive used in the treatment of the samples to enhance their rheological properties.

The recommended ratio of oxides of aluminum to silica in API standard bentonitesshould be 1/3 or 0.333. The values of ratio of Al_2O_3 to Si_2O recorded inthe samples studied ranged from 0.28 to 0.38 while values recoded for the commercial grade Wyoming bentonite was 0.38 thus indicating the good quality of the Nigerian bentoniticclays.

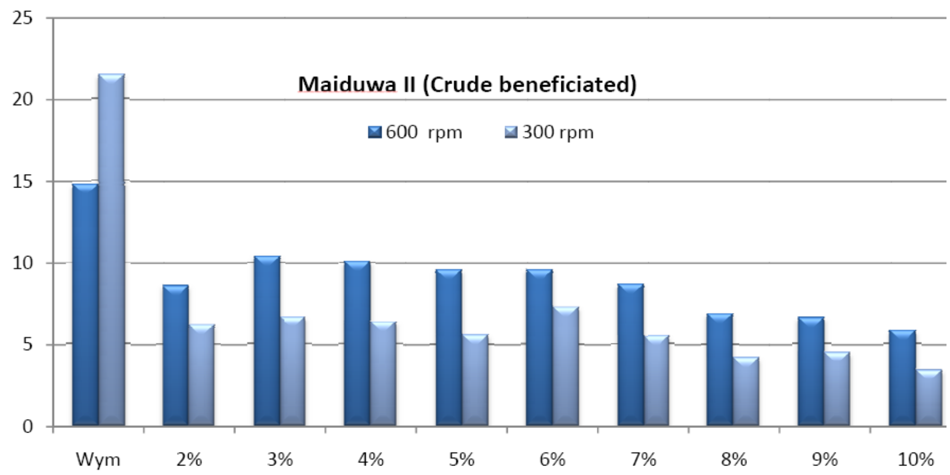

Fig 4: Viscosity variation with addition of 2 to 10% Na_2CO_3 to crude beneficiated samples

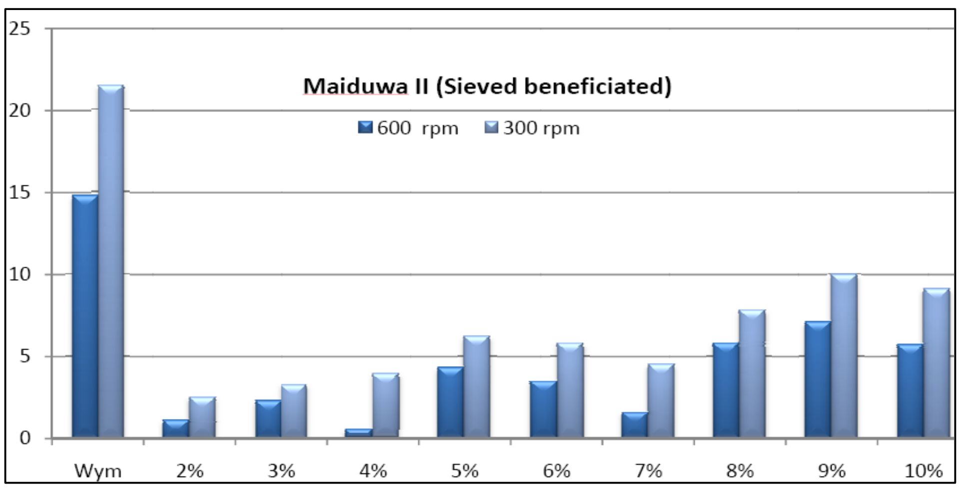

Fig 5: Viscosity variation with addition of 2 to 10% Na_2CO_3 to sieved beneficiated samples

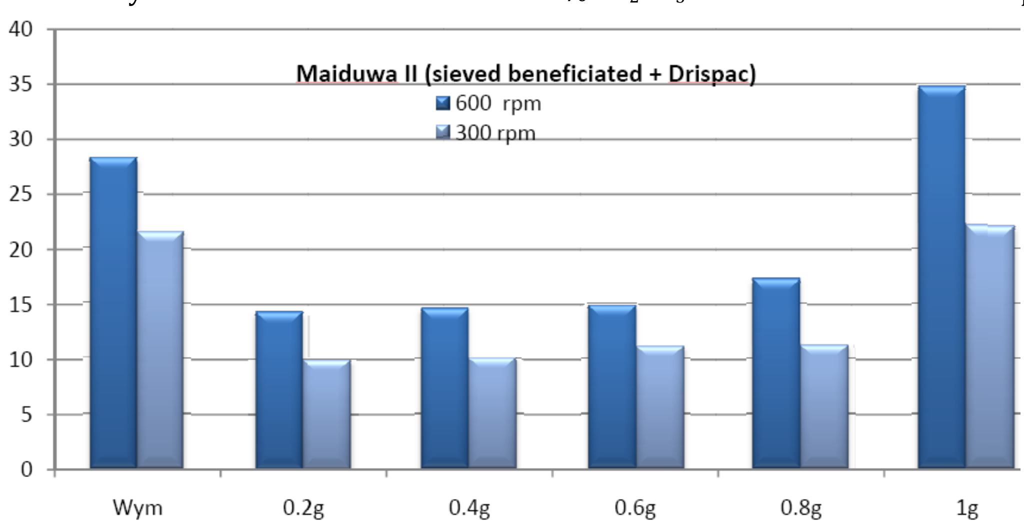

Fig 6: Viscosity variation with addition of 0.2 to 1g of viscosifier to sieved beneficiated samples

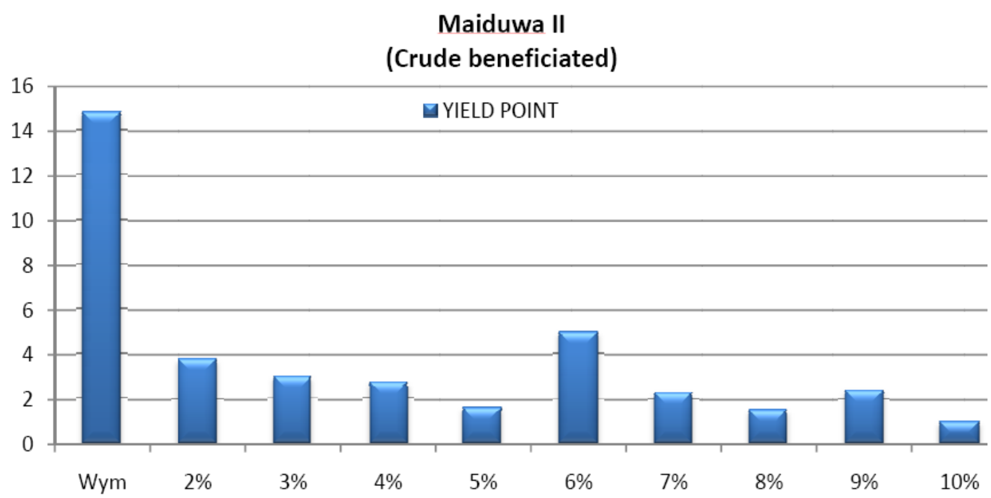

Fig 7: Yield point variation with addition of 2 to 10% Na_2CO_3 to crude beneficiated samples

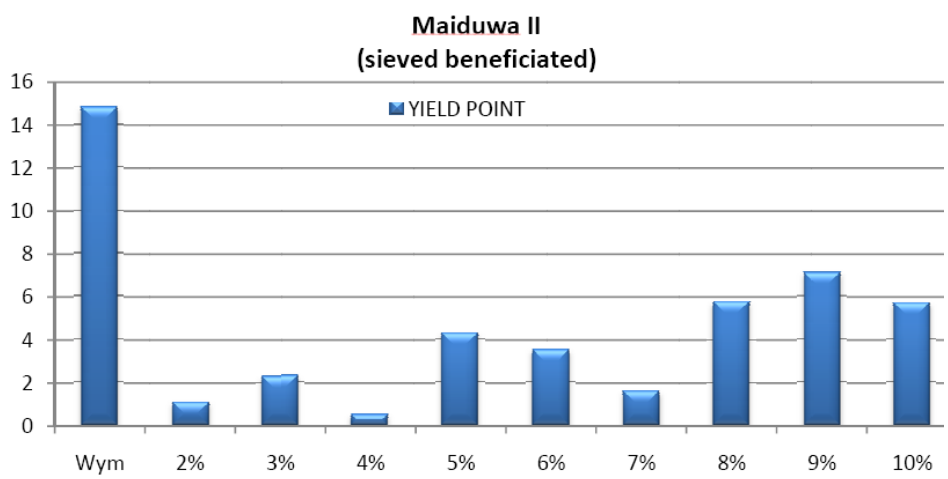

Fig 8: Yield point variation with addition of 2 to 10% Na_2CO_3 to sieved beneficiated samples

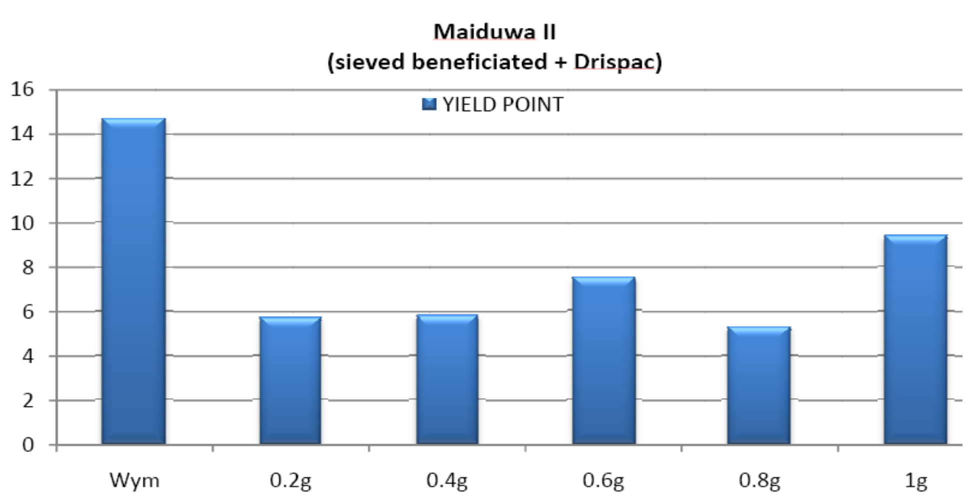

Fig 9: Yield point variation with addition of 0.2 to 1g of viscosifier to sieved beneficiated samples

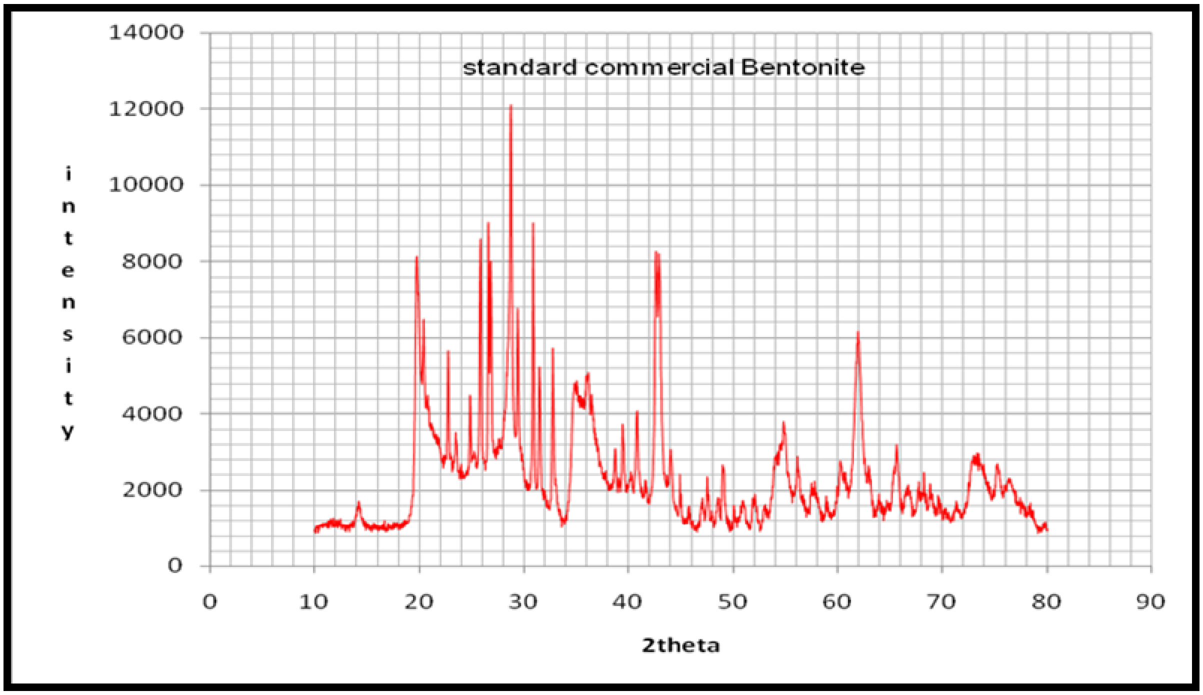

Fig 10: XRD spectra of a standard commercial Bentonite (Wyoming)

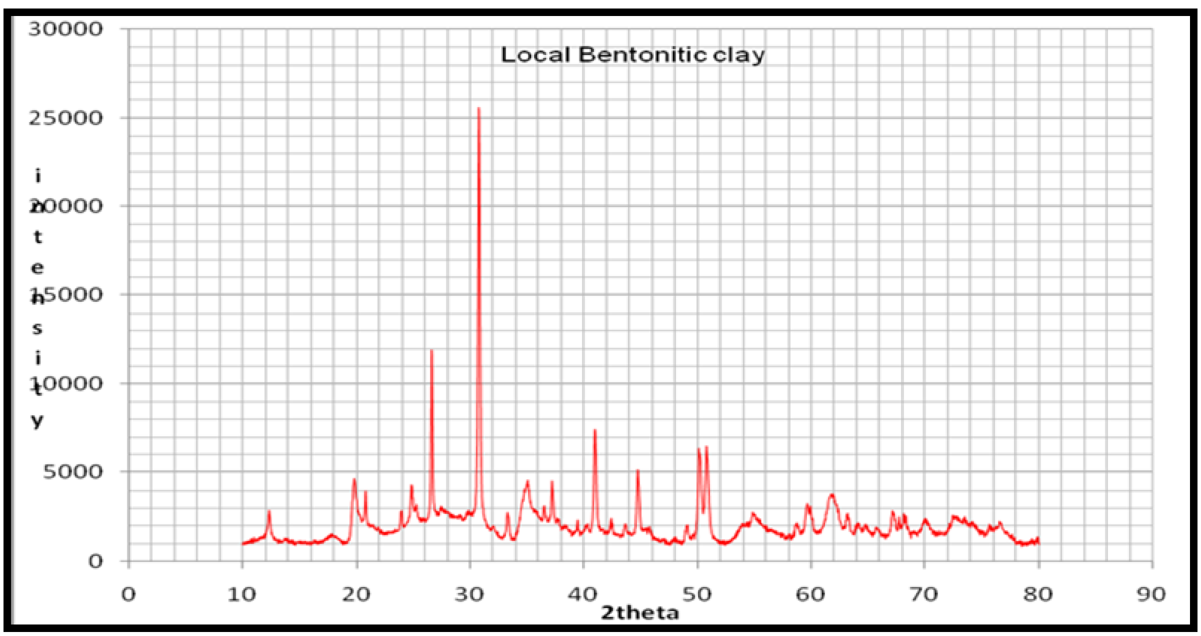

Figure 11: XRD spectra of locally beneficiated clay (Maiduwa I)

Loss On Ignition (LOI) recorded for studied samples are within the range of 8.77% to 9.73% while it is 10.64% in the Wyomingbentonite indicating the low level ofcombustible materials in the clays studied. This compared favourably well with the API commercial standard Wyoming and Myanmar clays used in the oil and gas industry. Moisture content in the sample studied range from 11.75 to 13.48% and in Wyoming bentonite, the value recorded is 27%. This shows that at room temperature, the Wyoming bentoniteabsorbs more water from the atmosphere than the studied samples.

The rheological properties of the clays improved with beneficiation of the clays. The viscosity, which is an important property for use as drilling muds, of the clays under study showed great improvements especially with the addition of viscosifiers. The results indicates viscosity range of <2 to about 10 at 600rpm in sieved beneficiated samples which improved to 34 on addition of a viscosifier, Drispac™. This surpasses the 25 recorded in the commercial grade Wyomingbentonite. Similarly, the yield point also showed some improvement especially after addition of the viscosifier. The values improved up to 10lb/s ton after addition of the viscosifier which compared well with the value of 15 lb/s ton recorded for the commercial grade Wyoming bentonite. This indicates that the bentonitic clays studied can have rheological properties improved to a level that can be used in the oil and gas industry.

CONCLUSIONS

Results of elemental analysis of the raw bentonitic clays from north-eastern Nigeria, the ones of Fika Formation in particular showed that the bentonitedeposits in these occurrences are Ca-rich. After beneficiation, it was found that there was improvement in Na contents of the samples, which is an indication that ion exchange procedure/technique is capable of treating bentonitic clays from these locations. Results of the rheological properties, especially the viscosity showed remarkable improvement after beneficiation. The results also showed that bentonitic clays from Fika Formation in north-eastern Nigeria can be beneficiated using ion exchange to improve its properties to commercial grades used in oil and gas well construction. Comparison of results/properties of the beneficiated Bentonitic clays of the Fika Formations with API grade Myanmar and Wyoming commercial bentonites showed that these clays can attain the expected quality of the commercial bentonitewith little beneficiation/improvement.

The results from this study showed that bentonitic clays from Nigeria, especially the ones we have studied can be economically beneficiated to grades of the commercial clays used in the oil and gas industry.

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