



# Beneficiation and Characterization of a Benetomite from Niger Delta Region of Nigeria

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**Abstract-** The characterization of a tropical bentonite (Niger delta bentonite) has been performed by different techniques for drilling application. While the chemical elements was determine qualitatively by measuring characteristic radiation of the X-ray fluorescence, the powder diffraction XRD of a random powder mount was used to obtain the definitive clay and nonclay components. The SEM was used to determine the particle size and geometry. The optimum sodium carbonate addition was observed between 2 and 3% which balance the exchangeable/surface cation such that a ratio of 56:23:21 for Na:Ca:Mg indicated a promising rheological property if the clay is applied for viscosity builing in any industrial application. The mixed monovalent divalent cation saturation in its crude state tends toward a better swelling index desired for drilling application with sodium carbonate activation. The clay mineral was found to be chemically stable, having a balanced surface charge distribution and the particles are highly colloidal with unique atomic structure as of a typical bentonite. The clay is a calcium bentonite and the chemical analysis reflects that an economical peptizing route is achievable.

**Keywords-** Bentonite; Cations; Swelling; Activation..

## I. INTRODUCTION

Bentonites are predominantly clay minerals of smectite group. It is ubiquitous in low concentration in soil formed by sedimentation in natural water bodies and airborne dust. Bentonites can be classified as sodium (Na), calcium (Ca), potassium (K) and aluminium (Al) depending on the dominant element in each. Of these elements, Na and Ca bentonites possess some physical properties, which make them valuable to a great variety of industries. Their importance is not only limited to rheological and absorbent properties, but also the cation exchange capacity, plasticity, high bonding strength, and swelling capacity. These properties are attributed to the clay mineralogy, the nature of exchangeable ion and its ion exchange capacity [1, 2].

The bentonite deposits found in Niger Delta region of Nigerian hold a probable reserve of about over 4 billion tonnes as reported by terra mines Edo state Nigeria [12]. The properties of the natural form of these deposits occur with significant impurities which adversely affect their quality for eventual application. Consequently, those bentonites need beneficiation to free them of the impurities and upgrading processing to improve their properties to an acceptable standard prior desired application [3, 4, 5]. Although several attempts were made to upgrade these low grade bentonites to meet OCMA/API specifications for drilling fluid and other industrial uses [6], the Na-exchange capacity is poor and rheological properties of these bentonitic clays were inferior to those of standard commercial bentonites [7, 8, 9, 11]. It is therefore of imperative to undertake a comprehensive beneficiation and upgrading investigation in order to meet the standard commercial bentonite for drilling fluid and plugging applications in oil industry.

## II. METHOD OF ANALYSIS

The samples used in this study represent an area located on the latitude 6 35' 54.6" N and longitude 5 18' 14.9"E and 49 metres above sea level depth 37.6m at the Niger Delta region of Nigeria. It has one layer of light beautiful clay with small inclusion of black bentonite. The materials with varying particle sizes were characterized by X-ray diffraction of bulk analysis using an untime3 theta-theta goniometer with a Cu  $k_{\alpha}$  radiation (40kV/30mA) and a SctSlit 2/3deg. The characterisation was done using the international catre for diffraction data for powder diffraction data. The sample was equally examined with the energy dispersive spectroscopy (EDS) on the scanning electron microscopy (SEM). The platelete photograph was taken for dimensionality. After characterization the swelling test and the exchangeable cation determination have been performed according to the methodology provided by petrology group British Geological Survey.

#### A. Specimen Preparation for XRD Analysis

Sedimentation and siphoning following the Stokes rule of thumb: A preliminary sieving was carried out to obtain 60microns and less. First sedimentation was carried out to obtain particle size less than 10microns by the first decantation. This was a supernatant liquid. Second sedimentation was carried out to obtain less than 4microns particle size using centrifuge and allowing the particles to settle. The sedimentations were carried out 20times and the new supernatant liquid had particle size less than 2microns. The less than two microns particle size was determined with scanning electron microscope. The distributed particle size were counted and matched with the circles of graded size. The diameter of the projected area is the particle size obtained. This is the Stokes diameter [11].

#### B. Extraction of the smectite

Sedimentation of the clay mineral was first carried out to obtain <2 $\mu$ m particle size of the clay. The use of a DENVER D12 laboratory flotation machine facilitated the floatation of smectite content of the clay sample by separating the different minerals into their respective fractions using their different physical and chemical surface characteristics. The addition of chemical flotation reagents then causes the valued minerals to attach to air bubbles (Hydro-phobic) and rise to the surface of the tank where they overflow as a concentrate.

#### C. SEM, XRD and XRF

Bulk mineralogy: the clay mineral identification was carried out using the XRD machine. It was first examined as a random powder mount. The JCPDS search procedure was carried out by comparing peaks height of particular minerals with those data already known by artificial mixtures. The impurity identified includes illite, kaolinite, quartz, calcite, gypsum and loss on ignition components. The XRF of the bulk mineral was carried out to obtain the major element.

Oriented mount of smectite this was used to examine the smectite content of the clay to determine the divalent or monovalent nature of the clay. (i.e. whether Ca<sup>2+</sup> or Mg<sup>2+</sup>) OR Na<sup>+</sup> which are the exchangeable cations. The basal spacing d<sub>001</sub> between 12.6 Å to 17.2Å were observed.

Use standard JCPDS search procedures; do bulk mineralogy to show minerals present such as christobalite, quartz, gypsum, etc which negatively affect rheology. The standard necessary procedure for XRD analysis of bentonite (clay) involves special specimen of less than 2 $\mu$ m at normal relative humidity, analysis should be done for both oriented mount sample and bulk sample/powder mount. The basal spacing to be used is d spacing d<sub>001</sub> and d<sub>060</sub> for a sample mixed with ethylene glycol or glycerol and normal air dried sample without any reagent. The values of angstroms at this spacing typically describe bentonite. Providing the atomic structure is also important, it could be dioctahedral or trioctahedral, the positions of Al, Mg, and Na are very typical for rheological property of the bentonite (clay.)

#### D. Determination of cation exchange capacity, swelling index and sodium, calcium and magnesium

The dry clay was sieved with less than 125 $\mu$ m sieve. 1g of the clay was placed in six different watch glasses. 1%Na<sub>2</sub>CO<sub>3</sub>, 2%Na<sub>2</sub>CO<sub>3</sub>, 3%Na<sub>2</sub>CO<sub>3</sub>, 4%Na<sub>2</sub>CO<sub>3</sub>, 5%Na<sub>2</sub>CO<sub>3</sub>, 6%Na<sub>2</sub>CO<sub>3</sub> was added respectively. The clay and the various %Na<sub>2</sub>CO<sub>3</sub> was mixed together while it is still dry. 1.5 mls of distilled water was added. The mixture was dried in an oven overnight at 60°C overnight. The clay was crushed and screened through 500 $\mu$ m and 250  $\mu$ m. 1g was weighed each of the 500 $\mu$ m and 250  $\mu$ m material out onto a watch glass. 10ml of distilled water was measured with a measuring cylinder. A filter funnel was placed in the neck so that the tip is about 1cm from the surface of the water. The clay sample was dividing into 8 portions roughly with a spatula. One portion was added slowly after every 5minutes. After each addition the bottom of the cylinder was lightly tapped to settle the clay. The final surface of the clay was levelled. The sample was left for 24hrs, the volume of the clay was read to the nearest 0.1ml the result was multiplied by 10. Sample of good bentonite will swell in excess of 10ml. the addition of clay will stop when the swelling approaches 9ml mark. The left over clay will be weighed and the swelling volume for the total 1gramme will be calculated. Cation exchange capacity CEC [9].

1ml of methylene blue chloride was added to 1g clay the absorption was allowed to last 5mins to observe that the clay takes up the dye by spotting a small quantity of the clay suspension dye solution on a filter paper and for each five mins interval a 1ml of methyl blue was added continuously. While the dye was seen absorbed by the suspension, the filter paper spotting is blue surrounded by clear distilled water until the uptake reaches an end point where the blue spot is surrounded by a halo of free dye. The methylene blue CEC is calculated from the amount of dye absorbed at the end point. Usually 80% is normal for true CEC. Ratio of monovalent and divalent cations present in bentonite

75g of ammonium acetate was dissolved in 1litre of water. The pH of the solution was adjusted to neutral 7 when low alkali was added and when high dilute acid was added. 1g of clay was transferred into a centrifuge bottle 30ml of 1M ammonium acetate solution was stirred for 30mins and centrifuged for 15 min at 2000rpm the supernatant liquid was decanted into 100ml volumetric flask. This was repeated three times. The solution in the volumetric flask was made up to 100ml with distilled water. The exchangeable cation concentrations (calcium, magnesium, sodium and potassium) were determined from an aliquot of the 100ml.

#### E. Swelling index and parameter for rheological properties

One gram of the sample was mixed with 10ml of distilled water mixed thoroughly for 20mins, reading taken after 24hrs, 48hrs and 168hrs.

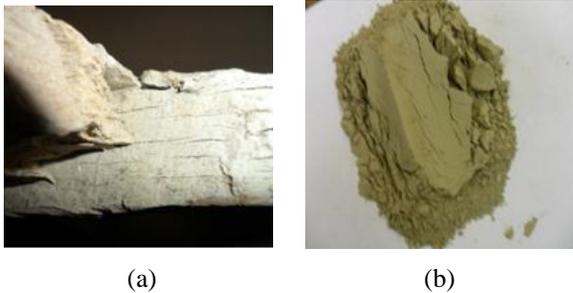


Figure 1. Bentonite collected from Niger Delta (a) Raw sample (b) Pulverized sample.

### III. RESULTS AND DISCUSSION

#### A. Characterization of samples

Elemental analysis of the Niger delta bentonite sample is presented in Table 1 and 2. The standard data base of the EDS and SEM was used to obtain the concentration of each element quantitatively. If the  $C_i$  is the concentration of element,  $I_i$ ,  $Z_i$  is the atomic number effect of atomic number of the emitter,  $A_i$  is the absorption of x-ray with bentonite specimen,  $F_i$  fluorescence effect for each element, then  $C_i = (ZAF)_i K_i$ . These three corrections factors play a vital role in obtaining an accurate quantity of each element in the sample. The values in Table 1 are  $\pm 1\%$  in accuracy when working with standards as a rule of thumb. Any inaccuracy in the atomic number effect may be traced to electron retardation and or electron backscattering. Because if they are not properly accounted for the values obtained for heavy element in a matrix of light element may be too low and a too high value may be observed for light element in a matrix of heavy element. However a secondary excitation of specimen is used as correction factors in our laboratory.

TABLE 1. POTASSIUM ELEMENTAL ANALYSIS OF RAW BENTONITE USING ZAF TECHNIQUES

	Mol %	K-Ratio	Z	A	F
O K	62.29	0.116	1.030	0.242	1.001
NaK	0.18	0.001	0.966	0.288	1.005
MgK	3.15	0.015	0.991	0.419	1.008
AlK	8.16	0.053	0.962	0.527	1.010
SiK	19.41	0.140	0.991	0.556	1.001
K K	0.54	0.008	0.940	0.844	1.015
CaK	4.10	0.066	0.964	0.889	1.004
TiK	0.25	0.004	0.883	0.919	1.006
FeK	1.93	0.044	0.884	0.989	1.000

The structural formula obtained is  $\text{Na}_{0.20}[\text{Al}_{1.9}\text{Mg}_{0.34}]\text{Si}_4\text{O}_{10}[\text{OH}]_2$ . The colour is grey with 5.73% of the oxide of iron, the viscosity at 5% concentration was 750mPa.s while the swelling ability was 15 times after 168hours.

The chemically property of the bentonite sample is comparable to the Wyoming bentonite chemical property. For example, the high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the bentonite

is an attribute well known for Wyoming bentonite. The  $\text{CaO}$  decreases content in the finer fraction while  $\text{MgO}$  and  $\text{Na}_2\text{O}$  content increases.  $\text{Mg}$  was found reasonable concentration in the octahedral site and would be responsible for the low alkaline concentration required for its optimum rheological property. Another interesting point worth mentioning is the contents of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  which are lower than in general purpose bentonites, which is reflected by the white colour of the bentonite.

TABLE 2. CHEMICAL ANALYSIS OF NIGER DELTA BENTONITE

Elemental oxide	Sample %	Wyoming bentonite %
$\text{SiO}_2$	47.4	49.28
$\text{TiO}_2$	1.18	1.48
$\text{Al}_2\text{O}_3$	20.97	22.28
$\text{Fe}_2\text{O}_3$	5.73	0.02
$\text{MnO}$	0.01	0.54
$\text{K}_2\text{O}$	0.98	0.90
$\text{CaO}$	4.23	3.43
$\text{MgO}$	9.48	5.70
$\text{H}_2\text{O}^+$	9.36	11.45
$\text{H}_2\text{O}^-$	12.80	9.62
Free volume swell	360	250

The clay sample is a multiphase material with typical peaks of crystalline and amorphous glass matrix of aluminosilicate close to the Na and Mg cations observed between 1-2kilielectronvolts (KeV). The distinctive peaks of calcium ions between 3.00-4.00 (KeV) energies reveals calcium as the dominant cations in the clay. Thus it is convenient to conclude that the material is calcium dominated clay since calcium was found both in the crystalline and amorphous phase at a higher percentage weight compared to other cations present. Sintering at elevated temperature will have to be carefully controlled while beneficiating for drilling application to avoid complete elimination of divalent cations. A beneficiation route to crystallize out the aluminosilicate could be a bypass process as the aluminosilicate content is high which has good application in catalytic reforming.

Figure 2 show the X-ray diffraction patterns of the bentonite clay sample. The tropical bentonite characterized in this work for drilling application show a dioctahedral smectite structure with a mixed monovalent/divalent cations saturation which makes it equally significant in viscosity application. The X-ray diffraction analysis of the clay sample with varying particle sizes show various peaks of the clay complexes, the varying reflections serve as reliable indices of  $d_{001}$  and  $d_{060}$  which are of particular interest when a less than 2microns particle sizes are analysed separately. The several homonic cations are however useful for the detailed characterization of the clay and non clay constituents since it will reveal a beneficiation route.

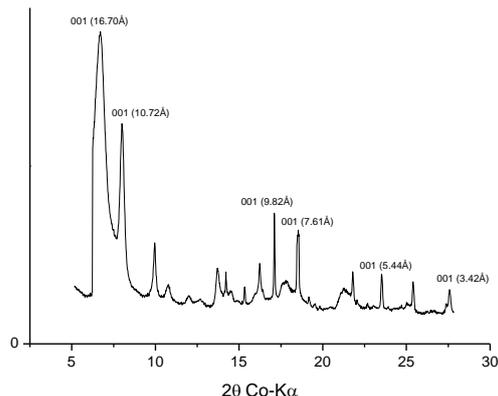


Figure 2. X-ray diffraction patterns of the bentonite clay sample.

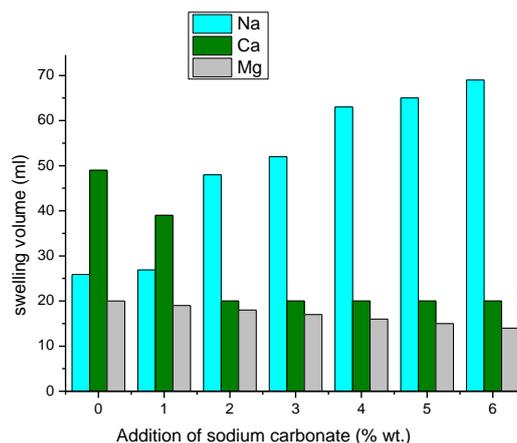


Figure 3. Na:Ca:Mg ratio of exchangeable cations in clay sample.

The XRD examination of the bentonite contains mainly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  exchangeable cations as shown in Fig.3. The experiment was performed at normal relative humidity. 16.7Å was observed at basal spacing ( $d_{001}$ ). A  $\text{Na}^+$  saturated cation present in the bentonite specimen shows a 14.35 Å at  $d_{100}$ . This is an exact submultiples of the initial 14.35 Å observed close to the 16.7 Å observed at 2θ of 7.5 Co-Kα. Therefore, with the bentonite having such a mixed monovalent/divalent exchangeable cation assemblage, the observed basal spacing which is between 14.35 Å and 16.7 Å and subsequent orders are not exactly submultiples of  $d_{001}$ . This mineralogical composition of smectite structure shows a mixed monovalent/divalent cations –saturate bentonite is peculiar for its application requiring viscosity necessary for optimum mineralogical properties of drilling mud. This is because it contains exchangeable Na to  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio of 3:2:2. With irregular series of peaks found in the air-dried specimen.

The scanning electron microscope reveals a typical sodium bentonite texture with curled and lighter edges due to the presence of opal-CT (Fig. 4). The platelet shape is equidimensional with 0.8 \*by 0.8by.001microns. The platelets shape of the particle of bentonite is due to the layer structure of the mineral. It is well known that the basal surfaces are hydrophobic, while the edge surfaces are hydrophilic.

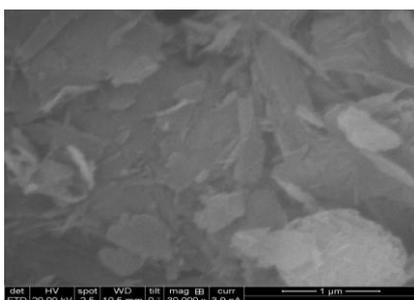


Figure 4. Scanning electron photograph of the bentonite clay sample.

Fig 5 shows the swelling value for raw clay as function of sodium carbonate addition. Its swelling ability was 13times its normal volume between 2% - 4% sodium carbonate addition. The Na:Ca:Mg ratio observed between 2% to 3% sodium carbonate addition shows a promising rheological property which is close to the recommended ratio of 3:2:2 figure stated by ingretrop et al as an indication of a very good rheology behaviour when bentonite is to be applied for viscosity purpose [10].

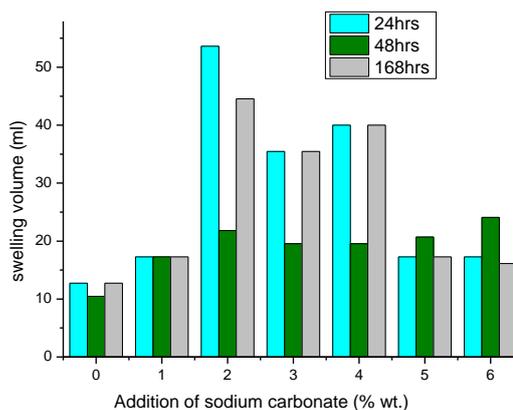


Figure 5. Swelling value for raw clay and 1-6 % sodium carbonate addition

TABLE 3. SURFACE CHEMICAL PROPERTIES OF NIGER DELTA BENTONITE

Na (meq/100g)	Ca (meq/100)	Mg (meq/100)	Na:Ca:Mg
25.9	49	20	2.6:5:2
26.9	39	19	04:4.2:02
48	20	18	3.08:02:2.1
52	20	17	3.76:2:2.24
63	20	16	08:2.5:2
65	20	15	8.6:2.6:02
69	20	14	9.5:2.72:2

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