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Determination of major elemental contents of some bentonitic clay in Akwa Ibom State, Nigeria

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ABSTRACT

Clay as a mineral resource remains an important material for most industries. They are varied in composition and as a result serve a multitude of purposes. To ascertain the industrial application of each clay type, knowledge of the elemental contents of the clay is important. For clays with montmorillonitic content, they are used in oil and gas industries mostly as drilling fluid viscosifiers. In this study, five clay samples obtained from clay deposits at Ibiono, Ini, Itu, Ikono and Uyo in Akwa Ibom State, Nigeria were characterized elementally to evaluate their montmorillonite content potential for use as drilling mud viscosifiers. X-Ray Fluorescence (XRF) coupled with samples dilution method and standard calibration of samples was used. The elemental analyses portray montmorillonite as the dominant clay mineral in the Ini, Itu Ibiono and Uyo clays. Abundance of major elements showed that SiO_2 (10.4 - 42.4%) and Al_2O_3 (4.4 -15.4%) constitute over 70% of the bulk chemical compositions. Other constituents included Fe_2O_3, K_2O, CaO, Na_2O, MgO among others. Additionally, notable disparities exist in the SiO_2 and Al_2O_3 contents of the clays, the Itu clay was the most siliceous while the Ikono clay was the least aluminous compared to the others. Furthermore, the XRF analysis of the clays showed that the Al_2O_3/SiO_2 ratio was higher than 0.38; as expected for montmorillonite content of clays. Therefore, the elemental characteristics of the studied clays revealed that they are suitable for use as drilling mud viscosifiers provided appropriate beneficiation is carried out on them to activate their Calcium-based to Sodium-based bentonitic clays.

Introduction

The geosphere of the Niger Delta region of Nigeria is endowed with abundant raw materials; one of which is clay. As reported by Terra mines in Edo state, Nigeria, the bentonitic clay deposits found in the Niger Delta region of Nigeria is estimated at a probable reserve of over 4 billion tonnes (Emofurieta, 2001). It is, however, worthy to note that the value of a raw material and its optimum use are recognized only by means of a thorough characterization. The comprehensive characterization of composition comprises of major and minor elements as well as major and accessory minerals. Partitioning of elements in coexisting phases and spatial distribution of mineral phases is crucial for eventual treatment and processing (Kuhnel, online {1995}). Therefore elemental or chemical analysis is an important step of establishing the nature of minerals such as clay (Newman, 1987). Thus, all the elements present in the clay samples are then expressed in their respective oxides, in such a way that their sum and that of water content approaches the sample weight. In the study of clay minerals for their structural formulae, elements such as Silicon (Si), Aluminum (Al), Iron (Fe), Magnesium (Mg), Titanium (Ti), Manganese (Mn), Phosphorus (P), Calcium (Ca), Potassium (K) and Sodium (Na) are essential (Mermut and Cano, 2001). In the literature, the most often used instrumental method for multi-elemental analysis of clay samples is the Neutron Activation Analysis (NAA). This method is highly preferred due to its ability to provide the required level of accuracy. However, it involves relatively high cost and difficulty to access a suitable nuclear irradiation facility (Garcia-Heras *et al*., 1997). Although X-Ray fluorescence (XRF) analysis cannot provide multi-elemental results of the same level as NAA, most researchers (Garcia-Heras *et al*., 1997; Dondi *et al*., 2001) prefer XRF as an alternative to NAA since it is less expensive and more accessible. In some studies, XRF is coupled to XRD to determine the chemical and mineral compositions of clay samples (Ehinola *et al*., 2009). Studies on Nigerian clays began in the late 1950s together with the development of clay-related industries. Interestingly, various researchers have looked at some of these Nigerian clays from diverse perspectives. Some researchers have analyzed the clays rheologically while others have done so mineralogically. For example, Porrenga (online, 2013) carried out mineralogical analysis of primary clay deposits from the Niger Delta and found out that the deposits contained kaolinite, montmorillonite and small amount of illite. In addition, he added that the montmorillonite content increases with water depth and distance to the shore. Interestingly, Olugbenga *et al*. (2013) carried out both mineralogical and rheological analysis on bentonitic clay deposits in some areas in the Niger Delta region. Their results showed that the bentonitic clays are predominantly calcium based. However, most of the studied areas in the Niger Delta region as documented in the literature are not in Akwa Ibom State. Therefore, it will be misleading to deduce from other researchers' findings that bentonitic clays in Akwa Ibom State are calcium based. Hence, this paper looks at the major elemental contents of clay deposits in Akwa Ibom State using XRF analysis approach.

Lithostratigraphy of the study area

For this study, the clay samples were collected from five different areas of Akwa Ibom State, Nigeria as indicated in Figure 1. According to onlinenigeria (2011), the whole of Akwa

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lbom State in South South Nigeria is underlain by sedimentary formations of Late Tertiary and Holocene ages. Deposits of recent alluvium and beach ridge sands occur along the coast and the estuaries of the Imo and Qua lboe Rivers, and also along the flood-plains of creeks. Inland, a greater part of the state consists of coastal plain sands, now weathered into lateritic layers, especially in Ini, Ikono, Etinan, Ikot Ekpene, Ibiono and ltu Local Government Areas (onlinenigeria, 2011). Additionally, a belt of shales associated with sandstones and limestones occur North of Nkari and Obotme, and extend down to ltu. The latter lithologies include the late Cretaceous Nsukka Formation at the base followed by the early Tertiary Imo Shale and the phosphatic Ameke Formation. Upwards, the geologic succession passes imperceptibly into thick sequences of clays, sands and gravel. Gravel beds and pebbly sands are commonly exposed on hillsides, road-cuts and stream channels in the north-eastern parts of the State.

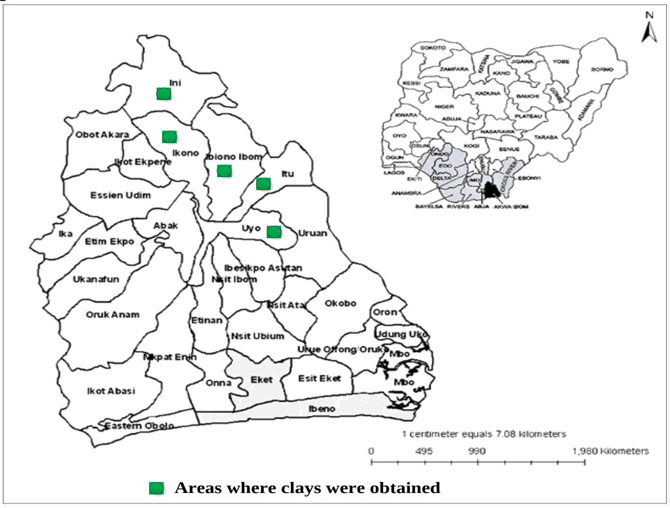
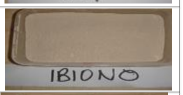
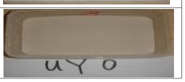


Figure 1: **Map of Nigeria (top right insert) and map of Akwa Ibom (enlarged) showing areas where clay were obtained**

Table 1: Description of clay samples used in the study

SAMPLE	LOCATION	PHYSICAL DESCRIPTION	PICTURE
A	**INI** **5° 24′ 0″N** **7° 44′ 0″E**	**Dark tan, slightly gritty feel**	
B	**IBIONO** **5° 14′ 0″N** **7° 53′ 0″E**	**Light grey, fine smooth feel**	
C	**IKONO** **5.210348 N** **7.793984 E**	**Light brown, fine smooth feel**	
D	**ITU** **5° 10′ 0″N** **7° 59′ 0″E**	**Brownish, fine smooth feel**	
E	**UYO** **5° 1′ 23.63″ N** **7° 55′ 26″ E**	**Light brown, fine smooth feel**	

Materials and Methods

Sample Collection and Preparation

The clay samples were collected from five different deposits: Ibiono Ibom, Ini, Ikono, Itu and Uyo Local Government Areas in Akwa Ibom State. In a bid to meet the homogeneity condition for XRF analysis, the clay lumps were dried and pulverized into very small size after which they were dissolved in water to form slurries. The slurries were sieved to obtain fine particles; as their clay content passes through as filtrate while sand and other organic contents were deposited as residue. These filtrates were allowed to settle for24hours, and then decanted to obtain clay mud of the different clay samples obtained. Thereafter, these clay muds were dried for about 8hours at temperature of 45^oC using vacuum oven to obtain clay cakes. Afterwards, the clay cakes of each clay sample were disaggregated and sieved to 125microns to obtain fine clay powder, as presented in Table 1.

Elemental Content Analysis

The elemental composition of the obtained bentonitic clays from Akwa Ibom State was performed with the X-Ray Fluorescence (XRF) method. This clay elemental analysis approach (XRF) was used as it is a non-destructive multi elemental analysis technique with sensitivity in the range 10^{-8} (IAEA, 2003b). Hence, the XRF analysis was conducted using the Bruker Tracer III-V analyzer. The analyzer was set with the filter composed of 1mil Titanium (Ti), 6mil Copper (Cu) and 12mil Aluminum (Al). This filter setting allows the analyzer to target potassium (K), calcium (Ca), iron (Fe), and titanium (Ti), among other elements in the clay samples. In addition, each clay sample was scanned at four locations with two reading per location for three minutes. This multi-location/multi-reading approach was adopted to allow for verification of the elemental composition reading consistency. Thus, the average elemental composition of each clay sample is presented in Table 2.Additionally, the obtained elemental compositions of the bentonitic clay samples were compared with Wyoming bentonite's (the clay of choice in drilling operation) composition.

Table 2: Major Elemental content of natural clays from the five locations

Samples	Location	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Al_2O_3 : SiO_2
A	INI	32.40	15.40	4.56	0.06	0.30	0.14	0.92	0.48
B	IBIONO	14.40	9.39	5.53	1.87	9.60	0.13	0.83	0.65
C	IKONO	10.39	4.40	6.63	0.14	0.72	0.27	2.07	0.42
D	ITU	42.41	13.43	7.12	0.09	0.43	0.14	0.71	0.32
E	UYO	18.43	7.41	5.63	0.08	0.43	0.15	1.01	0.40
Wyoming Bentonite (Dewu *et al.*, 2011)	WYOMING	47.37	17.82	1.72	1.5	1.41	15.41	0.88	0.38

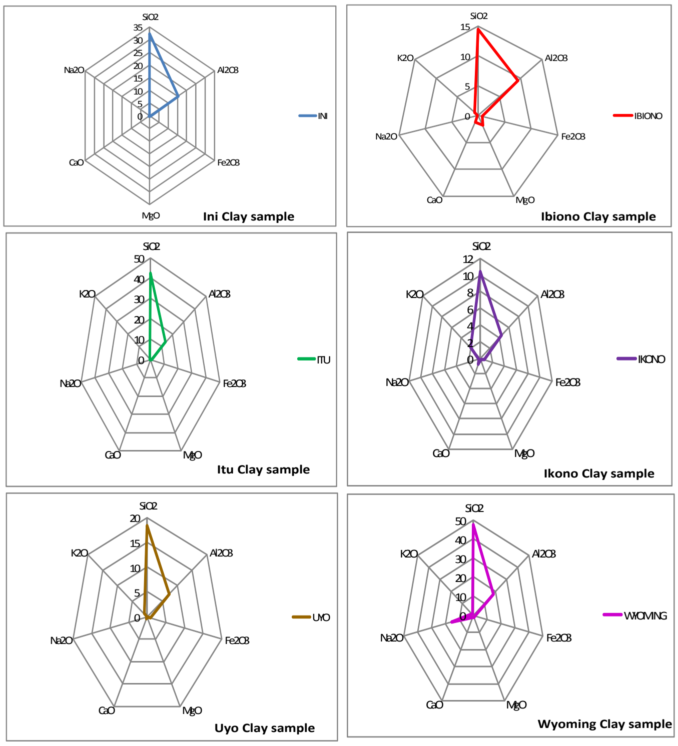


Figure 2: Web plot of major elemental oxides in clay samples studied

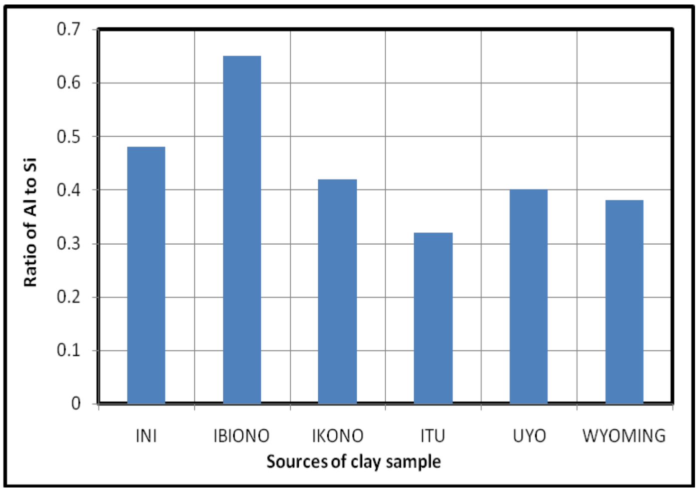


Figure 3: Comparison of the Al to Si ratio for the clay samples and Wyoming Bentonite

Results and Discussion

In this study, the readings from the XRF analyses were performed in duplicates and the average result recorded. Therefore, depending on the location of the clay samples, the percentage concentration of the bentonitic clay elements (as presented in Table 2) ranged between 10.4 –42.4 for Si, 4.4 – 15.4 for Al, 4.56 – 7.12 for Fe, 0.71 – 2.07 for K, 0.06 – 1.87 for Mg, 0.3 – 0.72 for Ca and 0.13 – 0.27 for Na. As observed from Table 2, Wyoming bentonite contains 47.4%, 17.8%, 1.7%, 1.5%, 1.41%, 0.88% and 15.4%, for Si, Al, Fe, Mg, Ca, K, and Na respectively (Dewu *et al*., 2011). A comparison of these results indicate that the Wyoming bentonite is Sodium-based while the studied bentonitic clays are Calcium-based, as the Calcium to Sodium content of the studied samples on the average was about 2.30 - 0.17% compared to 1.41-15.40% in Wyoming bentonite. Thus, this result depicts that the Calcium-Sodium ions content of the studied bentonitic clays and Wyoming bentonite was about 13.53 and 0.092 respectively. Meaning that, there is a higher content of Sodium in Wyoming bentonite than in the studied bentonitic clays. Figure 2 presents the web plots of the studied clay samples and Wyoming bentonite elemental compositions. In the figure, aside from the percentage composition and the NaO content of the Wyoming bentonite, three bentonitic clays: Ini, Itu and Uyo clays have about the same web pattern with Wyoming bentonite. This result indicates that these bentonitic clays can be improved to depict the same Wyoming bentonite characteristics. Additionally, comparisons of the bentonitic clays' elemental compositions indicate that Ibiono Ibom clay contained higher percentage of MgO and CaO than other samples; as observed in Table 2 and Figure 2. Also, the elemental results further indicate that Ikono clay contained higher K_2O than other bentonitic clay samples. Interestingly, the elemental composition results show that the studied clay samples contain significant percentage of SiO_2 and Al_2O_3 with comparable Fe_2O_3 content. However, the Fe_2O_3 contents of the studied bentonitic clays were higher than the Wyoming bentonite content. Thus, the studied clays may be seen or described as iron-rich bentonitic clay. Furthermore, Figure 3 shows the Aluminium-Silica ratio (Al/Si) of the studied samples compared with that of Wyoming bentonite.For the studied samples, the Al/Si ratio ranged between 0.32 and 0.65 while Wyoming bentonite was 0.38, indicating that the Al/Si of the studied sample has met the required standard for drilling mud formulation even before beneficiation.In summary, the XRF analyses of the studied bentonitic clays depict that the clay samples contain mixtures of montmorillonite and kaolinite in different proportions, which can be beneficiated to compare favourably with the API bentonite.

Conclusions

From the study, the following conclusions are drawn:

1. The major elemental contents identified in the study of the bentonitic clay samples from the five locations were Si, Al, Fe, Na, Ca, Mg and K. Thus, the local bentonitic clays are mixtures of montmorillonite and kaolinite depending on clay samples' location.
2. The Fe_2O_3 content of the local bentonitic clays was higher than Wyoming bentonite except for Ini clay. Additionally, the clays' Calcium oxide content was moderate; typical of Ca-bentonite with low concentrations of Magnesium oxide.
3. Except for the clay sample from Itu, the value for the Al/Si ratio for the other clay samples met the minimum value of 0.38 for clay viscosifier in drilling mud formulation. However, the studied clay samples require some beneficiation to meet the required standard for use as drilling mud viscosifiers.

Nomenclature

API	American Petroleum Institute
NAA	Neutron Activation Analysis
XRD	X - Ray Diffraction
XRF	X - Ray Fluorescence
Fe_2O_3	Iron Oxide
MgO	Magnesium Oxide
NaO	Sodium Oxide
CaO	Calcium Oxide
SiO_2	Silicon Oxide

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