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Comparative Analysis on Chemical Composition of Bentonite Clays Obtained from Ashaka and Tango Deposits in Gombe State, Nigeria

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ABSTRACT

A combination of some analytical techniques such as X-ray Flourescence (XRF), X-ray diffraction (XRD), infrared spectral (IR) analysis and Scanning electron microscopy (SEM) were employed to characterize bentonite samples from Ashaka and Tango (Gombe State, Nigeria). The results obtained for the two samples were compared. From the XRF analysis, the most abundant oxides in both the samples are SiO_2 and Al_2O_3. The silica (SiO_2), alumina, (Al_2O_3), iron (Fe_2O_3), calcium (CaO) and potassium (K_2O) contents of bentonite from Tango (GT) (49.87 wt%, 14.98 wt%, 5.12 wt%, 1.18 wt% and 1.76 wt%) are higher than those from Ashaka (GA) (48.16 wt%, 14.86 wt%, 4.80 wt%, 1.16 wt% and1.60 wt% respectively). From the FTIR spectra, both of the samples show OH stretching vibrations in the Si-OH and Al-OH groups of the tetrahedral and octahedral sheets at 3693$cm^{-1}$and 3622cm^{-1}. Bands at 1115cm^{-1} and 1113 cm^{-1}; 998 cm^{-1} and 1004 cm^{-1} were produced by the stretching mode of Si–O (out-of-plane) and (in-plane) for the GA and GT respectively. The basal spacing of samples GA and GT as determined from the XRD analysis is 15.23Å and 12.99Å respectively. Sample GT shows a SEM image with more phase separation between the particles. All the results of the analysis for the two samples were similar or close to reported literature values.

Keywords: Bentonite, XRF; XRD; FTIR; SEM; Basal spacing

INTRODUCTION

Bentonite is an aluminum phyllosilicate generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, mostly ***montmorillonite*** (MMT) (80-90 % by weight). Due to its special properties, bentonite is a versatile material for geotechnical engineering and as well as their demand for different industrial applications (James *et al.*, 2008; Asad *et al.*, 2013). For different purposes, different properties are emphasized and appropriate test methods have been developed. Mineralogical and chemical composition affects the properties of bentonite. On the other hand, the measured physical characteristics are frequently used to interpret the mineralogical composition of bentonite.

Two types of bentonite exist: swelling bentonite which is also called sodium bentonite and non-swelling bentonite or calcium bentonite. Majority of bentonites occurring worldwide are of the calcium type (Asad *et al.*, 2013; Ahmed *et al.*, 2012; Tijen, 2010; Ahonen *et al.*, 2008; RMRDC, 2007). Investigations by the Nigerian Mining Corporation established the existence of bentonitic clay reserves of over 700 million tonnes in different parts of the country which include the North-east quadrant; Borno, Yobe, Taraba and Adamawa (Apugo-Nwosu *et al.*, 2011).

Structure of clay particles is perceived in layers where each layer is composed of two types of structural sheets: octahedral and tetrahedral. The layers present in MMT are composed of a 2:1 structure i.e two tetrahedral silica sheets sandwiching a central octahedral alumina sheet (T-O-T). Due to an isomorphic substitution within the layers (e.g., Al^{3+} for Si^{4+} in the tetrahedral sheet and Fe^{2+}or Mg^{2+} for Al^{3+} in the octahedral sheet) the clay layers have negative crystal charge which is balanced by exchangeable cations such as Na^+, K^+, Ca^{2+} in the interlayer together with water molecules bonded by ion-dipole forces. The hydration of these inorganic cations causes the clay mineral surface to be hydrophilic (Xi *et al.*, 2007; Banik *et al.*, 2015; Rodriguez *et al.*, 2015).

Clay deposits and clay minerals generally vary in nature, no two or more deposits can have exactly same clay minerals and frequently different samples of clay from the same deposits differ. Their physical and chemical properties (swelling ability, plasticity, cation exchange capacity etc) vary typically within and between deposits due to the differences in the degree of chemical substitution within the smectite structure and nature of exchangeable cations present, and also due to the type and amount of impurities present (Trauger, 1994; James *et al.*, 2008; Asad *et al.*, 2013). The most common impurities in bentonite clay are

quartz, calcite, feldspar, cristobalite, beotite, kaolinite, mica and organic matter while hydrated iron oxide, ferrous carbonate and pyrite are being the minor impurities depending on the nature of their genesis (Holtzer *et al.,* 2011; Ahmad *et al.,* 2012).

The peculiar characteristics of bentonite clays; thixotropic, swelling and absorption/adsorption properties, have accounted for their demand for different industrial applications such as its use as detoxifier, sealant, binder, fillers for paper, pharmaceutical products, absorbent, adsorbent, catalyst, nanoclays, its use in drilling fluid, bleaching earth, etc (Trauger, 1994; James *et al.,* 2008; Asad *et al.,* 2013). A number of works has been carried out on the quantitative clay mineral analysis and characterization using different techniques such as infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), thermo gravimetric analysis (TGA) etc. This study demonstrates the use of some of these techniques for comparative characterization of bentonite from Ashaka and Tango (Gombe State), Nigeria.

MATERIALS AND METHODS

Materials

The bentonites used in this study were obtained from Ashaka and Tango deposits, Gombe State and were labeled as GA and GT respectively. The bentonite samples were obtained in milled powder form. The samples were pre-treated with 10% H_2O_2 to remove or oxidize any colored organic and inorganic matter in the clay (James et al., 2008). The suspension was then agitated and allowed to stand for 2 hr. The clear supernatant liquid was decanted and the clay re-suspended in 1 L 0.5 M NaOH solution for a period of 2 hr with moderate agitation using a mechanical stirrer. The supernatant was also decanted and rinsed with de-ionized water, dried and ground. The physico-chemical properties of the bentonites were reported elsewhere (Abdullahi and Audu, 2015).

Characterizations of the samples

X-ray fluorescence analysis (XRF): The chemical compositions of the bentonite samples were carried out using X-Ray fluorescence analysis (X-supreme 8000) instrument.

Fourier transform infrared spectroscopy analysis (FTIR): FTIR analysis was carried out using FTIR (Cary 630 Agilent Technology USA equipment) at Instrumentation Lab of Chemistry Department, Bayero University Kano, Nigeria. All FT-IR spectra were recorded in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

X-ray diffraction analysis (XRD): The Bragg angular zone was explored by X-ray diffraction (XRD) at GBC EMMA (Enhanced mini material) Analyzer, 40 kV and 40 mA, Cu Kα radiation source (λ = 1.5418). The diffraction angle 2θ was scanned from 2º to 65º at scanning rate of 2º/min and step size of 0.05 º. In order to calculate the distance between the silicate layers, Bragg's law was used.

Scanning electron microscopy (SEM): Scanning electron microscope (SEM) (Phenom Proxy, PW 100-002, magnification-255x, Accelerating Voltage- 10KV) was used to evaluate the surface morphology of the bentonite samples.

RESULTS AND DISCUSSION

The CEC values of the Ashaka and Tango bentonites were determined as 0.72Meq/g and 0.63Meq/g respectively, by ammonium acetate method.

X-ray fluorescence analysis (XRF):

The chemical compositions are shown in Table 1. Figure 1 summarizes the comparison of the chemical compositions of the two bentonite samples. The results of the chemical compositions of the two bentonite samples were similar to those of previous workers (Nweke *et al.,* 2015; Bendou and Amrani. 2014; Shah *et al.,* 2013; Abdallah and Yilmazer, 2011; Changchaivong and Khaodhiar, 2009; James *et al.,* 2008; Patel *et al.,* 2007; Tabak *et al.,* 2007). The most abundant oxides in both of the bentonite samples are SiO_2 and Al_2O_3. The silica (SiO_2), alumina, (Al_2O_3), iron (Fe_2O_3), calcium (CaO) and potassium (K_2O) contents of bentonite from Tango origin are higher than those of the bentonite from Ashaka origin, while for the sodium (Na_2O), titanium (TiO_2) and phosphorus (P_2O_5) contents, the values are higher in the Ashaka sample (Table 1). Nweke *et al,*. (2015); Kiviranta and Kumpulainen, 2011; Ahonen *et al.,* 2008; Tabak *et al.,* (2007); reported silica, alumina, sodium and calcium contents for Wyoming bentonite as (45 wt%, 17wt%, 2.7 wt%, 1.77 wt%; 61.55wt%, 20.55wt%, 2.41 wt% ,1.32 wt%; 61.80 wt%, 20.44 wt%, 2.1 wt%, 1.4 wt%; 48.35 wt% , 12.15 wt %, 3.65 wt%, 6.68 wt%) respectively. The silica (SiO_2) values of the Ashaka and Tango bentonites (48.16wt % and 49. 87wt %) are similar to the values reported by Nweke *et al,*. (2015) [45 wt%]; Tabak *et al.,* (2007) [48.35 wt%] for Wyoming bentonites. All the sodium contents of the bentonite samples (Ashaka and Tango) from this study (1.66 wt% and 1.43 wt %) respectively, have values lower than the Wyoming bentonites. Fe_2O_3 values reported for both the bentonite samples in this study are lower than those reported by Nweke *et al.,* (2015) [11.10 wt %]; Tabak *et al.,* (2007) [8.26] but higher than those reported by Kiviranta and Kumpulainen, (2011) 3.82 wt %]; Ahonen *et al.,* (2008) [3.84 wt %] for the Wyoming bentonites. All the values for the other oxides from

this study were similar to the values obtained for the different Wyoming bentonites.

Table 1: Chemical compositions of bentonites

Chemical oxide	GA (wt %)	GT (wt %)
SiO_2	48.16	49.87
Al_2O_3	14.86	14.98
Fe_2O_3	4.80	5.12
CaO	1.16	1.81
Na_2O	1.66	1.43
MgO	2.08	2.08
K_2O	1.60	1.76
TiO_2	0.94	0.87
P_2O_5	1.06	1.01

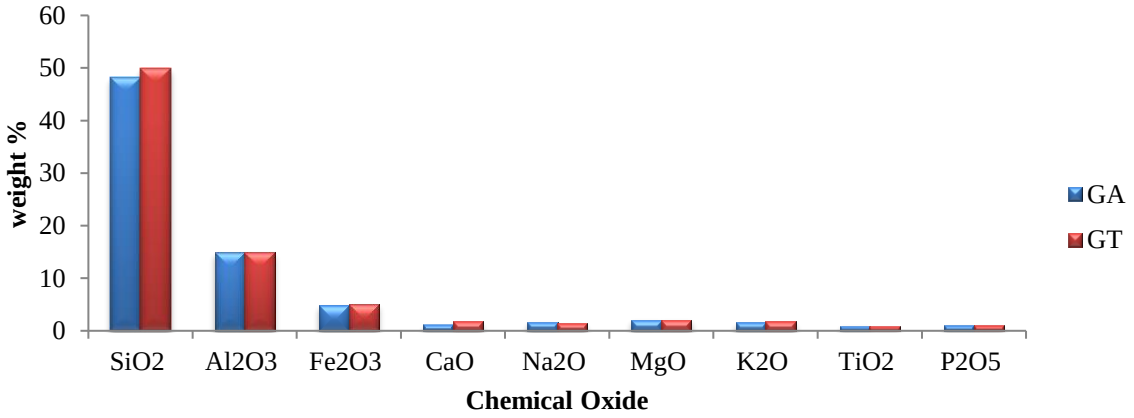


Fig 1: Chemical Compositions of the Bentonite Samples Analysed by XRF

Fourier transform infrared spectroscopy analysis (FTIR):

From FTIR spectra of the bentonite samples in this study, the bands at 3693cm^{-1}, 3693cm^{-1} and 3622cm^{-1}, 3622cm^{-1} are assigned to OH stretching vibrations in the Si-OH and Al-OH groups of the tetrahedral and octahedral sheets of the GA and GT clay samples. Bhattacharya and Mandot, (2014); Dutta and Singh, (2014); Aroke *et al.*, (2013); Patel *et al.*, (2007) reported values of 3698 cm^{-1} and 3620 cm^{-1}; 3693 cm^{-1}and 3620 cm^{-1}; 3695 cm^{-1}; 3698 cm^{-1} and 3620 cm^{-1} for the OH stretching vibrations in the Si-OH and Al-OH groups respectively. The band of low intensity located at lower frequencies at 1639cm^{-1} for both samples are produced by the bending vibration mode of adsorbed water, this was in agreement with the values reported by Dutta and Singh, (2014); Tabak *et al.*, (2007); Patel *et al.*, *(*2007); Abdallah and Yilmazer, (2011); Bhattacharyya and Mandot, (2014) of 1639 cm^{-1} and 1640 cm^{-1} respectively. Angaji *et al.*, (2013); Ezquerro *et al.*, (2015) reported values of 1630 cm^{-1} and 1636 cm^{-1} respectively.

The most intense bands of the spectrum were found in the low-frequency region. The bands at 1115cm^{-1} and 1113 cm^{-1}; 998 cm^{-1} and 1004 cm^{-1} for GA and GT respectively were produced by the stretching mode of Si–O (out-of-plane) for MMt and Si–O stretching (in-plane) vibration for layered silicates, respectively. Bands at 1110 cm^{-1}, 1115 cm^{-1}, 1116 cm^{-1}, 1125 cm^{-1} and 1150 cm^{-1}; 1007cm^{-1}, 1030 cm^{-1}, 1035 cm^{-1}, 1038 cm^{-1}, 1045 cm^{-1} were reported from different literatures for the Si-O stretching out of plane and in-plane respectively (Tabak *et al.*, 2007; Patel *et al.*, 2007; Abdallah and

Yilmazer, 2011; Angaji *et al.*, 2013; Aroke *et al.*, 2013; Dutta and Singh, 2014; Bhattacharyya and Mandot, 2014; Ezquerro *et al.*, 2015).

Bands at 912cm^{-1} are associated with the bending vibration of Al-Al-OH for both the samples which are in close agreement with values reported in some literatures; 914 cm^{-1}, 915 cm^{-1}, 919 cm^{-1}, 920 cm^{-1} .

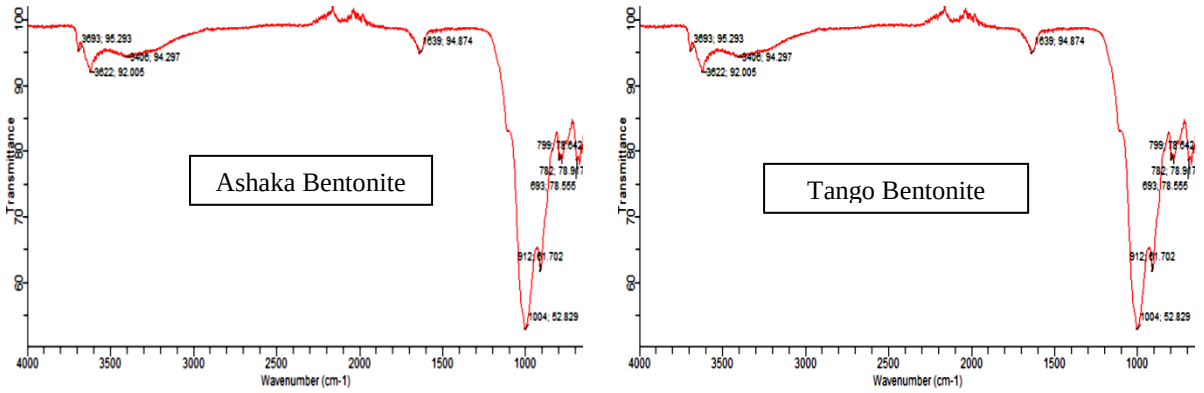


Fig 2: FTIR spectra of the Ashaka and Tango samples

X-ray diffraction analysis (XRD):

From the XRD patterns of the samples, basal reflections at angles 5.8°, 20.95°, 26.75°, 50.20 and 6.8°, 20.89°, 26.69°, 50.17° were observed which are associated to the presence of the smectite and impurities such as opal, quartz and calcite in the Ashaka and Tango bentonite samples respectively. In sample GT reflections at 29.47° was seen which is due to the presence of Feldspar in the sample. The basal spacing of samples GA and GT from the diffraction angles (5.8° and 6.8°) correspond to 15.23 (Å) and 12.99 (Å) respectively. These values are within the range of expected values (1.2 to 1.6 nm) for typical smectite minerals observed under ambient temperature and humidity (Massinga *et al.*, 2010).

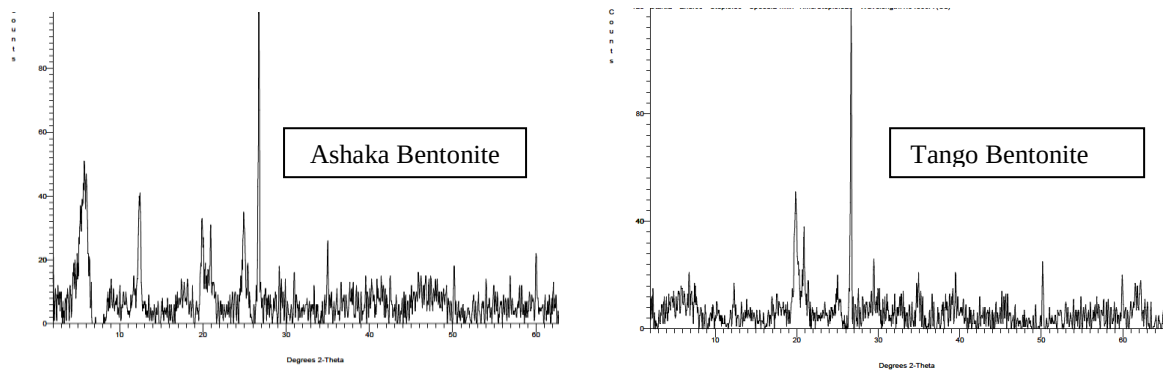
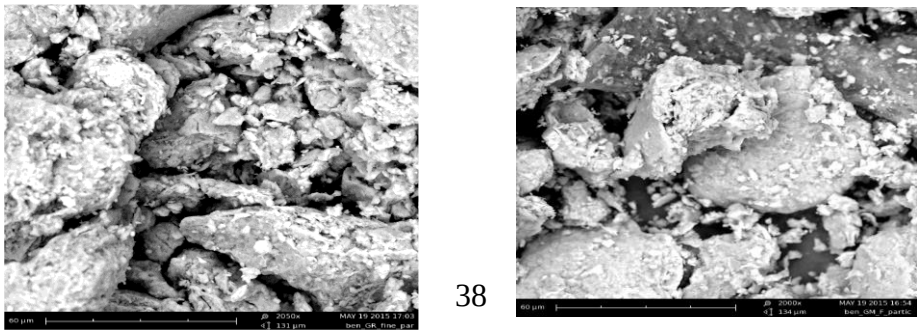


Fig 3: XRD diffractographs of the samples

Scanning electron microscopy (SEM):

In the SEM images of bentonite samples, massive plates with some phase separations are observed as a heterogeneous surface morphology. It showed a soft surface where large lamellas tend to form big agglomerates with a layer disposition. Sample GT shows a SEM image with more phase separation between the particles.



Ashaka Bentonite Tango Bentonite

Fig 4: SEM images of the samples

CONCLUSION

Some significant variations were observed from some of the results such as in the chemical compositions, basal spacing and SEM images of the samples, while in the FTIR spectra and wave bands, only slight variations were observed. These variations could be due to the fact that, the physical and chemical properties of bentonite clays vary typically within and between deposits due to the differences in the degree of chemical substitution within the smectite structure and nature of exchangeable cations present, and also due to the type and amount of impurities present. No two or more clay deposits or even clays from the same deposit can have exactly same clay minerals.

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