Supported by tetfund TERTIARY EDUCATION TRUST FUND

A GEOCHEMICAL ASSAY AND INDUSTRIAL UTILIZATION OF CLAYS FROM SABONGIDA-ORA, SOUTHERN NIGERIA

***Odokuma-Alonge,[1] O, Alonge,[2] P. O. and Chibuzor,[3] N. S.**
[1]Department of Geology, University of Benin, Benin City, Edo State, Nigeria
[2]Department of Science Laboratory Technology, University of Benin, Benin City, Edo State, Nigeria
[3]Department of Geological Sciences, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
*E-mail Address: ovie.odokuma-alonge@uniben.edu

Received: December 13, 2021 Accepted: February 20, 2022

ABSTRACT Five (05) clay samples from Sabongida-Ora in Edo State were analyzed using the X-Ray Flourescence (XRF) and X-Ray Diffraction (XRD) techniques to determine their chemical and mineralogical properties and hence industrial utilization. Results from the geochemical analysis reveal MgO content of 26.62 – 36.60wt%, SiO_2 of 14.20 – 20.18wt%, Al_2O_3 ranges from 5.30 – 9.16wt%, CaO ranges from 14.77 – 21.85wt% and Fe_2O_3 from 4.41 – 5.04wt%. The main minerals present are the vermiculite (45.45 – 68.52%), illite (10.93 – 20.00%), halloysite (5.47- 9.09%), magnesite (5.47 – 16.52%), tremolite (3.30 – 14.15%) quartz (5.79 – 17.19%) and hematite (2.83 – 17.19%). The SiO_2/Al_2O_3 (1.91 – 3.48) ratio is fair indicating clay minerals with both asymmetric (<2.5 SiO_2/Al_2O_3) and symmetric (> 2.5 SiO_2/Al_2O_3) structures and the ignition loss (LOI) (22.68 – 27.01). The study revealed the suitability of the clay for the production of bricks for construction purposes, if the amount of alkalis and silica content are increased to meet standard requirements.

Keywords: mineralogy, composition, clay, geochemical, utilization

INTRODUCTION

The demand for industrial raw materials by the fast growing industrial sector in Nigeria needs to be addressed. Clays are a very important industrial raw material needed for the production of a variety of items such as pottery, bricks paper, ink ceramic wares, roofing and floor tiles. Floor and wall tiles for instance are cheaper and more durable particularly under tropical conditions (Emofurieta *et al*., 1994). Clays can also be blended with other materials to improve on some desired characteristics of the finished products.

As a raw material, clay must contain a certain proportion of clay minerals to develop the required plasticity and filler such as quartz, fragments of feldspars and a proportion of fluxes like the alkalis, magnesium, calcium, iron as particles (Mitchell, 1983 and Michaiidis *et al*., 2010). The industrial utilization of these clay bodies depends on geological, mineralogical, chemical and physical properties hence, the need to evaluate the properties of any occurrence of interest. This is important for understanding of the technological properties of clay products and optimization of firing cycles in production (Teixera *et al*., 2001, 2004; Ferrari and Gualtieri, 2006). The aim of this study is to determine the geochemical (chemical and mineralogical) properties of clays from Sabongida-Ora in order to establish their suitability for the production of bricks.

Knowledge of clay availability in any region is important for its application and utilization. Several studies have been carried out on the physicochemical and the mineralogical properties of clay. Omotoyinbo & Oluwole, (2008) investigated clay deposit in Ekiti State and found it suitable for the production of crucibles and furnace lining. In southeast Nigeria, the clay deposits have good quality for economic and engineering purposes (Onyekuru *et al*., 2018). Residual and lateritic clays were analyzed in Ore area for their economic values. The clay layer has economic potential for ceramics, fertilizers and production of structural wares. This review is not exhaustive. The geochemical assay of clay mineral will provide useful information on clay minerals with regard to its applications in domestic and industrial purposes and utilization.

GEOLOGICAL SETTING

Sabongida-Ora is located in Owan West L.G.A of Edo State (Figure 1). The study area lies between longitudes 05˚56^{1}30^{11}E and 005˚56^{1}36^{11}E, and latitudes 06˚52^{1}44^{11} and 06˚52^{1}48^{11} (Figure 2). The clay body in the study area is probably transported from the existing Imo Formation. The study area forms part of the Anambra Basin Flank (Nwajide and Reijers, 1996) (Nwajide, 2013). The Imo Formation consists of thick clay shale, fine textured, dark grey to bluish grey with occasional admixtures of clayey ironstone and thick sandstone beds. Carbonized plant-remains maybe locally common and the formation becomes more sandy towards the top where it may consist of an alternation of bands of sandstone and shale (Wilson, 1925 and Kogbe, 1989). The age of the formation ranges from Paleocene - Lower Eocene (Bergren, 1960; Short and Stauble, 1967 and Nwajide, 2013). The geological map of the area of interest is shown in Figure 3.

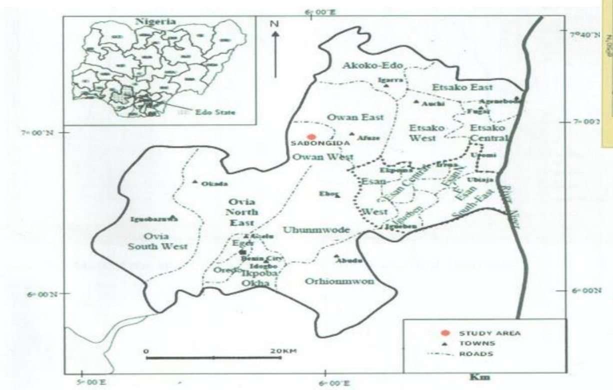

Figure 1: Map of Edo State showing the study area.

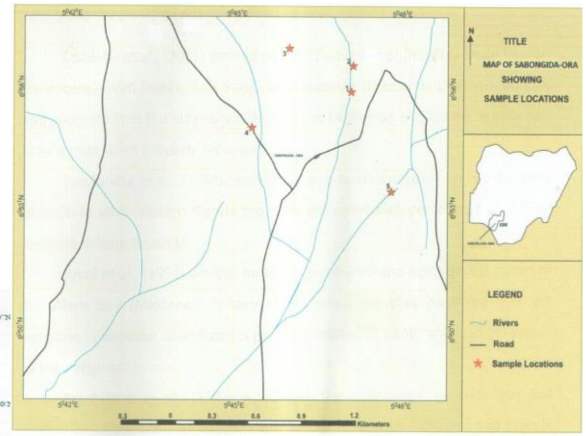

Figure 2: Sample locations (after GSN, 1974)

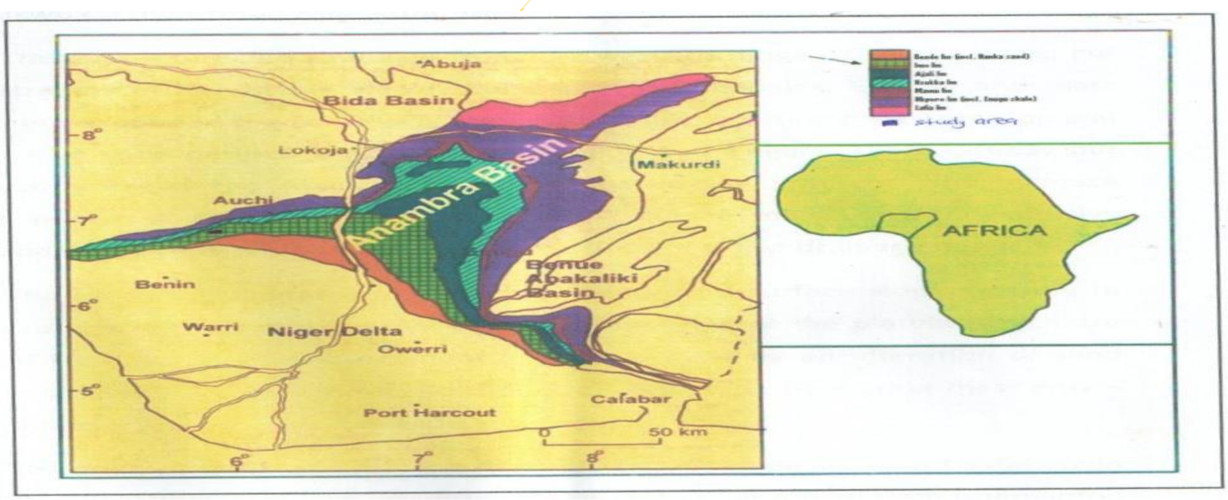

Figure 3: A geological map of the study area (modified after Nwajide and Reijers, 1996)

MATERIALS AND METHODS

Five (05) clay samples were taken from hand dug pits and trenches at a depth of 0.45m below the surface with the aid of a digger and shovel. The samples were put into well labeled sample bags with the coordinates of the area taken with the aid of a Global Positioning System (GPS) receiver.

preset time : 0.15 (sec)

The minerals present in each sample were identified based on their respective diagnostic lattice spacing (Chen, 1977). The relative proportions of the minerals are estimated in accordance with the method described by Carrol, (1971).

PROCEDURE FOR SAMPLE ANALYSIS

Pretreatment of samples

Each of the five samples was placed in a container with water for a few hours after which it was manually made into a slurry form and filtered for the removal of stones, organic matter and other impurities. It was allowed to settle and then the water was drained out. The samples were sun-dried and a few grams put into a well labeled sample bag and taken to the laboratory at National Steel and Raw Materials Exploration Agency, (NSRMEA), Kaduna for mineralogical and chemical analyses.

Pulverization of rock sample and mineralogical analysis

The dry sample was broken into pieces using a disc miller and finally a vibrating cup miller by setting the equipment at 6 – 8 rpm. Having obtained the powdered sample of particle size 100 mesh (0.15microns), the sample was ready for the X-ray Diffractometer. Mineralogical analysis was carried out with Schimadzu 6000 Diffractometer scanning between 0 – 54 theta Bragg angle under the following analytical conditions.

Measurement Condition

X-ray tube

target : Cu

voltage : 40.0(kv)

current : 30.0(mA)

Slits

divergence slit : 1.0000 (deg)
scatter slit : 1.0000 (deg)
receiving slit : 0.3000 (mm)

Scanning

drive axis : theta – 2 theta

scan range : 2.0000 – 55.0000 (deg)

scan mode : continuous scan

scan speed : 8.0000 (deg/min)

sampling pitch : 0.0200 (deg)

Sample Pelletization

The powdered sample was mixed with binder (Lithium tetraborate also called Borax) in a ratio 1:4 grams. This mixture was made even using Herzog vibrating cup miller at 8rpm. The mixture was loaded onto a cup of size 22 mm by 40 mm made of aluminum material. Pellets were thus formed. The required parameter for the XRF machine was set according to a standard which included pressure values set at 16Pa (Paschal), voltage recommended level was 45V and the current level is 40A.

RESULTS AND DISCUSSION

The results of the physical and chemical properties of the clay samples are presented in Table 1 and the mineralogical analysis result in Table 2. The predominance of MgO, CaO and Fe_2O_3 in the study area classifies these clays as probably transported clays with contamination from the surrounding limestone bodies hence the fairly high values of MgO (26.62 – 36.60 wt.%) and CaO (14.77 – 21.85 wt.%). The Fe_2O_3 values range from 4.41 – 5.07 wt.%. The SiO_2 content of the samples is fairly high and ranges from 14.20 – 20.18 wt% but is quite low compared to shale samples from Auchi area (Emofurieta, 1994). The low silica content may be due to washed or transported detritus material to other locations during weathering and erosion. The Al_2O_3 values 5.30 – 9.16wt.% are also very low when compared to previous studies and may also be associated to the enormous erosive activities in the area. The very low values of K_2O (0.15 – 0.88 wt.%) and Na_2O (0.01 – 0.02 wt%) may also be due to the reasons mentioned above. The TiO_2 and P_2O_5 content of the samples are 0.10 – 0.40 wt% and 0.01 – 0.04 wt%, respectively. The loss on Ignition (LO1) values range from 22.67 – 27.01. The fairly high values may be due to the presence of hydrous alumino-silicate minerals (vermiculite, tremolite) and also the presence of carbonate-rich minerals (calcite). The SiO_2/Al_2O_3 ratios gave values from 1.91 – 3.48 which indicate that the study area has both clay minerals with both asymmetric (<2.5 SiO_2/Al_2O_3 ratio) and symmetric > 2.5 SiO_2/Al_2O_3 structures, respectively (Krauskopf, 1979). The colours of the samples are generally dark brown indicating oxidation of iron.

Table 1: The physical and chemical properties of the clay samples

Parameter	Elemental oxides	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Reference sample
Chemical composition	SiO_2	16.88	15.42	14.20	20.18	17.04	38.67
	Al_2O_3	5.30	6.74	9.16	7.14	8.33	9.45
	MgO	36.60	30.65	28.14	26.62	30.24	8.50
	CaO	21.85	18.24	16.02	15.23	14.77	15.84
	Fe_2O_3	4.41	4.82	5.04	4.88	5.07	2.70
	K_2O	0.88	0.19	0.20	0.17	0.15	2.76
	Na_2O	ND	0.02	0.01	ND	0.01	2.76
	TiO_2	0.01	0.12	0.25	0.26	0.40	-
	P_2O_5	0.02	0.02	0.01	0.02	0.04	-
	MnO	0.04	0.06	0.14	0.10	0.17	-
	LOI	22.67	24.41	27.01	26.15	23.18	-
	SiO_2/Al_2O_3	3.06	2.82	1.91	3.48	2.52	4.09
Physical properties	Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	

Total Fe as Fe_2O_3 ND = Not Detected

Reference samples = Brick Clay (Murray, 1960), America Association of Testing Materials (ASTM). C62-17. Standard Specification for Building Bricks 2017, ASTM. International.

Table 2: The mineralogical composition of the clay samples from Sabongida-Ora area

Minerals	1	2	3	4	5	d-spacing value
Halloysite	-	9.09	-	5.47	-	7.50Å,7.20Å 4.50Å, 4.64Å

Tremolite	14.15	3.30	6.15	-	12.03	8.52Å
Magnesite	10.09	16.52	6.15	5.47	-	2.12Å
Quartz	5.09	5.79	6.15	17.19	7.40	1.81Å
Vermiculite	51.89	49.15	56.92	43.75	68.52	9.65Å
Hematite	2.83		-	17.19	12.03	2.16Å
Albite	2.83	-	4.61	-	-	3.57Å
Illite	13.20	16.11	20.00	10.93	-	25.80Å, 24.76Å

1Å (Angstrom) = 10^{-10m}

Table 2 shows the mineralogical composition of the clay samples. Vermiculite is clearly the most abundant mineral in the samples. Its occurrence ranges from 43.75 – 68.52% with d-spacing value of 9.65A˚. Illite occurs in fairly high amounts and ranges from 10.93 – 20.00% with d-spacing value of 25.80A˚ and 24.76A˚. Halloysite is similar to kaolinite, because they belong to the same group but is different depending on the way the successive layer of the clays being a two – layer structure are stacked (Krauskopf, 1979). It is observed in two samples (2 and 4) and range from 5.47 – 9.09%. The other minerals present are tremolite, magnesite, quartz, hematite and albite with their relative abundance from 3.30 – 14.15% and d- spacing of 8.52Å, 5.47 –16.52% with d- spacing of 2.12Å, 5.09 – 17.19% and d-spacing of 1.81Å, 2.83 – 17.19% and d- spacing of 2.16Å, and 2.83 – 4.61% and d-spacing of 3.57Å, respectively. They occur in minor to fair amounts. The diffractograms of the samples are presented in Figures 4 to 8.

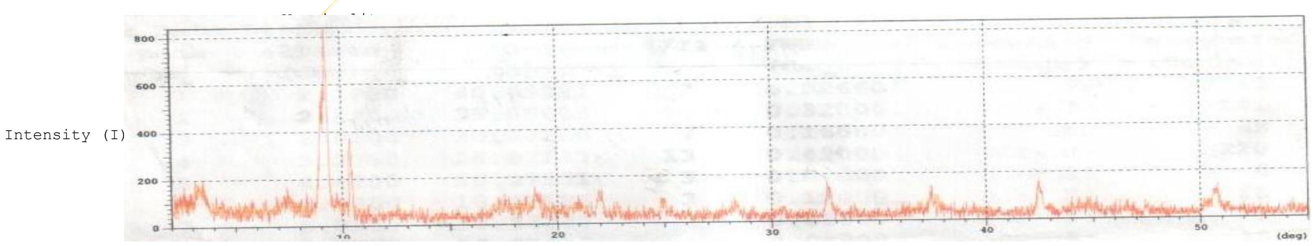

Figure 4: A diffractogram of sample one showing the major and minor minerals

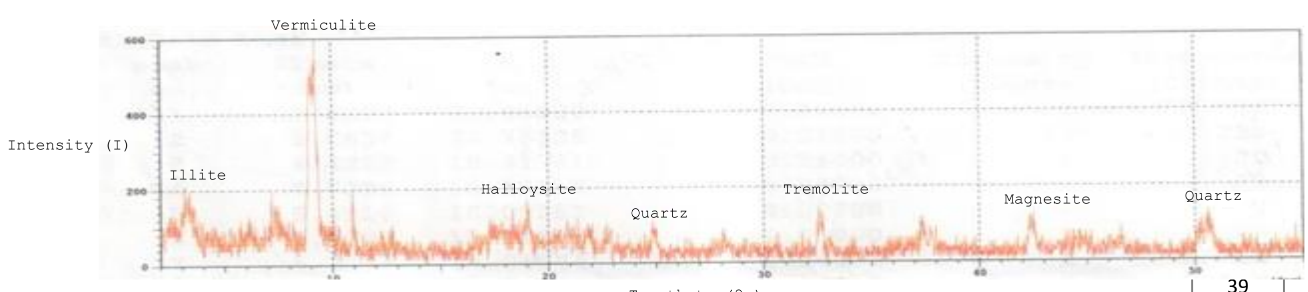

Figure 5: A diffractogram of sample two showing the major and minor minerals

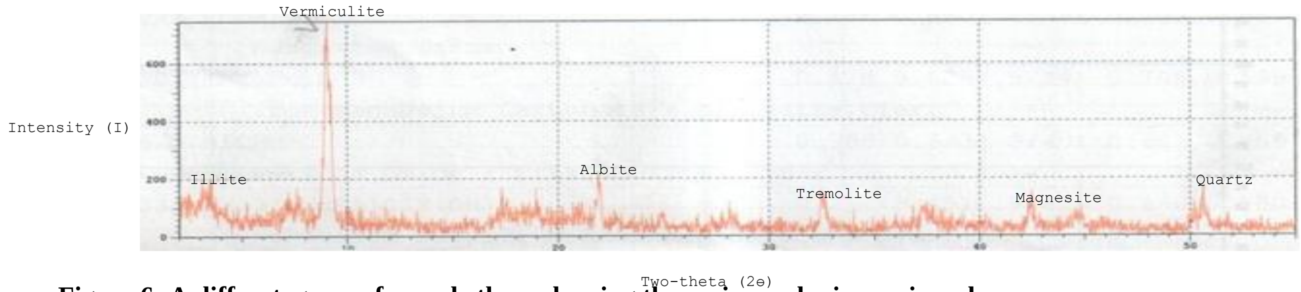

Figure 6: A diffractogram of sample three showing the major and minor minerals

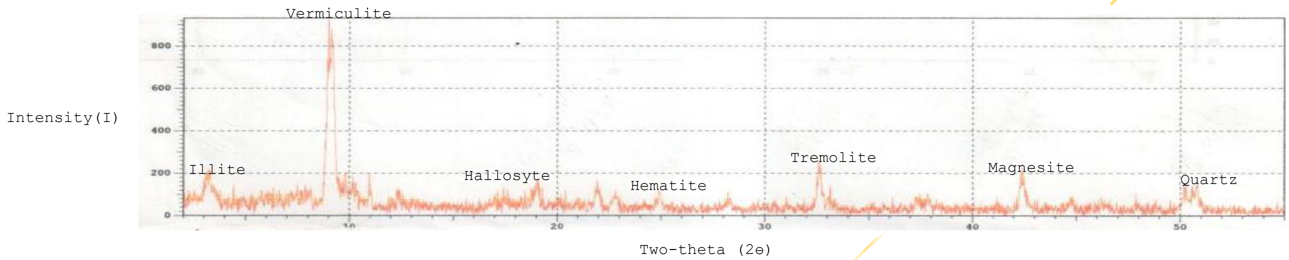

Figure 7: A diffractogram of sample four showing the major and minor minerals

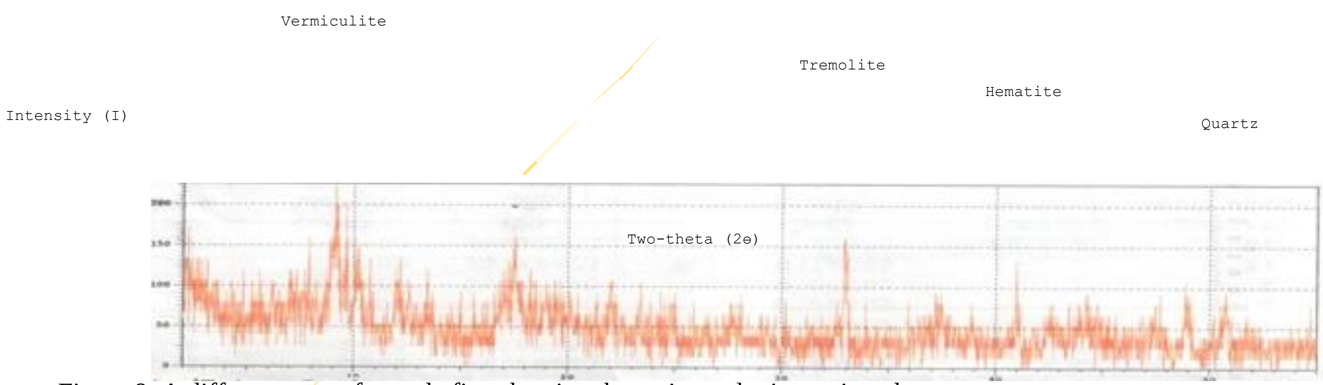

Figure 8: A diffractogram of sample five showing the major and minor minerals

From the study, the fairly high MgO and CaO content is not unconnected to the high vermiculite and fairly high magnesite content. The limestone body and shale around the study area must have probably being subjected to weathering. The high MgO content may be due to dolomitization process which affected the limestone in the area (Petters, 1978; Emofurieta *et al*., 1994). The studied samples when compared to the reference sample i.e. Brick clay (Murray, 1960 & 2007) (ASTM C62-17 Standard Specification for Building Bricks, 2017) have less SiO_2 content. But the Al_2O_3 content is fair. The K_2O and Na_2O contents of the studied samples are far less than the reference sample. The diffractogram shows the highest peak represent vermiculite, which exhibits the characteristics of expandable clay mineral and plasticity. The illite and halloysite are the non-expandable and soft clay minerals. The other minerals present are tremolite, magnesite, quartz, hematite and albite, and occur in minor-fair amounts. They add to the strength of the clay material. For the studied samples to be used for the production of bricks the alkali content must be increased. It would also be necessary to introduce silica into the system to achieve the desired result.

Table 3: Comparison between Sabongida-Ora clay & Standard brick clay (Murray, 1960 and 2007)

Paramenter	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3
Av. Comp. Sabongida-Ora Clay	17.22	30.45	16.74	7.33	4.84
Std. Brick Clay	15.84	8.50	38.67	9.45	2.70
Difference	+1.38	+21.95	-21.93	-2.12	+2.14

Table 3 shows the comparision between Sabongida-Ora clay and the reference standard. CaO, MgO, SiO_2, Al_2O_3 and Fe_2O_3 average values are 17.22wt.%, 30.45wt.%, 16.74wt.%, 7.33wt.% and 4.84wt.% which are the predominant oxides in the clay samples with difference of +1.30wt%, +21.95, -21.93, -2.21 and +2.14, respectively. The greatest deficiency in the clay is silica and can be sourced from compositionally mature sand and sandstones.

CONCLUSION

Chemical and mineralogical analyses were carried out on clay samples from Sabongida-Ora in Edo State. The results of the chemical analysis largely corroborates the diffractogram samples The analyses revealed a fairly high vermiculitic content when compared to the reference samples and are considered suitable for the production of bricks after appropriate beneficiation of the samples by increasing the alkali and silica contents.

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