



The Characterization of Local Clay from Anambra State Nigeria for Its Potential Applications in the Production of Ceramic Whitewares

F. O. Nnaneme^{1*}, T. U. Onuegbu¹, S. C. Agbo² and E. S. Okwute³

¹Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria.

²Department of Ceramics and Production, Project Research and Development (PRODA), Enugu State, Nigeria.

³Department of Pure and Applied Chemistry, University of Maiduguri, Maiduguri, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. Author TUO conceived the research and designed the research work. Author SCA designed all laboratory procedure. Authors FON, ESO and SCA carried out all literatures searches and conducted the laboratory work together with other authors. All authors read and approved the final manuscript.

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ABSTRACT

Local clay deposits from Ukpok in Nnewi South Local Government Area of Anambra State were characterized for its potential applications in the production of ceramics whitewares. XRF analysis of the clay revealed that it has high silica and alumina contents with some flux oxides. XRD analysis also revealed that of all the minerals present in the clay, quartz has the highest constituent followed by kaolinite and rutile. FT-IR analysis revealed that the bands corresponds to 3500 cm^{-1} to 4000 cm^{-1} indicating the presence hydroxyl groups (OH) and Si-O symmetry vibration stretch at 1206.207 cm^{-1} which confirmed the kaolinite structure of the clay. The SEM study showed a finely distributed uniform surface with isolated patches of granulated texture which explained the physical behaviour of the clay. The EDS spectrum of the formulated fired Ukpok clay indicated the presence of O, Al, K, Ca, K, Fe, and Si. The study revealed that an increase in the firing temperature and feldspar contents of the clay increases its bulk density, while the apparent density decreases with increase in

*Corresponding author: E-mail: felixnna22@gmail.com;

temperature. Apparent porosity showed that there was a decrease from 25% to 3%, and the water absorption increases with increase in the silica content and decreases with temperature and feldspar increase. The shrinkage increases with the increase in temperature. The results concluded that the clay sample could be utilized as an industrial raw materials for the production of ceramic whitewares.

Keywords: Ukpor clay; kaolinite; whitewares; ceramic; X-ray Diffractometer; FTIR.

1. INTRODUCTION

Clays are among the cheapest, abundant, environmentally friendly, ion exchangeable and non-toxic adsorbents that could be used to substitute the expensive commercial activated carbon in tackling environmental pollution problems. Clay could be defined as a tenacious ductile earthy material, hydrated aluminum silicate or earth crust [1]. Clays are available in different particles sizes and colours depending on their extent of migration from source (primary or secondary clays), inorganic impurities, organic matters, plasticity and minerals inherent in them.

They are anhydrous complexes of alumina (Al_2O_3) and silica (SiO_2) generally represented by the molecular formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [2]. Clay minerals are generally composed of aluminum silicates which are formed by tetrahedral and octahedral sheets that are linked together through sharing of oxygen atoms [3]. These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust; however, transformations in the geometric arrangement of atoms and ions within their structures occur due to weathering.

Ceramic whiteware products are often differentiated into classes according to their degree of Vitrification and resulting porosity. Proceeding from porous to vitreous, more particular product categories include earthenware, stoneware, china and technical porcelains. Earthenware is non-vitreous and of medium porosity. Clay from Mbaukwu in Awka South Local Government Area Anambra State of Nigeria was characterized physico-chemically by [4]. The results obtained showed the possibility of using the clay sample for different purposes. The study revealed that the clay sample has high silica and alumina content which makes it kaolinite in nature. The moderately lower content of alkali oxides (CaO, MgO, K_2O , Na_2O and MnO) in the clay qualifies it for use as refractory materials.

The scope of this study is to characterize the clay, determine other physico-chemical properties, hence utilizing the clay to produce ceramic whitewares (cups and plates).

2. MATERIALS AND METHODS

The Local clay used in this study was collected from a location at Ukpor in Nnewi South Local Government Area of Anambra State. It was then taken to the Ceramics Research and Production Laboratory of Projects Development Institute (PRODA), located in Enugu, south-eastern Nigeria for detailed study.

2.1 Sample Preparation for Physical Analysis

Some portions of the unprocessed clay sample was measured out and soaked in a calculated amount of water, then stirred vigorously in order to bring it to plastic state. It was allowed to stand for 30 mins for the suspended particles to be decanted. The sample was allowed to dewater for 5 days after which it was oven dried for 4 hrs. Processed sample were modified with lime, feldspar and quartz. Rectangular test pieces of dimensions' length 8 cm, width 4 cm, and height 1.5 cm were moulded for the water absorption, shrinkage test, density (bulk and apparent) and apparent porosity were determined by using standard procedures.

2.2 Physical Analysis of the Clay Sample

2.2.1 Determination of water absorption

Water Absorption was used to measure the maturity of fired clay body. The rectangular bar test pieces of dimension 8 cm x 4 cm x 1.5 cm were used for this study. The test pieces were fired to various temperatures, weighed and recorded as dry weight, M1 (g); after which the test pieces was soaked in water for 1hour, removed, reweighed and recorded as M2 (g).

The percentage water absorption was calculated using the equation 1 [5].

$$\text{Water of Absorption (\%)} = \frac{M_2 - M_1}{M_2} \times 100 \quad (1)$$

Where M1= dry weight
M2 = saturated weight

2.2.2. Determination of porosity and density

After the procedure described above was completed, the suspended weight of the test pieces was determined by the use of a lever and was recorded as M3 (g). The apparent porosity, apparent density and bulk density was computed using the equation 2 [5].

$$\text{Apparent porosity (\%)} = \frac{M_2 - M_1}{M_2 - M_3} \times 100 \quad (2)$$

Where M1 = dry weight
M2 = saturated weight
M3 = suspended weight

$$\text{Apparent density} = \frac{M_1}{M_1 - M_3} \quad (3)$$

Where M1 = dry weight
M3 = suspended weight

$$\text{Bulk density} = \frac{M_1}{M_2 - M_3} \quad (4)$$

Where M1 = dry weight
M2 = saturated weight
M3 = suspended weight

2.2.3 Determination of linear shrinkage test

The rectangular bar test specimen of dimension 8.0 cm x 4.1 cm x 2.1 cm with a line of 5 cm drawn at their centers was used for this test. The green samples were allowed to dry at room temperature while the others were dried and sintered at experimental temperatures inscribed on them. After sintering, the change in the 5 cm line drawn was recorded using a veneer caliper.

The drying shrinkage was determined using the Equation 5 [5].

$$\text{Total Shrinkage T.S} = SI \frac{L_d - L_f}{L_d} \times 100 \quad (5)$$

Where: SI = Linear (Dry-Fired) Shrinkage,
Ld = Dried length
Lf = Fired length.

2.3 Preparation of Sample for Chemical Analysis

The processed powdered sample was analyzed using Scanning Electron Microscopy (SEM), FTIR Fourier Transfer infra-Red and X-ray Diffraction (XRD) as described by [2]. The FTIR analysis was carried out in accordance with standard for testing of ceramics materials (AOAC, SON). The mineral phases within the raw clay samples were identified by powdered X-ray Diffractometer method. The samples were first subjected to X-ray scanning using the Philips PW 1830 X-ray Diffractometer with a Cu-anode. Thereafter, mineral peaks were identified using X Pert High Score plus software. X-ray Fluorescence XRF (Mini Pal for EDXRF), was used to determine the oxides composition of the raw clay samples [6]. For the Scanning Electron Microscopy, SEM model JEOL 840 was used to determine the morphology of the raw clay sample and formulated clay samples. Energy Dispersive Spectrum (EDS) was used to determine the quantitative analysis of the formulated clay sample using standard procedure.

2.4 Body Formulation

Whiteware bodies were formulated by varying the composition of the plastic (Clay) and the non-plastic (feldspar and quartz) materials with lime. The blending was done as given in Table 1.

2.5 Ceramic Whiteware Production

The production procedure followed in this study includes Raw Material Processing, Ball Milling, Body Formulation, Casting, Fettingling, Drying and Firing. This is shown in Fig. 1.

Table 1. Formulation of whiteware bodies

Ukpor Clay (%)	Feldspar (%)	Quartz (%)	Lime (%)
50	0	40	10
50	5	35	10
50	10	30	10
50	15	25	10
50	20	20	10
50	25	15	10
50	20	30	0

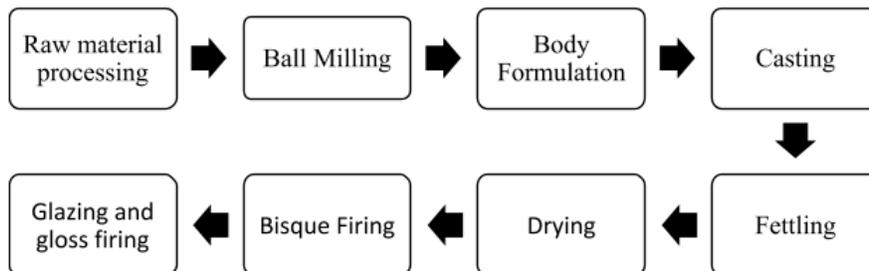


Fig. 1. Flow diagram for whiteware production

3. RESULTS AND DISCUSSION

3.1 Apparent Porosity

The result of apparent porosity showed a drastic decrease from 25% to 5%, this was as a result of closed pores by densification and gasification of the produced whitewares due to increase in high temperature (Fig. 2). High Apparent Porosity is not advisable in ceramic whiteware production, therefore it is reduced to 2% or even below by glazing the body and firing it at a high temperature of 1200°C.

3.2 Water Absorption

Water absorption measures the amount of water the sample is likely to retain in its body matrix. It revealed that the water absorption of the samples decreased from temperatures of 1000°C to 1200°C (Fig. 3). At temperature 1200°C, the change in water absorption was so obvious. This is because water absorption increases with increase in the silica content and decreases with

temperature and feldspar increase. The feldspar acts as flux which brings about the melting and vitrification of the body hence; the densification and sealing of pores thus; reduction in water absorption.

3.3 Bulk Density

The bulk density increases with increase in firing temperature and feldspar contents (as shown in Fig. 4). This is because of the shrinkage increase which gives rise to more compaction and densification of the whiteware body leading to an increase in the strength of the body.

3.4 Apparent Density

The apparent density decreases with increase in temperature (Fig. 5). This is expected because the apparent density always opposite the trend bulk density of fired clay bodies. The apparent density values obtained at temperature of 1000°C and 1200°C are within the standard range of 2.3-3.5 g/cm³ as reported by [7].

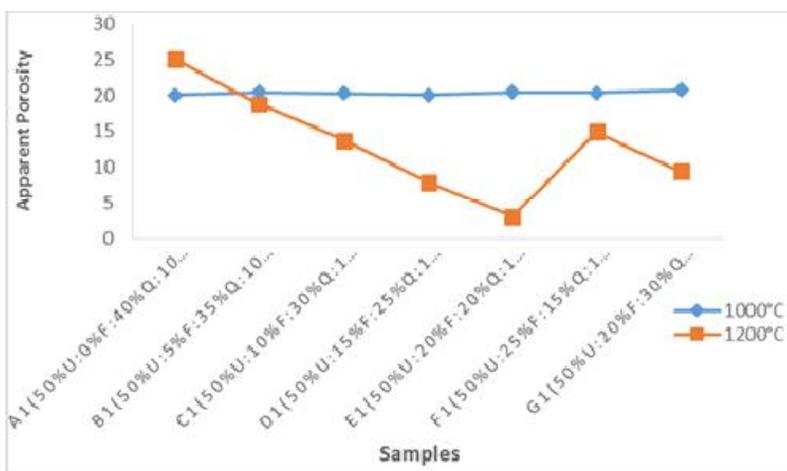


Fig. 2. Effect of temperature on apparent porosity of the clay

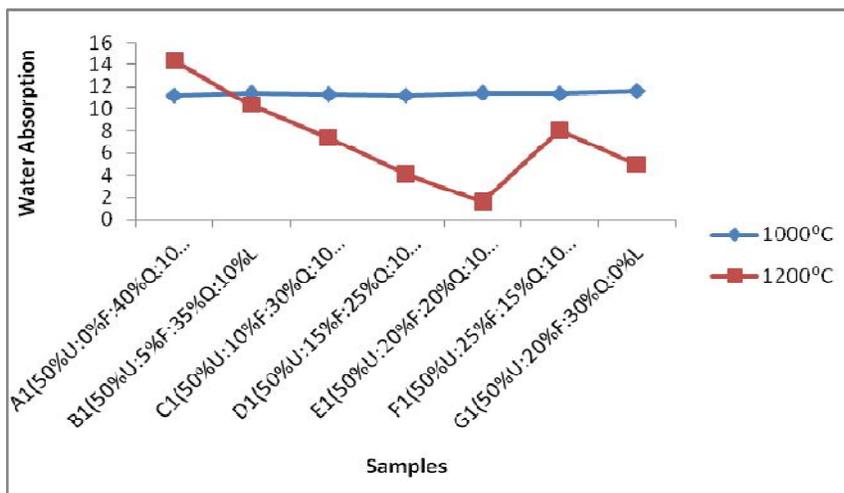


Fig. 3. Effect of temperature on water absorption of the clay

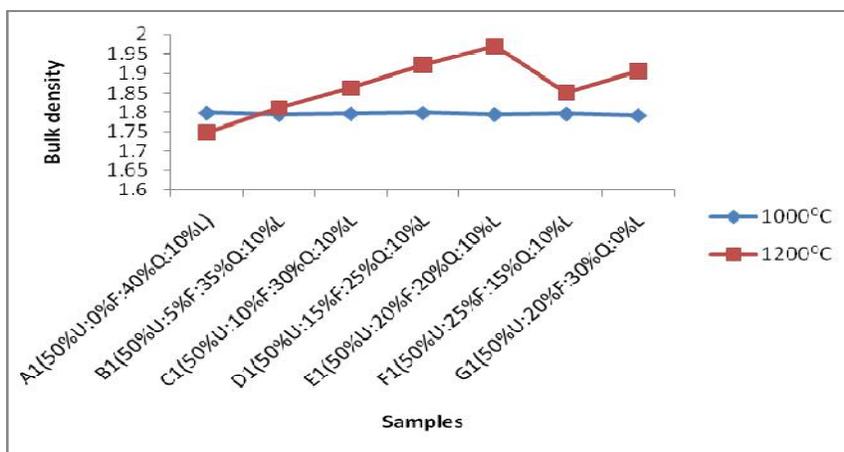


Fig. 4. Effect of temperature on bulk density of the clay

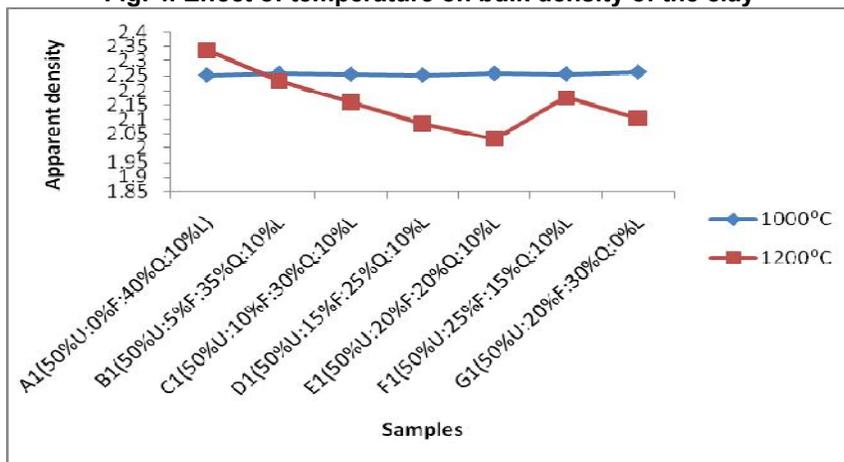


Fig. 5. Effect of temperature on apparent density of the clay

3.5 Total Shrinkage

Total shrinkage increases with an increase in temperature. The temperature increase was because of firing and drying. At temperature of 1200°C, the sample D had the highest shrinkage while the sample B had the lowest shrinkage. This could be attributed to the high content of silica in sample B as it helps to check the shrinkage of the ceramics body while the feldspar is inversely proportional in shrinkage changes as feldspar brings the maturing.

3.6 XRF Analysis of the Clay

The clay sample contained (Table 2) high alumina and silica with low flux oxides (CaO, Fe₂O₃, K₂O) which makes the clay very suitable for refractory application such as porcelain production (whitewares) [8]. Silica content of clay above 46.5% indicates free silica (Quartz) in the system which will enhance the ceramic properties [9, 10].

The Alumina content of 21.10% is slightly below the standard for ceramics, refractory, paper, and paints [11, 12]. The Fe₂O₃ content was 0.64 which is higher than 0.5 – 2.4% permissible limits for refractory bricks [12].

3.7 Results of X-ray Diffraction (XRD)

The Fig. 6 is a diffractogram of the local clay sample. The d – spacing value of the clay was sharp at 26.9Å. The d-spacing value of 26.9Å by spectrum showed the presence of quartz and

kaolinite as the major constituent then followed by anatase. These major mineral phases as seen above are in agreement with the X-ray fluorescence results [12]. The intense and sharp kaolinite peak observed in the spectra indicated the crystalline nature of Ukpor clay.

Table 2. Oxide compositions of Ukpor clay

Oxide composition	Ukpor clay
Al ₂ O ₃	21.10
SiO ₂	61.46
TiO ₂	3.45
Cr ₂ O ₃	0.038
Fe ₂ O ₃	0.64
CuO	0.021
Ga ₂ O ₃	0.015
As ₂ O ₃	0.006
SrO	0.019
ZrO ₂	0.34
BaO	0.092
PbO	0.014
L.O.I	12.74

3.8 SEM Result of the Raw Clay Sample

Fig. 7 and Fig. 8 showed the SEM analysis of Ukpor clay taken at different magnifications of 500x, 1000x, and the result revealed a finely distributed uniform surface with isolated patches of granulated texture which explains the physical behavior of the clay. The image showed some particles on the surface, these were likely due to the presence of non-clay minerals like potassium, iron, magnesium, sodium, calcium and manganese.

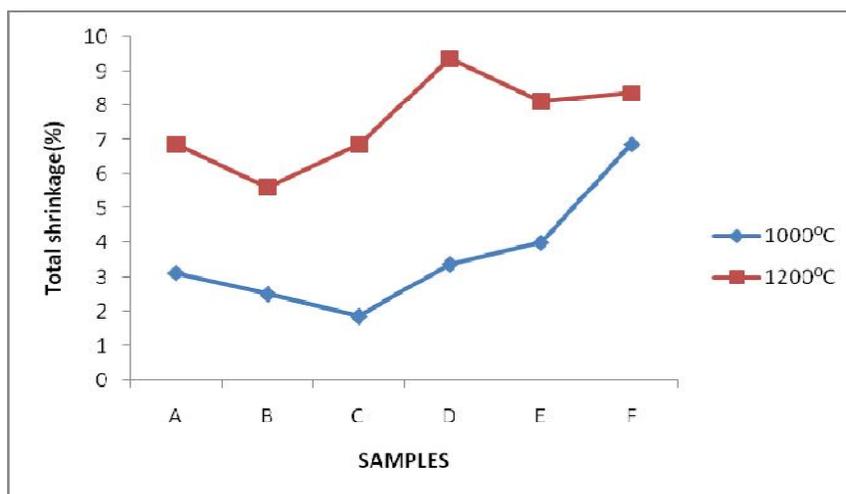


Fig. 6. Effect of temperature on total shrinkage of the clay

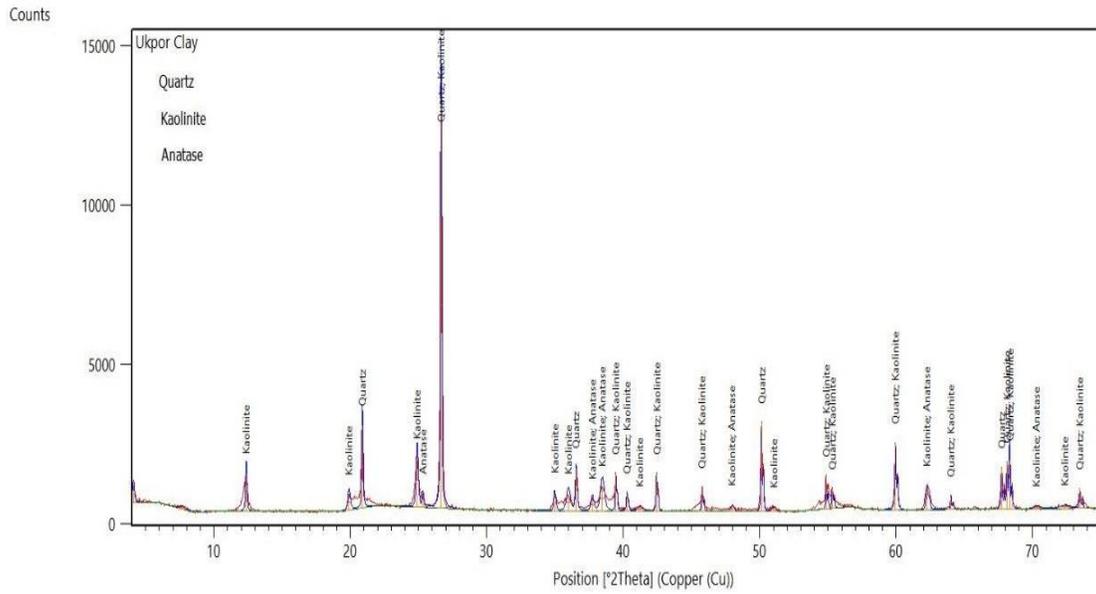


Fig. 7. X-ray diffraction (XRD) spectrum of Ukpor clay

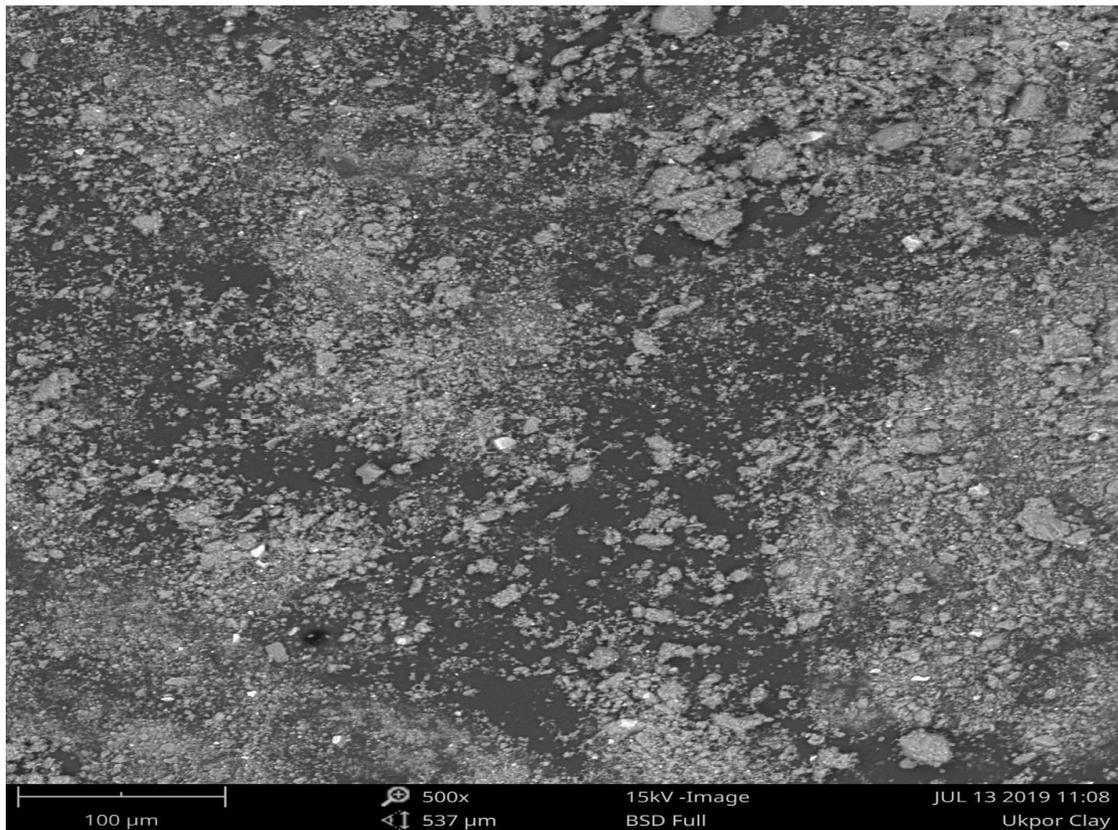


Fig. 8. Scanning Electron Microscope (SEM) morphology of Ukpor clay

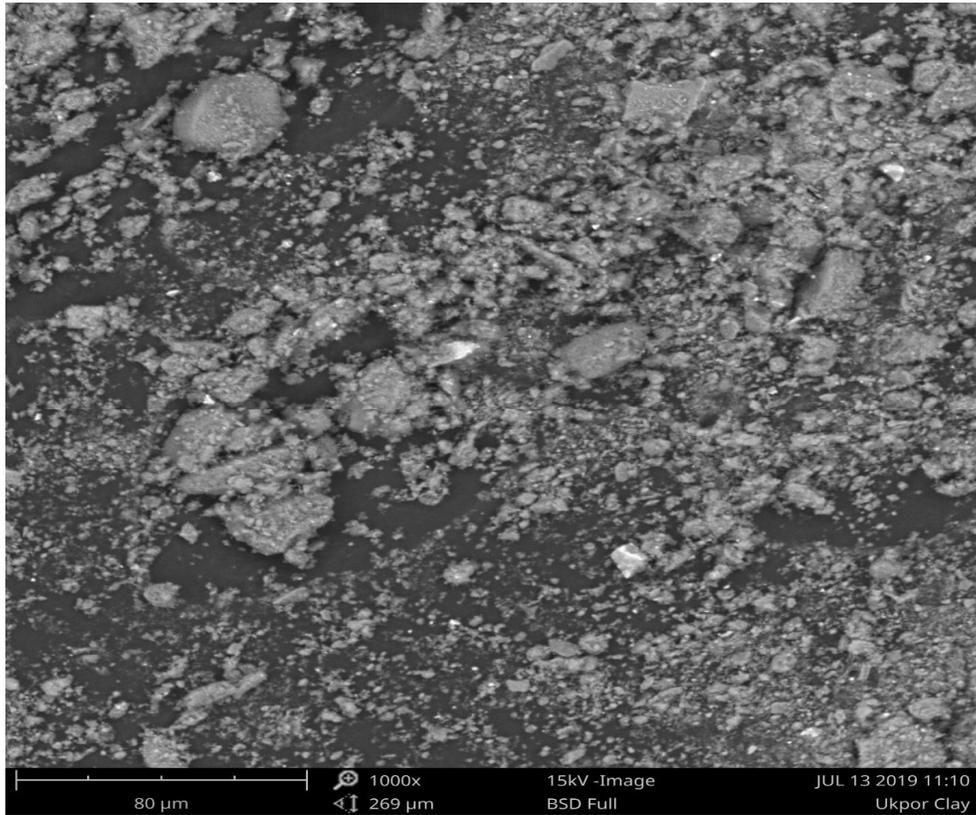


Fig. 9. Scanning Electron Microscope (SEM) morphology of Ukpok clay

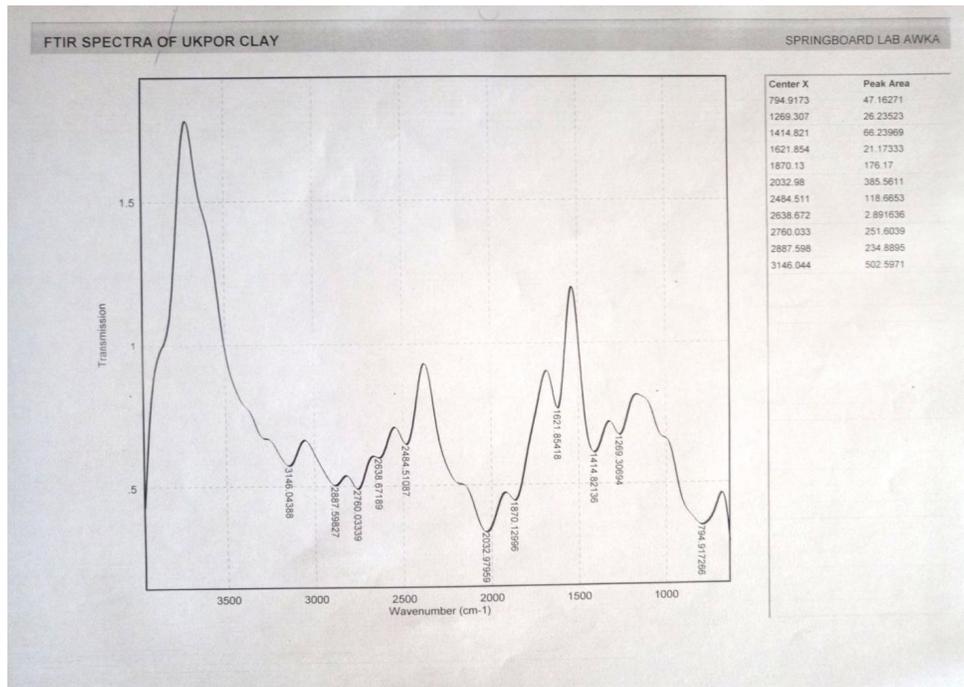


Fig. 10. FTIR analysis of Ukpok clay

3.9 FT-IR Result of the Raw Clay Sample

From Fig. 10, the bands correspond to 3500 to 4000 cm^{-1} which indicated the presence of hydroxyl groups (OH). The band is the stretching action of OH to OH groups as well [13]. The multiple bands at 3000 cm^{-1} to 2655 cm^{-1} corresponded to the C-H stretching vibrations of some organic materials. The high plasticity of the local clay is due to the low organic materials in the clay.

3.10 SEM/EDS Result of the Formulated Clay Sample

SEM/EDS is a powerful tool used to monitor the micro-structural evolution and densification behaviour of clay ceramics during firing. Figs. 11 and 12 below shows the SEM/EDS analysis for the formulated clay sample fired at a temperature of 1100 $^{\circ}$ C. They showed the SEM micrographs of sizes of the clay particles at ma. The EDS spectrum of the formulated fired Ukpok clay (Fig. 13) indicated the presence of O, Al, K, Ca, K, Fe, and Si.

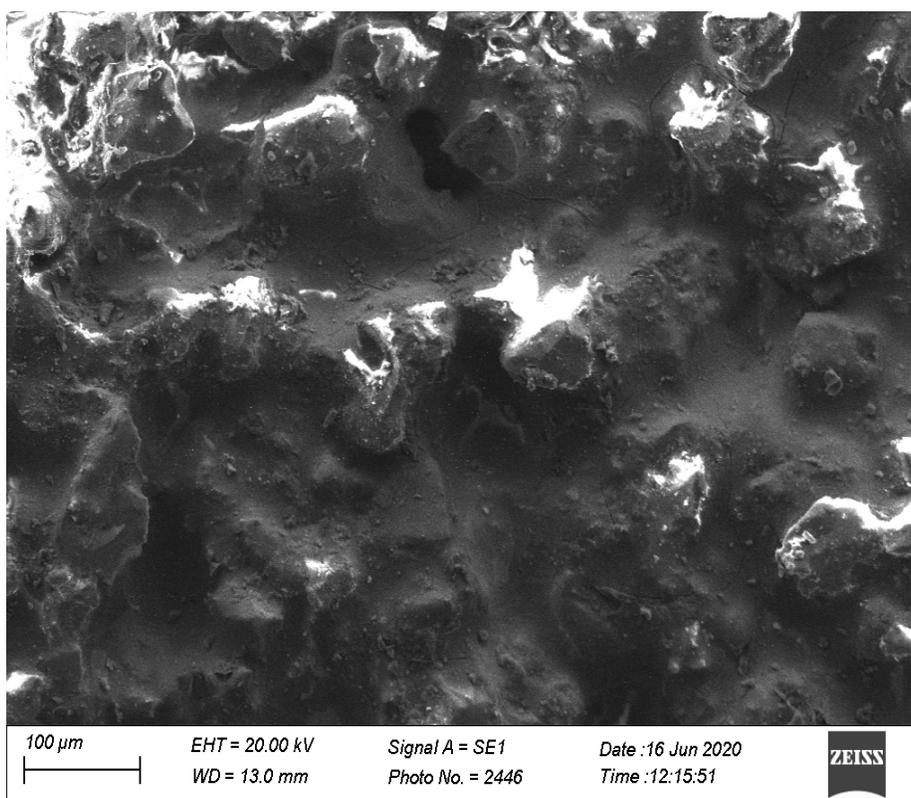


Fig. 11. SEM Morphology of formulated clay sample



Plate 1. Fettled ceramics whitewares

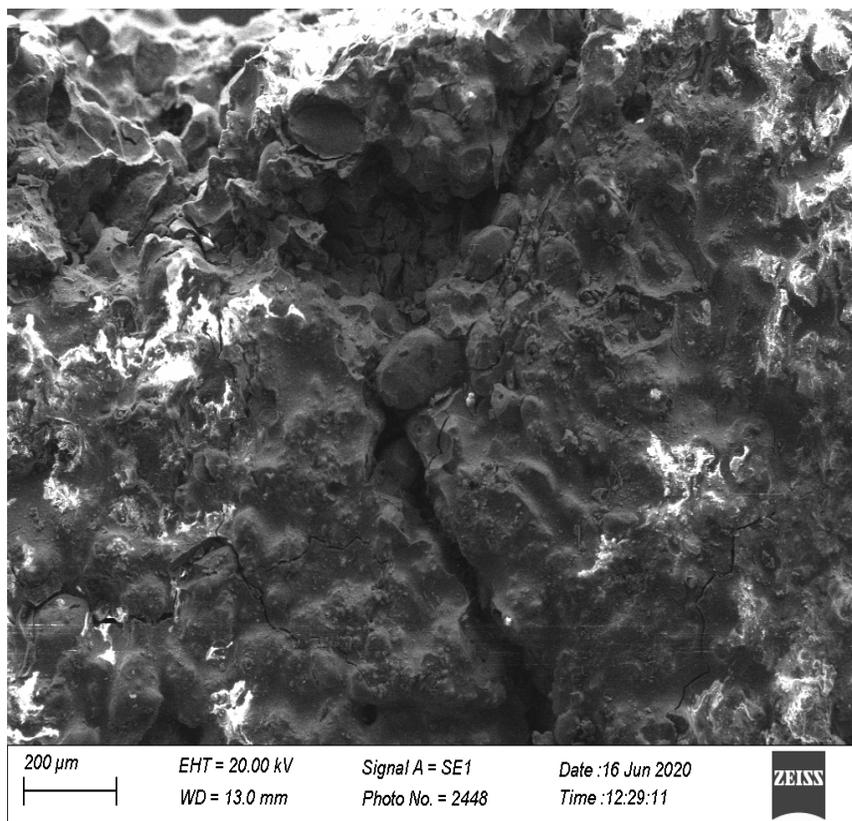


Fig. 12. SEM Morphology of formulated clay sample

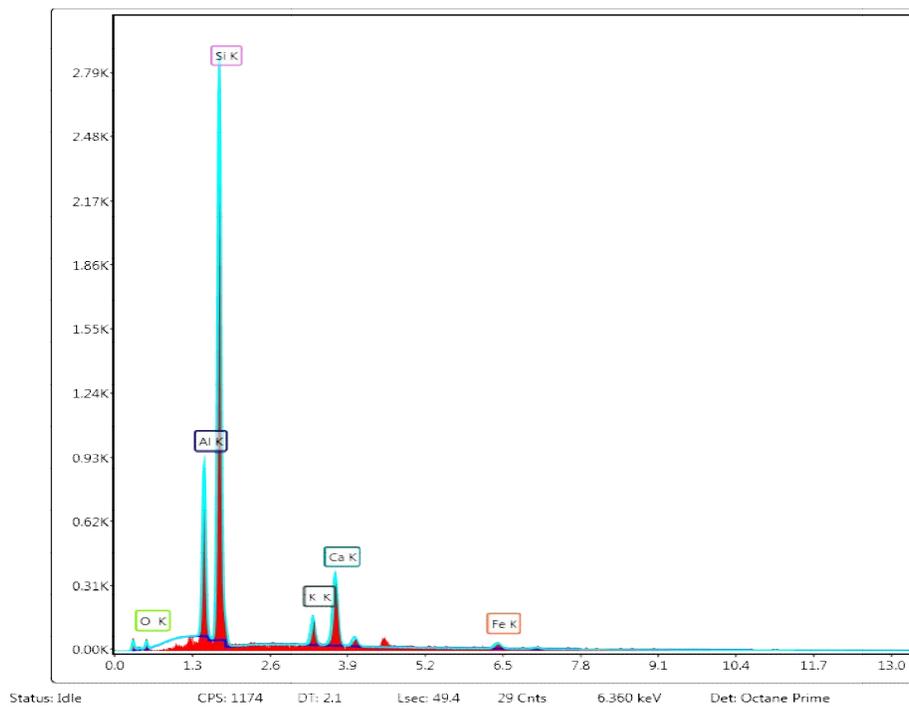


Fig. 13. EDS (Energy Dispersive Spectrum) of formulated clay sample



Plate 2. Ceramics whitewares produced

4. CONCLUSION

Local Clay was characterized to determine its suitability in the production of Ceramic Whitewares, the results obtained from the characterization showed that the clay sample can be used for different purposes. The XRD analysis confirmed the presence of kaolinite, quartz and anatase. The Kaolinite which was the major mineral content makes it suitable in ceramics production because of the non-expanding nature of the silicate clay (1:1 type). The SEM image shows some particles on the surface, these were likely due to the presence of non-clay minerals like potassium, iron, magnesium, sodium, calcium and manganese. The Fe_2O_3 content was 0.64 which is within 0.5 – 2.4% permissible limits for china wares and porcelain productions. The research conducted on this clay sample also revealed that the clay when utilized could be a major source of income for the people staying around Ukpok area. The abundant clay we have in Ukpok, Nnewi South Local Government Area of Anambra State, can be used to produce local ceramic whitewares, this was confirmed by the results from the tests conducted.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Manzuche SM. The role of clay in Technological Development Ashakwu. *Journal of Ceramics*. 2003; 1(1):6-9.
2. Ituma CG, Etukudoh AB, Abuh MA, Akpomie KG, Obioha CI. Utilization of Nkpuma-Akpatakpa clay in ceramics: Characterization and microstructural studies. *Journal of Applied Science Environmental Management*. 2018; 22(1):47-53.
3. Madejova MI. FT-IR techniques in clay mineral structures: Review. *Vibrational Spectroscopy*. 2003; 31(1):1-10.
4. Chikwelu GN, Onuegbu TU, Ezeofor CC, Akpomie KG. Characterization of Mbaukwu clay from Awka-South Anambra State Nigeria for industrial purposes. *Pacific Journal of Science and Technology*. 2018; 19(1):251-256.
5. Abuh MA, Abia-Bassey N, Udeinya TC, Nwannewuihe HU, Abong AA, Akpomie KG. Industrial potentials of Adiabo clay in Calabar Municipal of Cross River State, South- South Nigeria. *Pacific Journal of Science and Technology*. 2014; 15(1):63-75.
6. Dean B, Gano D, Knight K, Ofman J, Fass R. Effectiveness of proton pump inhibitors in nonerosive reflux diseases. *Journal of Clinical Gastroenterology and Hepatology*. 2004; 2:656- 664.
7. Ryan W, Radford C. *Whitewares: Production, Testing and Quality Control*, Pergamon Press / Institute of Ceramics; 1987.
8. Ekpunobi EU, Agbo SC, Ajiwe VIE. Evaluation of the mixtures of clay, diatomite, and sawdust for production of ceramic pot filters for water treatment interventions using locally sourced materials. *Journal of Environmental Chemical Engineering (JECE)*. 2019; 7(1):2213-3437. (Elsevier U K) DOI:<https://doi.org/10.1016/j.jece.2018.11.036>.
9. Singer F, Singer S. *Industrial Ceramic*, London Chapman and Hill Limited. 1993; 234.

10. Nwannenna O, Ogunro A, Apeh F. Comparative study on the addition of cullet to mowe and ibamajo clay for ceramic tiles production. Chem.Mater.Res. 2015; 7(4):16–25.
11. Chester JH. Refractories, production and properties. The iron and steel Institute. 1973; 3-13:295 -314.
12. Abubakar I, Birnin YA, Faruq UZ, Noma SS, Sharif N. Characterization of Dabagi Clay deposit for its ceramics potential. African Journal of Environmental Science and Technology. 2014; 8(8):455–459.
13. Franco F, Cecila JA, Perez-Maqueda LA, Perez-Rodriguez JL, Gomes CSF. Appl. Clay Sci. 2007; 35:119–127.

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