

Characterization and Evaluation of the Refractory Properties of Nsu Clay Deposit in Imo State Nigeria.

B.C. Chukwudi, M.Eng.

Department of Mechanical Engineering, Imo State University,
PMB 2000, Owerri, Nigeria.

E-mail: benkeke07@yahoo.com

ABSTRACT

The characterization and investigation of the refractory properties of the Nsu clay deposit in Imo State Nigeria, has been studied in this present work. The physical and mechanical characterization of the sample was carried out following American Society for Testing and Materials (ASTM) stipulated standards. The characterized/investigated properties were chemical composition, size and morphology, plasticity index, linear shrinkage, apparent porosity, cold crushing strength, thermal shock resistance, and refractoriness. An Atomic Absorption Spectrophotometer (AAS) and Scanning Electron Microscopy (SEM) were used to determine the chemical compositions, size, and morphology of the sample. AAS results revealed that the alumina content of the raw sample is 31.32 wt%, which appreciated in the fired sample to 36.21 wt%. SEM results showed a poorly developed hexagonal morphology and a size of about 3μ . The investigated properties proved that Nsu clay belongs to kaolinitic fireclay deposit.

(Keywords: kaolinite, fireclay, alumina, refractory material, plasticity index)

INTRODUCTION

Refractory materials are non-metallic materials that have unusual high melting temperatures and maintain their structural properties at very high temperatures. Principally, they are composed of oxides of silicon and aluminum. Refractories are employed in great quantities in the metallurgical, glassmaking, and ceramics industries, where they are formed into a variety of shapes to line the interiors of furnaces, kilns, and other devices that process materials at very high temperatures. Because of the high strengths exhibited by their primary chemical bonds, many refractory

materials possess unusually good combinations of high melting point and chemical inertness. Clay based refractories are the fireclay materials and are made from clays containing the aluminosilicate mineral-kaolinite ($Al_2[Si_2O_5][OH]_4$) plus impurities such as alkalis and iron oxides. The alumina (Al_2O_3) content ranges from 25 to 45 percent (Refractory, 2008; Clay Mineral, 2008). Refractories are classified based on the impurity content and the alumina-to-silica ratio (Al_2O_3/SiO_2).

Refractory materials are very useful and play very crucial roles in the industrial development of any nation. Aderibigbe, (1989), reported that virtually all the refractory requirements in all the pyro-metallurgical industries in Nigeria are imported. The Nigerian metallurgical industries are struggling today because of many factors which include short supply of refractory materials. Adondua (1988), reported that Ajaokuta Steel Complex requires about 43,503 tonnes per year of fireclay refractories for its operations; and these refractories are sourced abroad.

Despite having extensive clay mineral deposits in Nigeria, Nigeria continues to depend on external sources of refractory materials for many of its industries (Aliyu, 1996). Nigeria imported about 27 million metric tonnes of refractory materials in 1987 (Obadinma, 2003).

In view of all these facts, there is therefore every need to characterize and evaluate the refractory qualities of the Nsu clay deposit in Imo State Nigeria.

CLASSIFICATIONS, COMPOSITIONS AND PROCESSING OF REFRACTORIES

The composition and processing of refractories vary widely according to the application and the

type of refractory. Most refractories can be classified on the basis of composition as either clay-based or non-clay-based (Refractory, 2008). In addition, they can be classified as either acidic (containing silica [SiO₂] or zirconia [ZrO₂]) or basic (containing alumina [Al₂O₃] or alkaline-earth oxides such as lime [CaO] or magnesia [MgO]).

Among the clay-based refractories are fireclay, high-alumina, and mullite ceramics. There is a wide range of non-clay refractories, including basic, extra-high alumina, silica, silicon carbide, and zircon materials. Most clay-based products are processed in a manner similar to other traditional ceramics such as structural clay products (e.g., stiff-mud processes such as press forming or extrusion are employed to form the ware, which is subsequently dried and passed through long tunnel kilns for firing).

CLAY-BASED-REFRACTORIES

Most clay-based refractories are produced as preformed bricks. They include fireclay, high alumina and mullite.

Fireclay

The pillar of the clay-based refractories are the so-called fireclay materials. These are made from clays containing the aluminosilicate mineral-kaolinite (Al₂[Si₂O₅][OH]₄) plus impurities such as alkalis and iron oxides. The alumina content ranges from 25 to 45 percent. Depending upon the impurity content and the alumina-to-silica ratio, fireclays are classified as low-duty, medium-duty, high-duty, and super-duty, with use temperature rising as alumina content increases.

Fireclay bricks, or firebricks, exhibit relatively low expansion upon heating and are therefore moderately resistant against thermal shock. They are fairly inert in acidic environments but are quite reactive in basic environments. Fireclay bricks are used to line portions of the interiors of blast furnaces, blast-furnace stoves, and coke ovens.

High alumina

High-alumina refractories are made from bauxite, a naturally occurring material containing aluminum hydroxide (Al[OH]₃) and kaolinitic clays. These raw materials are roasted to produce a mixture of

synthetic alumina and mullite (an aluminosilicate mineral with the chemical formula 3Al₂O₃·2SiO₂). By definition high-alumina refractories contain between 50 and 87.5 percent alumina (Refractory, 2008). They are much more robust than fireclay refractories at high temperatures and in basic environments. In addition, they exhibit better volume stability and abrasion resistance. High-alumina bricks are used in blast furnaces, blast-furnace stoves, and liquid-steel ladles.

Mullite

Mullite is an aluminosilicate compound with the specific formula 3Al₂O₃·2SiO₃ and an alumina content of approximately 70 percent. It has a melting point of 1,850° C. Various clays are mixed with bauxite in order to achieve this composition. Mullite refractories are solidified by sintering in electric furnaces at high temperatures. They are the most stable of the aluminosilicate refractories and have excellent resistance to high-temperature loading. Mullite bricks are used in blast-furnace stoves and in the fore-hearth roofs of glass-melting furnaces.

MATERIALS AND EXPERIMENTAL METHODS

Kaolinite Sample

The Nsu clay was collected from Agbahara-Nsu, Ehime-Mbano Local Government of Imo State. The clay lumps were crushed, grounded and sieved.

Analytical Techniques

Atomic Absorption Spectrophotometer (AAS):

The chemical composition of the raw clay sample in wt % of (SiO₂, Al₂O₃, TiO₂, Fe₂O₃ etc) was determined using AAS Mode 320 carried out at Chemistry Department of University of Port Harcourt, Rivers State. The sample was washed and the effect on Na₂O and K₂O investigated. Also the fired sample was analyzed to determine its effect on alumina and silica compositions.

❖ **Loss on Ignition:** The water content %, of the clay was determined by measuring the weight loss of a known mass of the sample after firing in a furnace at 1000°C for one hour thirty minutes. Loss on ignition, (LOI) was calculated using this relation:

$$LOI, (\%) = \left\{ \frac{W_i - W_f}{W_i} \times 100 \right\} \quad (1)$$

where W_i and W_f are initial and final weight, respectively.

Scanning Electron Microscopy: The size and morphology of the Nsu clay sample was determined using SEM. SEM micrograph was obtained using a JEOL JSM-35C scanning electron microscope operated at 15kV with attached Kevex energy dispersive spectrometer. Secondary electron image photomicrographs was recorded with a digital camera. Images were digitally stored in tiff format. It was carried out at Alfa Research Laboratory Lagos.

Determination of the plasticity index

Plasticity index is the range of moisture or water content in which clay is plastic; the finer the clay, the higher the plasticity index (Smith, 1982).

Plasticity index (PI) = liquid limit (LL) – plasticity limit (PL). So to determine the plasticity index, liquid limit and the plastic limit must be determined.

Determination of the liquid limits: Liquid limit test BS1377 specifies two methods of determining the liquid limit of clay. They are the cone penetrometer method and the casagrande apparatus method. The casagrande apparatus method was adopted in this work. Liquid limit is the water content at which the clay stops acting as a liquid and starts acting as plastic clay. About 200g of the clay sample was sieved through a 425 μ m sieve, air dried, and thoroughly mixed. The sample was placed on a glass sheet and mixed with a little distilled water. The cup of the apparatus was half filled with the wet clay and leveled off. A 2mm groove was then cut in the sample using the grooving tool. The handle of the apparatus was rotated at a steady rate, which actuates the cam, causing the cup to lift 10mm and then fall onto the base. The number of blows needed to close the gap over 13mm was recorded and a portion of the sample just tested was removed and placed in a container for water (moisture) content determination both before and after oven-drying at 105°C. The groove was considered closed when two parts of the sample came into contact at the bottom of the groove; plastic flow caused the groove to close. The test

was repeated two more times, employing a little more water for each test. To obtain the liquid limit, the water content (w), % was plotted vertically against the number of blows (N) horizontally. Therefore the water content corresponding to 25 blows was taken as the liquid limit and expressed to the nearest whole number.

Determination of the plastic limit: This is the limit between plastic and brittle failure. About 20g of the sample prepared as in the liquid limit test was used. A rod of about 80mm long and 3mm diameter was used here. The sample was mixed on the glass plate with just enough water to make it sufficiently plastic for rolling into a ball, which was then rolled out between the hand and the glass to form a thread. When small cracks began to appear, the thread was divided into two parts. One part was formed into a thread, rolled until the diameter of the thread was reduced from 6mm to 3mm. The rod diameter assisted in determining the thread diameter. The sample is said to be at its plastic limit when it just crumbled at a thread diameter of 3mm. At this stage, a section of the thread was removed, placed in a container for water content determination both before and after oven-drying at 105°C. The test was repeated one more time.

Brick production

The sequence adopted in making refractory bricks are as follows: securing the clay, beneficiation, mixing and forming, drying, firing, and cooling. The raw sample was air dried and crushed to liberate the mineral constituents. It was washed so as to remove alkalis and other impurities (sodium, potassium) which are known to slow down mullite formation, and negatively affect refractoriness and strength of the brick. The sample was filtered and dried in the sun to facilitate crushing. Part of the dried sample was calcined by heating to 780°C for an hour, making the clay lose its plasticity by forming grog (firesand). Some portion of the dried and calcined sample was ground into powder, which was sieved using 600 μ m, 300 μ m, and 150 μ m aperture sizes according to ASTM standards. Those that passed through the 600 μ m sieve were used in firebrick making. Water was added to the sample and mixed very well to form a plastic paste. The water content of the moulding mass was determined by weighing the sample before and after oven drying at 105°C. A mould, cut from a mild steel square pipe with internal

dimensions of about 50mmx50mm and 100mm long, was used. After pressing the moulding mass into the mould, plunger was used to extrude the wet brick from the mould. The extruded brick was cut into different sizes; 50mmx50mmx50mm and 50mmx50mmx60mm, and was left overnight to air-dry in the laboratory. Oven drying at 105°C for 12hrs followed, before firing with an electric furnace up to 1250°C. Firing was done gradually.

Fired refractory analysis: The surface quality of the refractory brick was observed after furnace cooling. Also properties like apparent porosity, linear drying shrinkage and linear firing shrinkage, cold crushing strength, refractoriness and thermal shock resistance were investigated.

Determination of the apparent porosity: The 50mmx50mmx50mm brick was dried in an oven at 105°C for some hours. The weight of the dried weight in air (W_a) was taken, before sample was put into a boiling water for some minutes. It was allowed to cool while still in water. After which the weight of the soaked sample (W_s) was taken. The sample was removed from water and cleaned up and weighted again in air to know the saturated weight (W_{ss}). Apparent porosity was determined using the formula:

$$\text{apparent porosity} = \frac{\text{volume of water absorbed after boiling}}{\text{bulk volume}} \times 100$$

$$\Rightarrow \frac{W_{ss} - W_a}{W_{ss} - W_s} \times 100 \quad (2)$$

where W_a =weight of the sample dried in the air
 W_s =weight of the soaked sample
 W_{ss} =saturated weight of the sample in the air.

Determination of the linear shrinkage: Linear shrinkage was determined by measuring the dimensional changes in both the wet and fire bricks (50mmx50mm) using a vernier calliper. The linear dried dimensions were measured after air drying overnight. Only two sides of both bricks were measured. Linear shrinkage was determined using the relationship:

$$\frac{\Delta L}{L} \times 100 \quad (3)$$

where ΔL is change in length of the brick, L is the original length of brick.

Cold crushing strength determination: Two bricks samples were used here. The strength of one was tested vertically and the other horizontally and recorded. Samples were mounted in turn on a compressive strength tester and load was applied axially at a uniform rate by operating the pump handle in an up and down movement till it failed. Cold crushing strength in Mpa was taken as the maximum pressure shown by the gauge dial which was read off from the tester machine (Buehler hydraulic press).

Determination of the thermal shock resistance: A bricks size of 50mmx50mmx60mm was used. The sample was placed in a resistance heating box of an electric furnace, maintained at about 1100°C and soaked for 15 minutes, after which, it was air cooled and observed for any cracks. If none were observed, it was returned to the furnace and the same process repeated until the sample cracked. Thermal shock resistance is the number of cycles needed to cause conspicuous crack on the sample.

Determination of refractoriness: Pyrometric cone equivalent (PCE) was used to measure the refractoriness of the sample. Some standard cones were used along with the moulded cones of the test sample. Both cones were mounted on a refractory plaque and placed in kiln. The temperature was raised to about 1200°C at the rate of 10°C per minute, with a gradual reduction in the rate till the tips of the test cones bent touching the refractory plaque. The refractory plaque was removed, and allowed to cool before examining the test cones. Refractoriness of the tested cones is the number of the standard cones that has bent to the same level as the tested cones and the temperature similar to the cone number was determined from the ASTM Orton series.

RESULTS AND DISCUSSION

Chemical composition

The chemical composition of Nsu clay is presented in Table 1. Nsu clay had an alumina (Al_2O_3) content of 31.32wt % and alumina-silica ratio of 0.68. The alumina content agreed with Aderibigbe, (1989), who reported that in Nigeria, the major refractory clay deposits that is within the alumina-silicate raw materials are kaolin and fireclay deposits with alumina content of less than 45%.

Table 1: Chemical Composition of Nsu Kaolinite.

Composition	Raw clay wt %	Washed clay wt%	Fired clay wt %
SiO ₂	46.01		57.05
Al ₂ O ₃	31.32		36.21
TiO ₂	0.34		
Fe ₂ O ₃	4.78		
MnO	2.66		
MgO	1.45		
Na ₂ O	0.98	0.42	
K ₂ O	0.61	0.32	
H ₂ O (Ignition loss at 1000°C)	10.82		
Al ₂ O ₃ / SiO ₂ ratio	0.68		0.63

The washed sample also presented in Table 1, showed decrease in Na₂O and K₂O content from 0.98 wt% and 0.61 wt% respectively in the raw sample to 0.42 wt% and 0.32 wt% in the washed sample. However the alumina and silica content appreciated in the fired sample as shown in Table 1. This may be as a result of the removal of organic matters (LOI) in the fired sample.

SEM

The SEM micrograph showed moderately ordered flakes, with poorly developed hexagonal outlines as shown in Figure 1. However Zbik and co-workers (1998), suggested psuedohexagonal morphology. The edges of the particles are bevelled, somewhat ragged and irregular, an observation earlier reported by Grim (1968). The sample showed flake surface dimension of about 3μ that is within 0.3 to about 4μ suggested by Grim (1968).

SEM Result

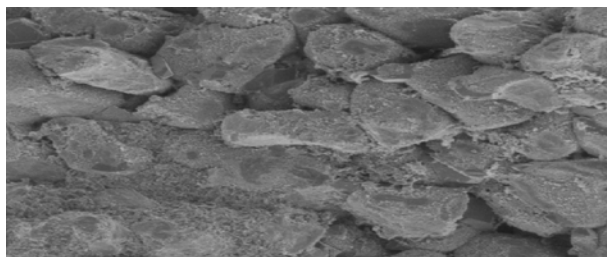


Figure 1: SEM of Nsu Clay Sample.

Plasticity index

Results of the liquid limit (LL) and plastic limit (PL) are shown in Tables 2 and 3 respectively. Figure 2 shows the plot of water content (w) as a function of number of blows (N) from which the LL was determined. Plasticity index derived from LL and PL is shown in Table 4. Nsu clay gave a plasticity index value of 25.3%. This value is within the recommended value of 10-30% for ceramic clays as suggested by Grimshaw (1971). In 1995, RMRDC, through Nigerian Mining cooperation Jos, investigated some kaolin deposit in Nigeria and came up with the following results-Major Porter deposit (PI =11.2%), Nahuta deposit (PI=19.92%), and Darazo deposit (PI=20.94%). The value obtained in this work, competed very well with these results.

Table 2: Liquid Limit Result.

Test	1	2	3
Container number	x	y	z
Number of blows, N	10	20	40
Container M (g)	19.3	19.4	19.0
Container plus wet clay, M _w (g)	38.5	40.1	36.3
Container plus dry clay, M _d (g)	30.6	31.8	29.7
Dry clay=(M _d -M)	11.3	12.4	10.7
Water loss,(M _w -M _d)	7.9	8.3	6.6
Water content,			
$w = \frac{M_w - M_d}{M_d - M} \times 100$	69.9	66.9	61.6

Table 3: Plastic Limit Result.

Test	1	2
Container number	x	y
Container, M (g)	16.7	16.9
Container plus wet clay, M _w (g)	30.5	30.9
Container plus dry clay, M _d (g)	26.8	26.7
Dry clay, (M _d -M)	10.1	9.8
Water loss,(M _w -M _d)	3.7	4.2
Water content,		
$w = \frac{M_w - M_d}{M_d - M} \times 100$	36.6	42.8
Mean		39.7

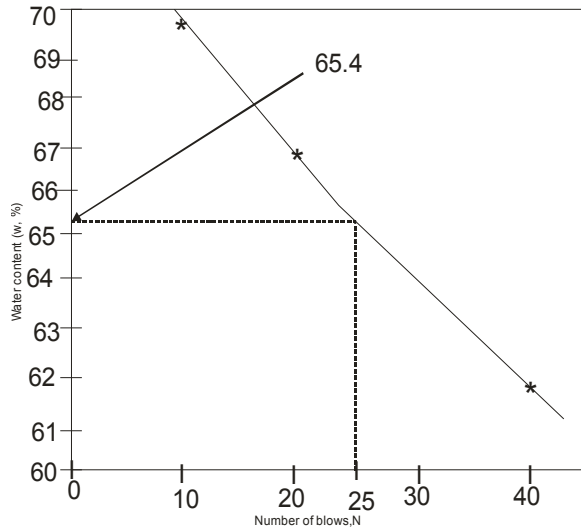


Figure 2: Water Content (w) as a Function of Number of Blows (N).

Table 4: Plasticity Index.

Details	Nsu clay
Liquid limit (LL)%	65
Plastic limit (PL)%	39.7
Plasticity Index (PI)	25.3

Linear shrinkage result

Results of the linear drying and linear firing shrinkage are presented in Table 5a. The result revealed that the linear drying shrinkage is 9.9%, while that of the linear firing shrinkage is 13.9%. RMRDC gave the linear drying shrinkage of Kankara deposit in Kastina State Nigeria to range from 9% to 12%; Chester, (1973), recommended linear shrinkage range of 7-10% for refractory clays. The results obtained in this work, showed that while linear drying shrinkage fell within the recommended range, linear firing shrinkage fell outside it.

Surface characteristics of Nsu clay

The observed surface characteristics are shown in Table 5b. No cracks were observed and the fired sample showed gray color. Fireclays are associated with light colors such as gray, buffs, cream and white (Firebrick, 2008).

Table 5 a: Linear Shrinkage.

Details	Nsu clay
Linear dried sample $L_{d(a)}$	41.88
Linear dried sample $L_{d(b)}$	45.51
Linear-drying shrinkage, % = $\frac{L_{d(a)} - L_{d(b)}}{L_{d(b)}} \times 100$	8.6
Linear fired sample $L_{f(a)}$	39.16
Linear fired sample $L_{f(b)}$	44.33
Linear-firing shrinkage, % = $\frac{L_{f(a)} - L_{f(b)}}{L_{f(b)}} \times 100$	13.2

Table 5 b: Observed Surface Qualities.

Details	Surface properties of Nsu clay
Color after firing	Gray
Surface crack	No cracks

Sieve analysis

Table 6 shows the result of the sieve analysis, while Figure 3 shows the plot of total undersize against particle size. The result shows that 50% of the sample particles have sizes finer than 400 μ m. This shows that the clay is not too fine and it may have contributed to the not too high PI recorded in this work. Therefore claim made by Smith (1982), that the finer the clay, the greater its PI, is justified.

Table 6: Sieve Results.

Details	Nsu clay		
Particle size (μ m)	600	300	150
Mass used, M_u (g)	200	200	200
Retained mass, M_r (g)	70.71	50.4	21.5
% mass retained = $\frac{M_r}{M_u} \times 100$	35.36	25.2	10.75
Total oversize, R	35.36	60.56	71.31
Total undersize, P=100-R	64.64	39.44	28.69

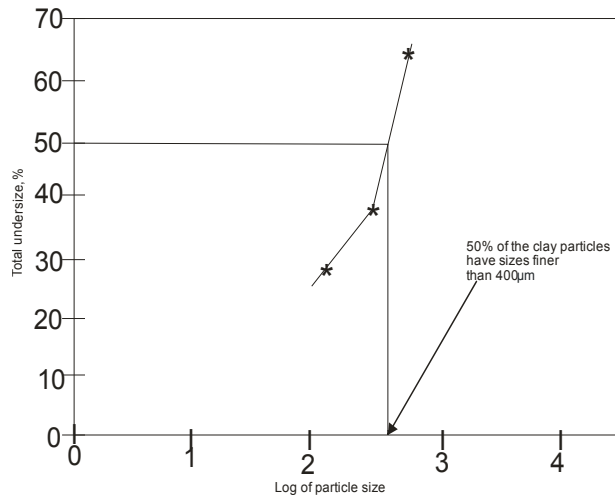


Figure 3: Total Undersize Plotted against Log of the Particle Size.

Apparent porosity

The result of apparent porosity is shown in Table 7. The sample gave apparent porosity value of 22.56% which is within the acceptable range (10-30%) suggested for refractory clays by Chester (1973).

Table 7: Apparent Porosity Result.

Details	Sample
W_a (g)	140.5
W_s (g)	78.62
W_{ss} (g)	158.53
Apparent porosity (%) = $\frac{W_{ss} - W_a}{W_{ss} - W_s} \times 100$	22.56

Cold crushing strength

Table 8 a shows the result of the cold crushing strength. Nsu clay gave a mean strength of 26.5Mpa. However, Chester (1973), recommended 5 Mpa as the minimum value for refractory clay materials. This shows that Nsu clay can comfortably withstand impacts at low temperatures.

Thermal shock resistance

Result of the thermal shock resistance is displayed in Table 8b. Result obtained gave the number of cycle to failure to be 32. This value narrowly fall outside the 20-30 number of cycles recommended

by Chester (1973). It may be as a result of the moderately high apparent porosity recorded by the sample. However, this value (32 cycles) is not too bad for refractory clay as thermal shock characteristics of a material may be improved by the introduction of some relatively large pores (Callister, 2003).

Table 8 a: Cold Crushing Strength.

Details	Sample
CCS_v (Mpa)	30
CCS_h (Mpa)	23
Mean strength (Mpa)	26.5

Table 8 b: Thermal Shock Resistance.

Details	Sample
Number of cycle to failure	32

REFRACTORINESS RESULT

Table 9 shows the refractoriness of the sample. The result shows that refractoriness of the sample occurred at a temperature of 1683°C. This may be due to appreciation of the alumina content in the fired sample (36.21wt %). It is a well known fact that the use temperature rises as alumina content increases.

Table 9: Refractoriness.

Details	Sample
Cone number	31
Temperature °C	1683

CONCLUSION

It was shown in this work that on the basis of the physio-chemical characteristics of this kaolinitic fireclay deposit, it can successfully be processed for use as refractory materials such as a ladle bricks, ramming mass, etc. Again almost all the investigated properties gave results that are acceptable for refractory clay materials. It is suggested that in processing Nsu clay for refractory purposes, impurities like alkalis should be reduced as much as possible.

REFERENCES

1. Aderibigbe, D.A. 1989. "Local Sourcing of Raw Materials and Consumables for the Iron and Steel Industries in Nigeria- Challenges for the Future". Raw Materials Research and Development Council of Nigeria (RMRDC). 55.
2. Adondua, S. 1988. "Indigenous Refractory Raw Materials Base for Nigeria Steel Industries". *Journal of the Nigerian Society of Chemical Engineers (NSCHE)*. 7(2):322.
3. Aliyu, A. 1996. "Potentials of the Solid Minerals Industry in Nigeria". RMRDC (Investment Promotion). 1-4.
4. American Society for Testing and Materials. 1982. "ASTM Standards Part 17: Refractories, Glass, Ceramic Materials, Carbon and Graphite Products". ASTM: Philadelphia. 7-9,51-61,190,498-508.
5. Callister, Jr, W.D. 2003. *Materials Science and Engineering: An Introduction. Sixth edition*. John Wiley and Sons: New York, NY. 667.
6. Chester, J.H. 1973. *Refractories, Production and Properties*. The Iron And Steel Institute: London, UK. 3-13, 295-314.
7. Encyclopædia Britannica. "Clay Mineral". Ultimate Reference Suite. 2008. *Encyclopædia Britannica*. Chicago, IL.
8. Encyclopædia Britannica. 2008. "Firebrick". Ultimate Reference Suite. 2008. *Encyclopædia Britannica*. Chicago, IL.
9. Grim, R.E. 1968. *Clay Mineralogy. Second edition*. 171-172.
10. Grimshaw, R.W. 1971. *The Chemistry And Physics Of Clay And Allied Ceramic Materials. Fourth Edition*. Wiley Interscience: New York, NY.
11. Obadinma, E.O. 2003. "Development of Refractory Bricks For Heat Treatment Facilities". *Journal of Science And Technology Research*. 2(2):13-17.
12. Raw Materials Research and Development Council of Nigeria (RMRDC). 1995. "Technical Brief on Minerals in Nigeria, Kaolin". Technical Brief No 1:3-10.
13. Encyclopædia Britannica. 2008. "Refractory". Ultimate Reference Suite. 2008. *Encyclopædia Britannica*. Chicago, IL.
14. Smith, G.N. 1982. *Elements of Soil Mechanics for Civil and Mining Engineers. Fifth Edition*. Granada Publishing Limited: London, UK. 3-18.

ABOUT THE AUTHOR

B.C. Chukwudi, is a lecturer in the Department of Mechanical Engineering at Imo State University, Owerri, Nigeria. He earned his master's degree (M.Eng) in Materials and Metallurgical Engineering from Federal University of Technology, Owerri Nigeria. His major research interests are mineral processing, environmental engineering and alloy development.

SUGGESTED CITATION

Chukwudi, B.C. 2008. "Characterization and Evaluation of the Refractory Properties of Nsu Clay Deposit in Imo State Nigeria". *Pacific Journal of Science and Technology*. 9(2):487-494.

 [Pacific Journal of Science and Technology](http://www.akamaiuniversity.us/PJST.htm)