

Full Paper

CHARACTERIZATION OF SOME NIGERIAN CLAYS FOR REFRACTORY UTILIZATION

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ABSTRACT

Clay deposits from four locations in Auchi, Enugu, Lagos and Uyo were characterized for ceramic applications. The major characteristics investigated were their chemical compositions, bulk density, apparent porosity, cold crushing strength, water absorption and linear shrinkage. Chemical analysis was conducted using Atomic Absorption Spectrometry method, while water absorption and water shrinkage were evaluated by sample heating and weighing methods. Results obtained showed that the samples belong to the fire clay class. Alkali oxide content was low, at an average percent of 0.045 for Enugu, 0.060 for Lagos, 0.025 for Uyo and 0.050 for Auchi, imparting high refractoriness on the clays and making them suitable for ceramics, specifically refractory materials. Moreover, the average 54% of SiO₂ and 42% of Al₂O₃ in Auchi and Uyo clays make them more suitable for the refractory purposes.

Keywords: clay, refractory, bulk density, porosity, absorption

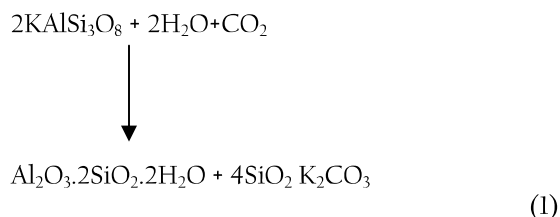
1. INTRODUCTION

Clays are versatile industrial raw materials needed for the manufacture of domestic and industrial products such as pottery and ceramic wares, bricks, electrical insulators, paper, paint, ink, drugs, soaps, toothpaste, roofing and floor tiles. They also find applications in the manufacture of cement, plastics, fertilizers and insecticides. The use of clay products for construction and building purposes has greatly aided many developed and developing nations to execute housing policies. Clay products such as ceramic wares, burnt bricks, roofing and floor tiles are cheaper and more durable building materials than cement, especially under tropical conditions (Nnuka et al,

2001). They can, therefore be utilized to reduce overdependence on cement particularly in Nigeria.

According to Nnuka et al, (1992), the wide application of clay in homes and industries is based on its intrinsic properties such as high chemical stability, high aesthetic value, wear resistance, high strength at elevated temperatures, thermal shock resistance and others. The basic constituents of clay are the alumino-silicates and other mineral oxides such as hematite, magnesium oxide, calcium oxide, sodium oxide, potassium oxide and soluble sulphide salts. The characteristic properties of clay which determine the areas of application are influenced by the chemical structure of the dominant constituent minerals, with important properties including plasticity, color, dry strength, drying and firing shrinkages. The percentage of the mineral oxides in the clay ultimately determines its areas of application, while the quantity of the alkali metal oxides such as Na₂O, K₂O, CaO, indicates their suitability for making ceramic products.

Clay is the product of weathering of exposed rock. The agents of weathering are water (especially with solid matter in suspension), wind (with sand grains in suspension) and glaciers. The formation of clay from parent rock is primarily a chemical processes by which fine particles are separated from coarser grains. One of the commonest processes of clay formation is the chemical decomposition of feldspar. Granite contains alkali feldspar, quartz, plagioclase feldspar and some biotite with hornblende (Clews, 1969). The alkali feldspar, orthoclase, typical of the group with formula KAlSi₃O₈, is slowly attacked by water containing carbon oxide in solution, which leaches away the potash and some of the silica, leaving the aluminum silicate, kaolinite and in the course of time the feldspar in granite is transformed by percolating waters to clay, as shown in Eq. (1)



1.1 Composition of clay

A pure clay mineral may be highly refractory but it may be very weak when burned owing to the absence of suitable



impurities which would, if present, form a verifiable bond to unite the clay particles into a mass of great strength. The proportion of impurities allowable in clay depends on the purpose for which it is to be used. Clay to be used as a refractory material must be as free as possible from fluxes (e.g. silica, calcite, magnesite) as these would reduce its resistance to heat. The principal chemical components of clays may be classified as; silica, alumina, alkali-bearing minerals, iron compounds, calcium compounds, titanium compounds, manganese, complex aluminosilicates often containing other elements, carbonaceous matter, moisture and colloidal water (i.e. water of constitution and of crystallization), exchangeable bases.

The particle size of clay is an important characteristic, since it influences other properties like plasticity and dry strength for instance, small particle size (< 0.1 microns) contributes to high drying shrinkage and great strength (Norton, 1956). Clay particles are small, hexagonal plate-like crystals, about 0.1 to 2 microns. This size lies in the colloidal range (0.001-1) microns and therefore clay has colloidal properties. The drying of clay is usually accompanied by shrinkage, which depends on the physical texture of the clay as well as the mineralogical compositions. As the film of water between the clay particles is drawn off by evaporation, the particles draw closer, thus making up the space previously occupied by water. The cumulative effect of the drawing close of each particle to its neighbour is the shrinkage of the entire mass.

Profound changes occur in clay during firing. A piece of fired clay differs both chemically and physically from raw clay. The first change is the completion of drying. At a kiln temperature range of 100°C to 150°C , all uncombined water (pore water and water of plasticity) in the clay evaporates and the clay dries completely. This final drying is carried out slowly to prevent bursting of the clay due to steam formation. The next change is dehydration of clay, which occurs between 350°C and 600°C . The chemically combined water, which is part of the molecular structure of clay, is driven off thus the clay loses its plasticity, becomes resistant to the slaking action of water, is porous and still quite fragile. As firing temperature increases, absorption decreases. The absorption value of clay is very important because it indicates how well the body has been fired, whether it is a vitreous or earthenware body, and something about its strength and water-tightness.

Between 350°C and 900°C , oxidation of organic compounds and inorganic sulphates present in the clay occurs. Complete oxidation of the carbon content yields carbon dioxide: in the case of insufficient oxygen in the kiln, partial oxidation occurs, yielding carbon monoxide.

Another change is quartz inversion. All clays have significant quartz content. Crystalline quartz has different forms, depending on temperature. When temperature increases, the quartz crystals arrange themselves into a slightly different order, accompanied by slight change in volume which is reversible. On cooling, the quartz changes and resumes its original crystalline form and size.

Finally, the clay is vitrified. The vitrification range starts about 900°C and extends up to the highest temperature clay can withstand without melting. Vitrification is the hardening, tightening and partial gasification of clay. It gives fired clay its characteristic hard, durable, dense and rock-like properties. Flux is usually added to reduce maturing temperature and hasten vitrification. Above red-hot heat, the fluxes start to soften and a glass is formed which acts like cement to make a strong body. Vitrification is accompanied by shrinkage in the clay which is caused by; a decrease in volume due to the

expulsion of water, CO_2 or SO_2 and the drawing together of the crystals by the capillary forces of the glass and the consequent expulsion of air from the pores.

Clays are of different types. Kaolin clay has its chemical composition approaches the formula of the mineral kaolinite. It is highly refractive clay with melting point of about 1800°C . Ball clays are blue or black but usually turn white when fired. They are fine; they have higher iron content, plasticity and strength and are more fusible. 'Fire clay' refers to refractoriness or resistance to heat and clay which vary widely in other properties may be called fire clay if they are refractory. Stoneware clays are plastic clays which mature or become vitreous between 1200°C to 1300°C . Their fired colour ranges from a very light gray. Earthenware clays contain iron and other mineral impurities in sufficient quantities to cause the clay to become tight and hard, fired at between 950°C to 1100°C . Bentonite clay major constituent is the mineral, montmorillonite. Although its chemical composition is like that of clay, the physical nature is different in that it contains more colloidal matter.

A clay body is a mixture of various clays combined with other ingredients where necessary, to give a working basis for the type of ceramic required. Important qualities of clay include texture, plasticity, and colour, durability when unfired, during and after firing. Clay that is too plastic may be added to another that is non-plastic. Ground glass is added to provide lower maturing point while grog (clay which has been previously fired and ground to fine size) is added for texture. By this, a clay body is produced with the desired workable qualities. Examples of clay bodies include porcelain, whose main clay content is kaolin. Typical porcelain contains 40% feldspar, 9% silica, 40% kaolin and 11% ball clay. It is blue – white and transparent when fired at high temperature.

Literature (Aderibigbe, 1989; Ajunwa, 1990; Abdulahi, 2003; Badejoko, 2006) clearly shows that clay abounds in Nigeria in large quantities and at various locations. However, the bulk of clay consumed in Nigeria is imported from the USA, United Kingdom and Japan (Iwuanyanwu, 1990). The cost implication of the importation of refractories (clays that can withstand very high temperatures) alone as at 1990 was put at \$3,000 to \$3,400 per ton (Nnuka and Adekwu, 1997). The estimate at current inflation rates can only be imagined. It is therefore imperative that alternative source of this important raw material be sought locally and hence this study is to characterize some Nigerian clays for ceramic application so that industrialists can utilize them instead of importing clay with similar characteristics. This characterization is limited to clay samples from four locations in Nigeria: Auchi in Edo State, Enugu in Enugu State, Ejigbo in Lagos State and Ikot Ekwere in Uyo, Akwa – Ibom State, some of its major deposits in Nigeria.

2. MATERIALS AND METHODS

The clay samples were collected from different deposits in Auchi (Edo State), Enugu (Enugu State), Ejigbo (Lagos State) and Ikot Ekwere in Uyo, (Akwa-Ibom state). Collected samples were air-dried, weighed and sieved through a 100-mesh sieve. Test pieces for various experiments were rolled and pressed, dried and fired at a temperature before the determination of different parameters. Half gram (0.5 g) of each of the samples was weighed, ground to pass through 100-mesh sieve, and transferred into a crucible. About 1.4g of flux ($1.2\text{g Na}_2\text{CO}_3 + 0.2\text{g boric acid}$) was added to the samples, mixed well and heated at 1200°C for 25 minutes. This was then removed, while about 1g of K_2CO_3 was added to melt the surface, the mixture

was heated again at 1200°C for about 5 minutes. The crucible was removed from the furnace and cooled in distilled water. It was then placed in a 250ml beaker and 60ml of 0.1M HCl added to form a solution which was left warm, agitated at intervals to facilitate complete dissolution. The solution was diluted to appropriate volume.

2.1 Linear Shrinkage

Test pieces were rolled in rods of 10cm. and marked along a line to maintain the same position after heat treatment. The samples were air-dried for 24 hours and oven-dried for another 24 hour, then fired at 800°C, 900°C and 1100°C, cooled to room temperature after each kiln temperature and measured. The fired linear shrinkage was calculated from equation 1. (Ekwere, 2005; Odo et al, 2003):

$$\text{Fired shrinkage} = \frac{DL-FL}{DL} \times 100\% \dots\dots\dots (1)$$

Where DL = dried length, FL = fired length.

2.2 Bulk Density

Clay samples were pressed into discs, air-dried for 24 hours, oven-dried and allowed to cool. Each specimen was weighed, and then suspended in a measuring cylinder containing water and the volume measured. The bulk density was calculated from equation 2 (Ekwere, 2005; Odo et al, 2003):

$$\text{Bulk density} = \frac{Md}{V} \dots\dots\dots (2)$$

When Md= dried mass and V = Volume.

2.3 Water Absorption.

To determine the water absorption capacity, the test pieces were dried for 24hours and fired to 800°C, 900°C and 1100°C at intervals. These were cooled and transferred into a 250ml beaker, filled with water. The specimens were allowed to soak in boiled water for 3 h and then left standing for 24hours. The soaked weight was recorded. The water absorption was calculated using equation 3 (Olubgade, 1999; Ekwere, 2005; Odo et al, 2003):

$$\text{Water absorption} = \frac{S-D}{D} \times 100\% \dots\dots\dots (3)$$

Where S = Soaked weight and D = Dry weight.

2.4 Apparent Porosity.

Test pieces were oven -dried for 24hours and fired at 800°C, 900°C and 1100°C respectively, cooled and transferred into a 250ml beaker. These were completely covered with water and boiled for 30mins. The soaked weight was recorded. The specimens were then cooled and weighed suspended in water

using a beaker placed on a balance. The apparent porosity was calculated using equation 4 (Ekwere, 2005; Odo et al, 2003).

$$\text{Apparent porosity} = \frac{W-D}{W-S} \times 100\% \dots\dots\dots (4)$$

Where W = Soaked weight, D = Dry weight, S = Suspended weight.

2.5 Cold Crushing Strength

Test pieces of clay samples were prepared into discs on a flat surface. The test pieces were fired in a kiln at 800°C, 900°C and 1100°C respectively and then cooled to room temperature. Each specimen was placed on a compressive strength tester and load was applied axially by turning the hand wheel at a uniform rate till failure occurred. Cold crushing strength (CCS) was then calculated using equation (5) (Ekwere, 2005).

$$\text{CCS} = \frac{\text{Maximum load (KN)}}{\text{Cross-Sectional area}} (\text{m}^2) \dots\dots\dots (5)$$

3. RESULTS AND DISCUSSION

The chemical composition, physical characteristics and firing characteristics of the samples obtained during the study are presented in Tables 1, 2 and 3 respectively. The principal oxides present in all the samples were silicon oxide and aluminum oxide, thus characterizing them as the fire clay class. The low amount of alkali compounds makes them highly refractory and the presence of iron oxide and organic matter i.e. carbaceous matter explains the colour variations in the raw and fired states (Tables 1 and 3).

The cold crushing strength is the load bearing capacity of fire clays. The presence of fluxes enhances bond formation at elevated temperatures. The strength behaviour of investigated clays was found to increase with rise in firing temperature for Auchi and Enugu clays.(Table 2). But the strength of the Lagos clay increased up to 900°C then reduced at 1100°C. The strength of the Uyo clay reduced at 900°C and rose at 1100°C (Table 2). Several factors can be responsible for the behaviour of Lagos and Uyo clays. These include the chemical composition of the clay, the physical properties, mode of preparation of the materials, mode of manufacturing of the article, conditions of drying, conditions of burning and the temperatures at which the material is used or at which the strength is determined. The lime in the clay components would have combined to form some considerably low-temperature melting compounds, which increased the strength of the test pieces on cooling.

The water absorption and porosity at 900 °C shows a decline for that of 800 °C and that of 1100 °C for all samples (Table 3). This might be due to the fact that vitrification starts at about 900 °C to the highest temperature clay can withstand without melting and gives it characteristic hard, durable, dense and rock like properties. Verification is accompanied by shrinkage in the clay as temperature increased from 800 °C to 1100 °C. This is caused by a decreased in volume due to expulsion of water, CO₂ or SO₂. The lesser the drying shrinkage, the stronger the clay and the less apt it is to crack.

Grimshaw (1971) and Chester (1973) show that the linear shrinkage, bulk density and the porosity of all the samples make them suitable for porous fire clay bricks. Auchi and Enugu clays may be suitable for building bricks; Auchi and Uyo clays may be



Table 1. Chemical composition of the clay samples

Clay Source	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI
Auchi	54.62	42.15	2.07	1.52	0.16	0.10	0.06	0.04	13.27
Enugu	46.72	37.38	0.68	1.30	0.12	0.09	0.07	0.02	13.72
Lagos	56.26	29.12	1.62	1.36	0.15	0.09	0.04	0.08	10.70
Uyo	53.42	44.03	1.47	0.38	0.12	0.10	0.04	0.01	12.42

Table 2. Physical characteristics of samples

Source	Bulk density (g/cm ³)		Cold crushing strength (KN/m ²)			
	800°C	900°C	1100°C	800°C	900°C	1100°C
Auchi	2.11	1.91	1.71	9,793	30,829	39,683
Eungu	1.84	2.00	1.98	25,128	39,785	50,273
Lagos	1.62	1.84	1.88	11,500	23,869	20,408
Uyo	1.78	1.92	2.58	20,555	16,011	19,412

Table 3. Firing characteristics of samples

Source	Linear shrinkage (%)			Water absorption (%)			Porosity (%)		Colour change				
	800°C	900°C	1100°C	800°C	900°C	1100°C	800°C	900°C	1100°C	25°C	800°C	900°C	1100°C
Auchi	5.18	3.67	4.20	16.50	10.92	13.5	20.00	15.24	18.74	Light brown	Reddish brown	Light brown	Light brown
Enugu	0.53	4.10	3.20	18.9	12.48	15.5	25.26	18.44	21.48	Red brown	Light red brown	Light brown	Light brown
Lagos	7.77	6.00	4.75	32.0	27.76	29.9	32.73	38.67	44.00	Off white	Off white	Yellow or white	Off white
Uyo	1.67	10.90	8.69	24.63	9.62	12.6	30.89	13.71	17.32	Dark brown	Pale brown	Light brick red	Buff

suitable for tiles while Enugu and Lagos clays may be suitable for fire clay brick. Enugu clay can be used for earthenware bodies. Due to their refractoriness they can be utilized as refractory materials for lining the walls of hot furnaces and other refractory applications.

5. CONCLUSION

The importance of sourcing for industrial raw materials locally has often been stressed by stake holders in the industrial sector, not only as a means of reducing dependency on imports and conserving foreign exchange but also as a way of reducing production cost and the consequent price of commodity. The physical and chemical properties of the clay samples from Auchi, Enugu, Lagos and Uyo, make them suitable for use as refractory materials. Refractories are needed to line the walls of a furnace, used in heat generation in many chemical processes. These refractories can come in form of bricks or tiles. Thus, Auchi, Enugu, and Lagos clay, are suitable for making fire clay bricks, while Uyo clay, as well as Auchi clay are suitable for making tiles. The clay samples are in commercial quantity (Badejoko 2006), so the problem of insufficient supply is adequately taken care of. It is hoped that industrialists will effectively exploit this cheap, abundant and versatile raw material for the nation's refractory needs and discontinue the practice of importing them.

REFERENCES

- Aderibigbe, D.A. (1989). Mineral resources in Nigeria and the potential for the manufacture of ceramic products. The Nigerian Engineer. Vol.24, no.4. pp 61-69.
- Ajunwa, J.C. and Oniklinam, E.P. (1990). Developing a domestic refractory industry. American ceramics society bulletin. Vol 69, no. 4, pp 656-657
- Badejoko, T.A. (2006). Opportunities in Nigeria Solid Minerals Participation. Proceedings of the 36th AGM, NSChE, Ibadan, Nigeria. Pp 110-132
- Chester, J.H. (1973). Refractories: production and properties. The iron and steel Institute, London. Pp 263-296
- Clews, F.H. (1969). Heavy clay technology. Second edition. Academic press Inc. (London). Ltd. pp1-16, 200-207
- Dinsdale, A. (1986) Pottery Science: materials, processes and products. Ellis Horwood limited. Pp 205-220
- Ekwere .I.I. (2005). Characterization of some Nigeria clays for ceramic Application. B.Sc. thesis. Department of Chemical and Polymer Engineering, Faculty of Engineering, Lagos State University, Epe Nigeria.
- Grinshaw, R.W. (1971). The chemistry and physics of clay. 4th edition. Ernest Benn limited. Pp 29-30, 271- 297, 807
- Iwuaanyanwu, E.C. (1990). Local sourcing of materials for the 1990s. proc. Of 1990 Annual conference of NSE. pp 12-30.
- Moore, F. (1965). 2. Rheology of ceramic systems. Maclaren and sons limited, London, England. Pp 51-67
- Nnuka, E.E, Elechikwu and Ogo, D.U.I. (1992). Sustainable refractory sourcing of our industries. Conference proc. Of NMS annual conference. Pp 18-20
- Nnuka E.E. and Enejore (2001). Nigerian Journal of Engineering Management. Vol 2, no.3. Besade publishing press. pp 9-13
- Norton, F.H. (1956). Ceramics for the artist potter. Addison Wesley publishing company Inc. pp 128-136, 208-218.
- Odo J.U and Nwajagu C.O. (2003). Possible Application of Eha-Alumona Clay Deposit in the Production of Refractories and Ceramics Ware. pp 109-111.
- Perry R.H. and Green. D.W. (1999) Chemical Engineer Handbooks. (7th Ed) Mc Graw Hill Co.Inc. New York. pp. 28-63.
- Rhodes, D. (1973). Clay and glazes for the pottery. 2nd edition, pitman publishing, Ptyled Melbourne. pp 13-18.