REFRACTORY CHARACTERISTICS OF KWI CLAY DEPOSIT IN PLATEAU STATE

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ABSTRACT

The Kwi clay deposit in Plateau State has been investigated to determine the chemical and mineralogical composition, refractoriness, apparent and bulk density, dry strength and dry shrinkage. Chemical and mineralogical composition were determined by x-ray analysis, density was determined using the pyrometric cone equivalence technique. Result obtained shows the clay to be composed of 31.69% Al_2O_3 and 37.63% SiO_2 placing the clay in the fireclay class of kaolins. The Fe_2O_3 content is notably high for kaolins (14.48%). The most interesting composition of the clay is certainly the high TiO_2 content, 2.97%. Mineralogical composition analysis shows the clay to be mainly kaolinite 88.88%. Apparent porosity is 39%, density at high temperature is 2.54 g/cm$_3$ while dry strength and dry shrinkage at high temperature (>1300°C) are 35.20MPa and 8.74% respectively. Refractoriness was found to be 1660°C. The clay is therefore recommended for ferrous and non-ferrous refractory application after reducing Fe_2O_3 content and more importantly for titanium extraction.

INTRODUCTION

Refractories are essential inputs in high temperature application especially in the foundry and metallurgical industry. In cement, ceramic, electrical and many other industries. In Nigeria the need for refractories is high especially in the metallurgical, foundry and cement industries. Table 1 shows the refractory requirement for these industries in Nigeria.[1]

Table 1: Refractory Needs for the Chemical and Metallurgical Industries 10^3 tons/year

Industry/ Type of Refractory	Delta Steel Company	Ajaokuta Steel Complex	Steel Rolling Mills	Cement	Ceramic Glass	Total
Alumino Silicates	18.0	36.4	3.0	4.0	2.24	63.64
Magnesites	27.0	5.0	5.0	5.9	1.04	43.94
Total	45.0	41.4	8.0	9.9	3.28	107.58

The bulk of this product is imported from far away America, Asia and Europe. The cost implication N2.27 billion per annum (Tables 1 and 3 refer) is enermous moreso when the demand is on the already lean foreign reserve. Furthermore, the security implication for the nation is undersirable especially when Nigeria plays the "big brother" politics in Africa. The only viable option is for the nation to develop its own refractory industry based on available local raw materials. Incidentally, the country is blessed with abundant raw materials deposits. Table 2 shows the locations, quantity and quality of the raw materials available in the country. [2]

The cost of refractories, Table 3, shows that it is economically viable to invest in refractory manufacture especially when it is also remembered that there is no country known to be producing refractory materials on a commercial scale in Africa today.

TABLE 2: LOCATIONS OF REFRACTORY RAW MATERIALS IN NIGERIA

Location & State	Class	Quantity (10^6 tonnes)
Osubulu, Anambra	Kaolin	4.2
Ukpor, Anambra	"	4.2
Enugu, Enugu	Fireclay	110.0
Enugu, Enugu	Clay	19.0
Nsu, Imo	Kaolin	0.1

Location & State	Class	Quantity (10^6 tonnes)
Umuahia, Imo	Kaolin	Undetermined
Ibere, Imo	Kaolin	2.0
Ogbuebule, Imo	Kaolin	Undetermined
Giru, Sokoto	Kaolin	2.0
Illo, Sokoto	Kaolin	Undetermined
Mararaba Rido, Kaduna	Clay	5.25
Farin Kasa, Kaduna	Clay	Undetermined
Bakin Kausa, Kaduna	Clay	Undetermined
Kachia, Kaduna	Kaolin	Large
Kankara, Kastina	Kaolin	3.40
Ikot-Ekpene, Akwa-Ibom	Clay	Undetermined
Obom, Akwa-Ibom	Clay	Undetermined
Mbiafor, Akwa-Ibom	Clay	Undetermined
Itu, Akwa-Ibom	Kaolin	Undetermined
Obomkpa, Bendel	Clay	Undetermined
Ukwunazu, Bendel	Clay	Undetermined
Ossioma River, Bendel	Kaolin	0.5
Igoriakhi North, Bendel	Clay	4.0
Igoriakhi South, Bendel	Clay	4.0
Warri, Bendel	Clay	0.75
Okpekpe, Bendel	Kaolin	3.0
Ibuzo, Bendel	Kaolin	3.0
Oshile, Ogun	Kaolin	Undetermined
Oke-Eri, Ogun	Clay	2.0
Imope, Ogun	Kaolin	1.0
Ilefun Hill Meko, Ogun	Kaolin	Undetermined
Onibode, Ogun	Kaolin	0.81
Dawakin, Kano	Kaolin	Undetermined
Tofa, Kano	Kaolin	Undetermined
Tsanyawa, Plateau	Kaolin	Undetermined
Nafuta, Plateau	Kaolin	6.0
Werron, Plateau	Kaolin	6.0
Major Porter, Plateau	Kaolin	3.0
Sabon Gida, Plateau	Kaolin	3.0
Kwi, Plateau	Kaolin	Undetermined
Ifon, Ondo	Kaolin	Undetermined
Oranyin River Ondo	Clay	0.075
Shagbon, Ondo	Kaolin	0.45
Alkaleri, Bauchi	Kaolin	Undetermined

It is certainly surprising therefore, that such huge reserve of the raw material is left untapped, while government and the private sector alike resort to importation of refractory materials. The cost of importation (N2.27 billion per annum) of these materials would have sufficed to establish manufacturing outfits for the product locally.

Table 3: Cost of Imported Refractories in Nigeria (1994 Estimate)

Refractory Type	Cost (₦/ton)
Fireclay bricks and shapes	15,000.00
Fireclay mouldable, mortars and masses	10,000.00
Medium alumina mouldables, masses and mortars	15,000.00
Medium alumina bricks and shapes	15,000.00
High alumina bricks and shapes	15,000.00
Magnesite bricks and shapes	28,500.00
High alumina mouldables, masses and mortars	17,000.00
Magnesite chrome bricks and shapes	23,500.00

Apart from considerations on the cost of importation, much more information is still necessary, especially with regards to the characteristics of the raw materials, the technological process involved, and the manpower requirement. This research aims at contributing towards solving one of these problems - providing information on the characteristics of the raw materials. Information on the refractory characteristics of the clay deposits in the country is scanty indeed. The location, class, reserve and chemical composition of some of the deposits are known but their mineralogical composition and refractory characteristics are not known. In this research, the chemical and mineralogical composition of Kwi clay is studied. Also studied are the refractory characteristics such as porosity, density, strength, shrinkage and refractoriness. It is hoped that the results emanating from this research will assist Nigerian entrepreneurs in venturing into the production of refractories from available raw materials.

REFRACTORY RAW MATERIALS

The majority of the good commercially esploitable kaolinitic fireclay from deposits in the country are used for the manufacture of structural clay products and

whitewares by the existing ceramic companies. For example, the Ukpor Clay in Anambra State is used by some paint manufacturers, the Nsu Clay in Imo State by the Modern Ceramics Industries, Umuahia, the Onibode, Oshiele and Orun deposits in Ogun State by the Porcelainware Ceramics and Richware Pottery, while the Ifon Clay in Ondo State is potentially applicable at the Nigerian-Italian Ceramics Company at Ifon[3]. So far refractory production in Nigeria is absent. It is therefore important that the basic raw materials content of refractories be highlighted.

Refractories primarily are materials which can withstand high temperatures. Their usefulness depends on their ability to maintain their mechanical strength at high temperatures, often in contact with corrosive liquids (slags) and gases. Most industrially used refractories are composed of a mixture of metal oxides. Besides, carbon, graphite and silicon carbides are now widely used as refractories. Other carbides, nitrides, silicides and borides are used in special applications, mostly in the space and nuclear industry. This group of refractories apart from refractoriness has an added advantage of stability in oxidising environments. The most commonly used refractory oxides are SiO_2, ZrO_2, Al_2O_3, Cr_2O_3, MgO and CaO. Refractories containing mainly Al_2O_3 or Zr_2O_3 are referred to as neutral, those comprising mainly of SiO_2 or ZrO_2 are acidic while those made of mainly MgO or CaO are basic. Refractories are used principally in the form of bricks but sometimes in the form of ramming mass. The following classes of brick are known and made:

Silica bricks consist mainly of silica (in the form of cristobalite, tridymite and quartz). Minor amounts of line, alumina, and iron (in the form of wollastomite) $CaOSiO_2$ and glass are often included. They are made from naturally occuring quartzites and silica gravels.

Semi silica bricks are made from siliceous clays and contain mainly cristobalite grain bonded with a glassy phase rich in alumina and silica. The composition is about 80% SiO_2 and 20% Al_2O_3.

Fireclay bricks are made from naturally occuring fireclays. Their refractoriness increases with increasing alumina content and decreasing impurity content (alkali oxides, haematite and titanium dioxide). The alumina range is 25% to 45%. High alumina bricks contain more alumina than pure calcined kaolin (45%). They are generally made from varying combinations of calcined bauxites, clays, silica sand and synthetic aluminium oxide. Their alumina content ranges from 45% to 100%. Chrome bricks are made from naturally occuring chrome ore (FeMg)O. $(CrAl)_2O_3$. Calcined magnesite is often added to the brick. The bricks are then called chrome-magnesite brick. Magnesite bricks consist mainly of the mineral periclase (MgO). When minor amounts of ore are added, the bricks are called magnesite-chrome bricks. Magnesite bricks are sometimes impregnated with pitch to increase their resistance to attack by basic slags.

Dolomite bricks are made from high calcined dolomite $CaCO_3MgCO_3$. Pitch is generally used as a binder for this type of refractory. Burnt dolomite bricks are often impregnated with pitch. Forsterite bricks consist mainly of the mineral forsterite, Mg_2SiO_2.

Zirconia-containing bricks consist mainly of the mineral zircon, $ZrSiO_4$ or of a mixture of zircon and alumina. The latter type of bricks is usually formed by casting from a melt. Refractories for use at temperatures above 300°C are made from synthetic, high purity, zirconia (ZrO_2). The bricks contain small quantities of lime, magnesia or yttria to stabilize the cubic crystal form of zirconia. High-alumina refractories production represents a demand for refractories to meet special industrial requirements. Tabular alumina made from Bayer alumina has also become popular for the manufacture of brick and refractory specialities. Tabular alumina (over 99% Al_2O_3) is sintered just below the fusion point of Al_2O_3 (2035°C). Bayer process alumina calcined to high temperatures to form corundum is also in use to a limited extent as the chief constituent or merely as an additive to refractories.

Mullite refractories, a special class of high alumina bricks are becoming ever more increasingly important in the refractories industry. This refractory class is historically significant as the first stage of refractories emanating from the adaptation of scientific data based on phase-equilibrium studies. The studies showed that mullite, $3Al_2O_3.2SiO_2$, was the stable compound in the alumino-silicate system at high temperatures.

Other refractory types include carbon, silicon carbide, zircon, zirconia and fused cast refractories. Fused cast refractories are a very recent development in the history of refractory manufacture. The novel

process employs the melting of refractory raw materials in an electric arc furnace and casting into shapes in a way similar to the production of iron castings. The technological process was initially applied to a mullite-corundum composition and has since been extended to other high-alumina and basic mixtures.

Bauxite consists mainly of the mineral gibbsite ($Al(OH)_3$), varying amounts of kaolinite and minor amounts of iron and titanium impurities. The loss on ignition is high. Therefore they are useful only after calcination at high temperatures. During calcination, the bauxite is reduced to a dense grain consisting mainly of corundum (Al_2O_3) and mullite $3Al_2O_3.SiO_2$. Refractory grade bauxite is a relatively scarce commodity as most bauxites have a high iron content which renders them unsuitable for refractory applications. For them to be useful as refractories, the iron content must be significantly reduced.

EXPERIMENTAL METHODS

X-ray Analytical Technique

X-ray analytical technique was used to determine the chemical and mineralogical composition of the clay. The clay was crushed into powder and binded with dextrin. It was then transfered into a sample cup. X-ray spectrometer was used to analyse the sample. The results was teledisplayed. A print-out was also produced by the attached print-out facility. The print-out was used to determine the chemical composition while mineralogical composition was obtained from the teledisplay. Detailed description of the X-ray analytical technique is available in the literature. [4]

EVACUATION TECHNIQUE

The evacuation method was used to determine bulk density, bulk volume, apparent solid density and apparent porosity. Three test pieces were used for each property determined. Each test piece had a volume of 50ml. It was ground, dried between 105°C and 110°C and cooled in a dessicator. Each test piece was weighed and the weight (WA) was recorded. It was then placed in an empty vacuum dessicator. An accuracy of 0.05g was maintained in all the weighings done. The pressure in the dessicator was maintained at a value not above 5mm Hg. and the immersion liquid was slowly admitted. The low pressure was maintained until the pieces were immersed and the immersed test pieces were allowed to stand for a few minutes. Air was then admitted into the dessicator. A test piece was then taken from the dessicator, slipped into a loop of fine cotton and transferred to a suitable container of immersion liquid (a glass beaker containing 400ml of liquid was suitable).

The balance bridge was put into position and the container was placed on the left hand pan of the balance bridge. The test piece was suspended from the balance hook by its loop of cotton thread (the test piece is prevented from touching the sides of the container or the surface of the paraffin when the balance beam is raised). The weight Wb of the immersed test piece was then recorded.

The container and test piece were removed from the balance bridge, the test piece slowly drawn from the paraffin by its cotton loop, and the residual liquid drops, below the test piece and between the cotton and the top of the test piece, were blotted out by brief contact with the edge of a piece of filter paper. The balance bridge was then removed while the test piece was again suspended from the balance hook and re-weighed. The weight (Wc) was recorded. Relevant data were obtained from the following formulae. [5]

The bulk density was calculated from the formula $D_b = \frac{Wa}{Wc-Wb} \times D_1$ where D_1 is density of paraffin at ambient conditions of test.

The bulk volume, $V_b = \frac{Wc-Wb}{D_1}$

Apparent solid density $Da.s. = \frac{Wa}{Wa-Wb} \times D_1$

Apparent porosity $Pa = \frac{Wc-Wa}{Wc-Wb} \times 100, \%$

$$= 100\left(1 - \frac{D_b}{Da.s.}\right)$$

Pyrometric Cone Equivalence (PCE)

The clay sample was dried and ground to pass a 30 mesh British Standard (B.S. 1610R 1942) test sieve and 50g were ground in an agate mortar to pass a 72 mesh sieve. Sieving was frequent to avoid excess of very fine powder. The sample was thoroughly mixed, made into a plastic mass with water and an organic binder (0.5% maximum ash content) was added. The test piece was then formed in a suitable mould. Calcination of the clay was conducted at 1000°C. The mould

was shaped into a pyramid with a triangular base. One edge of the pyramid was perpendicular to the base and 3.81cm long, each side of the triangular base is 1.27cm. A tolerance of 0.16cm was allowed in the dimensions of the base.

The test piece was mounted at the centre of a refractory plague and fixed with cement consisting of calcined alumina. The edge of the test piece perpendicular to the base was vertical. British Standard pyrometric cones were cemented to the plague but were oriented so that they would bend away from the test piece - their numbers facing inwards. The edges opposite the numbers were vertical. The test piece with the surrounding pyrometric cones were placed in the furnace the temperature was raised at a rate of 10 - 15°C/min to an estimated temperature of 200°C below the equatting temperature. Then the rate of temperature rise was maintained at 5°C/min. The temperature was checked by means of an optical pyrometer. The test was continued till the tip of the test cone had bent over level with the base. The plague bearing the specimen was removed from the furnace and the test piece examined when cold.

The refractoriness is the number of the pyrometric cone that has bent over to a similar extent to the test cone.

MECHANICAL TEST

Dry strength was determined by this method. A mechanical or hydraulic crushing machine which complied with grade B of B. S. 1610 1942 was used. One of the platers was on a seating designed to give axial loading. At least six pieces were tested varying the positions of the clay sample in each test. The test pieces were in cubic forms of 7.62cm - size. The direction of forming pressures was marked on each test piece. The two faces normal to the direction were prepared as bearing faces for the test by grinding to be plane and parallel to the forming direction.

Staw board of about 0.64cm thick was placed between the platers of the machine and the bearing faces of the test piece which was placed centrally on the plater. The rate of load application was 3.4 10^{-2} Nm $^{-2}$/ min, until the test piece fails to support the load.The crushing strength is the maximum load recorded.

RESULT AND DISCUSSION

Result of the experimental work is presented on Tables 4 to 6. Table 4 presents the chemical composition of Kwi clay while Table 5 presents the mineralogical composition of the same clay. On Table 6, the physical properties of the clay are presented.

Analysis of Table 4 shows that the clay is comprised predominantly of silica and alumina in such composition that place it in the fireclay class of kaolins. The silica content of 37.63% is relatively low while the alumina content (31.69%) is fairly high. The ratio of alumina to silica is high suggesting a negligible quantity of free quartz in the clay. The refractoriness of the clay is high as a result of the high alumina content which is the predominant determinant of refractoriness. The high percentage of ferric oxide (14.48%) is indicative of the presence of iron bearing minerals in the neighbourhood of Kwi. This high ferric oxide content should lend the clay a reddish to brownish colour on firing. The most striking component of the Kwi clay is obviously the high titanium oxide content (2.97%) which is sufficient to attract attention for benefication and extraction of titanium metal from the Kwi clay. Titanium is an expensive, strategic and scarce metal used in steel making as alloying element to impart special properties to steel. The lime and magnesia content is low too. The loss on ignition (L.O.I.) is on the high side (13%) and suggests the great potential of the clay for carbonaceous compound. It is a worthwhile endeavour to prospect for petroleum in the area. The remaining oxides are clearly impurities.

Analysis of Table 5 shows the mineralogical composition of the Kwi clay to be predominantly kaolinite at 88.88%. The quartz content of 8.00% must be in bonded form since the ratio of alumina to silica is high. The mineralogical composition confirms the deduction from the chemical analysis that the clay is in the fireclay class of kaolins.

The physical properties investigated, Table 6, shows, the apparent porosity of Kwi clay to be 39% at a temperature not exceeding 1300°C. This value is quite high and can be explained by the high loss on ignition and the attendant high cabonaceous content. The density as expected, is low. This is also true of the bulk density. Both loose density and compact

density depend on particle size, shape and size distribution. Compact density is always greater than bulk density so the result obtained confirms the rule. The difference between bulk and compact density is small suggesting that the particle size and shape difference is wide and that the particle distribution is even.

Therefore, the permeability value should be low as a result of the close packing of the particles. The dry compressive strength is low. This can be explained as follows: at a drying temperature of 110°C, most of the free water should have been liberated thereby creating vacant sites in the bricks at intersitices and pores. The cracks and pores in turn serve as sources of crack initiation and propagation. Furthermore, water of constitution is present in clays and many alteration products. The water in the clay constitutes a definite part of the crystal lattice and is only liberated at a comparatively high temperature when the mineral decomposes. Therefore, the water of constitution forms a continuously phase in the clay. It is also not liberated at the drying temperature since decomposition under conditions of slow rate of temperature rise occurs at about 4100C. Under such conditions, the water bond is weak and less force is required to ensure movement of particles. Already, discontinuities exist in the brick due to the vacant sites and the bond of the constitution water, so setting the stage for a friable brick which could shatter at the slightest application of load.

The dry shrinkage is low at 6%, and 8.74% at temperatures not greater than 1300°C and greater than 1300°C respectively.

The low value is indicative of the ability of the refractory, made out of the Kwi clay, to maintain fair stability in size at the operative range of temperature for most foundry furnace conditions.

RECOMMENDATIONS

The Federal Military Government is urged to establish a middle scale refractory and ceramic industry in Plateau State. The industries will be sourced locally from the Werron Clay and Kwi Clay both in Plateau State. Perhaps the most important recommendation emanating from this research is the call on the Plateau State Government to conduct a feasibility study on the extraction of titanium from its oxide richly present in Kwi clay. The State Government is also strongly urged to convince the Federal Ministry of Industries through the Raw Materials Research and Development Council to develop the Kwi and Werron clays for refractory and ceramic applications respectively.

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Table 4: Chemical Composition of Kwi Clay

Constituents	Composition, %
Al_2O_3	31.69
SiO_2	37.63
Fe_2O_3	14.48
TiO_2	2.97
MnO_2	0.03
MgO	0.12
CaO	0.03
Na_2O	0.12
K_2O	0.01
LOI	12.93

Table 5: Mineralogical Composition of Kwi Clay

Mineral	Composition, %
Kaolinite	88.88
Montmorillonite	2.62
Quartz	8.00
Haematite	0.50

Table 6: Physical Properties of Kwi Clay

Properties	≤1300°C	>1300°C
Apparent porosity, %	39.00	-
Compact density, g/cm³	2.59	2.54
Bulk density, g/cm³	1.56	1.96
Dry strength, Mpa	5.13	35.20
Dry shrinkage,%	6.00	8.74
Refractoriness, °C	-	1660