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THE STUDY OF CHEMICAL ANALYSIS OF CLAY DEPOSITS IN SOME STATES OF NIGERIA FOR REFRACTORY PRODUCTION

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Abstract

This paper discusses the results of chemical studies carried out in some clay deposits in three states of Nigeria. The clay samples were obtained from Ngala, Shuwari and Pulka representing Borno State, Eruemukohwarien and Ubulu-Uku, Delta State and Ijetu in Edo State. The results showed that alumina, silica and Lost-on-ignition (LOI) values for shuwari are 36%, 47% and 8.5% respectively; Pulka, 41.3%, 51.0% and 4.01%; Ngala, 38.0%, 46.8% and 11.63%; Ubulu-Uku, 40.0%, 39.0% and 12.0%, Eruemukohwarien, 29.0%, 45.8% and 14.7%; Ijetu, 41.5%, 45.8% and 10.2% respectively. These results placed the Shuwari clay in the group of siliceous fire-clay refractory; Pulka clay, medium duty, low-melting semi-acid fire-clay; Ngala, low-duty and low melting fire-clay refractory; Ubulu-Uku, under the super-duty, general purpose neutral fire-clay refractory; Eruemukohwarien, medium duty clay and Ijetu, was placed in the range of high refractory normal fire-clay group. The possible areas of applications of all the investigated clays have also been suggested in this paper.

KEYWORDS: Refractory production, alumina, silica, fire-clay.

INTRODUCTION

Refractory industry is important in any country aspiring to be technologically advanced. The refractories are absolutely essential for the lining of thermal unit such as kilns and furnaces, thermocouple sheaths, iron and steel, ladles, regenerators, tapping and teeming steel, foundry, cement factory, petroleum, refineries, gas plants, ceramic industries, non-ferrous furnaces, petrochemical industries and many others. The commonly used refractories include fire-clay, silica, high alumina, magnesia dolomite and carbon (Ibhadode, 1997; Oiks, 1977).

According to Krivandin and Morkov (1980) refractories can be classified by their properties and characteristic with distinct types in each;

A- Refractoriness:

1) Common refractoriness (upto 1580-177^{0}C)

2) High refractoriness (1770-2000^{0}C)

3) Highest refractoriness (above 2000^{0}C)

B- Chemical and mineral composition:

(1) Siliceous, in which the base is silica or quartzite ($Si0_2$); silica bricks have a fusion point of 1700^{0}C.

(2) Aluminum-siliceous; where components are $A1_20_3$ and $Si0_2$; fusion points between 1600^{0}C and 1800^{0}C.

(3) Magnesian; contains MgO (magnesite, dolomite, forsterite, talc and spinelides) fusion point 1800-2800^{0}C. Chromic; component includes Cr_20_3 and MgO (chromite, Chrome-magnesite and magnesite-chromite), fusion point above 1920^{0}C.

(4) Carbon; (carbon and graphite), fusion points above 1920^{0}C.

(5) Zircon; (ZrO); Zirconia and zircon-refractories. Fusion point of zirconia is 2700^{0}C while that of zircon is 2000^{0}C.

(6) Oxide; refractories composed mainly of pure oxide. (MgO, $A1_20_3$, CaO etc).

C- pH Range:

(1) Acid; with distinct acid properties (e.g. silica bricks, quartzite. This type contains typically 18-25% alumina and 72-98% silica (Micheal, 1989).

(2) Basic; distinct basic properties (magnesic brick; magnesite powder; magnesite-chromite with a high content of MgO; dolomite etc)

(3) Inert or neutral; with amphoteric oxide properties (fire-clay brick, chromite brick, etc; 30-45% alumina.

The chemical composition of a refractory determines its areas of application and to a large extent its refractoriness. As the alumina-silica ratio increases, the refractoriness usually increases (Michael, 1989); examples are carbonaceous materials such as ignite and humic organic matter (the later contributing in the high green strength of many clays). The amount of associate minerals like iron oxide (Fe_2O_3) and titania (TiO_2) also account for the fire colour of a clay (Grimshaw, 1971; RMRDC, 1996). The alkali oxide impurities, CaO, MgO, K_2O, Na_2O) supply the glassy phase during firing; this is needed for transparency (George, 1969). These alkali impurities and iron oxide are always kept to minimum because their presence also tends to reduce the refractoriness (Michael, 1989).

George (1969) suggested that the chemical composition can also be used to predict the extent of corrosion-destruction of refractory surface by chemical action on external agencies. For example acid refractories, contain a substantial amount on external agencies. Acid refractories, which contain a substantial amount of silica can react chemically with basic refractories, basis glass or basic fluxes.

In Nigeria, several economic deposits of refractory clay (Kaolin and fire-clay) have been located all over the country by the Federal Ministry of Solid Minerals and Natural Resources, and the National Steel Council (RMRDC, 1996). Vast deposits of Kaolin (China clay) have identified at Akinlabi village Oyo-State; Ukpor/Ozubulu areas Anambra-State; Nsu and Ozanogo, Imo-State; Okhuo an Ijetu Edo-State; Iguorbiaki/Ubulu-Uku-Delta State; and Giru-Sokoto-State; among others (Anagbo, 1981; Aneke, 1981; Orumwense, 1990)

Abundant amounts of fire-clay have also been reported in the coal fields of Enugu-State; Onibode/Oshiela-Ogun-State; Oturkpo (trough) Benue-State; Gwoza, Bama, Ngala, Biu, Damboa, New-Marte, Borno-State; (Brady and Clauser, 1991; Anagbo, 1981; BSH, 1990).

According to Nnuka et al (1992), the bulk of refractory needs in Nigeria are between 38,000-120,000 tons per annum. This amount is imported and the cost implication is enormous. Nevertheless, iron and steel making accounts for almost two-thirds of all refractories that are being presently used in the country (DSC, 1982). For instance, the Delta Steel Company (DSC) Limited, Ovwian/Aladja-Warri reported an annual refractory material (ramming mass) of about 72,000 tons per years.

Refractories generally reach the end of their useful life either by bending or cracking, although, there are other reasons such as attack by kiln atmosphere (lead vapour-glass-kiln) and slag attack (as in steel making, copper smelting) that may necessitate replacement.

The aim of this work is to study the chemical composition of some clay deposits in some states of Nigeria for refractory productions. This entails the determination of chemical analysis of clay samples taken from different areas of the country. The result will assist in refractory production in the country.

MATERIAL AND METHOD

Two zones in Nigeria were considered for collection of clay samples in this work. These are arid and equatorial zones, Shuwari, Pulka and Ngala representing the arid zone; Ijetu, Ubulu-Uku and Eruemukohwarien representing the equatorial zone. The soil of Shuwari is lateric, fine and medium sedimentary type which gives rise to Kaolin formation. Ngala shows alluvial type soil, reddish brown with bottom land. Pulka is ferrallitic granite rocks, rich in silica (IOB, 1990; Barthlomew, 1976). The relief of Pulka shows that the area is about 500m above sea level. The soil of Ijetu is composed of altered rocks often of the pegmatic type. The fine rocks and clay particles have been washed out of the original deposits and laid down. The kaolin deposits are usually formed by weathering of pegmatic. Generally Ijetu, Ubulu-Uku and Eruemukohwarien composed of altered pegmatic type which fine rocks and clay particles have been washed out of the original deposits and laid down in lakes and lagoons with some alteration during transport and after setting (Brindley and Nkahira, 1977; Okonji and Nwachukwu 1996). These areas are between 100-150m above sea level. Further information about these areas of collection is shown in Table 1.

EXTRACTION OF THE SAMPLES

Finely powered (5g) of each of the clay samples was admitted in a volumetric flask (100ml) containing a solution of NH_4OAl (1m, 30ml) to which a tetfon covered magnetic follower had been added. The flask was sealed and thermostated for 1hr at 25.20^{0}C in a water bath and stirring was effected by a magnetic stirrer. This was followed by further addition of NH_4OAl (1m, 30ml) while the stirring continued for another 30 minutes. The content of the flask was filtered using filter paper (0.45μ Millipore) and the volume was made up to 100ml with distilled water. These flasks were labeled A,B,C,D,E,F according to their localities. Each of these solutions was labeled stock solution and used for the various measurements.

DETERMINATION OF THE OXIDES

Magnesium Oxide:

The stock solution (10ml) was pipetted into conical flask (250ml) followed by addition of water (50ml), NH_3 solution (1M, 15ml), KCN, $K_4Fe(CN)_6$ (1:1, 50ml) and EDTA (0.1M, 10 drops) in that order. This mixture was allowed to stand for about 10 minutes and titrated to a permanent blue colour with EDTA (0.01M) using Erochrome black T indicator (EBT). The magnesium oxide of the final solution was determined by Direct Reading spectrophotometer (DR200) and the results are in Table 2.

Calcium Oxide:

The stock solution (10ml) was pipetted into conical flask (250ml) then distilled water (50ml) was added, NH_3 solution (1M, 15ml) KCN, $K_4Fe(CN)_6$ (1:1, 50ml) and EDTA (0.1M, 10 drops) were added in that order. Sodium hydroxide (10%) was then added until the pH becomes 12 on meter reading. The mixture was then titrated against EDTA to a reddish violet colour using murexide powder as indicator. The ensuring solution was analysed for calcium oxide using Direct Reading Spectrophotometer (DR200). Other oxides were analysed using the Direct Reading.

DETERMINATION OF LOSS-ON-IGNITION, (LOI)

The clay sample (5g) from each of the deposits was weighed into a clean platinum crucible (20ml). The crucible was partially covered with lid and placed in muffle furnace. The temperature was raised slowly to 1000^{0}C. The samples were ignited at this temperature for 30 minutes. The crucibles were removed from the furnace and cooled in a dessicator. The samples were reweighed and the weight recorded. The values obtained were used to calculate the Loss-on-Ignition (LOI). LOI=100-OT. Where OT is the total percentage of oxide in the clay (Leford, 1975).

RESULT AND DISCUSSION

Table 2 represents the results of the analysis of the clay samples from Shuwari (A), Pulka (B), Ngala (C), Ijetu (D), Ubulu-Uku (E) and Eruemukohwarien (F). The values of composition of normal fire-clay is also listed (Brindley, 1977). All these clay samples except F contains reasonably high content of alumina. This oxide is a determinant for refractoriness in clays (Leford, 1975), so the high values in these clays is a pointer to high refractoriness.

Sample A contains low amount of Fe_2O_3 (0.2%). This suggests that the main constituents of the clay are SiO_2 (47%) and Al_2O_3 (36%). The Shuwari clay can stand up well the action of high temperature (fire-clay). This property can be lost when the Fe_2O_3 is higher. (Leford, 1975; George 1969). Oiks (1977) pointed that as a result of this disruptive action of oxide of iron, fire-clay bricks cannot be used to line furnace elements in contact with slag or the furnace atmosphere. Sample B contains moderate amounts of alumina and silica of 41.3% and 51.0%. The LOI value is 4.01 which is on high side. The firing temperature of this clay is 1000^{0}C. This sample contains high amounts of Fe_2O_3 (1.95%). Sample B may give high plasticity clay. The oxide impurities present in the clay promote the formation of low melting glasses which tends to reduce the refractoriness (Brady and Clauser, 1991; Michael, 1989). The deposition of high amounts of iron in this clay may give rise to concentration of Fe to ore grade.

The Ngala clay (sample C) contains excellent chemical composition. However, its reaction upon firing makes it unsuitable for most structural and refractory application. With the alumina content of 38.0% and silica, 46.8%; one should expect high refractoriness. This could not be achieved, because of its high lime (CaO + MgO) content, and low firing temperature of 1000^{0}C. The reddish brown colouration of the clay at firing temperature is indicative of the presence of decayed vegetation, which burns out upon firing and yielding the high LOI value obtained (Brady, and Clauser, 1991; Aneke, 1981; Nnuka, et al, 1992). This reddish brown colour could be as a result of Fe_2O_3, but the amount is small (0.5%).

The chemical analysis of Ijetu clay sample D, revealed that the alumina content is 41.5%, silica, 45.8%, Fe_2O_3, 0.80%. The LOI value of 10.16 is high. The refractoriness is expected to be high and plasticity low due to low content of CaO and MgO. (Oiks, 1977; Leford, 1975; Okonji and Nwachukwu, 1996). The chemical analysis result of sample E (Table 2) gives the alumina content of 40.0%, silica, 39.0%; Fe_2O_3. 0.2% LOI, 12.01. The clay retained its original colour at 1200^{0}C (see Table 3). This result indicates presence of titania. Ubulu-Uku clay will possess a low plasticity because of the low content of alkali impurities. A value of 0.6% (Fe_2O_3) in sample F is high when compared with low amount of alumina (29.0%). This give the reddish colour at the firing, temperature of 1200^{0}C (Table 3). The alkali content is low, this may also result in low plasticity of the clay. Other possible areas which these clays can be used are as shown in Table 3.

Table 1: Sample Information

Sample	State	Location	Appearance	Zone
A	Borno	Shuwari on Maiduguri/Damboa Road	Grey	AR
B	Borno	Pulka, Gwoza L.G. Council	Brown	
C	Borno	Gamboru-Ngala, Ngala L.G. Council	Blackish	
D	Edo	Ijetu, Estako West L.G. Council	Brownish with dark patches	EZ
E	Delta	Ubulu-Uku, Aniocha South, L.G. Council	Reddish with gray patches	
F	Delta	Eruemukohwarien, Ughelli, North L.G. Council	Light Brown/Grey	

AR = Arid Zone
EZ = Equatorial Zone

Table 2: Composition of clay samples (A – F)

	SAMPLE (% COMPOSITION)						
CONSTITUENTS	**A**	**B**	**C**	**D**	**E**	**F**	**G**
SiO_2	47.01	51.00	46.80	45.80	39.00	45.80	40-60
Al_2O_3	36.00	41.30	38.00	41.50	40.01	29.00	25-45
Fe_2O_3	0.02	1.95	0.50	0.80	0.20	0.60	1-5
CaO	0.22	0.28	0.29	0.06	0.09	0.08	0.5-1.5
MgO	0.06	0.09	0.27	0.12	0.02	0.02	0.1-10
LOI	8.82	4.01	11.63	10.16	12.01	14.73	5-14
Other oxides	8.0	1.37	1.91	1.56	8.68	9.79	3

A = Shuwari; B = Pulka, C = Ngala, D = Ijetu,
E = Ubulu-Uku, F = Eruemukohwarien.
G = Normal Fire-clay (Leford, 1975; Orumwense, 1990, 1992)
LOI = Loss-On- Ignition (see Text).

Table 3: Colour changes at firing Temperature and possible areas of usage of the clay sample from different localities

Sample	Colour Eummited	Temperature ^0C	Possible Areas of Use
A	Reddish	1200	Line regenerator, laying the lower course of the hearth, ladle lining cement factory; burnt bricks and other ceramic application
B	Reddish	1000	Earth dam, canals and building bricks
C	Reddish brown	1000	As binders in foundry sand and as drilling muds.
D	Light brown	1200	Reheating furnaces, open-hearth furnace, soaking pits, boilers, kilns etc
E	Reddish with gray patches	1200	Reheating furnace, combustion chambers, Open-hearth furnace, soaking, pits, boilers, kilns, Also in structural building bricks
F	Reddish	1200	Reheating furnace, Open-hearth furnace doors and checkers, soaking pits, kilns. Boilers, Also in structural building bricks

CONCLUSION

It may be concluded that the Al_2O_3, SiO_2, Fe_2O_3, CaO and MgO form the major composition of these clay samples from the arid and equatorial zones of Nigeria. These contents can serve as a useful guide to the usage of these clays.

The Shuwari clay may belong to medium duty acidic siliceous fire-clay; Pulka clay may be classified as moderate duty, low melting fire-clay.

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