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Mathematical Modeling of The Refractory Properties for Kaolinite Clays in Nigeria

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Abstract: *The refractories need of Nigeria, a fast growing industrial nation, is potentially enormous. The country spends a huge amount of foreign exchange importing refractories. While, a lot of clay deposits are in this country, which can be processed to meet our local needs. The suitability of some kaolinite clays in Nigeria as refractory raw materials was investigated. A mathematical model was developed based on the concentration and absorbance of the metallic element present in the kaolinite clay. MATLAB was used to simulate the model data and results obtained were compared with experimental values of the four states. Mean square deviation of absorbance for experimental and model results for Abia, Akwa Ibom, Imo, and Rivers are 0.86%, 0.59%, 0.72%, and 0.60% respectively showing proximate agreement. The alumina-silica ratios of 0.54 for Abia; 0.34 for Akwa Ibom; 0.61 for Imo and 0.50 for Rivers (as compared to the theoretical value of 0.84 for pure kaolinite) makes the clays suitable for other industrial applications.*
Keywords - *Clays, Kaolinite, Mathematical Modelling, Raw materials, Refractory Properties.*

I. Introduction

Refractory materials are inorganic non-metallic substances, mainly mixtures of oxides, which can withstand very high-temperature conditions without losing their mechanical, chemical and integrity. Among the oxides found in refractory mixtures, the most common are those of aluminium (Al2O3) and silicon (SiO2), high alumina and silica (SiO2) are the chief constituents of all aluminosilicate minerals, particularly the clays. The potential use of aluminosilicate refractory raw material depends on the amount of alumina clay mineral present. Among the clay minerals, the kaolinites has the highest content of alumina (up to 39.50% by weight), as revealed by the chemical formula, Al2O3.2SiO2.2H2O.

The refractories need of Nigeria, a fast growing industrial nation, is potentially enormous. The country spends a huge amount of foreign exchange importing refractories. While, a lot of clay deposits are in the country, which can be processed to meet our local needs. Earlier research on various Nigerian clay deposits shows that many of them are rather high in silica content and low in alumina (NMDC, Jos, 1999; Hassan, 2001). Meanwhile, a number of deposits were found suitable for use as refractory raw materials; that is, if they are properly processed (Onyemaobi, 2002).

Complete chemical analysis of clays involves a true mineralogical analysis. Clays are basically aluminosilicates composed of alumina (A12O3) and silica (SiO2) with some ionic substitutions, and chemically bound water. Common impurities include compounds (usually oxides) of Ba, Ca, Na, K, and Fe, and some organic matter (Callister, 2003). A complete chemical analysis of clay, therefore, identifies the minerals and also shows the exact quantities of elements or compounds present (soilscijournals.org). One difficulty in the classical chemical analysis of clays is in finding a reagent specific for detecting the presence of certain element or mineral. However, classical methods (those based on wet chemistry techniques) are still very much in use today, but the modern instrumental methods are faster, and more, accurate (Reed, 1988; Chalmers, 1968). The relative proportions of alumina and silica (in the case of kaolinite or refractory clays) are relevant, since the higher the proportion of alumina, the higher the temperature (i.e. higher refractoriness) necessary to form the glassy ceramic bonding (vitrification) material which characterize ceramic products (ILO/UNIDO, 1984; Idenyi and Nwajagu, 2003).

The significant properties of any refractory depend on its mineral make-up, the particle size distribution of the minerals and furnace environments and the way these minerals react to high temperatures. Particles varying in size from 6mm to 7.4mm constitute the unfired refractories. Upon firing, the fines from a ceramic bond between the larger particles and the fired refractory consists of bonded crystalline mineral particles and glass or smaller crystalline particles, depending largely on the composition of the refractories (Ruh, 1986; Callister, 2003). When choosing a refractory for a particular application, a variety of physical properties must be considered, e.g. apparent porosity, bulk density and strength at room temperature (Ruh, 1986). The density, strength, and porosity of fired products are influenced by factors like quality of the materials, the size and 'fit' of the particles, moisture content at the time of moulding, pressure of moulding, temperature and duration of firing, kiln atmosphere and cooling rate (Idenyi and Nwajagu, 2003). The procedures in the brick making can be described under five headings: lay excavation and winning, clay processing or preparation, brick forming or moulding, brick drying, and brick firing (Nash, 1979; Rajput, 2004). Raw materials for the production of the fireclay refractories; their processing and testing methods. It is evident that in almost all the works cited, the researchers who worked on the refractory characteristics of various Nigerian clays did not add any inert (non-plastic) material to the clay. The addition of chamotte as a learner or inert substance to the plastic clay to form a moulding mass is where this investigation differs from previous works on the refractory properties of Nigerian clays. Viz.: Borode, et al (2000); Nnuka and Agbo (2000); Hassan (2001); Omowumi (2001); Obadinma (2003); Lawal, et al (2005); and Hussein, et al (2005). The addition of chamotte is said to diminish the shrinkage and cracking of fireclay bricks (Krivandin and Markov, 1980). This is already being exploited in the ceramic table and kitchen wares where the addition of grog, quartz or flint, and other non-plastic materials give strength to the ceramic body (Mark, 2003). It should be noted that the chamotte used have the same composition as the clay. So, at the appropriate high temperatures, they would fuse together and transform to mullite and tridymite/cristobalite.

Although Hassan (2001) added silicon carbide while Lawal, Amuda and Adeosun (2005) incorporated cow dung and graphite; the fact remains that these materials are foreign to clay composition. Silicon carbide or carborundum (rated as a first class refractory material and hence costly) was reported to enhance the refractory properties of the clay, whereas cow dung affected them adversely even though it was meant to provide the much-needed phosphate bond.

The addition of quartz or silica as did Samuel and Adeyemi (2004), in the case of ceramic tiles, may be considered nearer to what obtains in the SiO2 - Al2O3 system, but it will tend to lower the refractoriness (softening point), in the case of refractory bricks as predicted by the phase diagram. In contrast, however, the addition of a grog or chamotte made (especially) from the same clay would maintain the constitutional integrity of the refractory clay while improving its refractory properties. In fact, Schumann, Jr. (1952), and Krivandin and Markov (1980) alluded to the fact that the addition of a pre-fired or calcined clay (grog or chamotte) has the effect of reducing shrinkage, and increasing the packing density and strength. Of course, other processing parameters size distribution, moisture content, and moulding pressure must be adequately controlled. As already stated, this investigation differs from those cited earlier because it considered the use of pre-fired clay as a nonplastic additive. However, the testing procedures used in this study are in conformity with standard practices. So, it follows the same refractory testing methods used by previous investigators. This, of course, makes the results obtained to be comparable with those cited in earlier investigations using the same yardstick of measurement.

This study carried out experimental analysis on the refractory properties of Kaoloinite clay deposits in four Niger delta states. A model for analysing refractory properties of kaolinite clay deposits in four Niger Delta States was developed.

II. Model Formulation

The mathematical model was developed using the concentration and the absorbance of the metallic elements present. The equation of the line of regression of A on C is (Kreyszig, 1990).

$$A = \alpha_1 C + \alpha_O \qquad (1)$$

The coefficient of regression of A and C is and differs from one distribution to the other. If we sum equation (1) above we have:

$$\sum A = \alpha_1 \sum C + \alpha_O N \qquad (2)$$

If we multiply equation (1) by C and sum both sides we have:

$$\sum CA = \alpha_1 \sum C^2 + \alpha_O N \sum C \qquad (3)$$

Eqn (2) x $\sum C$ we have:

$$\sum C \sum A = \alpha_1 \sum C \sum C + \alpha_o N \sum C$$

$$\sum C \sum A = \alpha_1 \left(\sum C\right)^2 + \alpha_o N \sum C \qquad (4)$$

Eqn. (3) x N we have:

$$N \sum CA = \alpha_1 N \sum C^2 + \alpha_O N \sum C \qquad (5)$$

Subtracting (5) from (4)

$$\sum C \sum A - N \sum CA = \alpha_1 \left(\sum C\right)^2 - \alpha_1 N \sum C^2 \qquad (6)$$

Factoring out α_1 on the right-hand side of (6)

$$\alpha_1 = \frac{\sum C \sum A - N \sum CA}{\left(\sum C\right)^2 - N \sum C^2} = \frac{\sum C \sum A - N \sum CA}{N \sum C^2 - \left(\sum C\right)^2} \tag{7}$$

But $\overline{C} = \frac{\sum C}{N}$ and $\overline{A} = \frac{\sum A}{N}$ (8)

$N\overline{C} = \sum C$ and $N\overline{A} = \sum A$ (9)

Substituting (9) into (7) we have:

$$\alpha_1 = \frac{N \sum CA - N\overline{C}N\overline{A}}{N \sum C^2 - \left(N\overline{C}\right)^2} \tag{10}$$

Also solving (2) and (1) by eliminating α_0 gives

Eqn. (1) x N $NA = \alpha_1 NC + N\alpha_O$ (11)

Eqn. (2) x 1 $\sum A = \alpha_1 \sum C + \alpha_O N$ (12)

Subtracting (12) from (11) and dividing through by N we have

$$A - \frac{\sum A}{N} = \alpha_1 \left(C - \frac{\sum C}{N} \right) \tag{13}$$

Substituting (8) into (13)

$$A - \overline{A} = \alpha_1 \left(C - \overline{C}\right) \tag{14}$$

Substituting (10) into (14)

$$A - \overline{A} = \left(\frac{N \sum CA - N\overline{C}N\overline{A}}{N \sum C^2 - \left(N\overline{C}\right)^2} \right) \left(C - \overline{C}\right) \tag{15}$$

Equation (15) is the derived model.

III. Experimental Details

All experiments except those involving winning of clays and chemical analysis, firing, and softening point test; were executed at the Centre for Industrial Studies (CIS) and Institute of Erosion Studies (IES), Representative samples of the four clays were analyzed to determine their chemical constituents (quantity of SiO2, Al2O3, etc.) and mineralogical composition (amount of quartz or free silica, kaolinite, feldspar, etc). The analyses (chemical and mineralogical) were done. Atomic absorption spectrophotometer analysis, X-Ray Diffractometer analysis, liquid limit test and plastic limit test of the clay samples were carefully carried out.

Model Validation

The formulated model was validated by comparison of model results with experimental results using the root mean square error (RMSE). The deviation is given by

$$RMSE = \sqrt{\sum_{i=1}^{n} \frac{\left(A_{\exp,i} - A_{\text{mod}\,el,i}\right)^2}{n}} \tag{16}$$

Where $A_{\text{mod}\,el}$ = model result of the absorbance present in kaolinite clay

$A_{\exp}$ = experimental result of the absorbance present in kaolinite clay

n=Total number of observed values of Absorbance being predicted

IV. Results and Discussion

The mean square deviation of the Aexp and Amodel as seen from Fig 1 for Abia is 0.86%, Fig 2 for Akwa Ibom is 0.59%, Fig 3 for Imo is 0.72% and Fig 4 for Rivers is 0.60%. From the calculated mean square deviation for each state above we can observe that the values for the Aexp and Amodel are closely matched indicating that the model has been validated.

Table 1: Concentration "C" and Absorbance "A" of Metals in Clays from four Niger Delta States in Nigeria

	C	Si_A	Al_A	Fe_A	Mg_A	Ca_A	Na_A	K_A
Abia	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.20	0.006	0.004	0.003	0.007	0.001	0.001	0.009
	0.40	0.013	0.009	0.010	0.012	0.003	0.003	0.021
	0.60	0.018	0.011	0.010	0.019	0.005	0.006	0.028
	0.80	0.025	0.016	0.013	0.030	0.006	0.008	0.035
Imo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.20	0.007	0.005	0.004	0.008	0.002	0.002	0.010
	0.40	0.014	0.010	0.011	0.012	0.004	0.003	0.022
	0.60	0.019	0.012	0.011	0.019	0.006	0.007	0.029
	0.80	0.026	0.017	0.014	0.030	0.007	0.009	0.036
Rivers	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.20	0.005	0.003	0.002	0.006	0.009	0.009	0.008
	0.40	0.012	0.008	0.009	0.011	0.002	0.002	0.020
	0.60	0.017	0.010	0.009	0.018	0.004	0.005	0.027
	0.80	0.024	0.015	0.012	0.029	0.005	0.007	0.034
Akwa Ibom	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	0.20	0.014	0.002	0.001	0.005	0.008	0.008	0.007
	0.40	0.011	0.007	0.008	0.010	0.001	0.001	0.010
	0.60	0.016	0.009	0.008	0.017	0.003	0.004	0.026
	0.80	0.023	0.014	0.011	0.028	0.004	0.006	0.033

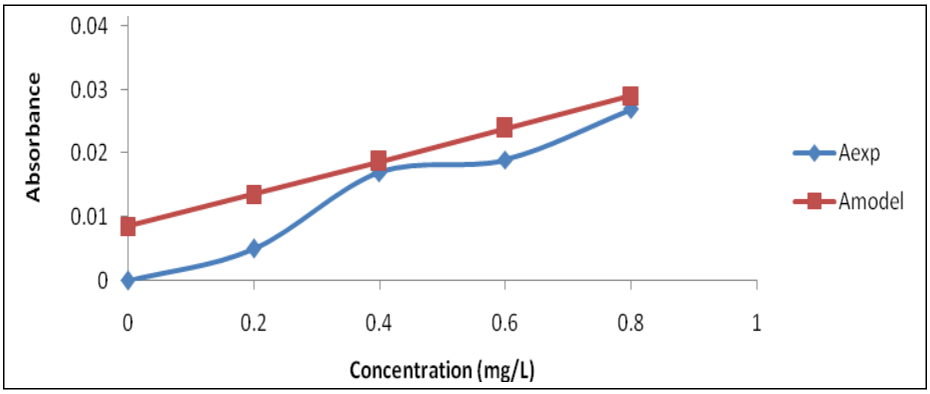

Fig. 1 Graph comparing model and experimental result of the absorbance against concentration present in kaolinite from Abia

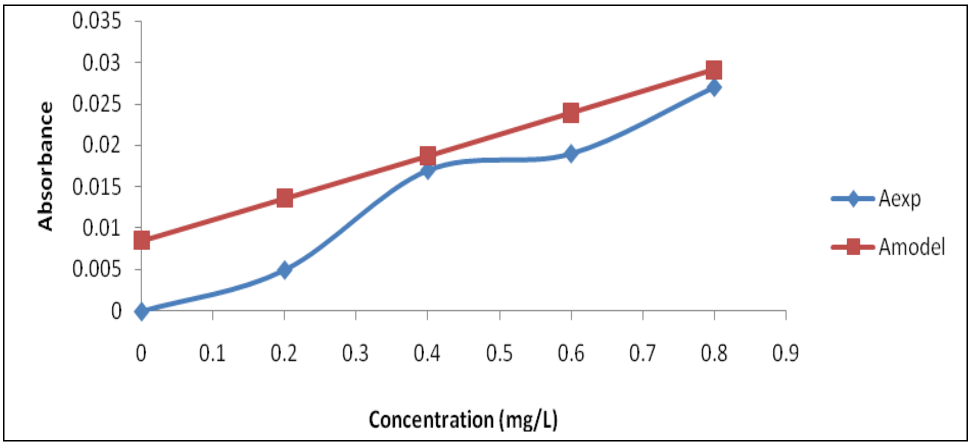

Fig. 2 Graph comparing model and experimental result of the absorbance against concentration present in kaolinite from Akwa Ibom

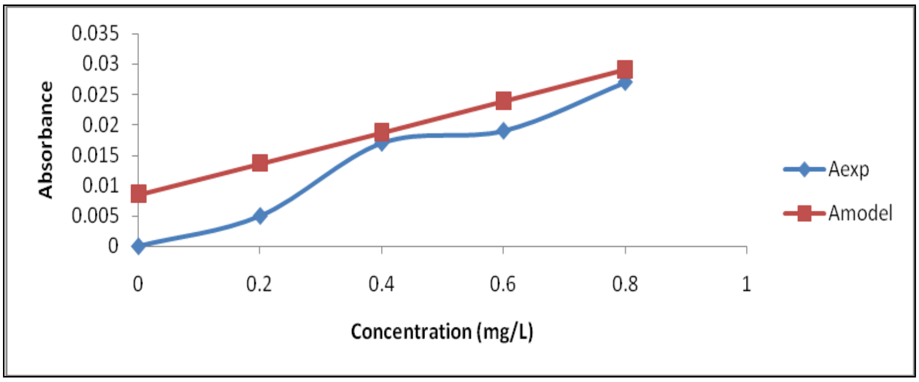

Fig. 3 Graph comparing model and experimental result of the absorbance against concentration present in kaolinite from Imo

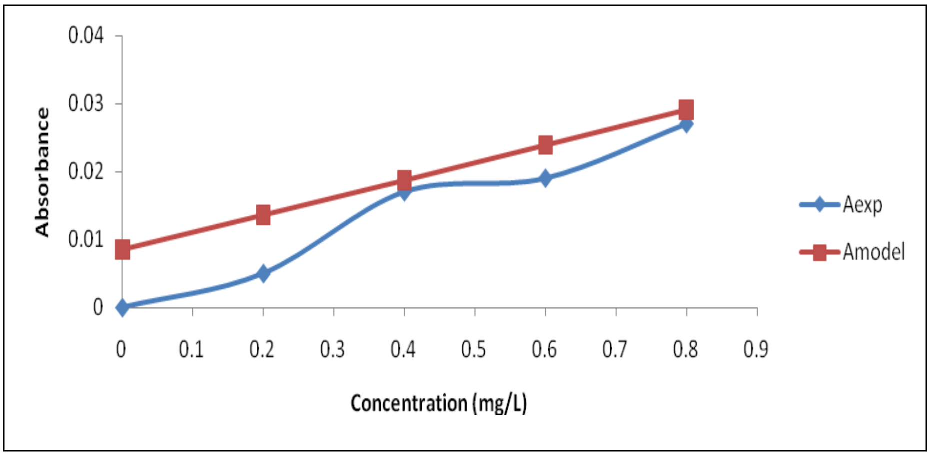

Fig. 4 Graph comparing model and experimental result of the absorbance against concentration present in kaolinite from Rivers

The procedures for obtaining the model (using the derived model) in the four Niger Delta States are shown below.

ABIA

Silicon			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.006	0.00012	0.04
0.40	0.013	0.0052	0.16
0.60	0.018	0.0108	0.36
0.80	0.025	0.0200	0.64
2.00	**0.062**	**0.0372**	**1.56**

A_{si} = 0.016x + 0.0092

Aluminium			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.004	0.0008	0.04
0.40	0.009	0.0036	0.16
0.60	0.011	0.0066	0.36
0.80	0.016	0.0128	0.64
2.00	**0.04**	**0.0238**	**1.56**

$$A_{Al} = 0.0103C + 0.00594$$

$A_{Abia} = 0.016C_{Si} + 0.0092 + 0.0103C_{Al} + 0.00594$ where $C_{Si} = C_{Al} = C$ *we have,*

$A_{Abia} = 0.0263C + 0.015$

AKWA - IBOM

Silicon			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.004	0.0008	0.04
0.40	0.011	0.0044	0.16
0.60	0.016	0.0096	0.36
0.80	0.023	0.0184	0.64
2.00	**0.054**	**0.0332**	**1.56**

$Ak_{Si} = 0.0153C_{Si} + 0.00468$

Aluminium			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.002	0.0004	0.04
0.40	0.007	0.0028	0.16
0.60	0.009	0.0054	0.36
0.80	0.014	0.0112	0.64
2.00	**0.032**	**0.0198**	**1.56**

$Ak_{Al} = 0.0092C_{Al} + 0.00272$

$A = 0.0153C_{Si} + 0.00468 + 0.0092C_{Al} + 0.00272$ $\qquad C_{Si} = C_{Al} = C$

$A_{Akwa\ Ibom} = 0.0245C + 0.0074$

IMO

Silicon			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.007	0.0014	0.04
0.40	0.014	0.0056	0.16
0.60	0.019	0.0114	0.36
0.80	0.026	0.0208	0.64
2.00	**0.066**	**0.0392**	**1.56**

$A_{Si} = 0.017C_{Si} + 0.0064$

Aluminium			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.004	0.0008	0.04
0.40	0.007	0.0036	0.16
0.60	0.011	0.0066	0.36
0.80	0.016	0.0128	0.64
2.00	**0.04**	**0.0238**	**1.56**

$A_{Al} = 0.0103C_{Al} + 0.0039$

$A_{Imo} = 0.017C_{Si} + 0.0064 + 0.00103C_{Al} + 0.0039$ $\qquad C_{Si} = C_{Al} = C$

$A_{Imo} = 0.0273C + 0.0103$

RIVERS

Silicon			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.005	0.001	0.04
0.40	0.012	0.0048	0.16
0.60	0.017	0.0102	0.36
0.80	0.024	0.0192	0.64
2.00	**0.058**	**0.0352**	**1.56**

$A_{Si} = 0.016C_{Si} + 0.0052$

Aluminium			
C	**A**	**CA**	**C^2**
0.00	0.00	0.00	0.00
0.20	0.003	0.0006	0.04
0.40	0.008	0.0032	0.16
0.60	0.010	0.006	0.36
0.80	0.015	0.012	0.64
2.00	**0.036**	**0.0218**	**1.56**

$A_{Rivers} = 0.016C_{Si} + 0.0052 + 0.0097C_{Al} + 0.0033 \qquad C_{Si} = C_{Al} = C$
$A_{Rivers} = 0.0257C + 0.0085$

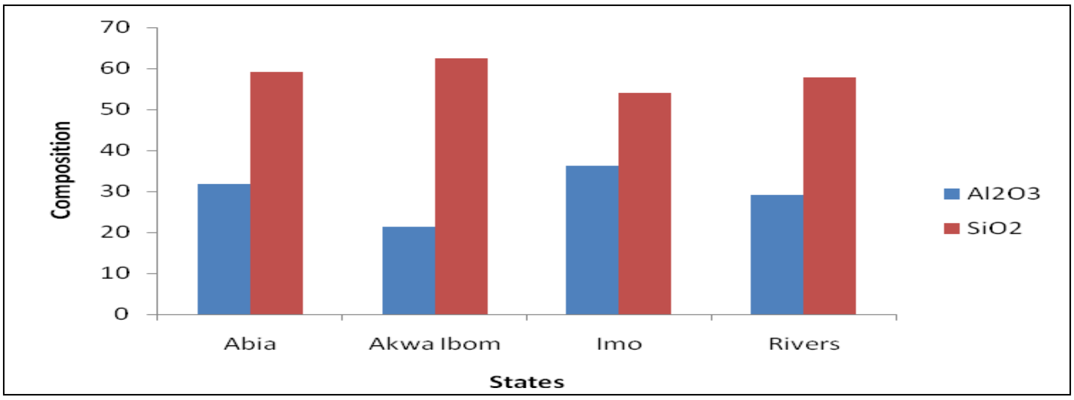

Fig 5: Atomic Absorption Spectrophotometer (AAS) Analysis of the Clay Samples

From Table 2, the alumina-silica ratio of Abia is 0.54; 0.34 for Akwa Ibom; 0.67 for Imo and 0.50 for Rivers. Table 1 contains the experimental result of concentration and absorbance of metals in Kaolinite clays from the four Niger Delta states. From previous literature, Si and Al are the chief constituent metals with very high content in clay minerals particularly Kaolinite clay. Therefore, Aexp= AlAl+ AlSi

Table 2: Composition of AL_2O_3/SiO_2 in fired Clay Samples (AAS)

Composition (%)	Abia	Akwa Ibom	Imo	Rivers
AL_2O_3	31.8	21.3	36.2	29.18
SiO_2	59.2	62.47	54.10	57.86
AL_2O_3/SiO_2 Ratio	**0.54**	**0.34**	**0.67**	**0.50**

V. Conclusion

Clays from four Niger Delta States in Nigeria have been characterized for refractory applications. Results of chemical and mineralogical analyses confirmed that the clays are kaolinitic. Physical and service properties tests confirmed that two of the clays (Abia and Imo) possess such refractory qualities that they can substitute imported fireclay refractories used in some metallurgical, ceramic, chemical and allied industries. The two clays belong to the medium duty fireclay class of aluminosilicate refractories. They are therefore suitable for processing refractory bricks needed for lining the walls of furnaces, soaking pits, ovens, ladles, crucibles and kilns. Akwa Ibom clay was found to belong to the semi-acid or semi-silica class of aluminosilicate refractories. However, blending with a more plastic-clay may be required to improve its properties. Rivers clay, though high in alumina content (26.22%), is not very good as a refractory because of its very poor thermal shock resistance. It should, therefore, be processed for other uses like fertilizer, paint, paper, etc. It is concluded that the incorporation of inert additives like grog or chamotte is imperative for optimum performance of refractory clays and that the quantity of grog in the moulding mass should increase with the plasticity of the clay. These clays can be beneficially processed and exploited for other industrial uses besides refractory bricks. Abia, Imo, and Rivers can be used as sources of alumina (via acid leaching) and hence, aluminium.

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