
Development of Aluminosilicate Refractory Crucibles from the Optimum Mix of Awo Quartz and Ikere Ekiti Clays

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ABSTRACT

Refractory needs in Nigeria are enormous but have not been fully met owing to over-reliance on importation. This has necessitated researches channeled towards local production of refractory materials in the country. In this research, the suitability of the quadraxial blend of Awo quartz, and Ikere Ekiti clays (ball clay and kaolin / kaolin grog) for refractory crucible production was tested. The test samples were fired in a gas kiln up to 1300°C for 6 hours. After firing, the optimum mix was determined by subjecting the test samples to standard tests such as linear shrinkage, water absorption, compressive strength and refractoriness. The result showed linear total shrinkage between 5.8%-11.77%; water absorption rates of 8.82%-18.51%; and refractoriness of 1698.5°C-1740.9°C. All the samples showed good refractoriness above 1300°C and ability to maintain good resistance to thermal shock. The optimum mix of the aluminosilicate materials was used in the development of refractory crucibles which are suitable for use in metallurgical, glassmaking, and ceramics processes.

Keywords: Awo Quartz, Ikere Ekiti Clays, Optimum Mix, Refractory Crucible, Quadraxial blend

INTRODUCTION

Refractories are heat resisting materials that are used where high temperature application is involved. American Standard for Testing and Materials (ASTM C71) defines refractories as non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems that are exposed to environments above 538°C (Folorunso, Olubambi and Borode, 2014). 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 (Aramide and Oke, 2014). Important properties of refractories are: chemical composition, bulk density, apparent porosity, apparent specific gravity and strength at atmospheric temperatures (Bhatia, 2012). The oxides of aluminium (alumina), silicon (silica) and magnesium (magnesia) are the most important materials used in the manufacturing of refractories (Atanda, Adeniji, and Oluwole, 2012).

According to Goski, Doza, DiSaia, and Lawrie (2014) refractory crucible is a type of refractory crucible typically made of various ceramic compositions. Adamu, Giwa and Opoku (2015) revealed that refractory crucibles are used in high temperature heat treatment in foundry applications such as metal, bronze and brass casting, coin minting and ore-assaying, in non-foundry applications as in glass and frit making, in laboratories by chemists as in chemical analysis and ash content determination. The Refractories Institute (1987) revealed that the development of refractories has paralleled the development of ceramic and metallic technology since ancient times, claiming that some refractories in some forms such as crucibles were necessary for metal processing as early as the bronze and iron ages, over 10, 000 years ago.

Adelabu (2012) indicated that a great emphasis is placed on exploiting the abundant solid minerals endowments in Nigeria with a view to diversifying the economic base of the country, improving Gross Domestic Product (GDP) and industrial activity. Unfortunately, there is no major specialized refractory industry in Nigeria despite the fact that there are abundant deposits of these rocks in the country (Lawrence and Ayo, 2012). Metallurgical, glass and ceramic industries are grossly concerned with transformation of solid minerals into useful products and hence hold great potential to thrive in Nigeria. For these industries to thrive in the country there is need for indigenous production of refractories such as refractory crucibles. The reason is that importation is not healthy for the country's economy owing to unfavourable foreign exchange rate. Apeh, Esezobor, and Lawal (2011) observe that huge savings could be obtained if local raw materials are properly exploited and harnessed towards the production of refractories. The refractories need of Nigeria, a developing nation, is potentially enormous (Aye and Oyetunji, 2013). As a result of this more researches are being carried out on the local production of refractory materials. According to Umaru, Aliyu, Mohammed, and Sadiq (2012), in the last few years, there has been an increasing awareness on the scope, and the importance of refractory materials in the industrial development of Nigeria. In the light of the aforementioned, the suitability of the quadraxial mix of Awo quartz, and Ikere Ekiti clays (ball clay, kaolin and kaolin grog) for the development of refractory crucibles was tested in this research.

MATERIALS AND METHODS

Raw Materials used

The raw materials used in this study are quartz, kaolin, ball clay and calcined kaolin. Quartz is the main source of silica for a ceramic body; it has the chemical formula SiO_2 , specific gravity of 2.65 and hardness (Moh's scale) of 7. Addition of quartz makes a clay body more refractory and opens up the body, thereby reducing shrinkage and drying problems. Kaolin is an hydrated aluminum silicate with the chemical formula, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, a specific gravity of 2.2-2.6 and hardness (Mohs' scale) of 2. It is also being referred to as primary clay or china clay. Kashim (2011) indicated that kaolin is the principal raw material needed for the production of technical ceramic items such as refractories; it gives plasticity to enable the body to be shaped and give adequate unfired strength so that it may be handled between the shaping and firing process. Chemically, ball clays are hydrous aluminum silicates, usually containing minor amounts of impurities such as potassium, sodium, calcium, magnesium or iron. Ball clay is essential for

ceramic production because of its high plasticity and strength. Hansen (2008) described calcined kaolin (kaolin grog) as a useful material for refractories and low expansion applications.

Sourcing of Raw Materials

The materials utilized in this study were sourced from Awo and Ikere Ekiti. Awo town is the headquarters of Egbedore Local Government Area in Osun State, Nigeria located on coordinates 7.7667°N and 4.4000°E. Ikere Ekiti is a city in Ikere Local Government Area of Ekiti State in Nigeria located on coordinates 7.5000°N and 5.2330°E. Both locations are situated in South West, Nigeria.

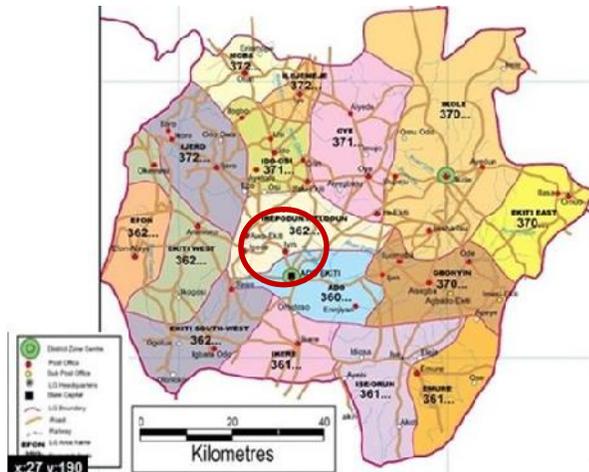


Figure 1: A map showing Ikere Ekiti and other Local Government Areas in Ekiti State, Nigeria.
Source: www.getamap.net/map, 2016.



Figure 2: A map showing Awo town (Egbedore Local Government Headquarters) and other Local Government Areas in Osun State, Nigeria.
Source: nigeriazipcodes.com/3972/local-government-are-in-osun-state/

Preparation of Raw Materials

Kaolin and ball clay were each soaked, sieved and dried. Part of the dried kaolin was calcined in a gas kiln to 1000°C for 6 hours. The resulting raw material, kaolin grog, was crushed, ground and sieved through 600µm and 300µm mesh British Standard Sieve. Quartz was thoroughly washed to remove physically combined impurities, dried and was calcined at 1000°C for 6 hours in a gas kiln. It was allowed to cool and was then manually crushed into pieces using a sledge hammer. It was further broken into smaller grains with the aid of the pulverizer, a type of jaw crusher in the department of Material Science and Metallurgical Engineering, at Federal University of Technology, Akure (FUTA) and was later sieved through 150µm and 75µm mesh British Standard Sieve.

Chemical Analysis of Raw Materials

After beneficiation and processing, the samples of the locally source raw materials were characterized using X-ray Fluorescence Spectrometer at The National Geosciences Research

Laboratories, Kaduna. The result of the X-ray Fluorescence Spectrometry analysis is as shown in Table I.

Table I: Chemical compositions of Ikere Ekiti Kaolin, Ikere Ekiti Ball Clay, Awo Quartz and Ikere Ekiti calcined Kaolin

Oxide	Ikere Ekiti Kaolin	Ikere Ekiti Ball Clay	Awo Quartz	Ikere Ekiti Calcined Kaolin
SiO ₂	58.6	61.9	98.69	52.8
Al ₂ O ₃	32.3	19	-	46.8
Fe ₂ O ₃	1.21	6.86	0.073	0.07
MgO	-	0.08	-	-
CaO	-	0.87	0.455	-
Na ₂ O	0.86	0.62	0.01	0.02
K ₂ O	3.46	4.4	0.11	0.19
MnO	0.027	0.14	0.01	0.01
TiO ₂	0.11	2.01	-	0.01

Source: The result of X-ray Fluorescence Spectrometry Analysis of the locally sourced raw materials carried out at National Geosciences Research Laboratories, Kaduna.

Formulation and Blending of Raw Materials

Carol (2008) explained that quadraxial blend can be used to blend four materials or recipes together. He gave out the layout of the 36 test recipes, given as percentages by weight of each of the four materials named as A-D as shown in the Table II below. This quadraxial blend was adopted for formulating the compositions for this study as follows: A= Ball Clay; B= Kaolin; C= Calcined Kaolin; D= Quartz

Table II: Quadraxial Blend of 36 test recipes

1.	2.	3.	4.	5.	6.
50A	50A	50A	50A	50A	50A
50B	40B	30B	20B	10B	
	10D	20D	30D	40D	50D
7.	8.	9.	10.	11.	12.
40A	40A	40A	40A	40A	40A
50B	40B	30B	20B	10B	
10C	10C	10C	10C	10C	10C
	10D	20D	30D	40D	50D
13.	14.	15.	16.	17.	18.
30A	30A	30A	30A	30A	30A

50B	40B	30B	20B	10B	
20C	20C	20C	20C	20C	20C
	10D	20D	30D	40D	50D
19.	20.	21.	22.	23.	24.
20A	20A	20A	20A	20A	20A
50B	40B	30B	20B	10B	
30C	30C	30C	30C	30C	30C
	10D	20D	30D	40D	50D
25.	26.	27.	28.	29.	30.
10A	10A	10A	10A	10A	10A
50B	40B	30B	20B	10B	
40C	40C	40C	40C	40C	40C
	10D	20D	30D	40D	50D
31.	32.	33.	34.	35.	36.
50A	40B	30A	20B	10B	
50B	50C	50C	50C	50C	
	10D	20D	30D	40D	50C
					50D

Source: Carol (2008)

Olasupo and Borode (2009) in a research on development of refractory ramming mass observed that 10% silica in the composition of the body enhanced low volumetric shrinkage after firing. They asserted that higher silica content will lower the cold compression strength of the mix and present a rough surface to the fired body. In agreement to this, Henrik (1987) stated that the addition of silica makes a clay mixture more refractory; however, items exposed to sudden temperature changes such as refractories should contain as little free silica as possible since some silica expand and contract suddenly at certain temperature. Based on these findings, blends with 30% quartz were considered too high for this study as it could have negative effect on the compressive strength and the thermal shock resistance of the refractory crucibles. Blends 8, 9, 14, 15, 20, 21, 26 and 27 were thus adopted since they consist of four materials as needed in this study. Eight (8) ceramic bodies were formulated as presented in Table III.

Table III: Formulated Ceramic Bodies for Refractory Crucible Production

	A	B	C	D	E	F	G	H
Ball Clay	40	40	30	30	20	20	10	10
Kaolin	40	30	40	30	40	30	40	20
Kaolin Grog	10	10	20	20	30	30	40	40
Quartz	10	20	10	20	10	20	10	20

Production of Refractory Crucibles

Slip casting method was used for the production of refractory crucibles. A drop of sodium silicate, the deflocculating agent was added to the mixed liquid ceramic body. The slurry was poured into the hollow POP mould, bound with rubber band so as to prevent sudden removal and pouring away of the slip. Within about five minutes after pouring, a film of firm clay appeared on the inner surface of the mould. When the desired thickness was developed, the excess slip was poured out. The remaining clay body continued to harden until it shrank away from the mould and the crucible was taken out. The process was repeated until all the prepared slip bodies were used up.

The formed crucibles were kept to dry under normal room condition. This was done in order to keep the drying rate of the crucibles at minimum in order to avoid cracking. Some of the samples began to show signs of drying after 2 days of casting while some lasted for 5 days before showing the sign of drying.

Firing

After drying, the crucibles were loaded to a gas kiln. Preheating was done for three (3) hours so as to preserve the crucibles from breakage in the course of thermal transformation. The firing was then gradually increased at intermittent interval, slowly at first and was later increased to the full firing stage. The refractory crucibles were dried and fired up to 1300°C. This was determined by the bending of the pyrometric cone 10 placed at the peep hole of the kiln. The total firing time was 6 hours. According to Cuesta and Bernardo (1987), 1300°C - 1996°C is the temperature at which alumina (Al_2O_3) in the raw materials react with silica (SiO_2) to form mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).



Figure 3: Slip casting of raw materials for crucible



Figure 4: Leather hard crucibles



Figure 5: Fired refractory crucibles

Mechanical Properties of the produced Refractory Crucibles

100g of each of the selected compositions was weighed and was thoroughly mixed, after which 10cm³ of water was added and mixed until it became considerably plastic and was then moulded into test samples of 70 mm x 40 mm x 15mm each. The wet length of each of the test samples was measured and after they were completely dried, the dry length was also measured and recorded. They were then fired in a gas kiln for 6 hours to 1300°C after which the fired length was measured and recorded.

Linear Drying Shrinkage

The Drying Shrinkage was calculated using the formula (ASTM C326-03, 2003):
 Drying Shrinkage = $\frac{L_w - L_d}{L_d} \times 100\%$, where L_w = wet length and L_d = dry length

Linear Firing Shrinkage

The Firing Shrinkage was calculated using the formula (ASTM C326-03, 2003):
 The Firing Shrinkage = $\frac{L_d - L_f}{L_d} \times 100\%$, where L_d = dry length and L_f = fired length

Linear Total Shrinkage

The Total Shrinkage was calculated using the formula (Oladiji *et al*, 2010):
 The Total Shrinkage = $\frac{L_w - L_f}{L_w} \times 100\%$, where L_w = wet length and L_f = fired length

Water Absorption

The water absorption test was conducted by boiling the fired test samples at 100°C for 24 hours, followed by an additional soaking in water for 4 hours. Water absorption was calculated as a function of the sample’s weight difference prior to and after water submersion using the formula (ASTM C20-00, 2010):

$$\text{Water absorption} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s = soaked weight after boiling at 100°C for 2 hours and W_d = dry weight

Refractoriness

The refractoriness of the refractory crucible was estimated using Shuen’s formula (Odewale, Obika and Tse, 2015):

$$K = \frac{360 + Al_2O_3 - RO}{0.228}$$

where, K = Refractoriness (°C), Al_2O_3 = Alumina Content in the clay, RO = Sum of all the oxides beside SiO_2 in the clay (or materials) 360 and 0.228 are constants.

Table IV: Summary of the standard tests carried out on the test samples

Sample	Linear Drying Shrinkage (%)	Linear Firing Shrinkage (%)	Linear Total Shrinkage (%)	Water Absorption (%)	Refractoriness (°C)
A	4.29	7.46	11.75	8.82	1711.1
B	5.71	6.06	11.77	11.30	1693.5
C	5.71	6.06	11.77	13.54	1725.6
D	4.29	4.48	8.77	15.13	1709.3
E	4.29	7.35	11.64	15.77	1740.9
F	4.29	7.46	11.75	16.43	1723.8
G	4.29	4.48	8.77	17.48	1715.5
H	2.86	2.94	5.8	18.51	1698.5

RESULTS AND DISCUSSION

As it can be observed from Table I, Kaolin contained 58.6% silica (SiO_2), 32.3% alumina, 3.46% potassium oxide (K_2O) and 0.86% sodium oxide (Na_2O) respectively. The coloured oxides present are 0.027% manganese oxide (MnO), 0.11% titanium oxide (TiO_2) and 1.21% iron (III) oxide (Fe_2O_3) respectively. Ball clay contained 61.9% silica (SiO_2), 19% alumina, 4.4% potassium oxide (K_2O), 0.62% sodium oxide (Na_2O), 0.08% Magnesium oxide (MgO) and 0.87% calcium oxide (CaO) respectively. The coloured oxides present are 0.14% manganese oxide (MnO), 2.01% titanium oxide (TiO_2) and 6.86% iron (III) oxide (Fe_2O_3) respectively. Quartz contained 98.69% silica (SiO_2), 0.11% potassium oxide (K_2O) and 0.01% sodium oxide (Na_2O), 0.455% calcium oxide (CaO) respectively. The coloured oxides present are 0.01% manganese oxide (MnO) and 0.073% iron (III) oxide (Fe_2O_3) respectively. Calcined kaolin contained 52.8% silica (SiO_2), 46.8% alumina, 0.19% potassium oxide (K_2O) and 0.02% sodium oxide (Na_2O) respectively. The coloured oxides present are 0.01% manganese oxide (MnO), 0.01% titanium oxide (TiO_2) and 0.07% iron (III) oxide (Fe_2O_3) respectively.

Silica exists as oxide of silicon in nature (SiO_2) which mainly occurs in quartz, sand and many other minerals. There can be other impurities incorporated in quartz but it generally has a high percentage of silica. The high content of silica in Awo quartz shows a significantly high level of purity of the material. Ikere Ekiti kaolin and ball clay show the quality of good aluminosilicate materials with relatively high percentage of silica and alumina and low impurities. The coloured oxides in the ball clay are expectedly higher than that of the kaolin. It can thus be inferred that Awo quartz and Ikere Ekiti ball clay and kaolin are good raw materials suitable for the production of aluminosilicate refractories.

Table IV shows the mechanical properties of the test samples as follows; A, B, C, D, E, F, G and H have total shrinkage of 11.75%, 11.77%, 11.77%, 8.77%, 11.64%, 11.75%, 8.77% and 5.8% respectively; water absorption rates of 8.82%, 11.30%, 13.54%, 15.13%, 15.77%, 16.43%, 17.48% and 18.51% respectively; and refractoriness of 1711.1°C, 1693.5°C, 1725.6°C, 1709.3°C, 1740.9°C, 1723.8°C, 1715.5°C and 1698.5°C respectively. This indicates that sample G has the lowest total shrinkage (5.8%) while B and C have the highest total shrinkage (11.77%). Sample A has the lowest water absorption rate (8.82%) while G has the highest water absorption rate (18.51%). Sample B has the lowest refractoriness (1693.5°C) while Sample E has the highest refractoriness (1740.9°C). All the eight samples show good refractoriness above 1300°C, and ability to maintain good resistance to thermal shock. Nevertheless, sample E gave the optimum composition for the production of refractory crucible since it has the highest rate of refractoriness. Therefore, Sample E was used for the development of refractory crucibles.

CONCLUSION

Four blended ceramic raw materials which include kaolin, ball clay, calcined kaolin and quartz can be used to produce refractories of good mechanical properties. All the Eight (8) different aluminosilicate compositions showed desirable mechanical properties. However, sample E which consists of 20% ball clay, 40% kaolin, 30% calcined kaolin and 10% quartz was found to be the optimum mix suitable for the production of refractory crucibles.

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