CERAMICS

MATERIAL SPECIFICATIONS FOR THE PRODUCTION OF HIGH DENSITY REFRACTORY BRICK WITH LOCALLY AVAILABLE HIGH ALUMINO-SILICATES

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ABSTRACT

An attempt was made to select refractory alumino-silicates and high alumina bearing minerals available in the country to develop dense refractory bricks for the metallurgical industries. Selective properties such as chemical analysis, mineralogy, % apparent porosity, cold crushing strength, pyrometric cone equivalent (P.C.E) were looked at with the view of finding out the best material for the development of dense refractories.

Awaso bauxite and Cape Coast clay were selected. Material specification, processing requirement, production and testing methods were reviewed. Cape Coast clay was successfully bench marked against known fireclays. The results obtained from the use of Awaso bauxite revealed that though Awaso bauxite has very high alumina content the bricks produced from it suffer very high re-heating shrinkage indicating low mineral stability in the grog. However, Cape Coast clay based bricks at 1350°C were found to have adequate properties with mullite crystallline phase which is decisive for high temperature behaviour of the bricks – a guarantee in service conditions and very comparable to the properties of refractory bricks from the U.K. Finally it was established that the higher the % apparent porosity the higher the re-heating shrinkage of the bricks produced from such compositions.

Keywords: *Re-heating shrinkage, apparent porosity, refractory, chemical and mineralogical analysis.*

INTRODUCTION

Refractories serve as the backbone to the growth and development of ferrous and non-ferrous industries as well as chemical plants, ceramic and glass industries. Structural and chemical inertness are the prime requirements in order to withstand various atmospheres from the high heat treatment of these industries. X-ray diffraction analysis usually reveals a comparatively high proportion of an amorphous phase (30-60%) usually specified as glass and some micro-crystalline phases. For use of bricks as lining materials the development of mullite and cristobalite are decisive for continuous use at high temperatures.

CLASSIFICATION OF REFRACTORIES

According to their chemical behaviour, refractories can be classified into three main types namely acid, basic and neutral [1]. The environment of production usually imposes strict material properties on the use of the refractories. For example, acid refractories are those that are easily attacked by basic slags. These include alumino-silicate refractories. Another group are the basic refractories which are attacked by acid slags and include alumina refractories and magnesite and dolomite refractories.

In Japanese industries, the material pyrophyllite is an added material principally to enhance the performance of fireclay bricks against slags. This is a siliceous material very close to our high silica clays. Therefore, it is not a major requirement here in Ghana.

Generally, most authorities [1, 2, 3] on refractories agree that the composition is of large grog or refractory – grain particles cemented together by a fine-grained clay bond.

A recent market survey carried out on behalf of the TCC/ITC of UK [4] identified the massive increase in the use of fireclay refractories in our metal industries. These are all imported into the country in large quantities.

FIRECLAY REFRACTORIES

Fireclay refractories are divided into several groups according to their properties and quality.

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For the development of this type of refractories, chemical analysis, apparent porosity and mineralogy are prioritised requirements since other properties can be deduced from the results.

The groupings of fireclay is done in relation to the quantity of Al_2O_3 in the material. The more the Al_2O_3 the higher the service temperature of the brick.

GROUP 1

This consists of fireclay 25-45%, Al_2O_3 refractories of 1600-1750°C. The Cape Coast clay was found among the Ghanaian raw materials appropriate for the production in this category.

GROUP 2

The make up of this group is fireclay enriched with calcined and fused alumina (Al_2O_3 50-60%). The refractories are approximately 1800°C, and working temperature of 1500°C. The Awaso bauxite falls into this category.

GROUP 3

This group represents sillimanite and mullite refractories containing 60-75% Al_2O_3 (also called high alumina refractories). These materials are available in the country in large quantities. The major limitation is the high temperature needed in stabilizing the grog. Sillimanite as a group name is justified only as regards the final raw material because the products always contain mullite. Naturally Kyanite which undergoes extensive expansion when inverted to mullite is normally calcined to 1350°C at which it expands by 17% [5]. Lower expansion is exhibited by sillimanite and still lower expansion by andalusite. These raw materials assume the function of grog, which however is not as chemically and mineralogically inert as fireclay. However, their expansion during inversion to mullite compensates for shrinkage of the clay component which takes up 10% of the mixture. The Al_2O_3 content in the minerals of the sillimanite group is theoretically 63% which correspond to a mullite yield of 86% [6].

In addition to the above, more advanced refractories of a new generation of materials are now available. Some of these are high alumina refractories modified with ZrO_2 additions up to 20%. These are fusion cast of the $Al_2O_3 - Si_2O_2 - ZrO_2$ systems which do not contain any glassy phase. These refractories are outstanding for their thermal shock resistance with their low thermal conductivity. They are usually the refractories used for development of assay crucibles and used extensively at the high stressed parts of glass and metallurgical furnaces.

The following table gives an overview of the nature and material properties of available refractories.

Table 1: Grouping for Alumino – Silicates

Type	Name	Composition	Class
Silica	High duty silica	98% SiO_2 0.7-1.5% Al_2O_3	Acid
	Semi silica	10-25%Al_2O_3	Acid
Alumina Silicates	Silicious Firebricks	25-32% Al_2O_3	Acid
	Common Firebrick	32-38% Al_2O_3	Acid
	Aluminous	38-45% Al_2O_3	Nr Neutral
	Kaolinite	45-50% Al_2O_3	Nr Neutral
High Order Alimina-Silicates	Sillimanite	45-65% Al_2O_3	Neutral
	Mullite	65-75% Al_2O_3	Neutral
High Alumina	Bauxite base	75-90% Al_2O_3	Amphoteric
	Corundum	90-100% Al_2O_3	Amphoteric

Table 2: Main types of refractories

Material	Chain-Composition Wt%	Prevailing Phase	Raw Material
Silica	93-97 SiO_2 0.2-2.5 CaO	Tridymite Cristobalite	Quartzite
Fireclay	15-46 Al_2O_3 50-80 SiO_2	$3(Al_2O_3)$ $2(SiO_2)$Mullite & glass	Clay
Sillimanite Mullite	60-75 Al_2O_3 25-40 SO_2	Mullite Al_2O_3	Sillimanite Kyanite and Clay
Corundum Corundum	80-98 Al_2O_3 0-18 SiO_2	Al_2O_3 Corundum	Corundum Clay

The purpose of this reviewed literature is to critically look at fireclay and high alumina bricks from available materials in the country and formulate a possible recipe for its proper development, production and use.

EXPERIMENTAL METHODS

(a) Forming of bricks

Finely processed Cape Coast clay designated as (CCC) Awaso bauxite also designated as AwB and Adankwame kaolin were batched up as indicated in Table 9. The mixture was then pugged and aged for 36 hours so that the water was absorbed by the clay and also to evenly hydrate the particles of the grog component. Forming was carried out by mechanical pressing up to 70 tons. About 7-9% water was used in the moulding. Firing was carried out in electrically powered kiln under full oxidising atmosphere for 12 hours to 1450°C and 1350°C respectively.

(b) Apparent porosity

Test specimens measuring 6.5cm x 6.5cm x 4cm were cut from the core of the fired refractory bricks using a cutting wheel. They were cleaned of any dust or loose particles adhering to its surface. The specimens were then dried in an oven at 110°C to a constant weight (D) with an accuracy of $\pm$ 0.1gm. The dried specimen was suspended in distilled water such that the specimen did not touch the bottom or sides of the container. It was boiled for two hours and while still suspended in water, cooled to room temperature and its weight (S) recorded. The specimen was removed from the distilled water and excess water was wiped off from its surface by lightly blotting it with a wet towel and then weighed in air (W). The apparent porosity (P) was calculated from the formula:

$$AP\% = \frac{\text{Volume of open pores of sample}}{\text{Total volume of sample}} - \frac{W-D}{W-S} \times 100$$

(c) Cold Crushing Strength

Test specimens were cut from the standard Awaso bauxite brick and Cape Coast based bricks. The test specimens were kept in between 5mm thick asbestos fibreboards to prevent any chippings while in the centre of a hydraulic compression-testing machine. The maximum stress required to crush the brick was recorded. A formula was then used to calculate the compressive strength

$$C = \frac{W}{A \times B}$$

where W is the maximum load (stress) A, B are the lateral and side dimensions of the pressure surface, C is the mean crushing strength.

(d) Pyrometric Cone Equivalent (PCE)

One kg of the material as a composite sample was crushed first in a jaw crusher then in a porcelain mill. The product was passed through a 20 micron sieve. The material was mixed with the desired quantity of water and an alkali free dextrine glue to a consistency that can be moulded. The mixture was then moulded into test cone which resembles a tetrahedron with 7mm (0.272") sides on the base and 27mm (1.081") height. The formed product was fired to hardness at 1000°C. During testing each cone was fixed on a plaque forming an angle of 82° with the horizontal. Standard segar cones were chosen as reference cones.

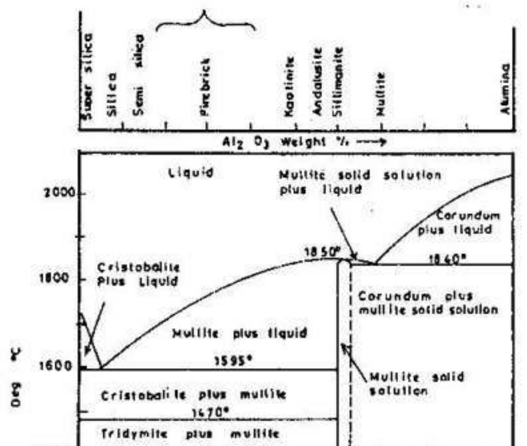

Figure 1: Silica – Alumina Binary System

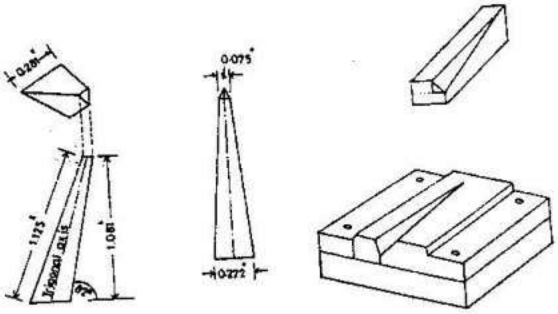

Figure 2: Standard pyrometric cone and split mould for making test cones Ref IS. 1528 of 1974 Part I

(e) Refractoriness under load

The test specimen comprises a cylinder of 50 ± 0.5mm diameter and $50 \leq 0.5$mm height. The sample dimensions were achieved by cutting, boring and grinding of the refractory. Heating was carried out in an electrical furnace consisting of a refractory tube of 100-120 ID, 120-150mm OD and about 500mm length. The specimen positioned in the furnace between carbon and mullite rods with about 5mm thick carbon plates interposed between the test specimen and the rods. A load of 2 Kgf/cm^2 was applied to the specimen. The results were automatically plotted by the R.U.L. heating furnace/plotter. The temperature was measured by an optical pyrometer.

(f) Permanent linear change

A specimen of 5cm x 5cm x 12.5cm was cut by a cutting off wheel from the refractory bricks under testing. The volume of the specimen was determined before heating in an oxidising atmosphere. The temperature was measured by a platinum, platinum-rhodium thermocouple up to 1450°C. After holding the test specimen at the maximum desired temperature, it was cooled to room temperature over 10 hours in the closed kiln itself. The test specimen was then removed from the kiln, and its volume measured again. The linear change was then calculated.

$$\text{Linear change (\%)} = \frac{\text{Fired length} - \text{original length}}{\text{Original length} \times 100}$$

(g) Spalling Resistance

Two samples each of Cape Coast based bricks and Awaso bauxite based bricks were placed in a pre-heated furnace at 1000°C. After every 15 minutes of heating a brick was removed from the furnace and cooled with forced air whilst another was introduced into the kiln. The exterior surfaces as well as micro and macro cracks were examined on the surface of the bricks and recorded. Each sample was taken through 10 cycles of heating and cooling the bricks.

(h) Chemical Analysis

Materials entering into refractory compositions needed to be as refractory as possible. Fluxing agents and impurities lower refractoriness. All the local materials investigated were screened by X-ray fluorescence spectrophotometry.

(I) X-ray Diffraction

Samples from the manufactured bricks were tested for the presence of mullite and cristobalite and other minerals. The inter planer distance corresponding to the peaks were matched with data provided in the files of the Joint Committee on Power Diffraction Standards (JCPDS).

RESULTS AND DISCUSSIONS

Materials Specifications

The manufacture of local refractory bricks was based on the alumino-silicates and bauxite. The essential material components of the bricks under investigation are:-

(a) Plastic Cape Coast clay;
(b) Pre-calcined Cape Coast clay (grog);
(c) Adankwame kaoline from the Ashanti Region; and
(d) Awaso Bauxite (grog)

From the available literature earlier on stated, Cape Coast clay has in it the Alumina content of 29.30% which is within the range of 15-46% as agreed on by most authorities. The other brick composition was based on Awaso bauxite 60.20% with Cape Coast clay as binder and Adankwame kaolin. From the percentage composition of the Al_2O_3, it is clear that the temperature of the grog calcination should be high. The temperature of calcination used here for the Bauxite grog production was 1450°C. The Cape Coast clay when fired to 1350°C for 2 hours shows no iron spots, blisters melt holes etc. [7]. The indication here is that the impurity content especially Fe_20_3 is low which is an important material requirement for fabrication of the bricks. In addition to the above, the alkalis and basic oxides which are usually harmful elements since they cause the formation of double silicates at lower temperatures are low. This, inter alia, gave us the confidence to benchmark our clay to known fireclays. Table 3 summarises the fine elements in the chemical analysis.

The total alkalis in the Cape Coast clay is 1.72% ref. Table 3. According to the available literature already deduced, the alkalis if present in excess of 1-2.5% may cause serious vitrification and lead to shrinkage and spalling in service. The other impurities e.g. titanium oxide, lime and magnesia have less effect. From the foregoing Cape Coast clay approximates quite closely to the known fireclays used in the manufacture of refractory bricks. To justify the inclusion of Adankwame kaolin into the composition, it is accepted that modern techniques demand the use of more than one type of clay. The desired properties of bricks are obtained by blending one clay with the other. Adankwame clay actually imparted a bleaching effect on the harsh colour of Cape Coast clay mainly because of its low iron content and high silica as it protects the bricks from excessive slag attack during use.

Grog Specification

One very important quality of a refractory brick is the nature and stability of the grog. The higher Al_20_3 content of the Awaso bauxite the higher the temperature of calcination [1, 2, 3]. The temperature of 1450°C was necessary to give lower firing shrinkage. The 6.70% of Fe_20_3 as found in this bauxite did not appear to lower its refractoriness in any way at all. This was confirmed by % apparent porosity measurements as in Table 7.

CCC and AwB were pelletised by judicious addition of water in a pan mill with rotation speed of 10 r.p.m and calcined to 1350°C and 1450°C respectively. The pelletised size was not more than 20mm. This enabled the heat to be uniformly distributed over the entire pellets. Since the grogs were intended to be used to prevent shrinkage the final shape was very important. The angular shapes which were very necessary were obtained by the use of a grinder instead of a ball mill. Rounded particles as obtained when ball-mills are used are avoided because of their decreased bonding capacity [1]. The temperature of 1450°C was the highest attained with the available facilities. From the % apparent porosity of the AwB it was clear that higher temperatures were more desirable than lower ones. This could have reduced the % AP hence a good chemical stability of the grog.

Process Specification (Forming)

Finely processed Cape Coast clay and Awaso bauxite according to the under listed recipe were mixed and pugged and aged for 36 hours so that the water was absorbed by the clay and distributed uniformly throughout the mass. Forming was carried out by mechanical pressing with a force of up to 70 tons. About 7-9% water was used in the case of the machine moulding.

Table 3: Chemical analysis of Alumino Silicates

Compound	Yorkshire fire clay	Indian fire clay % by Wt	Cape Coast clay % by Wt
Al_2O_3,	15.5-3.0	26-38	29.30
SiO_2	53.4-76.5	48-61	53.50
Fe_2O_3	0.8-2.8	0.6-2.5	2.8
TiO_2	1.0-1.6	Trace – 1.8	0.95
CaO	0.2-0.5	Trace – 1.3	0.13
Na_2O	0.1-03	Alkalis 0.15-0.9	0.3
MgO	-		0.36
K_2O	0.7-2.7		1.42
L.0.I.	5.3-12.6		11.05
Kaolinite	28.7-68.4		60.34
Mica	6.5-27.8		5
Quartz	19.0-58.0		10

Table 4: Chemical analysis of Adankwame Kaolin

Compound	% by weight
Al_2O_3,	17.80
SiO_2	72.50
Fe_2O_3	0.64
TiO_2	0.95
CaO	0.16
MgO	0.25
K_2O	2.31
Na_2O	0.14
L.0.I.	5.23

Table 5: Physical properties of Adankwame Kaolin

Mesh No.	Residue %	Temp °C	Shrinkage %	Strength (P.S.I) (M.O.R)	Apparent Porosity %	Atterberg
85	0.5	110	2		37.7	L.I 44.5
		1100	2		46.7	P.L 35.2
		1200	2	29.8	46.7	P.S 9.3
		1300	2	39.6	46.1	

Table 6: Chemical Analysis of Awaso Bauxite

Compound	% by weight
Al_2O_3,	60.20
SiO_2	0.81
Fe_2O_3	6.70
TiO_2	2.16
CaO	0.01
MgO	0.01
L.0.I.	29.90

Table 7: % Apparent porosity and % moisture absorption

Temperature	CCC grog		AwB grog	
	% MC	% AP	% MC	% AP
1250	12.8	25.9	40.1	79.7
1300	12.3	25.3	39.3	77.0
1350	8.0	17.85	38.3	76.6
1450			27.9	54.7

C CC = Cape Coast Clay grog
AwB = Awaso Bauxite

Table 8: Grog specification

CCC and AwB grogs were fired to 1350°C and 1450°C respectively and sieved as follows:-

45% Coarse	16 mesh
10% Medium	30 mesh
45% Fine	60 mesh

This classification gave us the highest packing density.

Table 9: Material composition

Material	Composition % by wt.	Grading	% Passing through various meshes
Cape Coast Clay (powder)	20	20 mesh	Passing through 75μ mesh
Adankwame Kaoline (powder)	20	40 mesh	Passing through 125 μ mesh
Cape Coast Clay grog		50% Coarse	16 mesh
		10% Medium	30 mesh
Bauxite grog	60	40% Fine	60 mesh

Table 10: Properties of high alumina bricks developed

	Results	
	Cape Coast baked brick	Awaso Bauxite baked brick
Apparent porosity %	25	30
Cold crushing strength (N/mm²)	15	10
Pyrometric Cone equivalent (No.)	18	32
Refractoriness under load	1300	1300
% Permanent linear change Spalling resistance	± 1.5 after heating at 1400°C for 5 hours10 cycles	± 1.5 after heating at 1400°C for 5 hours 10 cycles

The ageing and processing of the Cape Coast clay through 200 mesh gave us very good sintering property in the matrix. The reaction between the Cape Coast clay and Adankwame kaoline with the AwB helped to reduce the final percentage apparent porosity of the brick to 30% which was considered adequate. The testing of the final brick is reported in Table 10.

SPALLING RESISTANCE

Results of this investigation revealed very comparable results with imported bricks from Europe. For the spalling resistance, no material losses were experienced during the 10 cycles which shows the quality of the Ghanaian raw materials.

X-ray Analysis

The calculated d-spacing of the speaks on the diffractograms of the fired bricks were related to the data of the JCPDS for the Cape Coast based bricks, the presence of mullite and cristobalite were very pronounced. However there were few low peak of quartz. This diffractogram is shown in Figures 2 and 3.

The formation of mullite and cristobalite at a temperature of 1350°C with the Ghanaian raw materials is very encouraging. The processing and the recipe formulated could be the main features of formation of such stable forms of cristobalite and alumino sillicates. In most available literature mullite is known to be established at temperature above 1450°C. But it was not so in the investigation.

In the bricks composed with Awaso bauxite, the XRD revealed astonishingly high peak of quartz. This could be explained in a sense that the conversion of quartz to cristobalite was not completed. Generally, ceramic transformations are very sluggish and depends on a variety of factors i.e. particle size, presence of mineralizers and temperature. In this investigation, it would appear that the high $A1_20_3$ content of the Awaso bauxite with very low $Si0_2$ needed very high temperature before very stable phase of corundum and mullite could be established. The high re-heating shrinkage of this brick could be related among other factors to the unconverted quartz to cristobalite which would have high shrinkage during thermal treatment

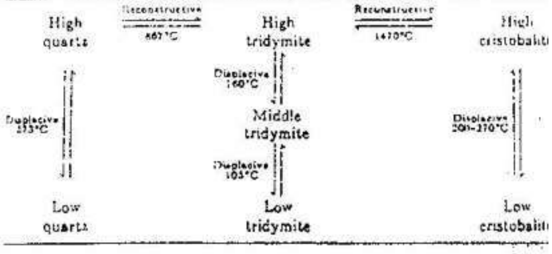

Figure 3: Polymorphic Forms of Silica

Another important consideration here is the displacive transformations between high and low temperature forms of each basic structure, as shown in the table above, which occur rapidly and cannot be restrained from taking place. In refractories, and other ceramic bodies the high low quartz transformation usually involves a substantial volume change, which inevitably leads to fracture of the quartz grains with reduction in the strength.

Re-heating shrinkage if high in the bricks as in the bauxite based bricks would produce high dimensional changes on the kiln wall whilst in use leading to gaps in the kiln structure, which increases heat loss through the kiln structure. This eventually would lead to poor efficiency of the kilns/furnaces and inefficient temperature distribution in the entire kiln e.g. some parts of the kiln would fire higher than other parts which would affect the products.

CONCLUSION

1. The stability of the brick during servicing depends on the temperature of calcination of the grog.
2. The moisture absorption of Alumino-silicates is twice the apparent porosity which is related to the $A1_20_3$ content of the bricks as well as the temperature of calcination of the grog.
3. The re-heating shrinkage is directly proportional to the apparent porosity of the bricks; the higher the % AP the greater the re-heating shrinkage.

4. Awaso bauxite has very high Alumina content therefore needed excessive temperatures of calcination to bring down the % AP. hence the production of quality bricks.

5. The cold crushing strength is indirectly proportional to the % apparent porosity and the alumina content.

6. The addition of Adankwame kaolin to the recipe helped in the promotion of mullite in the bricks as well as bleaching the harsh colour of the Awaso bauxite and the Cape Coast clay.

7. Strength at elevated temperatures, resistance to slag attack and many other properties identified here depends on the formation of cristobalite and mullite.

8. Ageing of the composition before moulding increases their plasticity. Therefore the 20% addition (CCC) to the recipe was enough to render the recipe workable during forming.

ACKNOWLEDGEMENT

The author would like to acknowledge the financial and technical back-up given us on this project by Technology Consultancy Centre, U.S.T. and Intermediate Technology Consultant, U.K. My sincere thanks go to Mr. Tuneyuku Nabeta of Mino Yogyo Refractory Ceramics, Japan for placing their equipment at my disposal in the testing and in the mineralogical work.

Finally, I would like to mention the services of Mr. Kofi Boateng and Mr. J. A. Donkor who performed some of the physical analysis with me.

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