"THE STUDY OF THE REFRACTORY PROPERTIES OF SOME NIGERIAN CLAYS"

BY

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DECLARATION

I, Hassan Suleman Bolaji, declare that this thesis is solely composed by myself and that it is the result of my own work. It has never been submitted and accepted anywhere for any higher degree. All literature cited have been duly acknowledged in the reference.



S.B. Hassan

June, 1990

CERTIFICATION

This thesis entitled "THE STUDY OF THE REFRACTORY PROPERTIES OF SOME NIGERIAN CLAYS" by HASSAN SULEMAN BOLAJI meets the regulation governing the award of the degree of Master of Science (Production Engineering) of Ahmadu Bello University, and is duly approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to those who have once cared, or who now care, and those who are to care, to give my life a purpose and its reason to be.

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ABSTRACT

Refractories are of immense importance in the metallurgical industries. Fireclay refractories, which are normally manufacture from mainly clays are the commonest type of refractory materials. These materials are imported in increasing quantities.

As a first step towards the local production of refractory bricks for metallurgical furnaces, clays from Oshielle, Bauchi and Onibode were collected and tested.

Onibode clays were powdery in texture while the other clays were harder and in lump.

Mineralogical analyses showed that Onibode clays contained the highest amount of kaolin of the clays. Chemically, the clays had Al_2O_3 and SiO_2 in the normal range for Alumino-silicate refractories, though the Bauchi clay had the highest silica content.

All the clays contain Fe_2O_3 except the Bauchi clay, and which gave the fired bricks the brownish appearance. Only Bauchi clay burnt white.

The following refractory properties of bricks produced from all the four clay samples were tested:

(1) Linear shrinkage

(2) Bulk and solid density

(3) Apparent porosity

(4) Cold crushing strength

(5) Thermal spalling resistance

(6) Refractoriness (Fusion)

(7) Refractoriness Under Load (R.U.L)

All the refractory properties of the bricks made from Onibode clays were found satisfactory with respect to most metallurgical requirements. Bricks produced from Oshielle and Bauchi clays had most of its properties being satisfactory. However, the thermal spalling resistances of the bricks from Oshielle and Bauchi clays were found to be low. Bricks produced from Bauchi clay had the highest apparent porosity, and slightly outside the range for dense refractory bricks.

The rising temperature behaviours of all the four clays showed that they can all be utilised in metallurgical furnace applications at operating temperatures up to 1500^{o}C.

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LIST OF ABBREVIATIONS

AAS : Atomic Absorption Spectrophotometry

ASTM: American Society for Testing and Materials

BSI : British Standards Institution

DSC : Delta steel company, Aladja, Warri

DTA : Differential Thermal Analysis

LOI : Loss on Ignition

MOR : Modulus of Rupture

PCE : Pyrometric Cone Equivalent

RUL : Refractoriness - Under - Load

CHAPTER ONE

INTRODUCTION

Refractory materials are generally considered as inorganic materials, consisting of mixtures of oxides obtained from naturally occuring minerals and capable of withstanding very high temperature conditions without an undue deformation, softening or change in composition (ASTM (1975)). They include aluminosilicates, silica, magnesite, chrome, chrome-magnesite, carbon and dolomite refractories. Others are zirconia, carbides, nitrides, silicides, borides and their compounds. Fireclay refractories are aluminosilicate refractories produced mainly from clays which have alumina content between 25 to 45%. They are probably the first refractories used by man and are the most commonest type of refractory materials.

It is generally accepted that high temperature processes considered here as those taking place above the red-heat, require refractory materials. In this respect, over 80% of the total refractory materials are being consumed by the metallurgical industries for the construction and maintenance of furnaces, kilns, reactor vessels and boilers. The remaining 20% being used in the non-metallurgical industries such as cement, glass and hardwares industries.

The most important aspects of a refractory material are that it must be able to provide necessary thermal properties, support metallic windings (for

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electrical resistance furnaces) and be capable of holding solid or liquid metals without entering into any undesirable chemical reaction with them.

Refractories are employed in kilns, furnaces, retort, crucibles, electrodes etc. The peculiar high temperature reactions associated with these equipments require the application of refractories which make up the furnace lining. The selection of a refractory for a specific use generally aims at two things:

(i) supporting the charge

(ii) minimization of thermal energy loss from the equipment by a way of restricting the heat to the heating source.

With the development of Iron and steel industry there has been a great increase in the use of refractory materials. For instance, the Ajaokuta steel complex on completion will require 36,000 tonnes of refractory bricks (Adondua (1985)) worth ₦20 million annually based on the cost of the bricks (Aderibigbe and Chukwnogo (1984)), for relining purposes. It is therefore projected that by 1990 about 30,000 tonnes of the refractory brick products worth ₦50 million will be demended in the country. Over ₦1.5 million worth of fireclay bricks are consumed annually in the steel melt shop of Delta steel company (DSC), Aladja and more than 80% of the refractory bricks to be required at Ajaokuta will be fireclays (Ahmed, K.S. (1986)).

The major raw materials for these products are clays which are plentifully and cheaply available in the country.

The development of our local materials for the production of refractories is therefore justified by the need to meet the technological requirements of the country. In particular, the production of raw material for the economic construction and maintenance of the metallurgical industries must now be met locally.

Some attempts have been made to examine the quality of the refractory properties of some of the local clays.[7-11,23,32] This project is therefore has the following objectives:

(i) To determine the essential refractory properties of Oshielle, Onibode (A & B) and Bauchi clay deposits in order to recommend them for appropriate uses,

(ii) To recommend procedurial changes to the manufacture of the refractories in order to achieve desirable properties for certain applications.

CHAPTER TWO

2.0 SURVEY OF LITERATURE

2.1 Refractories In General

Refractories belong to the class of ceramic materials which are employed for high temperature applications, usually above 1100°C. Most refractories are materials made from naturally occuring high melting point oxides, particularly silica (SiO_2), Alumina (Al_2O_3), Magnesia (MgO), chromium oxide (Cr_2O_3), Zirconia (ZrO) and Iron oxide (FeO).

Refractories may be used in any of the following forms:

(i) natural form without any formal processing
(ii) roasted condition or
(iii) synthetic form comprizing many artificially prepared refractories.

There is limited use, for metallurgical purposes, of spent refractory scraps coming from worked out and demolished refractory linings in furnaces and heat systems.

2.2 Classification Of Refractories

The refractories are primarily classified on three bases: chemicomineralogical basis, degree of refractoriness and metallurgical reaction behaviour.

The chemicomineralogical classification is based on the chemical and mineralogical composition of the refractory materials. Based on this, they are the followings:- Silica; Alumino - silicates; Chrome - Magnesites; Chromite; Magnesite; Dolomite; Carbon; Fosterite; Zirconia and Zircon.

The classification of refractory materials based on the degree of refractoriness are:- Low Heat Duty; Heat Duty; High Heat Duty and Super Heat Duty. Table 2.1 gives the details in this groups of refractories.

Table 2.1 Refractoriness Classification Of Refractories:

Group Of Refractories	P.C.E. NO.	Temperature Equivalent (^{o}C)
Low Heat Duty	19 - 28	1520 - 1630
Intermediate Heat Duty	28 - 30	1630 - 1670
High Heat Duty	30 - 33	1670 - 1730
Super Heat Duty	Above 33	Above 1730

On the basis of the behaviour towards metallurgical reactions, three main classes of refractories can be distinguished. These are:- acid, basic and neutral refractories. In this respect, their chemical reactions with metallurgical slags, fluxes and furnace gases are relevant.

Acid refractories are those containing considerable proportions of silica (SiO_2) and they react readily with basic slags and basic fluxes at elevated temperatures. Practically all fireclays, and all the refractories made from sand, flint, and ganister belongs to acid types.

The basic refractories are those in which silica is practically absent and they have their major constituent(s) as lime, magnesia or both and they do react chemically with acid slags or acid fluxes at elevated temperatures.

Neutral refractories are refractories that are chemically inert and resistant to chemical attack by both acid and basic slags or fluxes at high temperatures. Table 2.2 gives a listing of the refractory classification based on their chemical attacks by metallurgical slags.

Table 2.2: Refractory Classification Based On Their Chemical Attacks By Metallurgical Slags

Acid	Basic	Neutral
Silica	Magnesite	Alumina
Aluminiosilicates	Magnesite-chrome	Carbon
Zirconia	Mullite	Chrome
Zircon	Thoria	Fosterite
Sillimanite	Dolomite	Carborundum.
Andalusite	Beryllia	

A metallurgical classification of refractories is however shown in table 2.3 below:

Table 2.3: Metallurgical Classification, Chemicomineralogical Types, and Forms of Common Refractory Materials

Metallurgical Grouping of Refractories	Chemicomineralogical Types of Refractories	Form	
		Natural Condition (Form)	Roasted Condition(Form)
Silica	Silica	Quartzite, vein quartz, rock crystal, quartz schist, chalcedonites, quartz sand.	-
Aluminosilicate (Acid)	1. Aluminosilicate(Fireclay, multi-fireclay, tub and quartz-fire-clay) 2. High-alumina(Bauxite, mullite and corundum)	Clays and kaolins refractory schists, bauxites, andalusite, sillimanites, cyanite, natural corundum.	All natural ones except for andalusite.
Basic	1. Magnesia (magnesite, magnesite-graphite) 2. Chromomagnesia (chromite, magnesite-chromite, periclase-spinel) 3. Limestone-Magnesia(dolomite) 4. Silicate-Magnesia(forsterite).	Magnesite, Dolomites, chromite ores, Forsterites, Enstatites, Serpentinites, clivenites and Dunites.	All natural ones except for chromite ore.
Special (Acid, Basic and Neutral)	1. Silicon carbide(Available only in synthetic form) 2. Carbon (carbon, graphite-fireclay, graphite) 3. Zirconium base	- Natural graphite Zirconium dioxide and Zircon	- - -
Insulating	1. Fireclay 2. High-alumina 3. Corundum 4. Carbon	Raw materials for the production of silica and Diatomaceous earth Vermiculite and light marl.	All natural ones except for diatomaceous earth, vermiculite and light marl.

Source: Draft Report on Needs And Production Potentialities of Refractories in Africa. (United Nations Economic Commission for Africa). March, 1985.

2.2.1 Silica refractories:

Quartz is the most vital raw material from which silica refractories are manufactured. It has a chemical composition of SiO_2 and the crystal structure is such that there is very little space for accomodating excess atoms (Kingery, W.D. (1960)) nor can silicon be readily replaced by other cations. The quartz has a silica content close to 100%, in association with other minerals.

Silica brick have a high load-bearing capacity at elevated temperatures and consequently have been widely used for sprung arches as roofs for open-hearth furnaces, glass tanks, kilns, and coke ovens. In refractory production, silica bricks are manufactured from ground ganister rock (quartzite) containing about 98% SiO_2 to which is added some 2% CaO as milk of lime (Kingery, W.D. (1960)). The added lime serves as a mineralizer to control the transformation rate of silica during firing (Chester, J.H. (1973)).

2.2.2 Alumino-silicates refractories:

As the name implies alumino-silicate refractories are materials which consist mainly of alumina and silica and these form the largest group of refractories in use. Ordinary fire bricks belong to this group.

The best known refractory bricks are fireclay bricks which is often termed firebricks and they includes

bricks made of silica, alumina, magnesia, and other refractory materials. Fireclay bricks have a composition ranging from 35 to 55% aluminium oxide (Al_2O_3). They are based on mixtures of plastic fireclay, flint clay, and fire clay grog. Clays are the raw materials in the manufacture of these refractories which occur in the coal-measures and they owe their refractory properties to the fact that the bulk of the alkalis and other fluxing impurities become removed by the growing vegetations. They consists mainly of the clay minerals kaolinite associated with varying proportions of accessory minerals such as quartz, mica-type minerals, calcite, iron carbonate ($FeCO_3$), iron sulphide (FeS_2). Others in this group include, sillimanite, mullite, bauxite-base and corundum refractories with respect to their alumina content as shown below:

Table 2.4: Alumino - Silicate Refractories

Refractory Group	Alumina(Al_2O_3) content (%)
Fireclay	25 - 45
Sillimanite	45 - 65
Mullite	65 - 75
Bauxite-based	75 - 90
Corundum	90 - 100

Aluminosilicate refractories show a successive change in the oxide ratio $Al_2O_3.SiO_2$ which varies within

wide limits (from 10/90 - 100/0). These variations in the chemical composition reflect changes in their phase composition which in the final analysis dictates the refractory properties of the material. A binary phase diagram for the system Al_2O_3 - SiO_2 gives an idea of the change in phase composition of the refractories and their properties (figure 2.1). Accordingly mullite of (22 - 28% SiO_2) is found to melt at a high temperature of 1910°C. Outside this composition, low melting eutectics are formed. The one with higher alumina melts at 1850°C while it is evidenced from the phase diagram that as Al_2O_3 content is increased in the aluminosilicate refractories, their refractoriness changes from 1590°C (for % Al_2O_3 = 70) to 1850°C beyond this level.

Aluminosilicate refractories are utilised whenever a structure is required to withstand the action of heat, such as in furnace linings, hearths of furnace, boiler setting, and domestic fireplaces.

2.2.3 Chrome - magnesite refractories

The manufacture of these refractories is done by mixing about 70 per cent by part of coarse and medium chrome ore together with 30 per cent by part of fine magnesite.

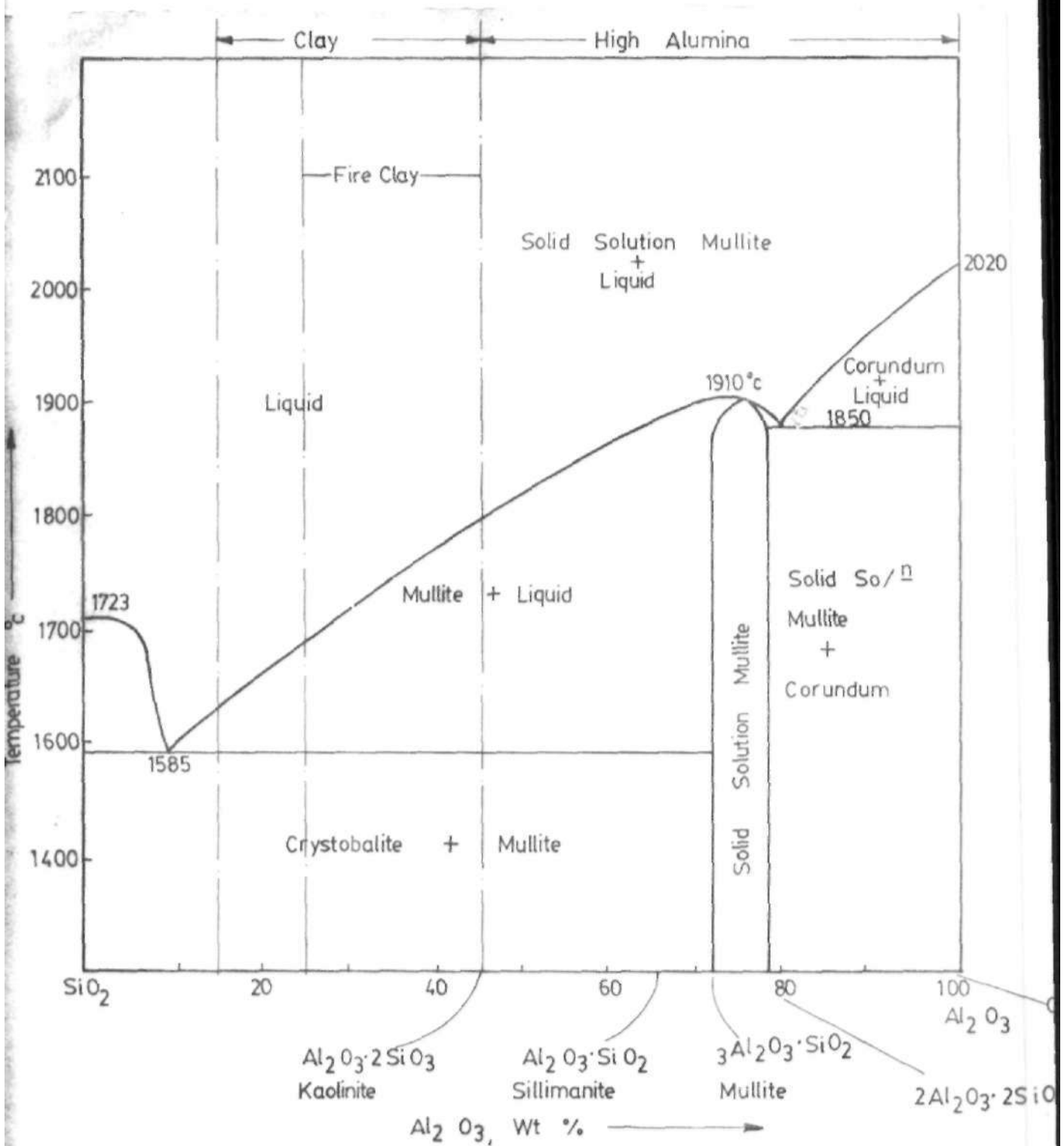


FIG. 2·1 : Phase Diagram of Al_2O_3— SiO_2 System .

2.2.4 Chromite refractories

These refractories are made from chrome ore containing up to 50 - 60% chromium oxide. The chemical composition of chromites is $FeOCr_2O_3$ and they are dark - brown in appearance due to the presence of iron oxide (FeO). They are unsuitable to use in electric induction furnaces used for melting steels, as the bricks tend to introduce chromium into the molten material which may not be required (Searle B.A. (1948)).

2.2.5 Magnesite refractories

Magnesite refractory are manufacture from magnesite minerals. The natural occuring magnesite is magnesium carbonate containing the equivalent of roughly 45% MgO, from which magnesia, (MgO) is produced by calcination.

Majority of magnesite refractories also contain large quantity of iron oxide which serves as source of the colour, but refractories exceptionally low in iron oxide is stained white. They are usually employed where refractories of basic character are needed such as in basic electric and open hearth furnaces (Gilchrist J.D. (1963)).

2.2.6 Dolomite refractories

Dolomite is essentially a mixture of the carbonates of calcium and magnesium ($CaCO_3$ and $MgCO_3$)

with a chemical composition of $CaCO_3$-$MgCO_3$.

Dolomite is the most readily available for use for basic refractories apart from limestone. When dolomite $[CaMg(CO_3)_2]$ is fully calcined, the carbon-dioxide is driven off and the product is simply a mixture of lime and magnesia (Chester J.H. (1973)).

Dolomite refractories are mainly used in the open hearth furnaces, stopper valves and laddle lining due to their basic character.

2.2.7 Carbon refractories:

The chief source of carbon for the manufacture of refractory bricks is from carbonized coal which are metallurgical coke, petroleum coke, graphite etc. Carbon is used not only as refractories, as a result of its peculiar properties, but also as electrodes in electric arc - furnaces. They finds applications in the area of blast furnace boshes lining, or protection of probes used in determining the temperature of molten steel. Other areas of application are in crucible fabrication, moderator, slab and fuel containers in Reactors.

2.2.8 Fostrite refractories:

The major raw material in the production of fosterite bricks is olivine. The fosterite has a chemical composition of $2MgO.SiO_2$. This type of

refractory brick do not have much advantage over other refractories but they can be utilised in some parts of furnaces where a basic refractories behaviour is necessary.

2.2.9 Zirconia refractories:

These refractories are produced from the oxide ZrO_2 which is known as baddeleyite. This is essentially ZrO_2, but is frequently found with 5-7 per cent each of silica and iron oxide. Stabilized zirconia refractories are also manufactured from zircon sand by fusing electrically with coke, iron borings, and lime until the silica is reduced to silicon which alloys with the iron (Chester J.H. (1973)).

Zirconia refractories are employed as nozzles or nozzle inserts for continuous casting. They are also used for the facing of high-temperature furnace linings.

2.2.10 Zircon refractories:

These are produced from raw natural zircon sand which is partially sintered to form grog. Zircon sand results from the weathering of the rock to produce sediments in which the heavy minerals (which include zircon) is further concentrated by wind and water.

The fired zircon bricks are mainly used in the glass and non-ferrous metal industry. They are also

employed in continuous casting as nozzles or nozzle inserts.

2.2.11 Composition of typical refractory:

Based on the foregoing discussion of the different metallurgical types of refractories, a typical composition of some common refractory materials is shown in table 2.5 below:

Table 2.5 Typical Composition Of Some Common Refractory Materials:

Refractory Material / Composition	Fire brick	Alumi-nous Fire bricks	Siliceous or Semi-silica	Silica	Sillima-nite ($Al_2O_3SiO_2$)	Magne-site	Chrome-Magnesite	Dolomite	Silicon Carbide
SiO_2	57.80	51.30	85.00	95.70	34.00	3.10	4.50	14.70	4.50
Al_2O_3	36.30	43.10	12.50	1.10	61.40	2.20	10.30	2.20	1.40
Fe_2O_3	2.40	2.10	0.80	0.70	0.70	4.50	12.70	4.00	1.00
CaO	0.90	0.50	0.20	2.10	0.90	2.50	1.00	39.00	-
MgO	0.20	0.30	0.20	0.10	0.40	87.50	41.00	40.60	-
Cr_2O_3	-	-	-	-	-	-	30.20	-	-
TiO_2	1.50	1.90	0.50	0.10	1.90	-	-	-	-
SiC	-	-	-	-	-	-	-	-	93.20
Alkalis	1.10	1.00	0.60	0.20	0.70	-	-	-	-

Source: Pritchard R., Guy J.J., Connor N.E. (1977).

2.2.12 Selection and Application of Refractories:

Refractories are generally used for lining, roofing and hollow ware casting in furnaces and other fire boxes constructions. The iron and steel industries are the major consumer of many types of refractory bricks and, as a result, a very close link has to be developed between the industries and the refractory manufacturers. Typical usage of refractories are shown in table 2.6 and table 2.7.

Both the design and operating condition of furnaces and fire boxes affect the choice and application of refractories. The availability, however, is an important factor that determines the selection. A replacement is normally sought for or the available ones may have to be employed, if what is needed is not available.

The use of a refractory for a particular operation may be removed by the nature of the material to be processed. An acidic or basic refractory material may need to be used, if the material to be processed is likely to give an acid or basic slag. Refractories that introduces alloying elements that are not required may not be employed in melting steels. For instance chromite bricks when used as refractory brick in steel melting, introduces chromium which is normally not required.

Table 2.6 Refractories used in Iron and Steel Smelting Industries

Type of Equipment	Material	Temperature Range (°C)	Slag Attack	Thermal shock	Abrasion
Blast Furnace					
Top	Low duty fireclay	200	None	Not important	Severe
In wall	Medium Fireclay	300-900	Slightly	Slightly	Slightly
Bosh	High duty Fireclay	1100-1600	Severe	"	"
Hearth	Carbon blocks	1300-1500	Severe	"	"
Stoves	High duty Fireclay	1150 maximium	None	Severe	Slightly
OPEN-HEARTH FURNACE(Basic)					
Hearth Walls	Magnesite	1650	Severe	None	Severe
Front	Silica and chromite	700-1650	"	Slightly	"
Back	Silica and chromite	700-1650	"	"	"
Roof	Silica or chrome-magnesite	800-1650	"	Severe	"
REGENERATOR	Fireclay	650-1200	Severe	Slightly	Slightly

Source: Hassan, S.B. (1985): Effect of certain Additives on Refractory properties of kankara clay.

Table 2.7 Typical Usage of Refractory Bricks

Industry	Installation	Location
Iron	Cupola, Blast Furnace, Blast Furnace stoves Torpedo-ladles, Hot metal mixers.	Linings Linings, checkers Linings.
Steel	Open Hearth Furnaces	Subhearth, doors, checker chambers, checkes.
	Arc Furnaces	Subhearth, doors
	Ladles	Linings
	Casting pit	All pouring pit hollow-ware.
	Soaking pits	Roof, side-walls.
	Reheating Furnaces	Hearth, roof, side-walls.
Non-Ferrous	Copper reverberatory furnaces	Subhearth.
	Lead dross furnaces	Hearth.
Glass	Pot furnaces	Pots, furnace linings.
	Tank furnaces	Regenerative system, flues
Carbonization	Coke Ovens	Sub-oven section: flues, regen-erators
Power Cement	Boilers	Walls, arches, flues
	Rotary kilns	Cooler sections.
Lime	Kilns	Most sections.
Chemicals and Petrochemicals.	Reactors and stills	Linings
Waste Disposal	Incinerators	Linings

Source: Chesters J.H. (1973)

The type of operation either continuous or batch form, also affect the choice of the refractory to be employed. In a continuous process the thermal spalling resistance characteristics of the brick becomes less vital requirement than the slag resistance. The thermal spalling resistance is more important in batch type operations. In both processes the temperature of operation also dictate the refractory to be used. Highly refractory materials are normally used in high temperature processes.

The type of furnace either reheating or smelting type also influence the selection of refractories. The property requirements of refractories to be used for particular type of furnace will definitely differ. In majority of the reheating furnaces, chemical attacks by slags and fluxes is completely absent. The mechanical strength required of the refractory will vary, depending on the load imposed on the lining and the mechanism of moving loads in the furnace.

Refractories may be required to have some qualities with respect to the nature of fuel used in firing the furnaces. Some furnaces may be required to be linned with refractories that possess an extremely low electrical conductivity while some may require high electrical conductivity refractories.

Finally the economical advantage of any process is highly important. Refractories are normally

expected to be cheaply available; interms of both the delivery and the installation costs.

2.3 Clays:

Clays are in form of naturaliy occuring fine-grained minerals which develops plasticity when mixed with the right proportion of water (Grims, E.R.(1968)).

They are natural argillaceous matters formed by decomposition of feispathic rock as a result of weathering action of wind and rain, and are of general chemical formula $mAl_2O_3\ nSiO_2.pH_2O$. Hence clays belong to the aluminosilicate group of refractory materials and are the most readily available sources of fireclay refractory bricks used in furnaces.

2.3.1 Structure of clays:

Clays are crystalline in structure. The chemical analyses of clays show them to be composed essentially of silica, alumina, and water, with appreciable amounts of iron, alkalies, and alkaline earth metals.

The lattice of most of the clay minerals are composed of two structural units. The first unit consists of closely packed six oxygen atoms or hydroxyls in the basal planes of an octahedral structure. Al, Fe or Mg atoms are embedded in the octahedral positions so that they are equidistant from

six oxygens or hydroxyls in the basal planes.

When aluminium is present, only two-thirds of the possible positions, required to balance the structure are filled. The structure containing aluminium ions is called the gibbsite structure and has the formula $Al_2(OH)_6$. When Mg is present, all the positions are filled resulting in a balanced structure, and this is known as the brucite structure with formula $Mg_3(OH)_6$.

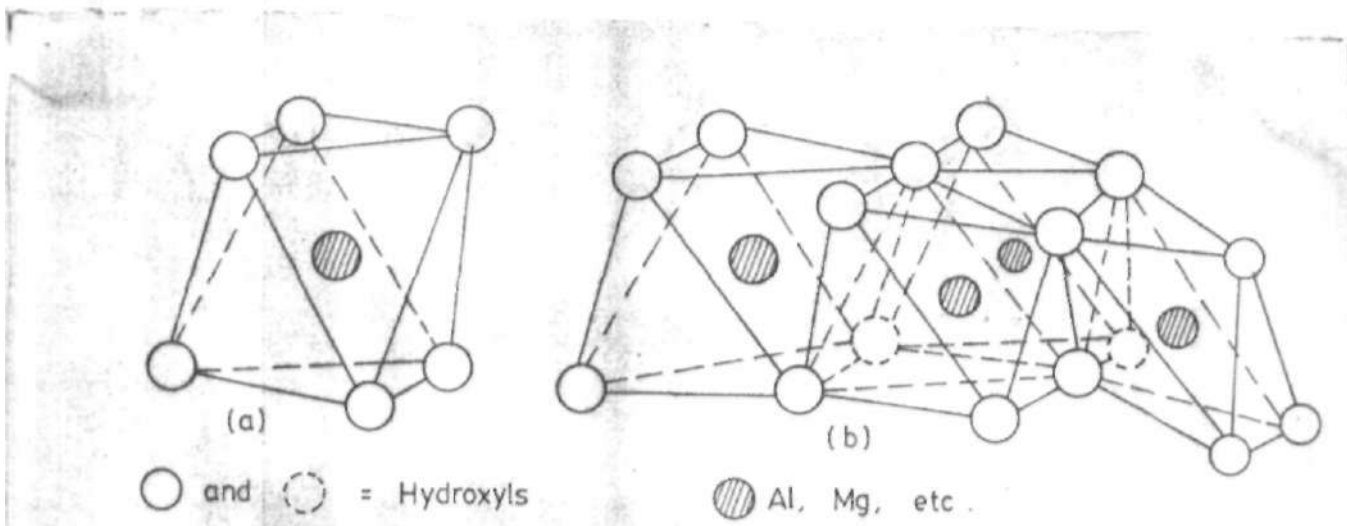


FIG. 2·2 : Diagrammatic sketch showing .
(a) Single Octahedral Unit .
(b) The sheet structure of the octahedral units (Grim, E. R-(1968)

The second unit has the silica structure made of units of tetrahedrons in which the silicon atom is centrally placed equidistant from the four oxygens, (or hydroxyls if needed to balance the structure).

The silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. This is shown below:

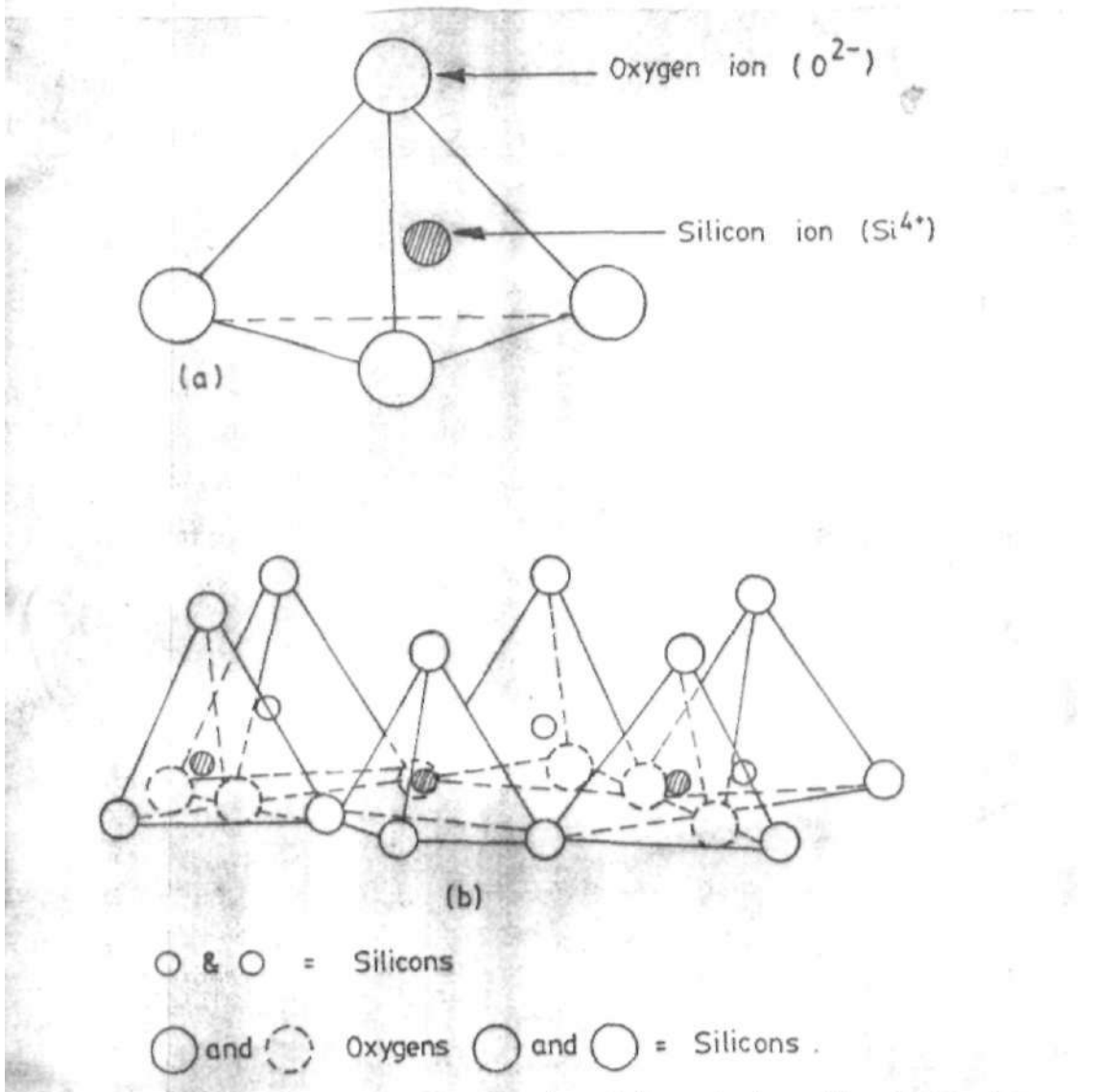


FIG. 2·3 : Diagrammatic sketch showing (a) a single silica tetrahedron . (b) the sheet structure of silica tetrahedrons arranged in a hexagonal net work .

The tetrahedrons are arranged so that the tops of all of them point in the same direction, and the bases of all tetrahedrons are in the same plane (Grim, E.R. (1968)).

2.3.2 Classification of clays:

Clays differ very considerably among themselves in structure, workability, plasticity, particle-size distribution, and mineralogical composition, and these differences lead to such terms as flint clays, plastic clays, kaolins, ball clays, and the like.

Clays are often classified mainly in two ways, and are based on mineralogical constituents and the properties of the clays.

On the mineralogical basis, clay minerals are divided into three major groups in accordance with their crystallographic structures.

(a) Kaolinite group which have the simplest clay mineral structure. These minerals all have the chemical formula $Al_2O_3.2SiO_2.2H_2O$, and include: kaolinite, nacrite, dickite, anauxite, halloysite and livesite.

(b) Montmorillonite group which comprises montmorillonite ($Al_2O_3.4SiO_2.H_2O$), nontronite $\left[(AlFe)O_3.3SiO_2.nH_2O\right]$ and beidellite ($Al_2O_3.3SiO_2.nH_2O$). Others are saporite ($2MgO.3SiO_2.nH_2O$) and sanconite ($2ZnO.3SiO_2.nH_2O$).

These minerals have the common properties of absorbing large quantities of water between adjacent layers, changing the basal spacing from 10Å to 20Å.

(c) Illite or hydromica group which have clay minerals that resembles the micas and they have large spaces which contain cations to keep the charges neutral. Their finely divided state, however, makes many of these cations accessible for exchange. Unlike the montmorillonites, water does not enter into the lattice itself and expand it, because the adjacent layers are held together to potassium ions. The general chemical formula is $(OH)_4Ky(Al_4.Fe_4.Mg_4.Mg_6)\ Si_{8-y}\ Aly O_{20}$ with y varying from 1 to 1.5.

Classification of clays according to their properties and therefore their applications are of great industrial relevance. The classification developed by Norton (1952) is as follows:

(a) White- burning clays commonly used in white ware consists of kaolins (residual and sedimentary) and Ball clays.

(b) Brick clays which are plastic clays, and contain iron-oxide. These are: Terra-cotta clays and face and common bricks.

(c) Refractory clays which have melting points above 1650°C but not necessarily white-burning. They are basically kaolins (sedimentary), Fireclays and High alumina clays.

(d) Stoneware clays (plastic containing fluxes)

(e) Slip clays which have more iron oxide content.

(f) Heavy clay-products clays which have low plasticity and containing fluxes. These consists of Paving brick clays and shales, sewer-pipe clays and shales and Brick and hollow tile clays and shales.

Ries (1927) also gave another classification which describes clays by their forming processes and locations. On this basis, two main groups exist: These includes residual (Primary) clays and sedimentary (colluvial or secondary) clays.

Residual clays are those which decompose at the site of the original rock and are characterized by relative purity. While sedimentary clays are those which have been carried on the beds of rivers or lakes. These class of clays possesses good plasticity but are relatively impure, since during their passage they will have been contaminated with impurities present in other rocks, which have similarly decomposed.

Three important clays, kaolin, Montmorillonite and Illite which are very relevant to this research work are therefore, discussed further.

2.3.3 Kaolinite minerals:

Singer and singer (1963) described kaolin as a corruption of the chinese 'kaoliang', meaning 'high ridge', a local designation for the area where a white china clay was found. A definition was given by Ross and Kerr (Grim, E.R. (1968)) as "the rock mass which is composed essentially of a clay material that is low in iron content, nearly white burning, generally of low plasticity and high refractoriness (1750-1770^{o}C). The kaolin form of clays are siliceous and after washing the chemical formular which approaches that of kaolinite ($2H_2O.Al_2O_3.2SiO_2$); which is predominant, and characterises most kaolins. Kaolins occur either as residual or as sedimentary deposits and are often grouped with fireclays due to their good refractory nature.

Pure kaolinite has the composition $Al_2Si_2O_5(OH)_4$ or $Al_2O_3.2SiO_2.2H_2O$ and occurs in the clays as minute, plate-like crystals. On heating, kaolinite loses its combined water between 450^{o}C and 550^{o}C. This leaves a residue consisting of Al_2O_3 and SiO_2 combined together.

The structure of kaolinite is composed of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tops of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer. All the tops of the silica tetrahedrons point in the same direction and toward the center of the unit made by the silica and octahedron sheets. (Grim, E.R.(1968)). The atoms common to both the tetrahedron and the octahedron layer are oxygens as shown below:

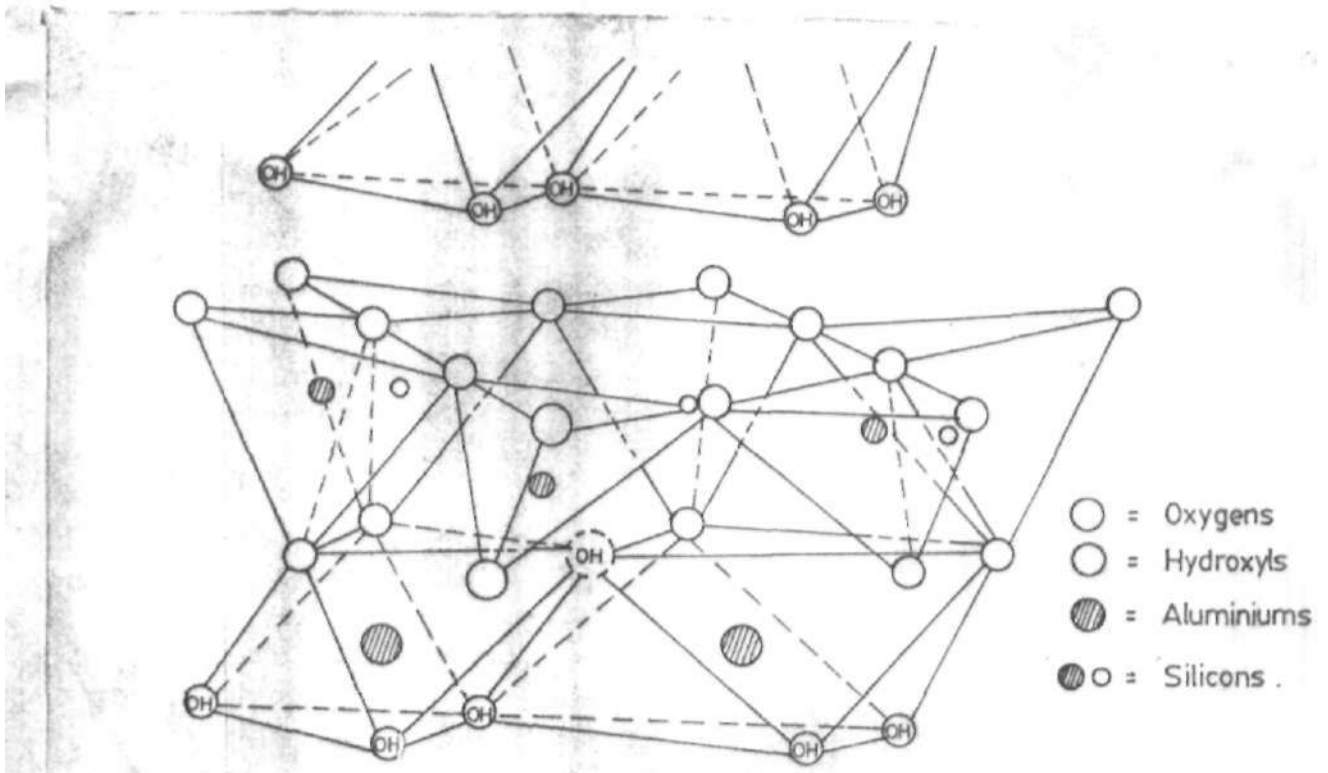


FIG. 2·4 : Diagrammatic sketch of the structure of the kaolinite layer. (After Gruner).

This structure unit consists of one silica unit and one aluminium unit. Hence the kaolinite

group of clays is said to have a 1:1 lattice structure. This is illustrated in figure 2.5 below

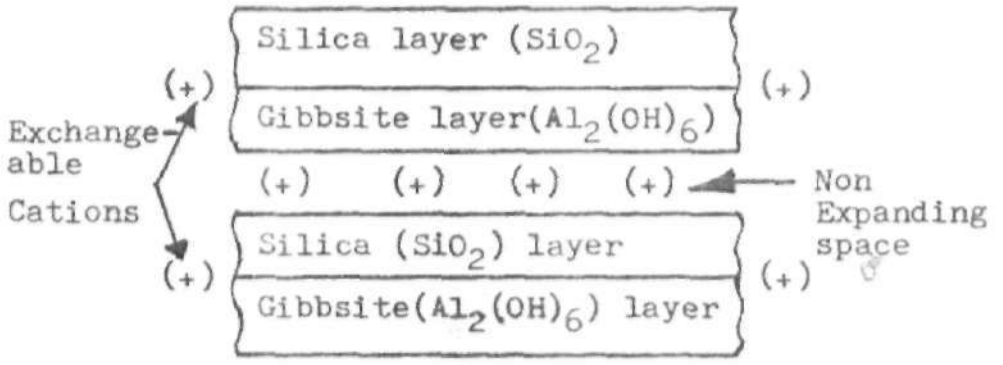


Figure 2.5 Diagram showing the lattice structure of kaolinite clay crystal.

The chemical formula of kaolinite is $(OH)_8Si_4Al_2O_{10}$ with a theoretical composition expressed in oxides is: SiO_2, 46.54%; Al_2O_3, 39.50%; H_2O, 13.96%. From this composition, it follows that this is the highest alumina content that can normally be expected in a fired clay brick. Usually it is lower than this due to the presence of accessory minerals and may be much lower if the clay contains much free quartz.

The analyses (Ross C.S. and Kerr P.F. (1931)) of many samples of kaolinite minerals have shown that there is very little substitution within the lattice. In the stacking of the silica and alumina layer, oxygen and hydroxyl ions are grouped in pairs, (O-OH), and this indicates that the layers are bonded together by hydrogen - or hydroxyl bond. This is a

strong bond, however, the bonds joining atoms within the layer structure are considerably stronger than this O - OH bonds between layers.

As the two sheets of each structure unit of kaolinite are held together tightly, and the structural units themselves are held together by strong hydrogen bonding, the kaolinite lattice is fixed, and no water and cations enter between the units, and no expansion normally occurs between them when the clay is wetted. The effective surface of kaolinite is thus restricted to its outer faces and its absorptive capacity for cations is very low. The cation exchange capacity of the kaolinite clay group is 3 - 15 milli-equivalents per 100g.

The strong bond between the kaolinite structural units favours the formation of larger particles and its surface area to unit weight is small compared to other minerals.

Less than half of the kaolin produced is utilised for ceramics, the rest being used as a filler in the paper, rubber, textiles and numerous other industries.

2.3.4 Montmorillonite minerals:

They occur only in extremely small particles. The structural units composed of layers made up of two silica (SiO_2) tetrahedral sheets with a central

gibbsite octahedral sheet by the mutual sharing of the unsatisfied oxygens on the apical side of the silica layers. All the tops of the tetrahedrons point in the same direction and toward the center of the unit. The tetrahedral and octahedral sheets are combined so that the tops of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. As there are two silica layers to every gibbsite layer in each structural unit, montmorillonite clays are said to have a 2:1 crystal lattice as indicated below:

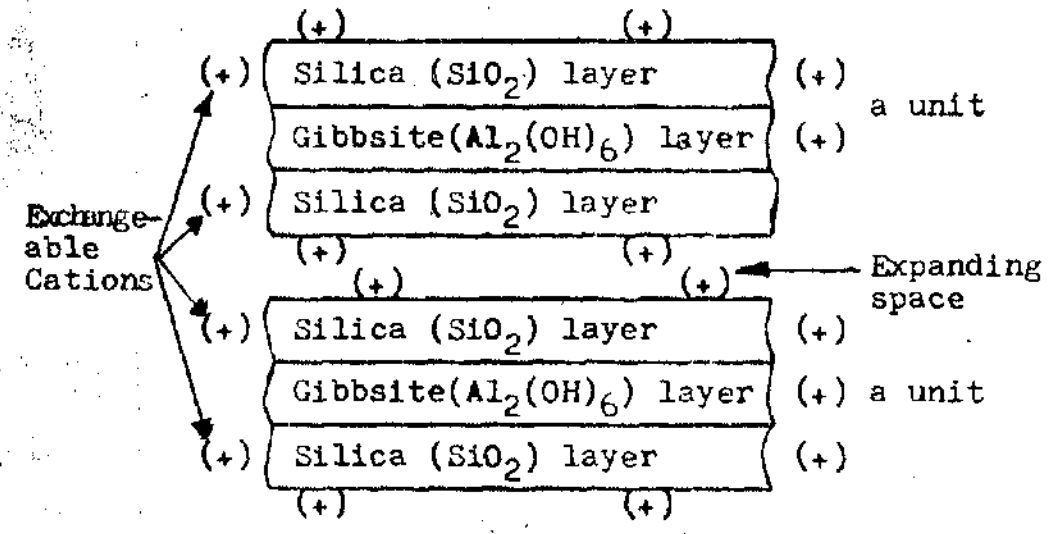


Figure 2.6 Lattice structure of Montmorillonite clay cystal.

The structural units in montmorillonite with the stacking of the silica-alumina-silica units are held loosely by the oxygen-oxygen linkage which is a very weak bond and can expand rapidly absorbing

water and cations between them when wetted. Montmorillonite clay minerals are said to have an expanding lattice which results in their excellent swelling properties.

As the bond between the structural units of this clay mineral are weak, their crystals may be fractured easily to give particles as small as structural units. The smaller size of the montmorillonite particle and its effective internal surface between the structural units (where water and cations can move in) provide it a larger effective surface area and thus provide a larger bonding power, plasticity, capacity for expansion on wetting and shrinkage on drying.

The theoretical chemical formula of this clay without taking lattice substitutions into consideration is $(OH)_4Si_8Al_4O_{20}.nH_2O$ with the theoretical composition of: SiO_2; 66.70%; Al_2O_3, 28.30%; H_2O, 5.0%.

The type of cations attached to the clay affects its properties to a great extent. As these cations are loosely held between the clay layers, they are easily exchanged with other cations and change the clay properties to a great extent. Montmorillonite clay has a cation exchange capacity of 80 - 150 milli-equivalents per 100g greater than that for kaolinite or Illite.

2.3.5 Illite minerals:

The structural units of Illite minerals is similar to that for montmorillonite and has the same 2:1 crystal lattice structure. But in illite about 20% of silicon ions (Si^{4+}) in the silica layer are always replaced by aluminum ions (Al^{3+}) and the resultant charge deficiency is balanced by potassium ions held between the structural units (Grim, E.R. (1968)) as in figure 2.7 below.

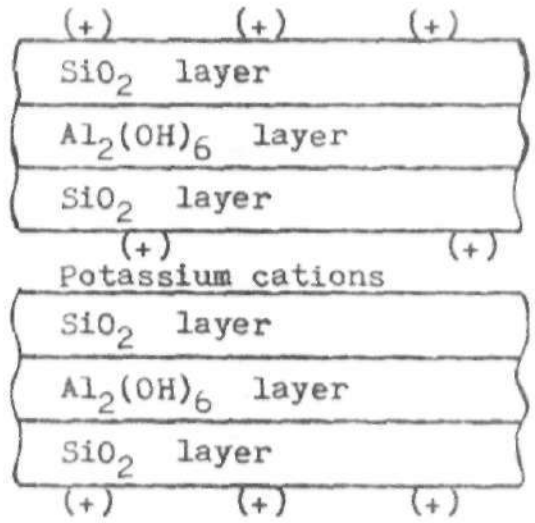


Figure 2.7 Lattice structure of Illite clay crystal.

The potassium ions provide a much stronger linkage between the structural units of illite than in montmorillonite and consequently water layers cannot enter between the units as easily as in the case of montmorillonite crystals. The illite crystals can also grow into bigger particles. Hence the properties such as hydration, cation adsorption (also cation exchange), swelling, shrinkage,

bonding strength, plasticity, etc., develop less intensely in illite than in montmorillonite, but more intensely than in kaolinite. The cation exchange capacity of illite clay minerals is 10 -40 milli-equivalents per 100g.

The structural formula of this clay is $(OH)_4k_2(Si_6.Al_2)Al_4O_{20}$ and the theoretical composition is: K_2O, 11.80%; SiO_2, 45.20%; Al_2O_3, 38.50%; H_2O, 4.50%.

2.3.6 Nigerian clays

A good number of clay deposits in Nigeria have been discovered. Some of these have been chemically analysed and their properties have been investigated. The known deposits include Orun, Ozubulu, Enugu, Nsu, Kankara, Giro, Majahota, Warram, Nafuta, Sabon Gida and Okpekpe. The location, chemical composition and refractoriness of these clays, as given by Aderibigbe and Chukwuogo (1984) are given in Table 2.8. Majority of these clays have been identified as kaolins but only a few of them burn white. Some of the commercial deposits have been leased and mining activities have already commenced at the sites (Table 2.9). More detailed analytical studies have been carried out on kankara clay by Robertson Research (1978) as reported by Ahmed, K.S. (1986). The chemical and mineralogical compositions of kankara clay, from a deposits, as obtained from the

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report (unpublished), are shown in table 2.10.

Table 2.11 presents the analyses of some good quality kaolins. Many of these compare favourably with the foreign kaolins with respect to quality. Kankara clay, for example, is a good quality china clay that appears even superior to the famous Cornish china clay in Britain. It contains less iron impurities, less total alkalis and is of higher clay content.

At present, the major consumers of the Nigerian clay materials being mined are ceramic tile, sanitary ware and dinner ware industries. There is no current use of the clays for industrial scale refractory production. Table 2.8 shows that many of the local clays have qualities that meet the requirements for refractory production demanded for the iron and steel making shop, that is minimum Al_2O_3 content of 32%, maximium Fe_2O_3 content of 2.5% and minimum refractoriness of 1730°C (Adigwe (1983)).

2.3.7 Chemical analysis of clay

Theoretically pure kaolins contain basically oxides in the percentages as shown below:

Al_2O_3 - 39.50
SiO_2 - 46.60
H_2O - 13.90

Table 2.8: Location, chemical composition and Refractoriness of some Nigerian clays

Clay	Location (State)		Al_2O_3 (%)	SiO_2 (%)	Fe_2O_3 (%)	CaO+MgO (%)	L.O.I. %	Refractoriness(P.C.E)	
								CONE NO	Equivalent Temp ^oC
Oshielle	Abeokuta	(OG)	28.30	53.40	1.35	0.88	15.00	33	1730
Orun	"	(OG)	34.55	50.50	2.05	1.10	15.50	33	1730
Onibode	"	(OG)	39.30	42.30	Trace	1.05	14.20	34	1760
Ozubulu	Nnnewi	(AN)	19.31	58.30	1.55	1.25	14.16	32	1710
Enugu	Enugu	(AN)	22.71	55.00	2.42	1.95	16.35	29	16.50
Nsu	Okigwe	(IM)	30.22	50.60	1.92	1.08	10.54	32	1710
Okpekpe	Auchi	(BD)	24.30	53.20	1.45	1.30	16.86	29	1650
Kankara	Kankara	(KT)	38.64	44.50	Nil	1.30	16.70	34	1760
Giro	Giro	(SO)	38.72	41.26	2.10	1.48	14.00	34	1760
Warram *	Warram	(PL)	37.13	43.54	1.15	0.58	14.20	34	1760
Sabon Gida	Jos	(PL)	25.88	25.32	13.10	3.20	18.36	27	1610
Majahota▲	Majahota	(PL)	-	-	-	-	-	-	-
Nafuta ▲	Nafuta	(PL)	-	-	-	-	-	-	-
Alkaleri	Bauchi	(BA)	25.43	54.30	1.05	1.00	15.73	33.5	1740

* Average values for two differently located samples.
▲ Data not available but vast reserves of white kaolins were reported.

Source: Ahmed, K.S.(1986): Development of Phosphate Bonded fireclay refractory castables.

Table 2.9: Reserve Estimates of some Nigerian clays

Clay	Type	Reserve Estimate (Tonnes)	Average clay content (%)	Current Lease Holder
Onibode	2^{o} kaolin	4,500,000	NA	National steel council
Kankara	1^{o} kaolin	891,000	90	Kaduna state Government
Majahota	kaolin	850,000	78	Bisichi Tin Company
Warram	kaolin	NA	88	Kaduna Prospectors Ltd.
Nafuta	kaolin	190,000	50	Kaduna Prospectors Ltd.

Source: Unpublished reports by Geological survey of Nigeria.

NA: Not Available

Table 2.10: Chemical and Mineralogical Composition of Kankara clay

Chemical Analysis			Mineralogical Analysis (Rational Analysis)		
Parameter	Whole	<10 µm	Parameter	Whole	<10 µm
SiO_2	48.46	54.27	Kaolinite	75.0	30.60
Al_2O_3	34.49	28.40	Allophane	9.0	40.70
Fe_2O_3	1.17	0.45	Free silica	5.6	16.90
MgO	0.95	0.56	Feldspars	2.5	3.90
CaO	0.31	1.11	Saponite	3.6	5.20
Na_2O	0.19	0.29	Muscovite	2.4	0.70
K_2O	0.33	0.10	Gypsum	0.1	-
H_2O(L.O.I)	13.19	14.60	Anatase	0.4	0.20
TiO_2	0.45	0.19	Geothite	1.3	0.50
MnO	0.01	0.03	Calcite	-	1.10
SO_4	0.05	N.D			
Total	100.00	100.00		100.00	99.80

N.D - Not Detected.

Source: Ahmed, K.S.(1986): Development of Phosphate Bonded Fireclay Refractory Castables.

Table 2.11: Analyses of some Foreign Clays:

Name	Cornish china clay	Zettlitz Kaolin	Kemmiltz Kaolin	North Caralina Kaolin	Sergeant China clay
Country	Britain	Czechoslo-vakia	Germany	U.S.A.	U.S.A.
SiO_2	45.45	46.09	58.30	48.46	44.90
TiO_2	0.34	-	-	0.06	1.32
Al_2O_3	38.33	39.28	29.31	36.53	38.90
Fe_2O_3	0.55	0.76	0.87	0.15	0.40
MgO	0.12	-	Trace	0.03	0.10
CaO	0.06	0.15	0.51	0.13	0.06
Na_2O	0.43	0.03	1.26	0.21	0.22
K_2O	2.22	0.12		1.34	0.20
L.O.I	12.44	13.58	10.62	13.03	14.20
Clay Substance	-	98.30	54.90	-	-
Potash-mica	-	-	-	-	-
Soda-mica	-	1.20	43.80	-	-
Quartz	-	0.40	1.30	-	-
Feldspar	-	-	-	-	-

Source: Singer and singer (1963)

After calcining, the percentage of these oxides are Al_2O_3 - 46.60; SiO_2 - 54.00. Apart from these principal components clays in the as-mined condition contains certain amounts of impurities. The commonest of them is quartz which are evenly distributed. Up to 1300° - 1350°C quartz is inert and plays the part of a non plastic filler. But at 1350°C and above quartz becomes an active fluxing agent, forming low-melting multi-component eutectic with the clay (Budnikov. P.P. (1964)).

Another common impurity of clays is some form of ferruginuous compounds. These include pyrite, mascasite (FeS_2), siderite ($FeCO_3$) and Iron oxides. At fairly high temperatures these could cause spalling, swelling and sometimes stains on the surfaces of the bricks. Hence Iron oxides are often said to cause appreciable deterioration of the refractory properties of the clay (Budnikov P.P. (1964)).

Fluxing agents such as CaO, MgO, Na_2O and K_2O are also found in clays. Otehrs are calcite ($CaCO_3$), gypsum ($CaSO_4$), rutile (TiO_2) and organic mater of vegetable origin. Hence the complete chemical analysis of clays would normally comprise the determination of the following oxides:

Loss on Ignition

SiO_2

TiO_2

Al_2O_3

Fe_2O_3

CaO

MgO

Na_2O

K_2O

Other oxides

Loss on Ignition: The hygroscopic and combined water, carbonate and carbonaceous matter are rarely required in normal practice. However, these with the exception of hygroscopic water, are included in the Loss On Ignition. Loss On Ignition is determined as a pre-step to silica determination by heating a dried sample to 1000°C for 30 minutes (Bennett, B.H. and Read, R.A. (1971)).

Classical technique for chemical analysis: The traditional techniques of chemical analysis is by chemical "Wet" method. The 'classical' method as it is called, gives considerable accuracy but a great length of time is required for better results. Recent developments have favoured instrumental techniques which, once, properly caliberated, do not require as much skill as the classical method. These include X-ray fluorescence, direct-reading spectrometry and atomic absorption spectrophotometry (A.A.S). According to Bennett & Read (1971), it was observed that classical method still serve two main purposes in

providing the analyses on which the instrumental analyst can base his comparison as well as simple techniques for those laboratories which do not perform enough analyses to justify the expensive equipment .

In classical method there are two standard alternative methods of silica determination - single dehydration method and coagulation method. Coagulation method is now preferred in practice, because the silica residue is less and the method is appreciably faster without loss of any accuracy (Bennett, B.H. & Read, R.A. (1971).

Instrumentation technique: In the x-ray fluorescence, the sample is either pressed in powder form into a compact or, better still, fused with a suitable flux (e.g Borax) to form a glass disc. A thin pencil of x-rays from a tungsten or chromium tube is allowed to fall on the specimen; this causes elements of lower atomic number to be excited and produce secondary or fluorescent x-rays which are characteristic of the elements in the sample.

Atomic absorption spectrophotometry (A.A.S) is another method that is commonly employed. However Bennett and Read (1971) gave their reservations concerning the use of the method for the determination of Aluminium and silicon which are main constituents in clays. According to them Atomic absorption spectrophotometry is ideal for the determination of

calcium in magnesite and chrome-bearing materials, while, determination of elements like Mn, Fe and Cr bring the atomic absorption technique into direct competition with direct-reading spectrometry.

A number of different techniques are employed for the determination of the mineralogical composition of clay, the most commonest being x-ray diffraction, differential thermal analysis and infra-red-absorption.

The differential thermal analysis depends on the detection of the heat given out or absorbed when a phase change occurs in a substance which is being heated. The apparatus used for this parameter consists of a refractory specimen holder, divided into two compartments; the material to be tested, in the adjoining compartment is usually placed on an inert material which does not undergo any phase changes and this acts as a reference material. The specimen holder is provided with a set of thermocouples for measuring the temperature T of the inert material and also the difference in temperature between the inert and the test sample (ΔT). To obtain temperature uniformity the specimen holder is placed inside a cylindrical refractory brick, which in turn fits closely inside an electrically heated tube furnace. The latter is controlled so that its temperature is raised uniformly from room temperature up to the desired maximum temperature (usually 1000 - 1250^{o}C) at a recommended

constant rate of 10°C/minute. The thermocouple readings is recorded automatically on a chart recorder.

When a reaction involving a heat change occurs, the temperature of the test sample will deviate from that of the inert, depending on whether the reaction is exothermic or endothermic. Therefore if ΔT is plotted against T, a peak will occur whenever a phase change occurs. The 'zero line' on the graph is called the base line. It is then clearly possible from the graph to determine the sign of the heat change (exo-or endothermic), the approximate temperature at which it commences and, from the magnitude of the peak, the approximate proportion of reactive material.

The temperature of the inert material increases regularly as the temperature of the furnace increases. When a thermal reaction takes place in the sample, the temperature of the sample is greater or less than that of the inert material, depending on whether the reaction is exothermic or endothermic, for an interval of time until the reaction is completed and the temperature of the sample again comes to the temperature of the furnace.

Figure 2.8 shows an idealized DTA curve for kaolinite. The endothermic reaction between about 500 and 700°C correspond to the dehydration of the material. The curves illustrates that the differential

method is a dynamic rather than a static one. The thermal reactions are not instantaneous, and they are recorded as functions of the furnace temperature, which is continuously increasing as the reaction takes place.

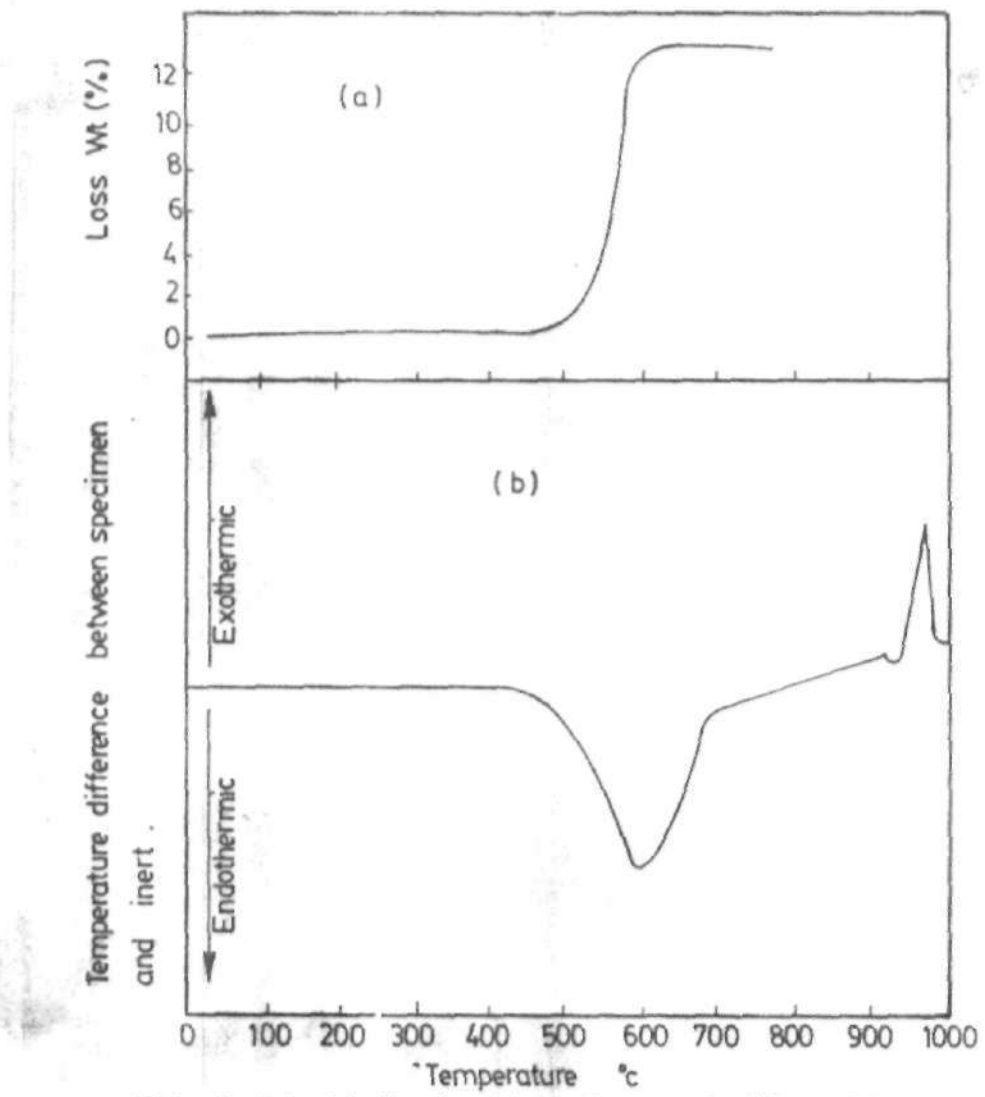


FIG. 2·8 : Idealized dehydration and differential thermal curves for Kaolinite .

According to Grim (1968), the temperature at which the dehydration begins corresponds to the start

of the endothermic reaction. The temperature of the peak of the endothermic deflection varies, depending on the details of the procedure followed, the character of the reaction involved, and the material being investigated.

Typical thermal analysis curves for kaolinite and montmorillonite are shown in figure 2.9. From the curves it can be seen that a small endothermic peak occurs with kaolinite at about 110°C as a result of the evolution of absorbed water. At about 520°C the main endothermic peak commences, the tip of the peak being at about 600°C, corresponding to the decomposition of the mineral, and elimination of the hydroxl groups as water. A further peak, which is exothermic, occurs at about 1000°C, and is associated with a recrystallisation process. According to Worrall, W.E. (1975), this has been variously attributed to the formation of mullite, of alumina and of silicon spinel.

The main differences found between well - crystallised kaolinite and disordered kaolinite was also reported by Worrall, W.E.(1975). In disordered kaolinite, the initial peak due to adsorbed water is often larger than for well-crystallised kaolinite. The main endothermic peak is somewhat lower-usually at about 600°C - and the exothermic peak is smaller and broader.

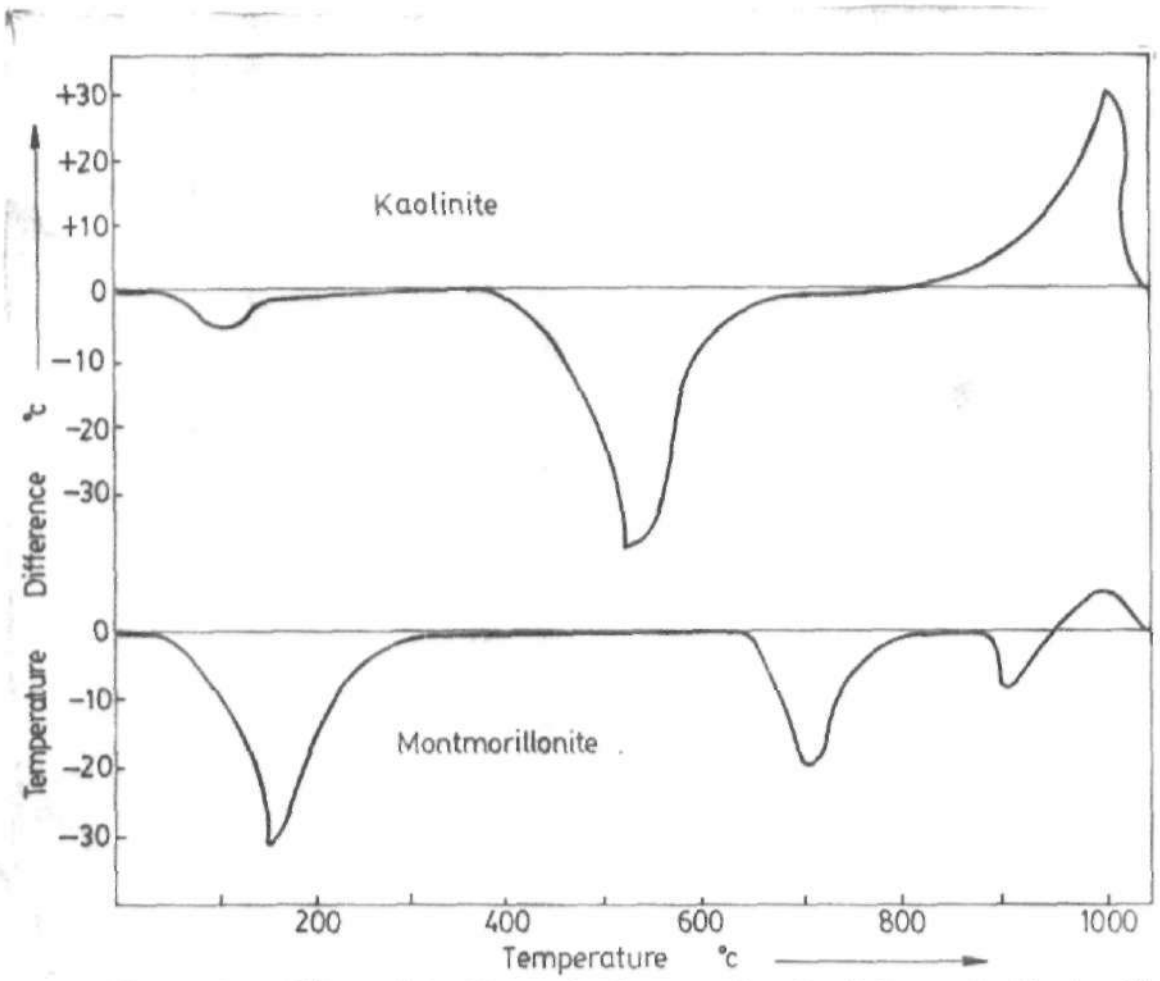


FIG. 2·9 : Differential Thermal Curves for Kaolinite and Montmorillonite.

The montmorillonites all have in common a large endotherm at about 150°C, corresponding to the evolution of inter-layer water and water associated with the exchangeable cations. The peak varies in size and shape according to the nature of the cations and the lattice substitutions. The main endotherm corresponding to the thermal decomposition of the mineral, occurs at about 710°C and there is a final exotherm at about 1000°C as for kaolinite.

2.4 Manufacturing And Method Of Testing Refractories

2.4.1 Methods of refractory manufacturing:

The production of a refractory body starts generally with granular or particulate materials, and by various steps and procedures these materials are finally incorporated in a single coherent body, such as a brick or a furnace bottom, with some mechanical strength. Beginning with raw materials, the process of forming the refractory body can be varied in many ways to obtain a variety of final structures with widely different properties.

Refractories are normally manufactured from the followings: refractory raw material, water and additive (if required). The conventional method of manufacturing refractories from the raw material involves a number of steps, principally; purification which consists of crushing, washing and grinding; screening to reduce the raw material to a suitable size and size distribution; mixing and blending. This is followed by forming or molding, which involves tempering with water or other bonding agents to form a body which can be shaped by molding, pressing or, in the case of hollow - ware, by extrusion. Final processes include drying and firing on a heated chamber or in kilns at temperatures normally between 1100^{o}C and 1400^{o}C depending on the quality of the clay. The properties and characteristics of the raw material, the size and shape of the final product, and

the requriements of the fired products, will determine the details of the various processes just enumerated. However a simple flow diagram of the major processes involved is shown in figure 2.10.

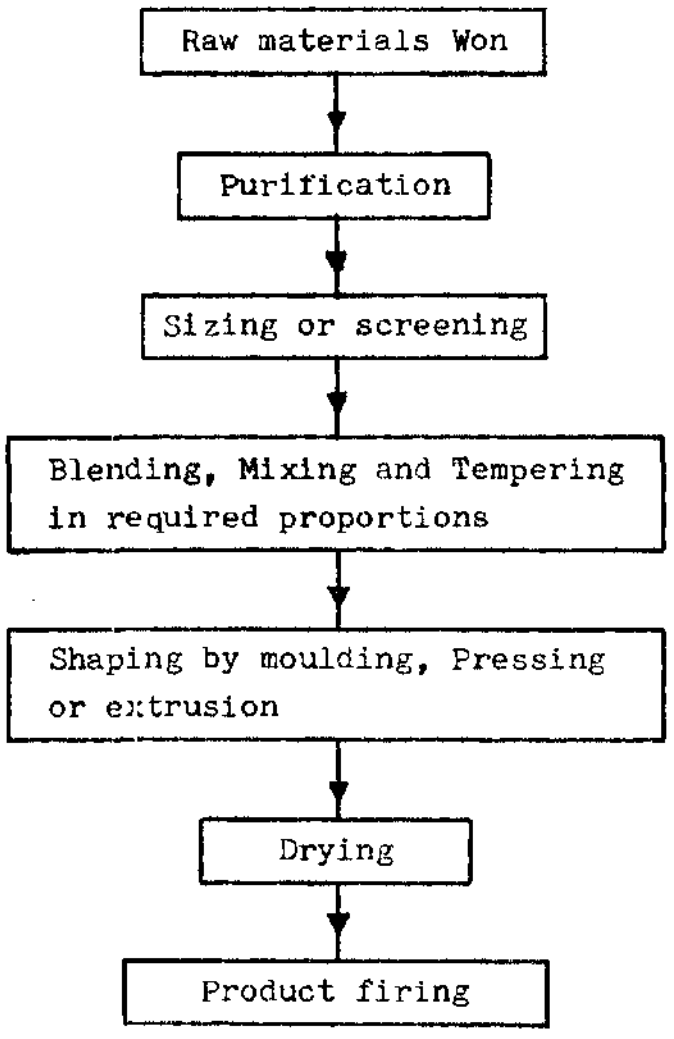


Figure 2.10: Flow diagram of the major processes involved in the Manufacturing Refractories.

2.4.2 Purification of the as-mined clays:

Clays in the as-mined conditions undergo some degree of purification in order to remove various

associated impurities present - before being used for manufacturing bricks. The method of purifing depends on the type and origin of the raw material that will be used.

One method most frequently used is that of sedimentation which results in the separation of minerals on a size basis; since no two minerals are likely to have exactly the same size distribution. This involves the crushing, washing and grinding of refractory raw material. This method is effective in separating clay from sand, silt and quartz.

Another method of purifying clay material is by sieving. This also separates impurities on a size basis and it is sometimes preferred to the sedimentation technique due to the fact that it is much faster to accomplish. Sieving is achieved by soaking clay in water, drying and sieved through a selected sieve. The choice of sieve size is guided by the knowledge of the particle size distribution of the clay.

Generally clays are purified to free them from their impurities such as dead organic materials which usually act as source of porosity in the refractory bricks. Some inorganic impurities may also need to be removed depending on the area of application of the refractory bricks.

2.4.3 Sizing and size distribution

Suitable size and size distribution are achieved by crushing, grinding and screening by comminution equipments. This is necessary to improves the manufacture of high packing density products.

Robson (1962) explained that low porosity can be attained by using a "closepacking grading" such that interstices between the largest particles are filled by a smaller grade. Thus there is some control on the ultimate porosity and strength, for the maximum number of contacts will also be made with the closest packing.

However, theory predicts that the use of three particle size fractions (coarse, medium and fine), with each fraction being an order of magnitude smaller, will produce an optimum dry packing and the porosity obtained is as low as 20%.

The controlling of the particle size distribution in addition to absolute size in the manufacture of refractory bricks is very crucial. The ground material are normally screens into 3 - size fraction, referred to as the coarse, medium and fine fractions. The coarse particles should pass through an 8-mesh sieve (2.057mm i.e. 2000 μm), and retained on a 22-mesh sieve (0.69mm i.e 710 μm), the medium particles should pass through the 22-mesh and retained on 72-mesh sieve (0.212mm i.e. 212 μm), while the fine particles should pass through 72-mesh sieve. The recommended gradings fall between

the 60 coarse: 10 mediums: 30 fines type and the 45 coarse: 10 mediums: 45 fines (Thring M.W. (1962)). Higher plasticity and dry strength but slower drying rate are obtained for fine particle grades and this is normally accompaned with high shrinkage. In coarse particle shrinkage is much more less.

According to Kingery W.D, it was shown that the use of two - particle size decreases apparent porosity from about 45% obtainable in one - particle size to about 15%. This minimum porosity occured at 70% coarse content of the two - particle mix.

2.4.4 Blending and mixing

The composition of a refractory is adjusted by blending the raw materials with the binder (if any). Blending is, however, not only by composition but also by size. The aggregates are blended and mixed proportionally with adequate amount of water to make it viscous, prior to forming. Three major procedures are normally adopted; and these are:

(a) Wet or slip mixing

(b) Semi-dry or plastic mixing

(c) Dry mixing

Wet or slip mixing involves the addition of about 25 - 30% by weight of water to make the aggregate into a slurry form. The amount of water added in this

method, is controlled by that quantity adequate to form the required slurry and it is molded to form the required shape. This method is normally employed for ceramic and pottery wares.

Semi-dry mixing employs the addition of approximately 15% by weight of water and then pressed to form the required shapes. Mixtures that are capable of developing adequate plasticity when water is added uses the semi-dry method of mixing.

Dry mixing involves low water levels. The aggregates are blended and mixed dry or about 5% by weight of water may be added. The resulting mix is either compressed in an hydraulic or water pressure presser depending on whether the 5% water is added or not.

2.4.5 Forming and shaping of refractories:

The refractory material can be classified according to the mix involved into shaped refractory material (bricks) and unshaped refractory material (castable, plastic, etc.) from the view point of shape. Refractories are made into various shapes according to the structural requirements of the furnace. Figure 2.11 shows the standard size and shapes of refractory bricks commonly used in industry.

Refractory bricks are usually formed into shape by the application of a pressure of the order 200kg/cm^2

or more. Bricks produced by this method usually have the least final shrinkage of the products; and also, there is an achievement of greater dimensional accuracy.

The commonest laboratory method of shaping refractories is by subjecting the final mix to a pressure of 6 - 8kg/cm^2 while in the plastic condition. The water content (18 - 22%) by weight of the plastic mix is considered to be adequate though it results in high shrinkage. However, excellent mouldability and good surface smoothness of the product is achieved. Generally, the lower the water requirement of the clay to develop optimum plasticity the better. Plastic method is generally used for the production of intricate shapes.

Wet or slip casting is employed for mixes containing 30 - 45% by weight of water (slurry). The forming procedures involves pouring the slurry into a plaster of paris of the required shape. The porous plaster absorbs the water in the slurry and casting is allowed to continue until the layer of cast material is of the required thickness and the excess slip is poured away. This method is mostly employed in the manufacture of hollow wares.

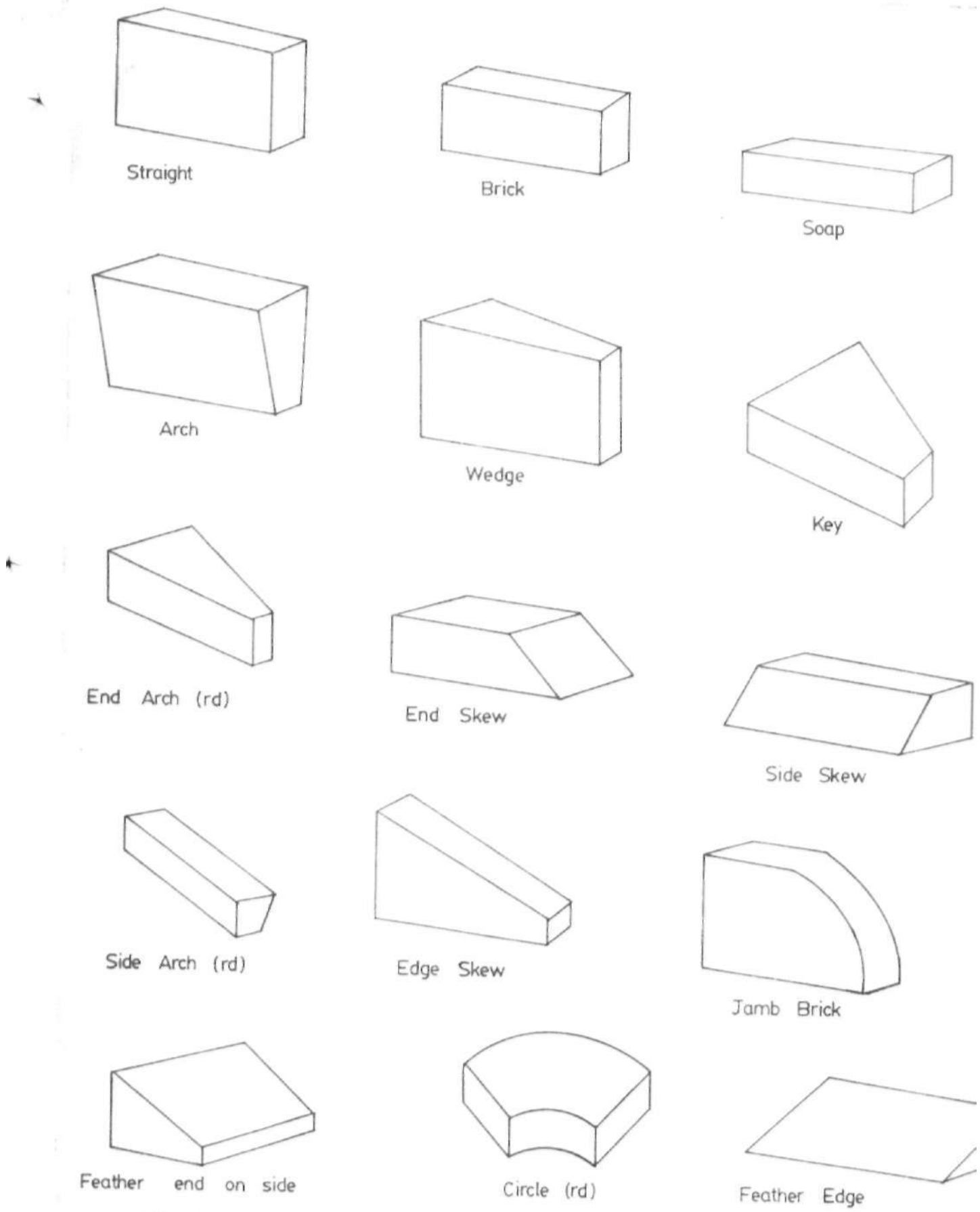


FIG. 2·11 : Standard shapes of refractory bricks (Reinhardt S. Jr; 1952 · Pritchard R; 1977)

2.4.6 Drying of refractories

The prepared shaped product is then dried in open air for a day or more, then followed by oven drying for minimum of 12 hours at 110°C prior to curing (firing). Clays generally, possess the ability to shrink in volume on drying or firing as the particles come closer together. This enables clay to be made into parts with the required density and strength. During drying in air, most clay gradually gives up water, at first at a constant rate and subsequently at a decreasing rate until it losses all the free water. During the constant - rate period the surface is always equally moist and shrinkage of the whole piece occurs. Thereafter the surface begins to appear dry and evaporation takes place within the piece, with little or no shrinkage occuring during this stage. The more water a clay has absorbed the higher is the drying shrinkage so that high plasticity is offset by the danger of cracking due to too rapid drying and irregular shrinkage.

The oven drying is carried out either on a heated floor or in the tunnel type furnace to reduce the drying time. If they are not properly dried, the drying shrinkage that results may lead to deformation, distortion or cracking of the product. Since some materials shrink appreciably during drying, care is necessary at this stage to avoid rapid drying because

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the gradients of moisture content set up may cause warping or cracking. Hence, the rate of drying is usually controlled and it differs according to the type of refractory material. It is generally recommended that drying rate should be very slow to avoid cracking. When completely dried, the product acquired a considerable strength which is further enhanced by firing.

2.4.7 Firing and changes occuring during firing of refractories

The dried mass is next fired in a suitable muffle furnace to a high temperature obtainable in the furnace. According to M.W. Thring (1962) the object of firing is to develop the so-called ceramic bond, which is responsible for the strength and hardness of the fired product, and also to give a volume - stable product which will not unduely shrink or expand when it is subsequently put into service. The process by which this ceramic bond develops is known as vitrification. The onset of vitrification begins at about 950^{o}C and this is a phase transformation accompanied with volume increase. Consequently, unless mineralogical changes which give rise to expansions are taking place, vitrification is usually accompanied by shrinkage and it is very important that this should not be too great if warping and cracking are to be avoided. This is usually achieved by controlling the

particle size of the original mixture since an aggregate of coarse particles shrinks less than an aggregate of fine particles during firing.

Worrall, W.E. (1975) explained that during firing it is generally believed that adsorbed water was first removed at just over 100°C. At temperatures up to 300°C, the water of plasticity is driven off and the clay becomes rigid but not strong. At temperature between 300°C and 400°C the organic matters present in the clay burn away and may result in an unfavourable packing of particles.

The kaolinite clay minerals decompose at about 460°C by losing its hydroxyl groups as combined water. The dehydration is represented by the chemical equation shown below. The dehydration is completed at about 800°C.

$$Al_2Si_2O_5(OH)_4 \xrightarrow{460^{\circ}C} Al_2Si_2O_7 + 2H_2O$$

Kaolinite — Metal kaolin — Water

The product is known as metakaolin. However, organic matters are oxidised during firing and this occurs at about 550 - 900°C. Decomposition reaction takes place, in which the carbonate or hydrated compounds decompose to form oxides and gaseous products such as carbondioxide (CO_2), and water (H_2O) (Ryan W;(1968)). At still higher temperatures the metakaolin undergoes further reactions to form crystalline compound, end-products being cristobalite (free silica) and

mullite ($3Al_2O_3.2SiO_2$). The relative percentage of SiO_2 and Al_2O_3 being 22 - 28% and less than or equal to 70% respectively. Brindly G.W. (1955) first proposed the entire process and this is represnted by the following chemical equations:

$$2(Al_2O_3.2SiO_2) \xrightarrow{920^oC} 2Al_2O_3.3SiO_2 + SiO_2$$

Metakaolin — silicon spinel

$$2Al_2O_3.3SiO_2 \xrightarrow{1100^oC} 2(Al_2O_3.SiO_2) + SiO_2$$

Silicon spinel — pseudo-mullite

$$3(Al_2O_3.SiO_2) \xrightarrow{1400^oC} 3Al_2O_3.2SiO_2 + SiO_2$$

Pseudo-mullite — mullite cristobalite.

In many cases the refractory body does not attain equilibrium since they contains impurities other than SiO_2 and Al_2O_3 (Reinhardt S; (1952)). Theoretically, melting should begin at 1600°C, the eutectic temperature for Al_2O_3-SiO_2 system. The eutectic is formed with 5.5% Al_2O_3 at the temperature of about 1600°C as compared to the melting point of pure silica (SiO_2) at 1724°C. The liquid formed above 1600°C is very viscous and may partake of the nature of a glass more than of a common liquid. On cooling, this liquid tends to remain as a glass. This complex glass is responsible for the vitrification and fire strength of such clays. Quartz in naturally occuring clays is coarse-grained and therefore reacts little, and it often appears unchanged after heating; any that is fine enough to react is probably incorporated in the

glassy phase. Hence, the principal products of fired clays are mullite, a complex glass, cristobalite (if undissolved by the glassy liquid) and some unchanged quartz, if any.

Owing to these chemical changes that occur during firing, there are considerable changes in volume of the clay. These changes are irregular due to rapid expansion or contraction associated with the rapid chemical changes. Linear shrinkage, porosity, bulk density and water absorption rate are the common properties mostly affected by firing stage.

2.5 Properties Of Refractories

Before a refractory can be accepted and recommended to the user as having the required qualities, certain properties have to be satisfied. The primary requirements are such that it:

(a) has to be rigid and be able to maintain its dimension and strength at all working temperatures.

(b) should possess adequate resistance to chemical attack by whatever gas, slag or material likely to be encountered during operation.

(c) should have the ability to withstand thermal shock associated with heating up and cooling down of furnaces. These are the thermal

fluctuations to which furnaces are normally subjected.

The specific properties such as cold crushing strength, thermal expansion, thermal conductivity, apparent porosity and permeability and resistance to wear serve mostly as indirect guides to and measurements of the quality of a given refractory material. Infact they are usually considered as of secondary importance with respect to the primary properties.

To provide a means of assessing and for the purpose of assessing the suitability and controlling the quality of a refractory for a given application, the following properties are commonly measured:-

(a) Drying and firing shrinkage.

(b) Bulk density.

(c) Apparent porosity and permeability.

(d) Cold crushing strength.

(e) Modulus of rupture.

(f) Refractoriness (Fusion point).

(g) Refractoriness - Under - Load (RUL).

(h) Thermal conductivity.

(i) Specific Heat capacity and thermal Diffusivity.

(j) Thermal shock Resistance.

(k) Resistance to slag attack.

(l) Linear Expansion or contraction.

The role each of these properties plays in determining the suitability of a refractory brick for a specific application is enumerated below:

2.5.1 Drying and firing shrinkage

Drying or firing shrinkage of refractory bricks is more commonly expressed in linear relationship than by volume. Drying linear shrinkage accompanies loss of water from between the clay particles. It is generally believed that each clay particle is surrounded by a water - film that becomes progressively thinner during drying. Drying linear shrinkage could be determined either on the basis of the wet (as formed) dimensions, or the dry (uncured) dimensions. The percent linear drying shrinkage on the green basis is given by:

$$\%LDS_w = \frac{L_A - L_B}{L_A} \times 100 \quad \text{---------- (1)}$$

The one based on the dry (uncured) dimensions is given by:

$$\%LDS_d = \frac{L_A - L_B}{L_B} \times 100 \quad \text{---------- (2)}$$

where LDS_w = linear drying shrinkage based on wet dimensions

LDS_d = linear drying shrinkage based on dry dimensions

L_A = the green dimension

L_B = the dry dimension

The higher the amount of water present in the formed mass, the greater the linear drying shrinkage. Excessive shrinkage may cause warping and cracking of the mass. It is therefore necessary for drying shrinkage to be as low as possible.

Firing shrinkage of refractory bricks is usually based on the cured dimensions, as given below:

$$\%LFS = \frac{L_B - L_D}{L_B} \times 100 \quad \text{---------- (3)}$$

where L_D = fired dimension.

The firing shrinkage is found to be the most useful and relevant for the production of refractory bricks.

2.5.2 Bulk density

The bulk density of a refractory body is its weight divided by total volume including pores, and this is the figure used in various engineering calculations of weight and volume of refractory structures. This property indicates whether or not the refractory was well fired. It is normally determined by dividing the test brick mass by the exterior volume. The typical bulk density value of fireclay refractories is 1.90g/cm^3 (Gilchrist, J.D. 1963).

2.5.3 Apparent porosity and permeability:

Porosity originates from the voids which are created within the bulk. These pores are of two kinds;

open and closed pores.

The open, or otherwise known as apparent porosity measures the fraction of void volume to the material volume. The open pores are usually interconnected so that they provide passages through which gases or liquid can pass through. This constitutes permeability and are responsible for the penetration of the liquid or gases into the refractory body. It is also directly related to many other physical properties of a refractory such as resistance to chemical attack.

Practically all furnace refractories have appreciably high porosity levels. The major source by which porosity is induced is through the presence of dead organic materials in the natural raw materials. Another source is from the production process in respect of the size and distribution of the particles composed in the aggregates. Though high forming pressures may be used, voids are always present, and these are not completely eliminated even on firing, and with the observed volumetric shrinkage not withstanding.

It is usual to begin with the porosity test when faced with the problem of ascertaining the suitability of an unknown refractory brick. The porosity level often provide useful (vital) indicators of other properties. In general, bricks with the low porosity levels have the high values for cold crushing strength, high thermal conductivities, resistance to deformation

under load at operating temperatures, heat capacity, and resistance to attack by slag and gases (Harold E.M; 1971). However, such refractories have low resistance to thermal shock (Chester J.H; 1975). A typical value of apparent porosity for silica brick is 26.5% (Chesters J.H; 1975).

The determination of porosity involves measuring the real and apparent densities by standard methods. The British standard method of testing this property which involves the soaking of the brick in water, normally yields three figures, namely: the apparent porosity Pa, the bulk density Db, and the apparent solid density Das. The three parameters are interrelated in the manner shown by the equation below:

$$Pa = 100\ (1 - \frac{D_b}{D_{as}})\% \quad \text{---------- (4)}$$

According to Chester J.H; (1975), one of the methods involves cutting samples (test piece) from a whole brick. Each specimen is at least 50ml in volume. The test piece is first dried in oven at between 105 - 110^{o}C for a period of 12 hours and then rapidly transferred into a vessel of boiling water. With the specimen immersed in the boiling water, boiling is continued for at least 10 minutes. Heating is discontinued and the hot water is displaced by a continuous replacement with cold water for about 30 minutes. The weight W_B, of the specimen suspended in

cold water is recorded. It is then removed from water and its weight, W_C, suspended in air is taken. The dry weight W_A being recorded. A relation between these three weights is used for calculating the apparent porosity of the sample as follows:

$$\text{Bulk volume, } V_b = \frac{W_C - W_B}{D} \ (cm^3) \text{---------} \quad (5)$$

$$\text{Apparent volume, } V_a = \frac{W_A - W_B}{D} \ (cm^3) \text{----------} \quad (6)$$

$$\text{Bulk density, } D_b = \frac{W_A . D}{W_C - W_B} \ (g/cm^3) \text{----------} \quad (7)$$

$$\text{Apparent Density, } Da = \frac{W_A . D}{W_A - W_B} \ (g/cm^3) \text{----------} \quad (8)$$

$$\text{Apparent Porosity, } Pa = \frac{W_C - W_A}{W_C - W_B} \times 100\% \text{ ----------} \quad (9)$$

$$\text{True Porosity, } Pt = \left(1 - \frac{D_b}{D_t}\right) \times 100\% \text{ ----------} \quad (10)$$

D = density of immersion liquid

Dt = true specific gravity of refractory powder.

The true specific gravity (Dt) is determined by the specific gravity bottle method. Sample of the refractory brick is ground to pass through 120-mesh B.S. sieve(410μm) and then dried in the oven at about 110°C. About 15g of the specimen is introduced into the specific gravity bottle and the weight, W_2, of the specimen together with the bottle is recorded. The weight, W_1, of the empty bottle had earlier been taken. About 20 - 30cm^3 of displacement liquid, mainly water,

is first introduced into the bottle by means of pipette to eliminate splashing and finally the bottle is filled with water. The total weight, W_3 and that of bottle filled with water alone, W_4, are taken. Then the true specific gravity of the powder is calculated as follows:

$$Dt = \frac{W_2 - W_1}{(W_4 - W_1) - (W_3 - W_2)} \times 100 \text{ ------- (11)}$$

Permeability:

This is a function of porosity created as a result of interconnected pores which allow the passages of gases or even liquids through the brick. In general, high apparent porosity causes failure due to penetration by slag melts or gases. Permeability is governed by the number and size of the connected pores which are continuous from one side of the brick to the other.

The permeability of a refractory is measured by determining the volume of air which will pass through a specimen of know dimensions in a given time with a known pressure drop across the specimen. The permeability index is given by the formula:

$$\text{Permeability} = \frac{VH}{TAP} \text{ mm/sec. ----------(12)}$$

where:

V = volume of air in mm^3 passing through the specimen

H = Height of specimen (mm)

T = Time taken in seconds for the air to flow through the specimen.

A = Cross-sectional are of specimen

P = Pressure head under which the air has passed (mm of water).

2.5.4 Cold crushing strength

This is an ability of a refractory to withstand adequate load (compressive) at low temperatures. These mechanical properties serve as some measure of the extent to which the ceramic bond has been developed in firing and sometimes may be correlated with certain structure - sensitive service characteristic of the brick.

This property is needed to assure the user that the refractory bricks is capable of withstanding a high handling conditions within shop or during shipping.

It is very rare for refractories to fail due to dead loading in the cold condition. Test of this property are therefore generally carried out with a view to checking indirectly some other property, e.g. abrasion resistance.

Chesters (1973) explained further that the indirect value of cold-crushing strength data lies in examples such as those given below:

(a) Low value of cold - crushing strengths in refractory bricks are generally an indication of underfiring and frequently suggests the desirability of further checks, e.g. of permanent linear change on refiring.

(b) Extremely low values of this property are liable to result from the use in chrome-magnesite bricks of chrome ores susceptible to growth in alternating oxidizing and reducing atmospheres. Since it is found that repeated firing of such bricks leads to further deterioration, similar difficulties may occur in service.

The method of testing involves making a specimen of size 76.2mm cube and marked to indicate the direction of forming pressure during manufacturing. The two faces normal to this direction is prepared as the bearing faces for the direct compression test. A compressive load is applied using a universal crushing testing machine at a rate of 2 tonf/minute until the maximum recorded load is taken as the cold crushing load value. The typical cold crushing value of fireclay refractories is 15,550 in the direction of forming (Chesters J.H; 1975).

2.5.5 Modulus of rupture (MOR):

This is a measure of the fracture strength (by bending) of a refractory. At the room temperature

it is known as the cold modulus of rupture while the hot modulus of rupture is that at elevated (close to operating) temperatures. It is generally believed that the cold modulus of rupture usually has a slight bearing on strength at high temperatures. Modulus of rupture (Hot) is another property of refractories similar to cold crushing strength, in that the brick is normally loaded until failure occurs. Hence, it tends to be more useful in predicting the behaviour of refractories in service than the cold crushing strength.

The MOR test procedure involves supporting a long bar of rectangular cross section of refractory sample 150x25x25mm at the desired temperature near its ends and loading it at a rate of 58kN/m^2/s at the centre (three-point-loading). The loading of the specimen is continued until it fails by fracture. The loading arrangement of the specimen is shown in figure 2.12. The MOR value for such a specimen is calculated by the following formula:

$$MOR = \frac{3WL}{2bh^2} \ N/m^2 \qquad \text{----------(13)}$$

where:

W = Load at which the specimen failed (N)

b = Width of specimen (m)

h = Height of specimen (m)

L = distance between the centres of the two supports (m).

MOR = Modulus of rupture in N/m^2

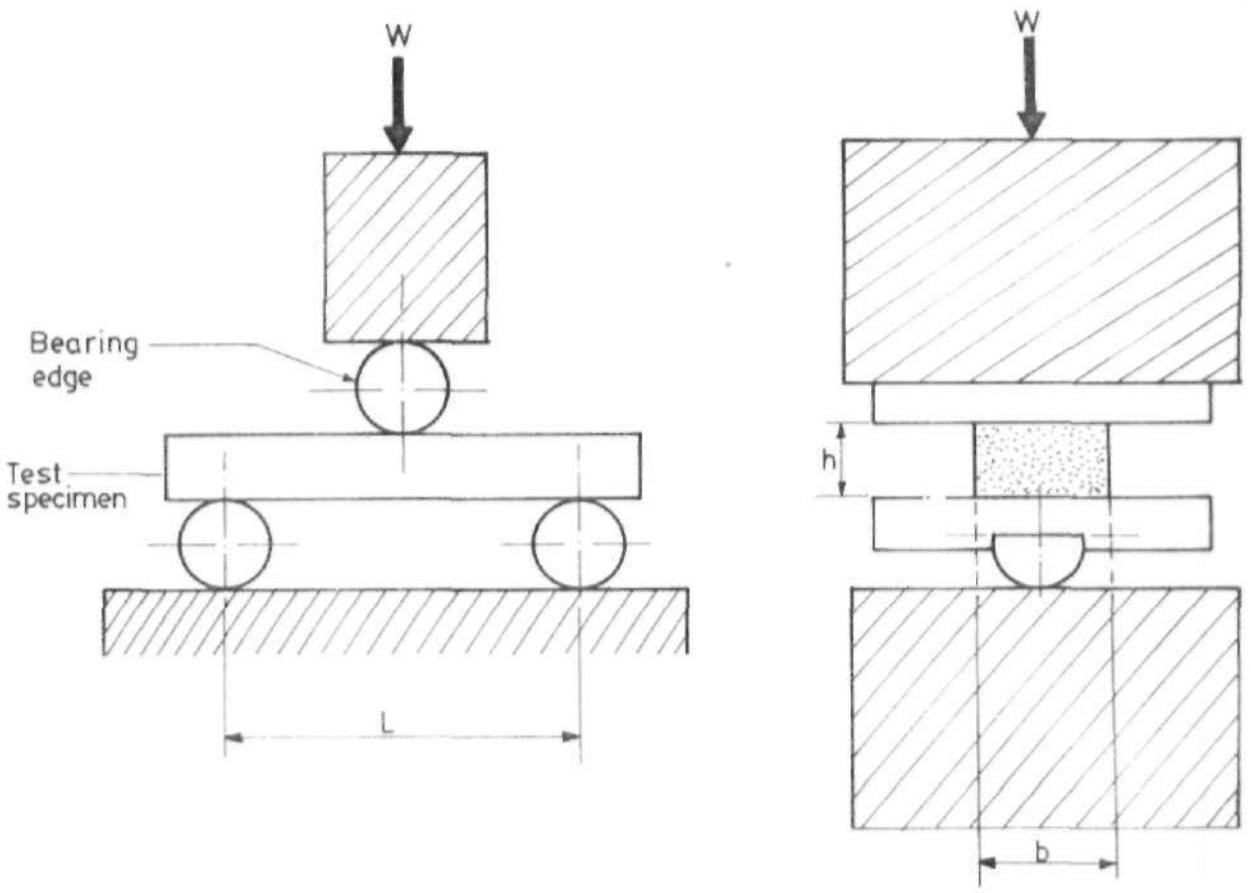


FIG . 2·12 : Three – point loading method of Testing refractories for modulus of Rupture

According to Chester (1973), hot modulus of rupture is rapidly replacing the refractoriness - under - load test, both as an index of quality and as an indication of probable performance in service.

2.5.6 Refractoriness (Fusion point):

Fusion and softening temperatures of a refractory logically come first in the list of service properties, since the first requirement for a refractory material is that it should withstand the high temperature at which it is to be used.

Refractoriness is the property of a refractory to resist and withstand the effects of exposure to high temperatures, without melting or softening. Softening of refractories indicates the maximum temperature to which it can be subjected at normal operating condition. Melting is said to have taken place when the refractory becomes so soft that it can no longer be able to support its own weight. These are only guides to and not an index of quality since these temperatures are usually much higher than the practical or working temperatures for the refractory brick because of their chemical complexity, most furnace refractories, melt progressively over a range of temperature. In this respect, the most common and widely used method of assessing this property is by means of the cone fusion test (Thring M.W; 1962). The test involves the determination of the pyrometric cone Equivalent (PCE), by the procedure standardized as ASTM Test C-24.

In determining the P.C.E, the sample is pulverized to minus 65 mesh and then formed into a test cone having the shape and dimensions shown in figure 2.13. The cone is mounted on an inert and more refractory disc, care being taken to ensure that the perpendicular edge of the cone is vertical, along with a series of standard Pyrometric cones with which the behaviour of the sample is to be compared. The

standard cones are oriented so that they will bend away from the test cone, by having their perpendicular edges facing outward.

The refractory disc with its assembly of cones is then heated at a specified rate in a suitable furnace with uniform temperature distribution having a neutral or oxidizing atmosphere. The heating rate over the last 200°C below the estimated fusion temperature is carefully controlled at 5°C/minute. Softening of a cone is indicated when the cone bends over until its tip level with the base or touches the disc. The heating is discontinued and the P.C.E of the test sample is reported to be the number of the standard Pyrometric cone which most nearly corresponds in time of softening to the test cone.

This procedure actually measures not softening temperatures, but the softening behaviour in comparison with standard materials. During a heating cycle of controlled time and temperature, the PCE's is always converted to approximate softening temperatures, since the behaviour of the standard cones has been carefully measured.

Table 2.12 gives the temperature corresponding to the end points of the standard Pyrometric cones measured under known heating rates.

Depending on the material being tested and on the application to be made of the material, various other ways of measuring softening behaviour may also be adopted. One of such methods is the observation of the behaviour of the test cone while temperature is measured with an optical pyrometer.

Table 2.12: Temperature End Point of Pyrometric(SEGER) Cones:

Seger Cone No	Temperature Equivalent(°C)	Seger Cone No	Temperature Equivalent(°C)
1	1145	20	1560
2	1165	23	1580
3	1185	26	1600
4	1220	27	1620
5	1230	28	1640
6	1260	29	1660
7	1270	30	1680
8	1295	31	1700
9	1315	32	1710
10	1330	33	1730
11	1350	34	1760
12	1375	35	1780
13	1395	36	1800
14	1410	37	1830
15	1440	38	1860
16	1470	39	1880
17	1500	40	1900
18	1520	41	1940
19	1540	42	1980

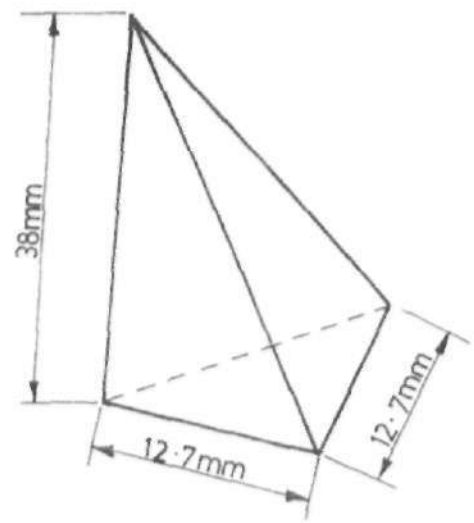


FIG. 2·13 : A Standard Pyrometric Cone (ASTM) for Testing of Refractoriness .

2.5.7 Refractoriness under load (R.U.L):

This is also known as hot strength, and it is the ability of a refractory to withstand a specified load at a chosen working conditions. It may give the maximum temperature at which the refractory brick can be subjected without fear of failure. Neither the PCE nor the ultimate temperature of complete melting give the temperature at which a refractory will collapse under some loading. The results of the refractoriness - under load test are of more practical significance than refractoriness figures in that, refractories fail not only because of fusion, but also mechanical loading facilitates failures of refractories at much lower temperatures. Refractoriness - under load is a good index of quality, since practically all

refractories will fail to function satisfactorily beyond certain temperature levels which are normally less than their melting or softening temperatures.

Gilchrist J.D. (1963) reported that refractory bricks expand first and then contract when heated under load. The temperatures at which these occur differs from one refractory to another. Harold (1971) also noticed that the plastic flow that occurred in the contracting stage will depend solely on:

(a) Crystalline structure of the solids,

(b) Amount and viscosity of liquid present at a given temperature and

(c) The amount of applied load and the rate of application, if the load is not constant.

The temperature of deformation of refractories is greatly affected by the presence of fluxing agents, the degree of firing, and apparent porosity. The fluxing agent in particular, reduce the temperature of allowable deformation. The greatest reduction is caused by those fluxing agents which increase the amount and reduce the viscosity of the liquid so formed. For fired clay refractories the most harmful oxide is sodium oxide (Na_2O).

Higher porosity also reduces the resistance to deformation under load, mainly because the presence of many voids provides opportunity for the brick to

compress and effect pore closure. Hence, well fired brick has much better resistance to deformation than soft fired brick made of the same refractory material.

One method of testing the refractoriness - under-load is to heat the refractory test - piece at a defined rate under a prescribed compressive load and the temperatures at which the initial subsidence and final collapse take place are noted. This is known as the rising temperature test. In this test the recommended heating rate is $10^{o}C$/minute and the heating is continued until the specimen shears or until 5% subsidy has occurred, which ever is the earlier (Thring M.W; 1962).

Another method of testing is to measure the percentage subsidence which occurs within a time interval, for a given amount of loading and temperature which is usually 2 hours. If the refractory collapses under loading at this temperature before the time, the time to collapse is then noted. This mode of testing is the maintained temperature test. In this method a heating rate of $10^{o}C$/minute is specified but this is decreased to $5^{o}C$/minute as the testing temperature is approached.

In so far as it assesses the behaviour of the refractory when continuously loaded over a period of time at the test temperature, the maintained-load test method gives a more realistic index of refractory

behaviour in service. Both forms of the test are more regarded as giving an index of refractory quality rather than providing a figure which can be used in furnace design. Typical values for a very good fireclay refractories are between 1400°C and 1500°C (Budnikov (1964)).

In the British standard test (Thring, M.W; 19 62), the test piece may either be a prism measuring 53.5mm high by 44.45mm square base or a cylinder 53.5mm high by 50.8mm in diameter and with a compressive load applied of normally 3.5kg/cm^2 for silica bricks and 2kg/cm^2 for other materials.

In the American test, two whole bricks or cut specimens of equivalent size of 228.6 x 114.3 x 53.5mm are used and the load applied is 1.765kg/cm^2.

2.5.8 Thermal conductivity:

This is the ability of the refractory brick to conduct heat to the surroundings. The inherent thermal conductivity of the brick is an important factor determining the normal value of refractory brick in service. The thermal conductivity of a refractory depends on the intrinsic conductivity of the material of which it is made and also on the porosity, decreasing as the porosity increases. A low thermal conductivity is required in such applications as external furnace walls and roofs to prevent excessive heat loss.

The production of low thermal conductivity property in insulating bricks is normally achieved by the addition of combustible dead organic matters such as saw - or coal dust to the clay material. These then burns off at the firing temperature and voids created constitutes porosity in the clay body and this result in a low thermal conductivity value of the brick.

There is no standard method developed for the determination of this property. A general method involved measuring the heat flow through a unit thickness of the brick per unit area. It is usually measured on the whole brick with its maximum surface area on a hot plate. The quantity of heat flow past the brick is determined by suitable means. The following equations are used in calculating the thermal conductivity value of a refractory brick:

$$Q = \rho A \frac{(\theta_1 - \theta_2)}{t} \text{ ----------(14)}$$

Hence,

$$\rho = \frac{Qt}{A(\theta_1 - \theta_2)} \text{ ----------(15)}$$

where: A = area of the whole brick

t = thickness of the brick

Q = Total heat flow through the sample.

$\theta_1 - \theta_2$ = Temperature gradient.

ρ = Thermal conductivity of the sample.

2.5.9 Specific heat capacity and thermal diffusivity:

The internal stress developed in the refractory body as a result of temperature gradient during heating and cooling constitute the spalling characteristics of the refractory body. This temperature differential is affected by the heating condition as well as thermal diffusivity βd. Thermal diffusivity is the rate at which the temperature is propagated when a body is heated and this is related to thermal conductivity and specific heat capacity in the following way (Budnikov P.P; 1964).

$$\beta d = \frac{K}{c\rho} \ m^2/hour \text{ ---------- (16)}$$

where: K = Thermal conductivity

c = Heat capacity

ρ = Bulk density

βd = Thermal diffusivity

When thermal conductivity is associated with low specific heat capacity, uneven stresses are reduced, and the refractory body rapidly acquires a uniform temperature.

The typical thermal diffusivity value of fireclay refractories is between 0.25-0.27m^2/hour.

2.5.10 Thermal shock resistance:

This is the ability of the refractory to withstand fluctuation in temperature resulting from

heating and cooling without fracture. It is otherwise known as spalling resistance. It is another source of failure of refractories as a result of exposure to rapid temperature changes. This causes the establishment of a temperature gradient within the brick. Large temperature gradients cause unequal expansion in different parts of the brick, and generate stresses large enough to cause failure by shear or tension.

High stresses may result also when the heating or cooling passes through a temperature at which an allotropic change occurs, with a sudden volume change in a small range of temperatures.

Norton, R.H; (1949) described spalling as failure of the refractory brick resulting from any of the following causes:

(i) Temperature gradient in the bricks, as a result of non uniform heating or cooling that is sufficient to set up stresses of such magnitude as to cause failure.

(ii) Variation in coefficient of thermal expansion between certain layers or portions in the body of the brick. This may be as a result of slag attack or any structural changes in service.

The thermal shock resistance of a refractory brick is a somewhat complex property depending on a number of properties of the material as well as on the size and shape of the body. The method of production has considerable influence on the spalling resistance of a particular type of brick. The method of shaping, whether cast or dry-press leads to different, sometimes unpredictable, results. In addition another complicating factor with furnace refractories is that they are porous, and crystallographically heterogeneous and this tends to stop the propagation of cracks so that complete fracture does not necessarily follow immediately from the initiation of the first crack (Thring M.W; 1962). Majority of the refractories tend to fail progressively on being subjected to repeated thermal shocks which are not severe enough to cause failure from a single shock. As a result of this, refractories are usually tested by subjecting a standard specimen of the brick to repeated cycles of shock of defined severity and recording the number of cycles to cause the test - specimen to separate into at least two pieces.

In the British form of the test, a test-piece sample size of 50.8mm square base by 76.2mm high is used. The specimen is heated to a temperature between 1000-1200^{o}C (450^{o}C in the case of silica bricks) for 30 minutes in the first instance and then withdrawn to cool

on a brick floor for 10 minutes. The brick (test - piece) is then loaded in a standard test rig shown in figure 2.14 made for the purpose. The specimen is returned into the furnace for another 10minutes and the cycle of heating, cooling and testing is repeated until failure occurs or for 30 cycles if failure has not occurred earlier. The material is reported to have excellent spalling resistance if failure has not occurred earlier. Otherwise the number of cycles to failure is reported (Chester J.H; 1973).

Another method, according to BSI specification, involves heating standard prisms of refractories to a high temperature of about 1000 to 1200^{o}C and removing it from the furnace to cool rapidly. After cooling, a pull is exerted on the test specimen. The thermal cycle is continued until the specimen can be pulled apart; the number of cycles is recorded.

The American standard test for this property involves a panel of whole bricks at least 457.2mm square alternately heated to 1400^{o}C and cooling until the surface peel off (Thring M.W; 1962).

The nearest approximation to service is provided by the ASTM panel spalling test, whose wider adoption has only been prevented by the laborious operations involved and the inevitably high cost of obtaining test data (Chesters J.H; 1973). The method involves a panel

of the refractory to be heated on one side in the wall of a furnace, and is then artificially cooled by a fan. After a number of such cycles the spalling resistance of the test specimens is determined from the total weight loss.

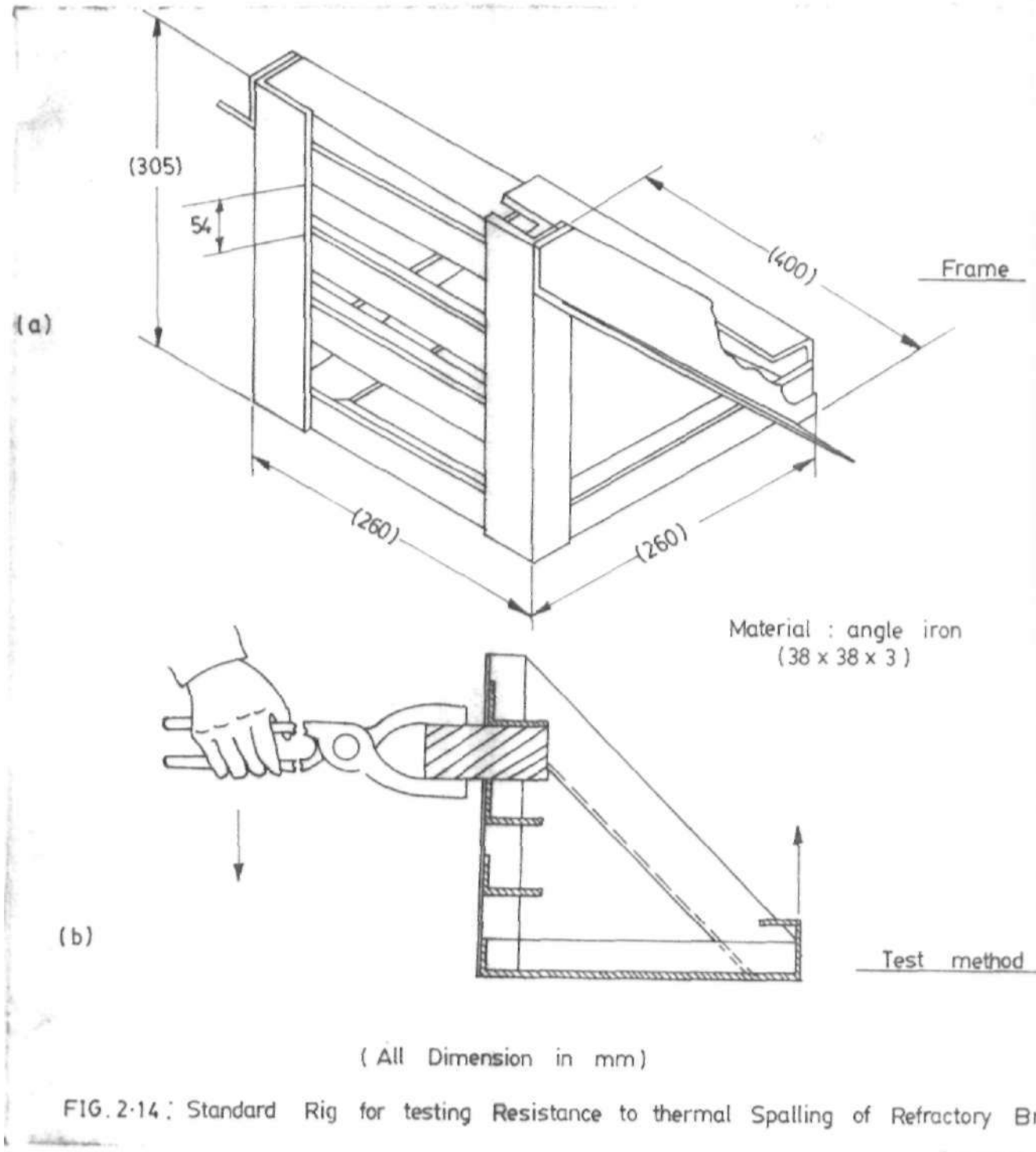


FIG. 2·14 : Standard Rig for testing Resistance to thermal Spalling of Refractory Brick

2.5.11 Resistance to slag attack:

This is the ability of a refractory to resist the chemical action of the hot charge and slag in the furnace, or of the furnace gases Chemical attack, especially by slags, is all-important in the choice of refractory materials for many applications, since even with the most suitable refractory materials corrosion is one of the prime causes of refractory failure.

The common refractory oxides are the same oxides as those forming slags, so that only very rarely is it possible to find a refractory which is insoluble in the slag. Rather the problem is to minimize the rate of slag attack. Many factors affect rate of slag attack, so that in any given case a careful study of the mechanism of the attack may be required to find the best means of overcoming slag action or of bringing it within tolerable limits (Reinhardt S.Jr; 1952).

When a slag remains in contact with a refractory wall for any period of time, the action between the two is generally not confined to a geometric interface separating them but instead usually results in the development of several transitional zones from the interior of the homogeneous slag to the unaffected interior of the wall. What happens in these zones determines the rate of corrosion of the wall. With factors such as melting points, viscosities, diffusion constants, and reaction - rate constant, it is apparent

that slag temperatures and temperature gradients at and through the wall will have large effects on the rate of corrosion.

Chemical attack is involved in a variety of refractory failures other than direct slag action. Erosion by dust-laden gases is accelerated often by slagging reactions between the dust and the refractory.

No simple laboratory tests have been developed which afford a reliable prediction of the rate of slag attack of a refractory. However, the quantitative measurement involves drilling a hole in a brick of the refractory material and packing it with sample of a typical slag likely to be encountered in service. The sample is then heated to a standard temperature and maintained at this temperature for a period of time, preferably one hour. It is then cooled and sectioned to examine the degree of attack and penetration of the slag.

A similar test involves direct firing with pulverised coal to study the effect of coal ash on the refractory. A proportions of the slag or fluxes are mixed with the refractory material in the pulverised form, and made into standard cones and its fusion point determined by heating in a suitable furnace.

2.5.12 Linear expansion or contraction:

This is the expansion and contraction behaviour of a refractory brick. It is the major factor

influencing the thermal spalling property of a refractory material. Refractory materials gradually show this characteristic during thermal expansion due partly to polymorphic transformation which take place on heating. Hence the risk of thermal spalling is greatest when a furnace is being heated up from cold. At temperature above red heat the risk is usually less since the refractory tends to become slightly plastic and can accommodate the stresses more readily.

The expansions/contractions of refractory material usually result in adverse effects, and it has been found that the cracking of a refractory brick associated with heating and cooling can be reduced, if the coefficient of thermal expansions is low. It is obvious, therefore, that a low coefficient of thermal expansion is desirable in refractories. The coefficient of thermal spalling is directly proportional to the coefficient of thermal expansion, and the greater the coefficient of thermal expansion, the smaller the resistance to thermal spalling of the brick. There is usually an expansion of the brickwork as a whole when a furnace is heating up, and small allowanced called expansion gaps are always provided to accommodate this characteristics and these are expected to be closed up at high temperatures. These expansion gaps are usually filled with sheets of combustible material which burns off during heating. Excessive expansion on the other hand is not desirable as wide gaps will have to be

provided in the furnace walls which may cause considerable loss of heat release from the system before they are finally closed up.

In addition to reversible thermal expansions, refractories may undergo permanent deformations when subjected to high temperatures (Thring M.W; 1962). This behaviour is known as irreversible thermal expansion and this causes permanent dimensional changes. This is usually the result of chemical or physical changes which have not been completed during the firing process and which proceed towards completion when the brick is heated in service. The amount be which a refractory brick changes permanently (volume stability) on reheating is usually measured by the standard permanent linear change (P.L.C.) test.

This test is carried out on a test piece measuring 53.5mm high by 50.8mm square base, having the 50.8mm square bases ground flat and parallel (Thring M.W; 1962; Chester J.D; 1973). The specimen is heated in a furnace with an oxidizing atmosphere at the rate of $5^{\circ}C$/minute to the testing temperature. The temperature is then maintained for a period of 2 hours after which the heat is discontinued and the specimen is furnace cooled and its dimensions at room temperature after firing are compared to its original dimensions before firing. The change is length being expressed as a percentage of the original length.

In the British standard test, neither the temperature nor the duration of the test are the same for all refractory materials. For fireclay refractories having a refractoriness of 1680°C and above, a period of 2 hours at 1410°C is adopted. While for fireclay refractories with lower refractoriness value, a period of 2 hours at 1350°C is recommended. For silica bricks, a period of 2 hours at 1450°C is adopted.

In the American "Reheat change" test method (Thring M.W; 1962), a whole brick size 228.6 x 114.3 x 53.5mm are tested, at a test temperature which may be 1200°C; 1350°C; 1400°C or 1600°C according to the type of brick (Chesters J.H; 1973) for a period of 5 hours.

For the majority of applications, refractories must fulfil many requirements other than that of mere refractoriness. No single refractory material can be expected to meet all the requirements. The final selection of a refractory for a particular application is, therefore, frequently a compromise in which less essential properties may have to be sacrificed so that essential requirements may be met.

CHAPTER THREE

3.0 PREVIOUS STUDIES ON NIGERIAN CLAYS

3.1 Introduction

Kankara, Onibode, Nafuta, Majahota and Warram clays are some of the Nigerian clays on which some work has been done. These clays have their applications limited to local industries particularly ceramics or pottery. However, most of it has been in the continuing search of raw materials for the consumption of the Iron and steel industries. Investigation done so far are in the following areas:

(i) Chemical Analysis

(ii) Investigation for suitability in foundry applications.

(iii) Production of refractory crucible and castables

(iv) Refractory use

3.2 Chemical Analysis

The chemical composition of kankara, Onibode, Nafuta, Majahota and Warram clays has been analysed by many individuals and group of people. Some of the analyses are shown in tables 3.1, 3.2, 3.3 and 3.4.

These chemical analyses were done with different interests to be served. For example, Mathew, P. was

searching for clays to be used in foundry sand aggregates. Others were searching for clays to be used as refractory castable and bricks for containing molten metals.

Table 3.1 Chemical Analysis of kankara clay (P. Mathew, 1977)

Oxides	Percentage average Compositions
SiO_2	46.00
Al_2O_3	35.00
H_2O	18.09
Na_2O and K_2O	0.91

Table 3.2 Chemical Analysis of Kankara Clay (Mckay and Schellman, 1983)

Oxides	Percentage (%)	Oxides	Percentage (%)
SiO_2	44.55	K_2O	0.32
Al_2O_3	31.45	CO	0.28
H_2O	18.09	Na_2O	0.17
FeO	1.07	MO	0.01
MgO	0.87	Other sulphates	0.05
TiO	0.41		

Table 3.3 Chemical Analysis of Kankara Clay (Aihevboloria A.C. 1985)

Oxides	Percentage (%)
SiO_2	45.35
$Al_2O_3 + TiO_2$	23.99
CaO	7.07
MgO	14.89
L.O.I*	9.18

* Loss on Ignition

Table 3.4 Chemical Composition of Five Nigerian clays (Ahmed K.S; 1985)

Clay sample / Constituent Parameter (%)	Kankara	Onibode	Nafuta	Majahota	Warram
L.O.I	14.00	14.04	8.69	11.73	14.10
SiO_2	47.23	45.54	67.29	51.10	45.59
Al_2O_3	38.54	38.27	21.76	35.76	36.44
Fe_2O_3	ND	0.72	0.20	0.67	1.00

N.D: Not Detected.

Judging from the silica and alumina contents of these clays, they belong to the alumino - silicate or fireclay class.

3.3 Suitability in Foundry Sand Applications

Mathew (1977) found that the kankara clay was suitable for the use in the preparation of synthetic foundry sand. It was discovered that a limit of 15% of the clay could be added to impart the necessary plasticity to foundry sand. It was also reported to be kaolinite with an AFS clay content of 80.4%.

3.4 Production of Refractory Crucible and Castables

Kankara clay was reported suitable for the production of castables when mixed with about 50% Fondu cement (Musa, T.M. 1984). The castables were reported to be capable of being used as refractory insulators. Some crucibles were also produced from this clay for melting glasses for laboratory purpose (Oyedepo, R.O; 1984). The evaluation of the products was limited to shrinkage properties.

The refractory properties of kankara, Onibode, Nafuta, Majahota and Warram clays were investigated by K.S. Ahmed (1986). The investigation was aimed at establishing conditions for the production of refractory castables using phosphoric acid as a binder which is totally based on local raw materials.

3.5 Refractory Bricks Production

J.A. Aniyi (1985) investigated the refractory properties of bricks made from kankara clay. He found

out that kankara clay possessed the following characteristics:

(i) Shrinkage value of 5.8% which was adequate for refractory bricks.

(ii) Excessive apparent porosity value of 38%.

(iii) Low thermal conductivity value of about 0.48W/m^{o}C.

(iv) The cold crushing strength was 15,527.25 kN/m^{2} which was found to be barely adequate.

(v) Firing the bricks produced from this clay at temperature of 1300^{o}C and above, shows excessive vitrification.

(vi) During the rising temperature refractoriness under load tests, kankara clay began to soften at 1200^{o}C and gave 5% subsidy at 1400^{o}C. A subsidy of 0.42% was obtained during refractoriness under load test in the maintained temperature mode. Hence, the refractoriness of kankara clay was rather low.

S.B. Hassan (1985) also investigated the effect of certain additives on some refractory properties of kankara clay. Sawdust, graphite and asbestos were the additives included in the refractory clay mixes in order to influence the thermal conductivity values. It was discovered that a good thermal insulating fireclay bricks can be produced from this clay by the additions

of graphite and sawdust (15%). It was also found out that, a dense fireclay brick, capable of possessing adequate strength at operating temperature can be made by mixing the clay with upto 25% asbestos.

With the above characteristics, kankara clay did not meet the requirements for metallurgical refractory bricks. This then causes the need to look for clay deposits which satisfy the needs of the metallurgical industry.

CHAPTER FOUR

4.0 EXPERIMENTAL PROCEDURE

4.1 Introduction

Four different clays from the following locations: Bauchi, Oshielle and two from Onibode (A & B) were obtained from different states and locations. Bauchi clay was obtained from Alkaleri village in Bauchi state while the Onibode and the oshielle clays were obtained from Onibode and Oshielle villages respectively, all near Abeokuta, in Ogun state.

The clays in the as-mined condition were in the lump form and all were grounded into powder form (-250 μm). In each case the quality and appearance of the clay varied from deposit to deposit. However, collection of samples which were a good representative of the deposit as a whole were made. The clays were then characterized with respect to their physical appearance, mineralogical composition (DTA) and AFS (American Foundry standard) clay content.

4.2 Characterization

The following preliminary investigations were carried out by a way of characterizing the four clay samples.based on:

(a) Physical appearance

(b) Mineralogical composition.

4.2.1 Characterization according to physical appearance

The clays were characterized according to colour and physical form. Table 4.1 below gives the physical characteristics of the four grades of clays.

Table 4.1: Physical Characteristics of Four Nigerian clays

Clay sample	Appearance (Colour)	Physical Form
Oshielle	Brown Stains Cream	Hard lumps with smooth touch.
Onibode (A)	Brown	Moderately hard, with soft touch
Onibode (B)	Light Brown	Soft, smooth powdery lumps
Bauchi	White	Very hard lumps of coarse texture

4.2.2 Characterization according to mineralogical composition

Differential thermal analysis (DTA) was used for the qualitative study of the crystalline phases present in the clays. A portion of each clay powder was used for the DTA runs. A sample weighing 0.4g was used at a time with the same quantity of burnt kaolin serving as blank. For each run the double pen chart recorder produced thermographs of both the samples and the standard kaolin under the same operating conditions.

The quantitative evaluation of a DTA curve in practice involves heating the sample to be tested simultaneously with a reference material and the temperature difference between substances is measured. Because the reference substance will show no reaction in the investigating temperature range, the reaction of the substance to be tested has to be measured as a temperature difference against the inert (reference) substance.

The equipment normally used for this test consists of the pick-up attachments for the samples (here marked as measuring head), the heating furnace, a working stand, a base cantilever and adjusting devices. The measurements of the thermal effect are carried out at continuous temperature changes and registered via direct current voltage measuring amplifiers by point printers, two - line recorder as shown in figure 4.1 and 4.2.

Then the curve of a material of known enthalpy change is recorded simultaneously with that of the test sample, and the magnitude of enthalpy change of the transformation in question is evaluated on the basis of the sizes of the area defined by the two curves.

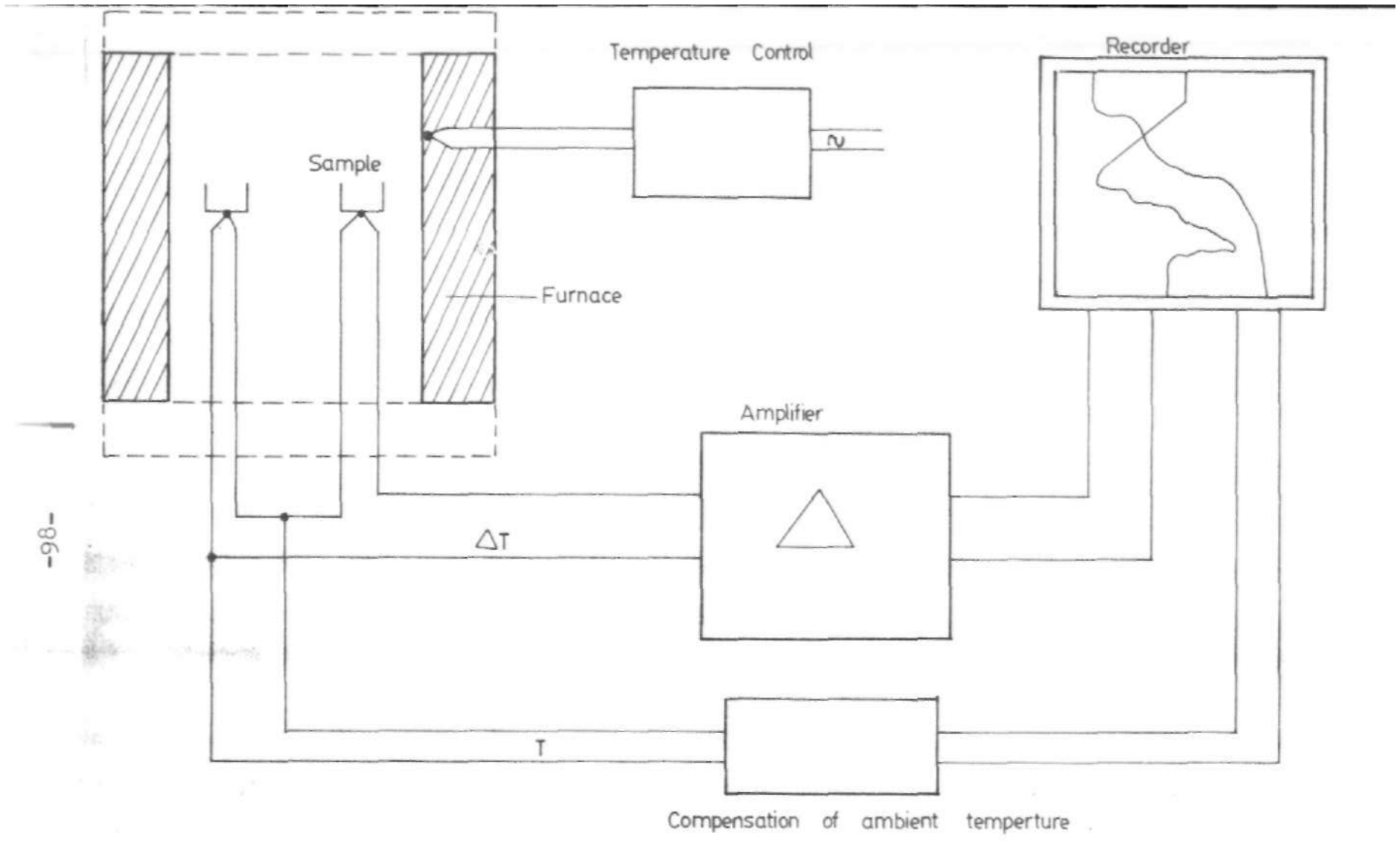


FIG. 4·1 : DTA Measuring Arrangement (Schematically)

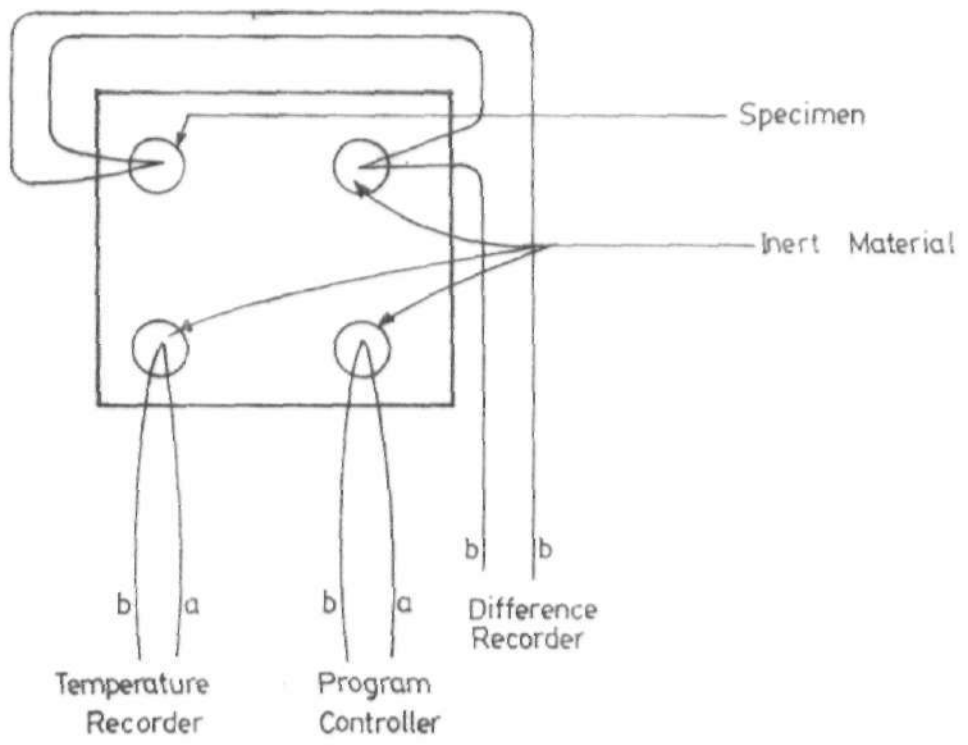


FIG. 4·2 : Thermocouple arrangement for DTA .

The factors that do affect the accuracy of DTA evaluation include:

(a) Abrupt changes in the base line of a DTA curve. This give rise to much more difficulty than the measurement of the area under the curve. This is shown in figure 4.3.

(b) The determination of the shares of two overlapping areas in the double maximum of two transformations partly overlapping. Mackenzie (1970) suggested that the graphical method should be employed for

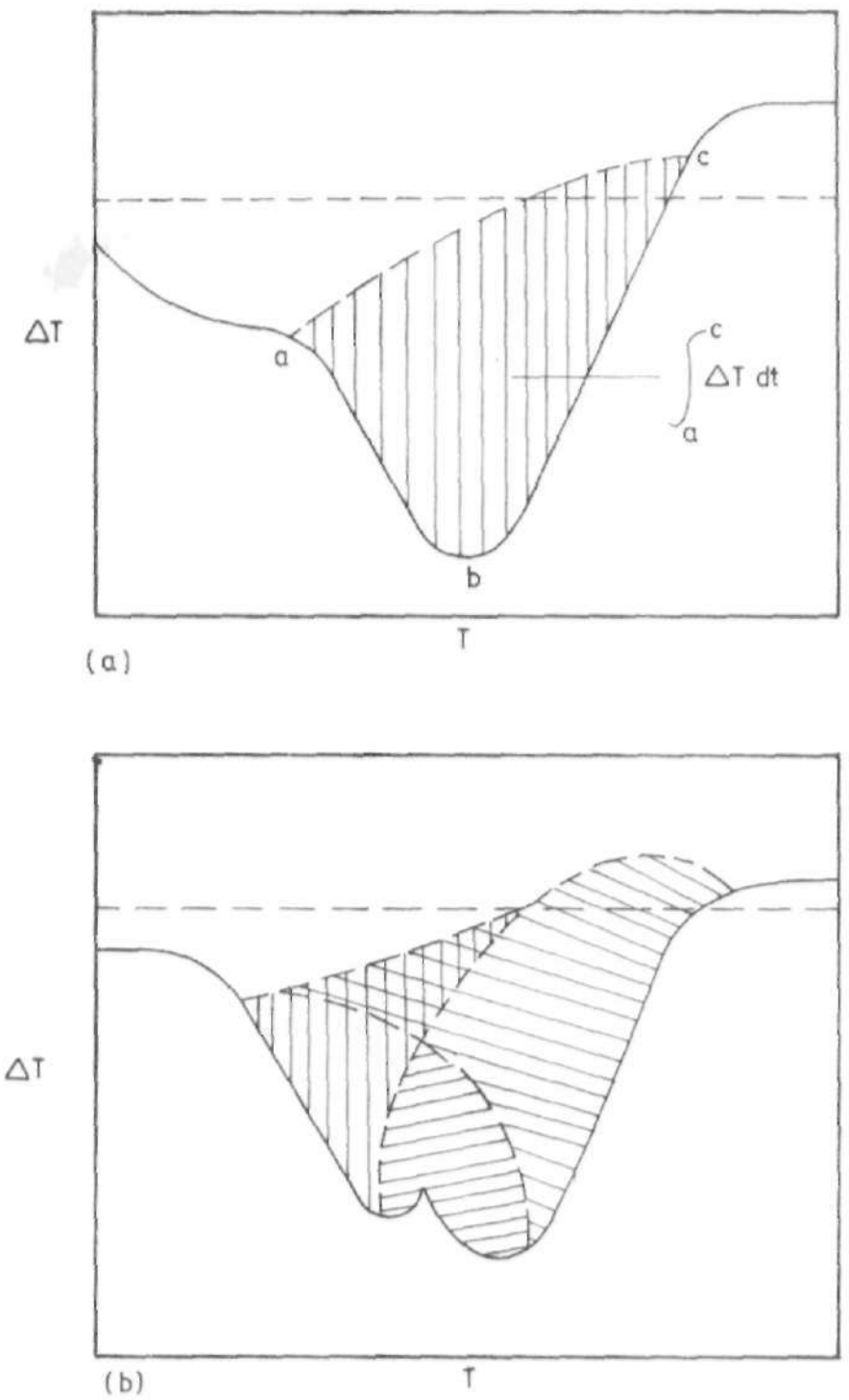


FIG . 4·3 : Factors Affecting the Accuracy of Qualitative DTA Evaluation
(a) Abrupt Change in Base line .
(b) Over lapping Transformations .

the determination of the boundry lines of areas under peaks.

The area under the peak is markedly affected by the following factors:

(i) The design of the apparatus, such as the sensitivity of the galvanometer and the size of the sample crucible.

(ii) The physical properties of the test sample and the reference (inert) material; such as the heat capacity and the thermal conductivity of the sample.

(iii) The heating rate of the furnace.

The kaolinite content of each clay was then determined from the endothermic peak around 600°C by comparing the chart obtained with the standard charts. The percentage of clay mineral content was read out from the standard chart that marches the plotted experimental curve. The results for these test are shown in table 5.2 and the chart obtained are shown in figures 5.1(a),(b), (c), and (d) for the clay samples.

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4.2.3 Chemical analysis

For each of the clay samples, the dried clay was crushed and grounded into powder. The sieve analysis was carried out by selecting the clay that passed through sieve size 106 μm as the optimum size for the chemical analysis.

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The chemical analysis of the four clay samples were carried out using the traditional techniques known as "Wet method" as given in the literature.

The clay powder was pre-treated by adding 7.0 gramme of anhydrous sodium carbonate (Na_2CO_3) as a fluxing agent to 1.0 gramme of clay sample in a nickel crucible and then thoroughly mixed. The crucible was then covered with its lid and heated in a muffle furnace slowly at first and vigorously for one and half hour until there was complete fusion of the clay sample. The covered crucible and their contents were allowed to cool in a dessicator after which the fused clays were transfered into a porcelain dish containing distilled water. The porcelain and its contents were warmed in a water bath to disintegrate the fused sample. 9.5ml of 36% HCl was added to the fused sample to decomposed it and this also produced an acidic effect on the medium. It is then warmed again in a water bath until the evolution of carbon dioxide (CO_2) ceased. The nickel crucible and its lid were thoroughly washed and rinsed with both distilled water and dilute HCl.

The sample was then completely evaporated to dryness and dehydrated in an oven at 110^{o}C. Then the dried clay samples were stored in a dessicator.

The pre-treated clay samples were then used for the determination of oxides in the clay samples. The

following oxides were determined: Moisture content, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and Loss on Ignition. The results for the chemical analysis of the four clay samples are shown in table 5.3.

4.2.4 Determination of AFS clay content and Fineness number of the clay samples

Sylvia (1972) explained that the AFS clay in a foundry moulding sand are the particles which fail to settle down at the rate of 25.4mm/minute when suspended in water. These particles are usually less than 20 μm in size and they include very fine minerals.

The AFS clay content of each of the four clays was determined by putting 50g of the clay in a standard clay content-tester having beaker of volume $1000cm^3$. About $25cm^3$ of sodium hydroxide (NaOH) solution (0.3ml NaOH) was added to it and the beaker was then filled with water to the required level. The contents of the beaker was stirred mechanically by the stirrer incorporated with the system. The particles were allowed to settle for 10 minutes and the water above the clay was siphoned out. The next cycle involved the addition of fresh water to fill the beaker, stirring, and leaving it to stand for 5 minutes before siphoning the water out. This cycle was repeated until the water in the beaker above the clay was clear of suspended particles after 5 minutes of standing. The residue in the beaker, mainly sand, was

dried at 110°C and weighed. The weight were recorded for the four clay samples. The sieve analysis of the clay were then conducted. The A.F.S. clay contents were then determined for each, and the results of the analysis are shown in table 5.4.

4.2.5 Determination of optimum moisture levels

It is most desirable to use as low moisture level as possible while the quality of the bricks are not sacrificed. In this work, the optimum water level was determined for each of the clay samples on the basis of adequate green strength. The required amount of moisture level for each clay, was selected by preparing bricks from the raw clay at different water levels starting from 10% by weight and using mannually operated press. Bricks were then examined for strength sufficient for handling in the wet condition. The Oshielle and the first Onibode clays were found to develop enough plasticity to hold the particles together in shape under the moulding pressure as from 18% water by weight. The second Onibode and Bauchi clays developed enough strength and plasticity at higher moisture levels of 20% and 22% respectively.

A reasonable densification and better surface finish were obtained for the bricks in the green condition for 10kg/cm^2 pressure as compared with those obtained for the standard pressure of 8kg/cm^2.

4.3 Production Of Refractory Bricks:

The initial processes of the clays commenced by crushing the raw clays as mined, soaking for two or three days, washing and then followed by drying in the sun. The soaking was necessary to get the alkalis dissolved and also to remove light dead organic matters. The inclusion of these alkalis in large amount tends to lower the refractoriness of clays and hence retards the formation of mullite.

The dried clay was then ground in the muller into powder and sieved to pass through the following grades. The coarse aggregates were those retained on 22-mesh sieve (710 μm), while the medium and the fine aggregates were those retained on 44-mesh (355 μm) sieve and 100-mesh (150 μm) sieve respectively. The preparation of test specimens involved the mixing of freshly sieved clays with water and then pressed to shape by the application of 10kg/cm^2 pressure. The 10kg/cm^2 pressure was applied instead of the recommended pressure of 8kg/cm^2 for improved properties in the green condition, particularly the surface smoothness.

The specimens were then dried, first in the open air on the laboratory floor for 24 hours followed by oven drying for 12 hours in the case of samples for testing of the following properties: shrinkage, apparent porosity, thermal shock resistance,

refractoriness and refractoriness under load, while oven drying for 24 hours in the case of samples for test of the cold crushing strength due to the size of the samples, at a temperature of 110°C. The rate of drying in the oven was controlled by a built-in fan which was set at the low position to ensure the required slow rate of drying. Thus was followed by full firing in an electric furnace at a designed heating rate of 7°C/minute. The firing procedure adopted involved heating and soaking the samples at various temperatures, as shown below:

(i) at 350°C for 6 hours
(ii) at 650°C for 4 hours
(iii) at 950°C for 3 hours
(iv) at 1300°C for 8 hours

The firing procedure normally encounter in industry for fire bricks, recommended a longer time at both low and high temperature. A period of 12 - 48 hours is recommended for temperature of 300°C and 12 to 18 hours for temperatures in the range 1200 - 1400°C. However, because of the limitations due to furnace elements and capacity, the above laboratory procedure was adopted and found to be satisfactory. The samples were furnace cooled at a cooling rate of about 1.5°C/minute.

4.4 Tests Procedure

The refractory properties tested among many properties in this project were listed below:

(i) Linear shrinkage

(ii) Bulk density and Apparent Porosity

(iii) Cold Crushing strength

(iv) Thermal shock resistance

(v) Refractoriness

(vi) Refractoriness Under Load (R.U.L.)

These properties were selected on the basis of their importance and the availability of equipment. However, Refractoriness and Refractoriness Under Load (R.U.L.) were performed at D.S.C. (Delta Steel Company) Aladja, Warri.

The test procedures were as recommended in the literature. However, in a few cases, slight deviations were made as a result of practical limitations imposed by the equipment in the laboratory.

4.4.1 Linear shrinkage:

The shrinkage properties of the pressed bricks were determined by measuring the green dimension of the bricks, which was 84 x 81 x 53mm, and comparing it with the fired dimensions. The linear shrinkage was then calculated as a percentage of the original green dimensions. The results of the tests for the bricks made from the four clay samples are shown in table 5.6.

4.4.2 Bulk density and apparent porosity:

For each of the clay samples, four test bricks were made and were used for the determination of Bulk density and Apparent porosity. Each brick was 40mm cube. Before the test, the brick was dried in the oven overnight at 110°C and quickly transferred into and suspended in a vessel of boiling water for 10 minutes. At this time, the boiling was discontinued and the hot water was gradually displaced by continuous addition of cold water. This was done for at least 30 minutes and with the brick still suspended in the cold water, the weight of the brick was measured and recorded (W_B). The soaked brick was then taken out of the water and weighed in air (W_C). The dry weight of the brick was earlier measured and recorded as W_A. From the relation given below, the bulk density, apparent solid density and apparent porosity of the brick were determined.

$$\text{Bulk density, } D_b = \frac{W_A}{W_C - W_B} \ (g/cm^3) \quad \text{--------- (a)}$$

$$\text{Apparent solid density, } D_{as} = \frac{W_A}{W_A - W_B} \ (g/cm^3) \quad \text{--------- (b)}$$

$$\text{Apparent porosity, } P_a = \frac{W_C - W_A}{W_C - W_B} \times 100\% \quad \text{--------- (c)}$$

The results of the tests for the bricks made from the four clay samples are shown in table 5.7.

4.4.3 Cold crushing strength:

Standard bricks, which were 76.2mm cube, were tested for the cold crushing strength using a universal Denison strength testing machine in 200kN range. The strength values of the bricks both in the direction of forming and the direction normal to the direction of forming were recorded. Two samples were tested for each of the directions and the results are shown in table 5.8.

4.4.4 Thermal shock resistance:

A standard brick measuring 76.2 x 50.8 x 50.8mm was put in the furnace, which was maintained at temperature of 1100^{o}C and soaked at this temperature for 30 minutes. After this time, the hot brick was brought out to cool in air for 10 minutes. The brick was tested for failure using a fabricated rig (figure 2.12) if failure does not occur, the brick is then put back into the furnace and heated for a period of 10 minutes. This cycle of heating, cooling and testing was repeated until failure occurred.

The results obtained from this test showed that the bricks had poor thermal shock resistance at temperature of 1100^{o}C. It was therefore considered necessary to test this property at higher temperatures. Hence, the bricks were heated to temperature of 1300^{o}C for 30 minutes and then cooled

in air for 10 minutes. The procedure was the same as previously done at 1100°C. The test was concluded when all the specimens were broken. The number of complete cycles required to produce failure in each specimen was noted.

This test was done for each of the clay samples, and the results are shown in table 5.9.

4.4.5 Refractoriness:

The sintering test was initially carried out. This test was performed prior to refractoriness test because it served as a guide for the selection of seger cones needed for the refractoriness test.

The powder form of the clay samples, contained in separate discs, were heated in the furnace at a heating rate of 10°C/minute. At temperatures above 1000°C, the clay samples were constantly checked for commencement of sintering. This situation was indicated by the powder sticking to the disc. The temperature at which sintering occurred was noted for each of the different clay samples and are shown in table 5.10.

Two test samples were made from each of the clays and were tested for refractoriness. The test samples were made into seger cones with the dimensions shown in figure 2.12. The cones were mounted on an inert refractory disc, along with the

appropriate standard pyrometric cones selected on the basis of the results of the sintering tests. The refractory disc with its assembly of cones were then heated in the furnace at the heating rate of $5^{o}C$/ minute. The heating was discontinued when the test cone bent over and levelled with the base of the disc. Then the pyrometric cone equivalent (P.C.E) of the test sample was recorded to be the number of the standard pyrometric cone which most nearly corresponded in time of softening to the test cone. The result of the test is shown in table 5.10.

4.4.6 Refractoriness Under Load (R.U.L)

The Refractoriness-Under Load was performed for the rising temperature test mode and in accordance with the standard procedure. The cylindrical test specimens of the dimension 50.8mm diameter by 53.5mm high as recommended were made for all the four clay samples.

Rising temperature tests were run for the specimens using a $1800^{o}C$ DIETERT RUL furnace. The equipment consists of an electric furnace console capable of being raised up or lowered for heating the specimen. There are two loading alumina refractory posts; the upper and the lower posts purposely for the application of pressure. The upper post is capable of being raised by an hydraulic system for applying pressure. The displacement of the movable

post is measured using a micrometer dial gauge actuated by a lever mechanism (figure 4.4).

In the test the specimen was placed vertically in-between the two refractory posts. The heating chamber was then lowered so as to contain the test specimen within the chamber. At this stage, a load of 2kgf/cm^2 (1.93×10^5N/m^2 or 28 psi) was applied and the specimen was heated at a recommended rate of 10^{o}C/minute. The displacement which is the deformation of the test specimen was read on the dial gauge and recorded at 50^{o}C interval. This was continued until more than 5% subsidy was recorded.

The result of the refractoriness under load tests were done for the four clay samples and are shown in table 5.11.

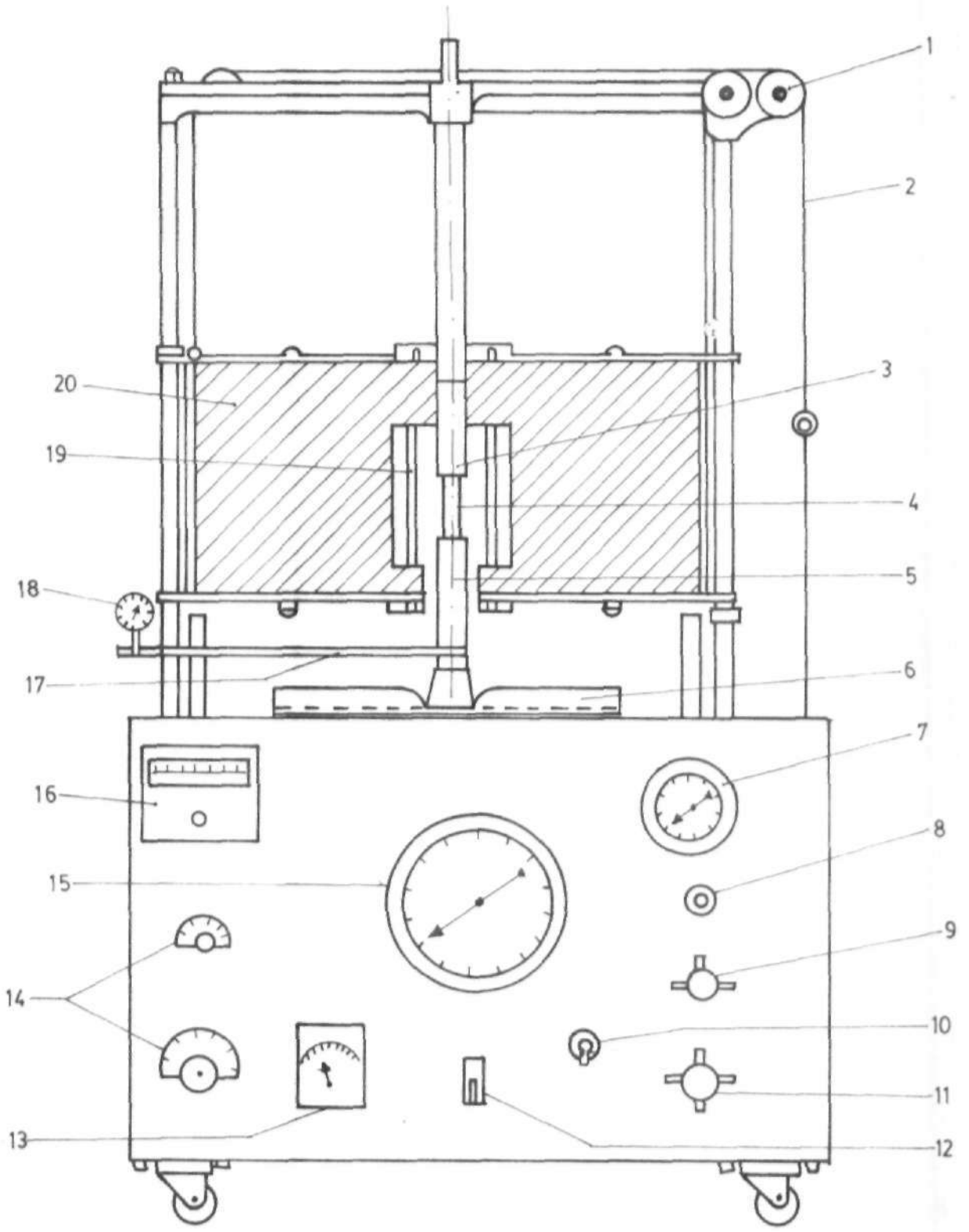


FIG . 4 . 4 : Dietert Dilatometer .

Dietert Dilatometer Components

1. Pulley,
2. Cable for lifting furnace
3. Upper refractory post,
4. Refractory brick sample,
5. Lower refractory post,
6. Collecting pan,
7. Small pressure guage,
8. Pressure presetting valve
9. Small guage shut-off valve,
10. Compressor switch
11. Pressure release valve,
12. Main switch,
13. Ammeter,
14. Voltage selectors
15. Bigger pressure guage,
16. Temperature indicator,
17. Amplifying lever,
18. Dial guage,
19. Graphite Electrode (heating element)
20. Refractory bricks.

CHAPTER FIVE

5.0 RESULTS AND DISCUSSIONS

5.1 Preliminary Tests

It was found that at water additions less than 18%, the plasticity and the compactibility of the moulded mixture were low for all clays. They were too dry. It was found, that adequate plasticity was obtained at 20% water addition for the Oshielle and Onibode (A) clays. However, higher water addition of up to 24% was required to obtained requisite plasticity in respect of the Onibode (B) and Bauchi clays. Hence, by comparison of the characteristics attained both before and after curing, the optimum properties of the Oshielle and Onibode (A) clays were found to be achieved at water addition of 18% while, the optimum properties of the Onibode (B) and Bauchi clays were found to be achieved at 20% and 22% water addition respectively.

5.2 Characteristics of the clay samples:

5.2.1 Physical appearance of samples:

The clays had varying physical characteristics as it is shown in Table 4.1.

Oshielle and Onibode (A & B) were quite similar in colour, and texture. The three of them were brown, though the Oshielle clay had cream stains. It was also lumpy while the Onibode clays were powdery. Bauchi

clay had white colour, not powdery and was in very hard lumps, which were not easily crushed by hand.

5.2.2 Particle size distribution

The results of the particle size analysis of the four clay samples are presented in Table 5.1(a) and 5.1(b).

It is pertinent to note that the percentage of material with particle size that fall between 710 μm and 75 μm sieve (Table 5.1(b)) are fairly high and hence show that these clay can be economically utilized for refractory production. This is because the refractory bricks are normally made from clays with particle size in this range.

However, there is a relatively higher percentage of coarse aggregates particularly in the Oshielle and Bauchi clays. They also gave the least percentage for constituents retained on the pan. This is reflected in the low AFS fineness numbers for these clays as shown in table 5.1(a). The constituents with particle sizes greater than or equal to 710 μm were found to be basically silica in appearance.

Hence, it could be assumed that bricks made from the Oshielle and Bauchi would contain more silica than those of Onibode clays.

The fineness numbers obtained are also indications of the crushability of the different clays in the as-mined condition, and they confirm what was expected from the physical appearance of each clay samples. It may also be presumed that the smaller the AFS fineness number, the higher the clay content.

Table 5.1(a): Particle Size Analysis of Four Selected Nigerian Clays:

Sieve Grade			Weight Percentage (%) of Particle Retained				Multiplying Factor x Weight %			
Sieve Opening (μm)	Sieve Mesh	Multi-plying Factor	Oshielle	Onibode (A)	Onibode (B)	Bauchi	Oshielle	Onibode (A)	Onibode (B)	Bauchi
1000	16	14	18.37	9.63	7.64	7.28	257.18	134.82	106.96	101.92
710	22	16	12.28	8.95	12.67	19.88	196.48	143.20	202.72	318.08
420	36	22	26.03	26.46	25.53	28.42	572.66	582.12	561.66	625.24
300	52	36	6.58	7.49	7.54	7.47	236.88	269.64	271.44	268.92
250	60	52	6.68	6.23	6.48	6.89	347.36	323.96	336.96	358.28
150	100	60	18.08	14.98	15.09	18.24	1084.80	898.80	905.4	1094.40
106	150	100	6.39	7.88	7.06	5.53	639	788	706	553
75	200	150	4.72	13.91	14.60	5.53	708	2086.50	2190	829.50
53	300	200	0.59	3.79	2.81	0.49	118	758	562	98.00
Pan	-	300	0.30	0.68	0.54	0.29	90	204	162	87.00
TOTAL			100.02	100.00	100.00	100.02	4250.36	6054.22	6005.14	4334.34
FINENESS NUMBER							42.50	60.54	60.05	43.34

Table 5.1(b): Approximate Proportion of Silica, Clay and Silt in the Five clay samples

Particle size (μm)	Clay Samples				Remark
	Oshielle	Onibode (A)	Onibode (B)	Bauchi	
> 710	30.65	18.58	20.13	27.16	Silica
75-710	68.46	76.95	76.52	72.06	Clay
< 75	0.89	4.47	3.35	0.78	Silt

5.2.3 Differential Thermal Analysis (DTA) of the Clay samples:

The Differential Thermal Analysis charts for all the four clay samples are shown in figures 5.1(a),(b), (c) and (d). These figures show the endothermic and exothermic peaks which were matched with appropriate standard charts, from which the relative proportions of clay minerals were determined and are as shown in table 5.2.

All the four clay samples contain kaolinite and Illite mineral and none of the clay samples showed traces of Montmorillonite mineral. Onibode clays has a high percentage of kaolinite mineral and Onibode (B) is predominantly kaolinitic in nature. Oshielle and Bauchi clays are low in kaolinite content.

Table 5.2: Differential Thermal Analysis of the clay samples

Clays	Peaks		Composition		
	Endothermic	Exothermic	% Kaolinite	% Illite	% Montmo-rillonite
Oshielle	650	1003	25	75	-
Onibode (A)	630	1002	50	50	-
Onibode (B)	620	1000	90	10	-
Bauchi	630	1010	25	75	-

5.2.4 Chemical composition

The results of the chemical analysis of the four clay samples as performed in the laboratory are presented in Table 5.3, which showed the major constituent parameters that influence the refractory properties of the bricks.

Bauchi clay was found to be free from Fe_2O_3, which agreed with the white physical appearance. Others have 0.4% for the Oshielle and Onibode (B) clays. Only the Onibode (A) clay has 0.8% Fe_2O_3. This explains the brownish colour in the as-mined condition of the three clays.

The Alumina content (Al_2O_3) of these clays ranged from about 25-36%. This range falls within that for Aluminosilicate clays (Table 2.4), which is 25 - 45%. It is the Bauchi clay which has the least Al_2O_3 content, and may be expected to have poor refractoriness.

Onibode (A and B) clays have adequate and comparable alumina content and will be expected to possess superior refractoriness. They also have composition similar to the zettlitz kaolin of Czechoslovakia and sergeant China clay of United States of America (Table 2.10).

It should be noted that all except Oshielle clay have relatively a high percentage of CaO and/or MgO and will be expected to improve their refractoriness. There are only traces of fluxing materials such as Na_2O, K_2O and TiO_2 and small percentages of Fe_2O_3. In this respect, and at these levels, their presence is expected to cause adverse effects on the refractory properties.

The combustible matter lost on ignition for each clay sample is about 15%, and is a little bit on the high side, though it is often specified to be less than 16%. One will expect this to affect shrinkage and porosity values to some extent.

Table 5.3: Chemical Composition of Four Nigerian clays:

Oxides Contents	Clay samples			
	Oshielle	Onibode (A)	Onibode (B)	Bauchi
Moisture	0.10	0.20	0.12	0.20
SiO_2	45.70	50.00	49.00	56.50
Al_2O_3	36.00	30.00	33.60	24.95
Fe_2O_3	0.40	0.80	0.40	N.D
CaO	1.00	4.00	3.00	1.00
MgO	1.00	2.00	0.80	2.33
Na_2O	Trace	Trace	Trace	Trace
K_2O	Trace	Trace	Trace	Trace
TiO_2	Trace	Trace	Trace	Trace
L.O.I	16.13	13.98	14.85	15.32
TOTAL	100.33	100.98	101.77	100.30

5.2.5 AFS clay content

The clay content for each of the clays is seen in table 5.4. Onibode (B) is found to have the highest clay content of 91.2%, followed by Onibode (A) and Bauchi clays with about 80%. Only Oshielle clay had a relatively low clay content. This result was predicted from the particle distribution test. With the low clay content, one will presume that the Oshielle clay will probably have the most inferior properties.

Table 5.4: AFS Clay Content of the Four Selected Nigerian clays

Clay Samples	Initial Weight of clay sample (g)	Weight of Residue (g)	AFS clay content (%)
Oshielle	50	19.20	61.60
Onibode (A)	50	9.50	81.30
Onibode (B)	50	4.40	91.20
Bauchi	50	9.40	80.20

5.2.6 Surface appearance of fired bricks

The appearance of the dried and cured bricks formed from all the four clays, are described in Table 5.5.

There were slight colour changes in the bricks after firing at 1300°C as follows:

(i) Oshielle clay - from brown to light cream

(ii) Onibode (A) clay - from brown to dark cream

(iii) Onibode (B) clay - from light brown to light cream.

However, the Bauchi clay retained its white colour after firing.

The change in colour from brown to lighter shade of cream may be due to reactions involving Fe_2O_3. Only Bauchi clay which had no Fe_2O_3 and retained its original colour.

Bauchi and Onibode (B) clays fired at 1300°C developed no cracks, while the bricks produced from Oshielle and Onibode (A) clays were cracked on firing at 1300°C. However, these cracks may probably result from the differential thermal expansion between the clay particles and the constituent quartz grains (Singer and Singer (1963)).

Table 5.5: Surface Appearance After Firing

Clay Sample	Appearance			
	After dried at 110°C for 24 hours		After fired at 1300°C	
	Colour	Crack Formation	Colour	Crack Formation
Oshielle	Brown stains cream	No crack	Light cream	Cracks
Onibode (A)	Brown	No crack	Dark Cream	Less Cracks
Onibode (B)	Light Brown	No crack	Light Cream	No Crack
Bauchi	White	No crack	White	No Crack

5.3 Physical and Mechanical Properties:

5.3.1 Linear shrinkage characteristics

The linear shrinkages of the bricks made from the four types of clays were determined and are shown in table 5.6. Low average shrinkage values of 3.62% and 5.58% were obtained for Oshielle and Bauchi clays respectively. It is seen that these values are less than the shrinkage values of between 7 and 9%

(Budnikov (1964) which are common for kaolins.

However, higher values were obtained for the Onibode clays. The Onibode (A) clay had 7.17% shrinkage and that for the Onibode (B) clay was considerably higher, being 11.81%. It should be noted that the total shrinkage for each set of bricks is made up of two components.

(a) Shrinkage during drying

(b) Shrinkage during firing.

The firing shrinkage is calculated from the difference between the total and the drying shrinkages.

The drying shrinkage was rather appreciable for the Onibode (B) clay. Hence, this is an indication of its ability to absorb water and its swelling characteristics. Onibode (A) and Bauchi clays were found to have moderate drying shrinkage values. However, Oshielle clay had very low drying shrinkage showing its low ability to absorb water. This is not unexpected because of its low clay content (Table 5.4). This clay would be expected to have low plasticity.

The linear shrinkage during firing, shown in the table indicated that very little shrinkage took place in all the clays. This is quite unexpected in the light of the amount of the volatile matter contained in all the clays as shown by the loss on ignition values.

The firing shrinkage for the Bauchi clay was particularly very low, 0.06%, indicating that at the firing temperature of 1300°C, the clay was probably not properly sintered. Infact only the Onibode (B) clay gave what may be considered reasonably fired bricks. Its however suffered from a rather excessively high drying shrinkage and which resulted in a total shrinkage much higher than normal.

Table 5.6: Drying and Firing Shrinkages of clay samples

Clay Sample	Shrinkages		
	Drying shrinkage (%)	Total shrinkage (%)	Firing shrinkage (%)
Oshielle	2.51	3.62	1.11
Onibode (A)	5.91	7.17	1.26
Onibode (B)	8.92	11.81	2.89
Bauchi	5.52	5.58	0.06

5.3.2 Bulk and apparent solid density:

The results of the density and porosity measurements are shown in table 5.7. Of the four clays, the Onibode (B) clay produced bricks with the highest bulk density, which was 2.21g/cm^3. However, the Bauchi clay gave bricks with the lowest bulk density of 1.50g/cm^3. Typical bulk density values for dense fireclay refractory bricks are about 1.90g/cm^3

(Gilchrist, (1963)). Only the Bauchi clay could be considered to produce a rather low density bricks. The remaining had satisfactory bulk density values. These results again point out to the fact that the Bauchi clay may not have undergone adequate sintering during firing.

Three of the clays gave fired bricks with practically the same apparent solid density values between 2.20 - 2.43g/cm^3. However, fired bricks from the Onibode (B) again gave a significantly higher apparent solid density value of 2.88g/cm^3. This suggest that the Onibode (B) fired bricks contained certain heavy minerals to justify the exceptionally high apparent solid density values. This is infact confirmed from the chemical composition analyses in table 5.3 where it is this clay which contained higher quantities of heavy metallic oxides of Fe_2O_3 and CaO.

5.3.3 Apparent porosity:

The results in table 5.7 contain apparent porosity values, and it is seen that bricks produced from the Onibode (A) and Oshielle clays had apparent porosity values of 20.00% and 16.67% respectively. These values are rather low when compared with the recommended values of between 20-30% for dense fired bricks (Gilchrist (1963); Chester (1973)). The Bauchi clay gave fired bricks with the highest porosity values, and above 30% value. Hence it is only the

Onibode (B) clay which produced bricks with porosity values which fall well within the recommended range.

The high prosity value of the Bauchi clay still indicates the possibility of undercuring. However, another contributive factor may also be due to the presence of a high content of volatile matters as seen from the high loss-on-ignition value. Both of these may be the cause of the very low firing shrinkage value obtained for this clay. The high clay content and the moderate drying shrinkage relate very well. But the observed low firing shrinkage, low bulk density, and hence high porosity cannot be full explained yet.

The low porosity values obtained for the Oshielle and Onibode (A) clays are probably due to the low volatile contents in the aggregates, and acceptable firing shrinkage.

Table 5.7: Density and Apparent Porosity of clay samples

Clay Sample	Average Weights (g)			Average Densities (g/cm^3)		Average Porosity $(\frac{WC-WA}{WC-WB})$ (%)	L.O.I values (%)
	W_A	W_B	W_C	Bulk $\frac{WA}{(W-WB)}$	Solid $\frac{W-WA}{(WA-WB)}$		
Oshielle	110	60	120	1.83	2.20	16.67	14.10
Onibode (A)	97	57	107	1.94	2.43	20.00	13.80
Onibode (B)	95	62	105	2.21	2.88	23.25	15.10
Bauchi	90	50	110	1.50	2.25	33.33	16.20

5.3.4 Cold crushing strength

From table 5.8, all the bricks had good cold crushing strength values in the direction of pressing. They all have cold crushing strength values above the recommended minimum of 15,000 kN/m^2 (Chester (1973)) for dense fired bricks. The Oshielle bricks barely met this requirement, while the Onibode(B) bricks possessed extremely high cold crushing values (31,830 kN/m^2) which was more than double the recommended minimum. This is due to the favorable mineralogical composition and sintering characteristics. The latter was measured by the high firing shrinkage. A very good cold crushing strength values of nearly 20,000 kN/m^2 were obtained for the Onibode(A) and Bauchi clays. That the Bauchi bricks had comparable cold crushing strength values with Onibode (A) bricks was not expected.

Similar results were obtained for cold crushing strength values in the direction normal to forming. They have values higher than the recommended minimum of 5,000kN/m^2 (Chester (1973)), and the Onibode (B) bricks had very high values followed far behind by the Bauchi bricks.

Table 5.8: Cold Crushing Strengths of clay samples

Clay Samples	Average Cold Crushing Strength (kN/m^2)	
	Direction of forming	Normal to forming direction
Oshielle	15,200	5,030
Onibode(A)	19,420	5,610
Onibode(B)	31,830	18,620
Bauchi	19,210	7,100

5.3.5 Thermal shock resistance:

All the bricks tested at 1100°C failed before the 30^+ cycles were reached. This showed that none of them had any outstanding thermal shock resistance since the best of them (the Onibode (A) and (B) clays) failed after 20 cycles. Infact the Oshielle and Bauchi bricks failed after 12 and 3 cycles respectively, showing poor thermal shock resistance for these bricks. These results are shown in table 5.9.

The spalling tests done at 1300°C for these bricks showed improved thermal shock resistance as seen by

failure taking place at a higher number of cycles for each type of brick. This is due to soft phases being formed at 1300°C which on cooling harden and improve thermal shock resistance. Hence spalling tests are commonly done at temperatures below which softening occurs. These are usually between 900 and 1200°C, and depending on the type of refractory brick and operating temperatures.

Spalling tests done at 1300°C did not cause bricks made from the Oshielle and Bauchi clays to fail after a considerable number of cycles. Infact the Oshielle bricks failed after 18 cycles while the Bauchi bricks failed only after 6 cycles. This may also be due to incomplete firing or curing. Only the Onibode(A) and particularly Onibode (B) bricks which gave good thermal shock resistance for spalling tests at 1300°C.

The actual testing rig was not available and the one used was fabricated based on the calculated equivalent torgue. This may actually be heavier than the standard rig.

Table 5.9: Thermal Shock Resistance of clay samples

Clay Samples	Spalling Tests at 1100°C		Spalling Tests at 1300°C	
	No. of cycles	Remarks	No. of cycles	Remarks
Oshielle	12	Poor	18	Acceptable
Onibode (A)	20	Fair	30	Good
Onibode (B)	20	Fair	28	Good
Bauchi	3	Very poor	6	Very poor

Note:

> 30 - Excellent

25-30 - Good

20-25 - Fair

15-20 - Acceptable

10-15 - Poor

< 10 - Very poor

5.3.6 Refractoriness of the refractory bricks

The refractoriness of these bricks were examined first under no load conditions. The results of these test are shown in table 5.10. It is seen that the sintering temperatures, represented by the sticking temperatures, are quite high. In all cases they are 1500°C, for the Oshielle and Bauchi clays, but higher temperatures of 1600 and 1650°C were obtained for the

Onibode (A) and Onibode (B) clays respectively. It is surprising that the sintering temperature for the Bauchi clay was less than the Onibode clays, because it was thought to be improperly sintered to give low firing shrinkage.

The high sintering temperatures of these clays are indications that they have good refractoriness. These are confirmed by the refractoriness value of 1700°C or above for any one of them. Again Bauchi and Oshielle have the least refractoriness. The Onibode(B) clay had refractoriness above 1730°C that is beyond the measuring range of the furnace used.

Table 5.10: Refractoriness of the clay samples

Clay Samples	Sintering temperature (°C)	Refractoriness	
		Seger cone Number	Refractoriness (°C)
Oshielle	1500	31	1700
Onibode (A)	1600	33	1730
Onibode (B)	1650	> 33	> 1730
Bauchi	1500	32	1710

5.3.7 Refractoriness - under load:

The refractoriness - under load behaviour of each type of brick in the rising temperature condition

for the four clay samples is shown in table 5.11. Figure 5.2 presents the RUL curves obtained for all the four clays. The curves show the expansion and contraction regions. Bauchi and Oshielle clays gave maximum expansion at 1350°C. The Onibode specimens recorded maximum expansion at 1400°C and 1450°C for the (A) and (B) clays respectively. Beyond this temperature the test specimens began to contract and reaching the original (or zero subsidy) as seen in the table 5.11. The 5% subsidies were obtained at varying temperatures from 1500°C for the Oshielle specimens, and 1680°C for the Onibode (B) specimens. These are also contained in table 5.11. It is note worthy that these bricks meet very well the minimum RUL specification for dense bricks of between 1500°C and 1600°C. It should be noted that the temperature at 5% subsidy are practically the same as those for the sintering (sticking) temperatures in table 5.10.

Again that the Bauchi specimen softened at a lower temperature indicates that the bricks were properly sintered. The low firing shrinkage, and poor thermal shock resistance might have come from other sources.

Table 5.11: Refractoriness under load characteristics

Clay Samples	Refractoriness Under Load (^{o}C)		
	Maximum Expansion	Zero subsidy	5% subsidy
Oshielle	1350	1455	1500
Onibode (A)	1400	1575	1640
Onibode (B)	1450	1610	1680
Bauchi	1350	1530	1580

Table 5.12: Refractoriness-Under Load (Rising Temperature) Characteristics of Oshielle Clay

Specimen size = 63.5mm high

Temperature (^{o}C)	Expansion/contraction (mm)	Expansion/contraction (%)
100	0	0
150	0.0508	0.08
200	0.2032	0.32
250	0.3048	0.48
300	0.4064	0.64
350	0.4801	0.76
400	0.5791	0.91
450	0.6248	0.98
500	0.7112	1.12
550	0.7772	1.22
600	0.8255	1.30
650	0.8788	1.38

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
700	0.9373	1.48
750	1.0160	1.60
800	1.0668	1.68
850	1.1176	1.76
900	1.1684	1.84
950	1.2192	1.92
1000	1.2700	2.00
1050	1.2929	2.04
1100	1.3335	2.10
1150	1.3716	2.16
1200	1.3843	2.18
1250	1.4224	2.24
1300	1.4326	2.26
1350	1.4478	2.28
1400	1.3843	2.18
1450	0.2032	0.32
1460	-0.4064	-0.64
1480	-1.2700	-2.00
1500	-3.3020	-5.20

Table 5.13: Refractoriness-Under Load (Rising Temperature) Characteristics of Onibode(A) clay

Size of specimen = 63.5mm high

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
50	0.1524	0.24
100	0.2033	0.32
150	0.3048	0.48
200	0.3556	0.56
250	0.4572	0.72
300	0.5588	0.88
350	0.6604	1.04
400	0.7620	1.20
450	0.8636	1.36
500	0.9144	1.44
550	0.9906	1.56
600	1.0668	1.68
650	1.1176	1.76
700	1.1836	1.86
750	1.2700	2.00
800	1.3335	2.10
850	1.4224	2.24
900	1.4732	2.32
950	1.5494	2.44
1000	1.6256	2.56
1050	1.6383	2.58
1100	1.7272	2.72
1150	1.7907	2.82

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
1200	1.8288	2.88
1250	1.8796	2.96
1300	1.8923	2.98
1350	1.9304	3.04
1400	1.9431	3.06
1450	1.8923	2.98
1500	1.6891	2.66
1550	1.1684	1.84
1560	0.2540	0.40
1580	-0.4064	-0.64
1600	-1.2700	-2.00
1620	-1.8796	-2.96
1640	-3.2385	-5.10

Table 5.14: Refractoriness-Under Load (Rising Temperature) Characteristics of Onibode(B) Clay

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
100	0	0
150	0.2032	0.32
200	0.2794	0.44
250	0.3556	0.56
300	0.4953	0.78
350	0.6350	1.00

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
400	0.7239	1.14
450	0.8128	1.28
500	0.8636	1.36
550	0.9208	1.45
600	0.9779	1.54
650	1.0668	1.68
700	1.1430	1.80
750	1.2192	1.92
800	1.2954	2.04
850	1.3716	2.16
900	1.4478	2.28
950	1.5240	2.40
1000	1.5773	2.48
1050	1.6256	2.56
1100	1.6764	2.64
1150	1.7272	2.72
1200	1.7399	2.74
1250	1.7780	2.80
1300	1.7907	2.82
1350	1.8288	2.88
1400	1.8415	2.90
1450	1.8796	2.96
1500	1.8415	2.90
1550	1.4859	2.34
1600	0.2540	0.40

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
1620	-0.3556	-0.56
1640	-1.2700	-2.00
1660	-1.5240	-2.40
1680	-3.1115	-4.90

Table 5.15: Refractoriness-Under Load (Rising Temperature) Characteristics of Bauchi clay

Temperature (°C)	Expansion/contraction (mm)	Expansion/contraction (%)
50	0	0
100	0.0635	0.10
150	0.1524	0.24
200	0.2591	0.41
250	0.3556	0.56
300	0.4572	0.72
350	0.5588	0.88
400	0.6299	0.99
450	0.7239	1.14
500	0.7849	1.24
550	0.8636	1.36
600	0.9195	1.45
650	0.9754	1.54
700	1.0312	1.62
750	1.0820	1.70

Temperature (°C)	Expansion/contraction (mm)	Expansion/contractio (%)
800	1.1684	1.84
850	1.2319	1.94
900	1.2903	2.03
950	1.3437	2.12
1000	1.3919	2.19
1050	1.4732	2.32
1100	1.4961	2.36
1150	1.5469	2.44
1200	1.5977	2.52
1250	1.6459	2.59
1300	1.6815	2.65
1350	1.6967	2.67
1400	1.5977	2.52
1450	1.4224	2.24
1500	0.7620	1.20
1520	0.1524	0.24
1540	-0.4572	-0.72
1560	-3.0480	-4.85

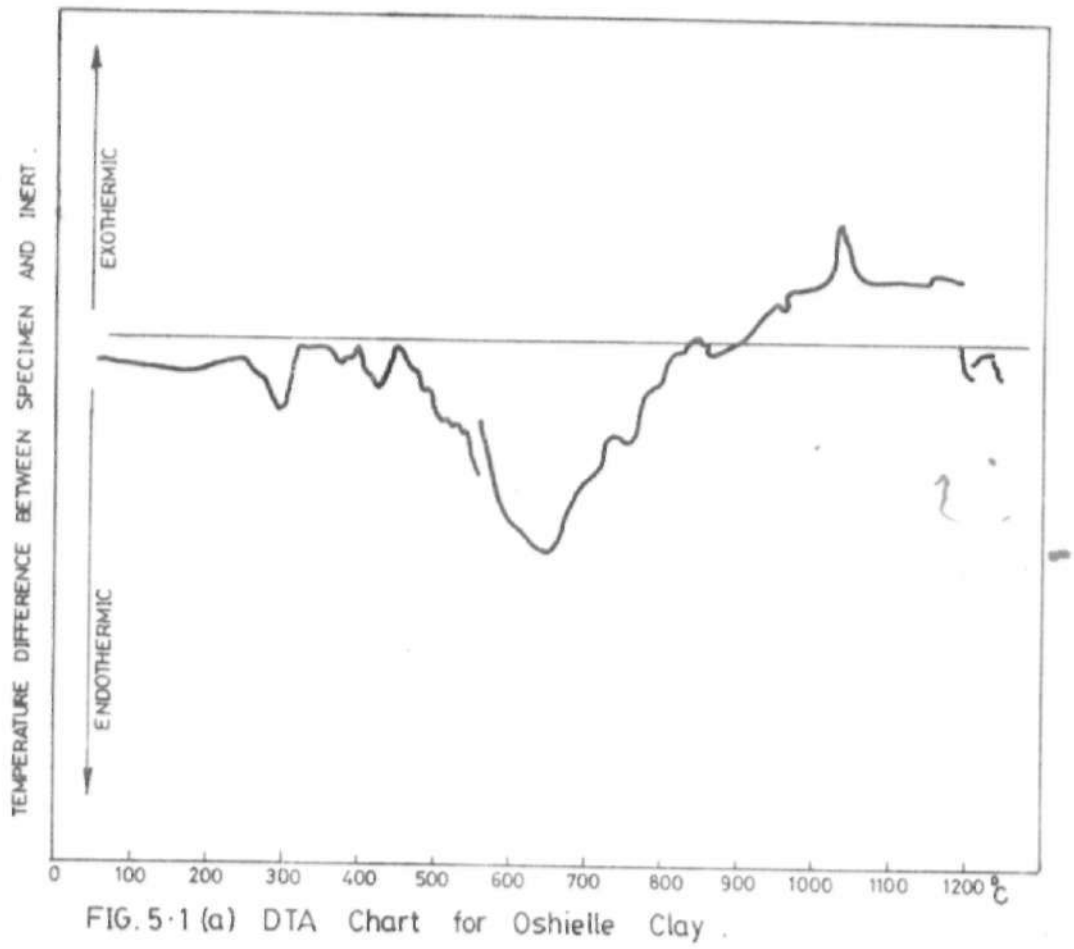
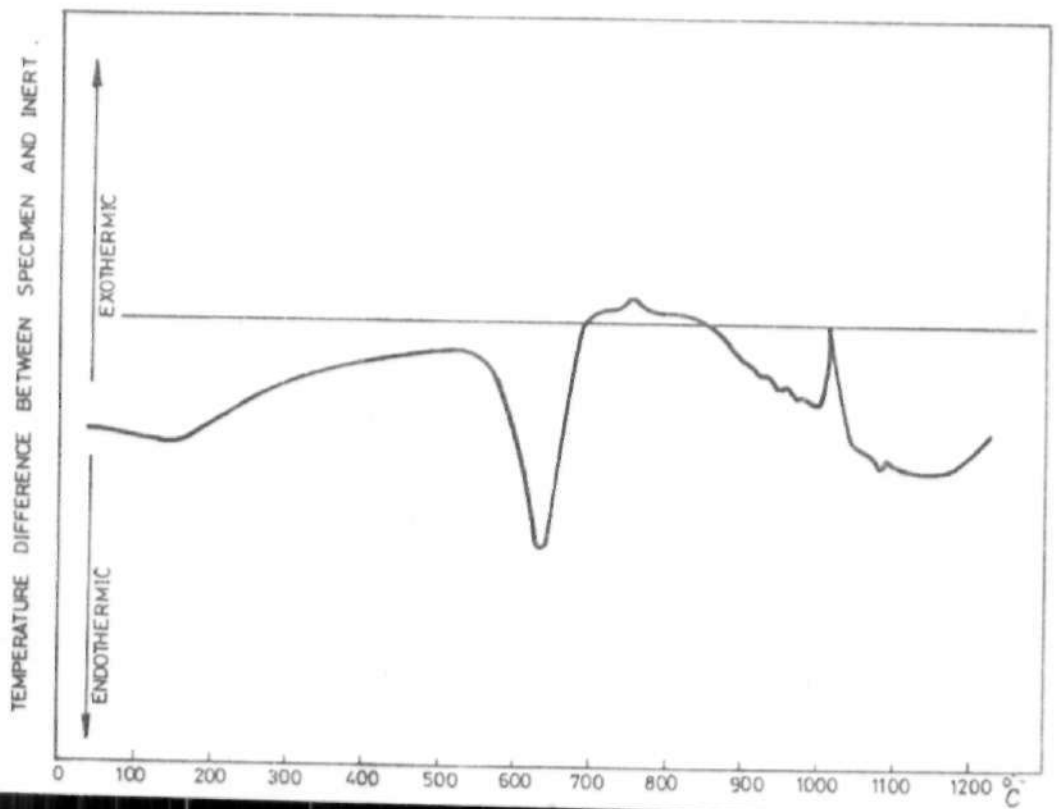


FIG. 5·1 (a) DTA Chart for Oshielle Clay.



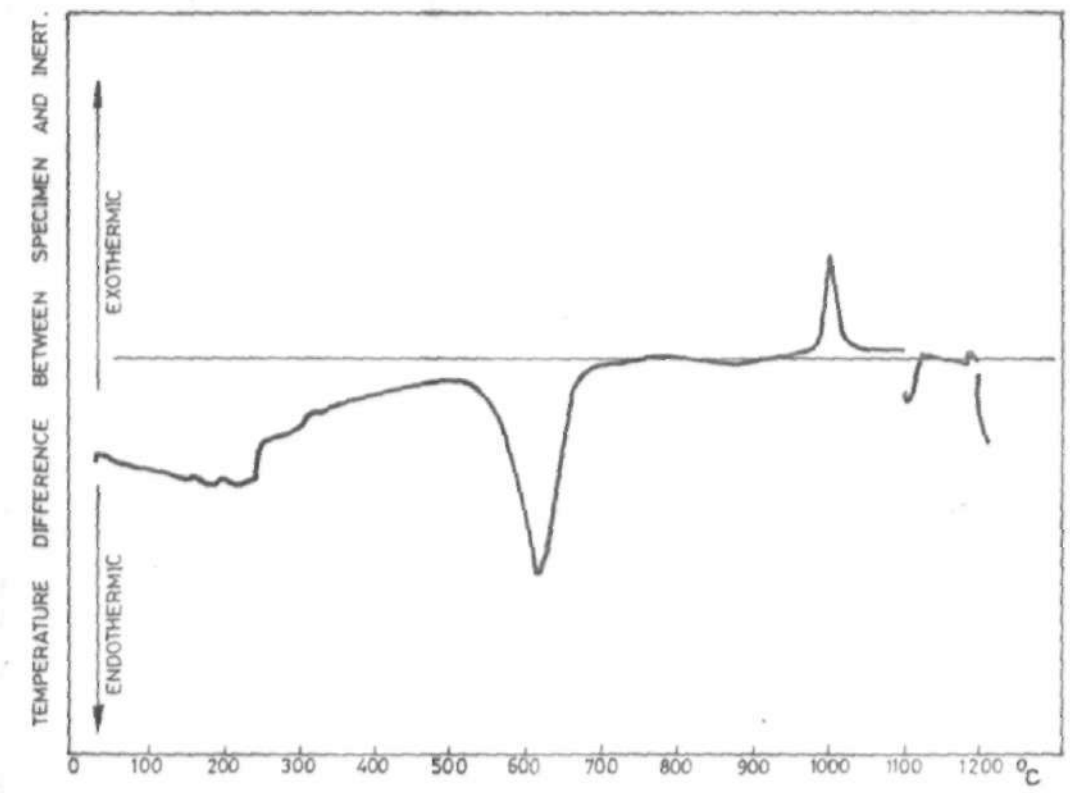


FIG. 5·1 (c) DTA Chart for Onibode (B) Clay .

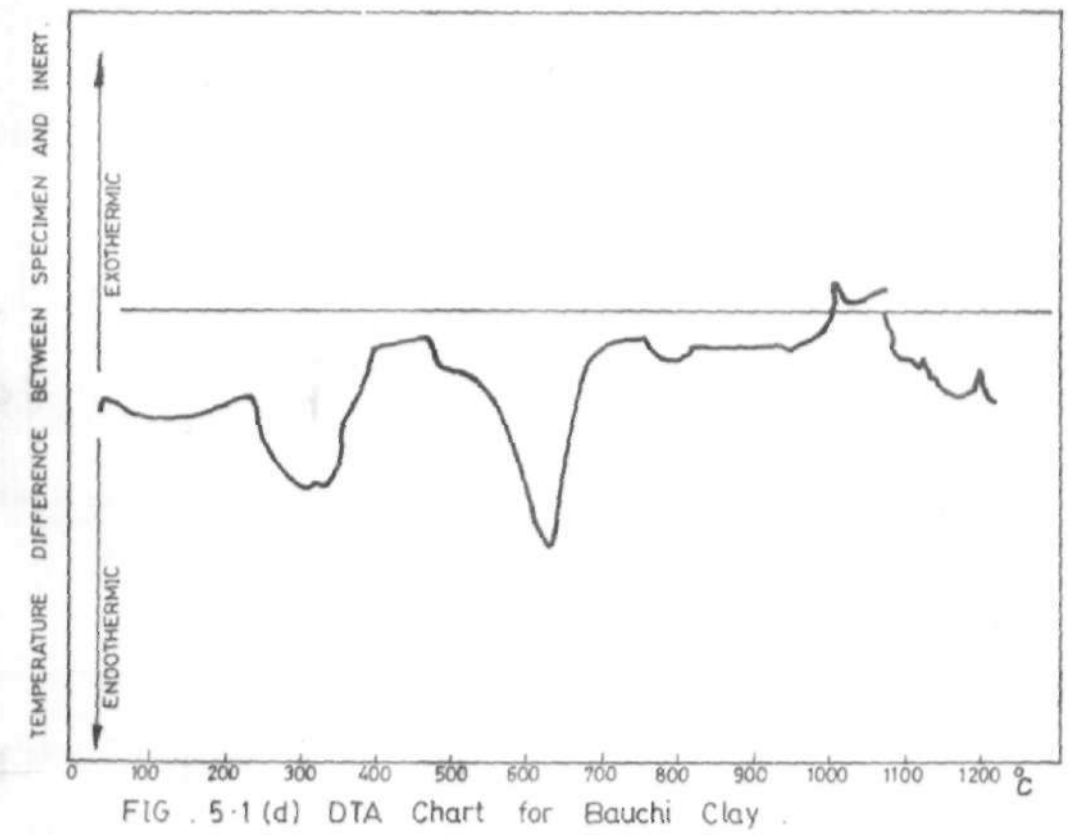
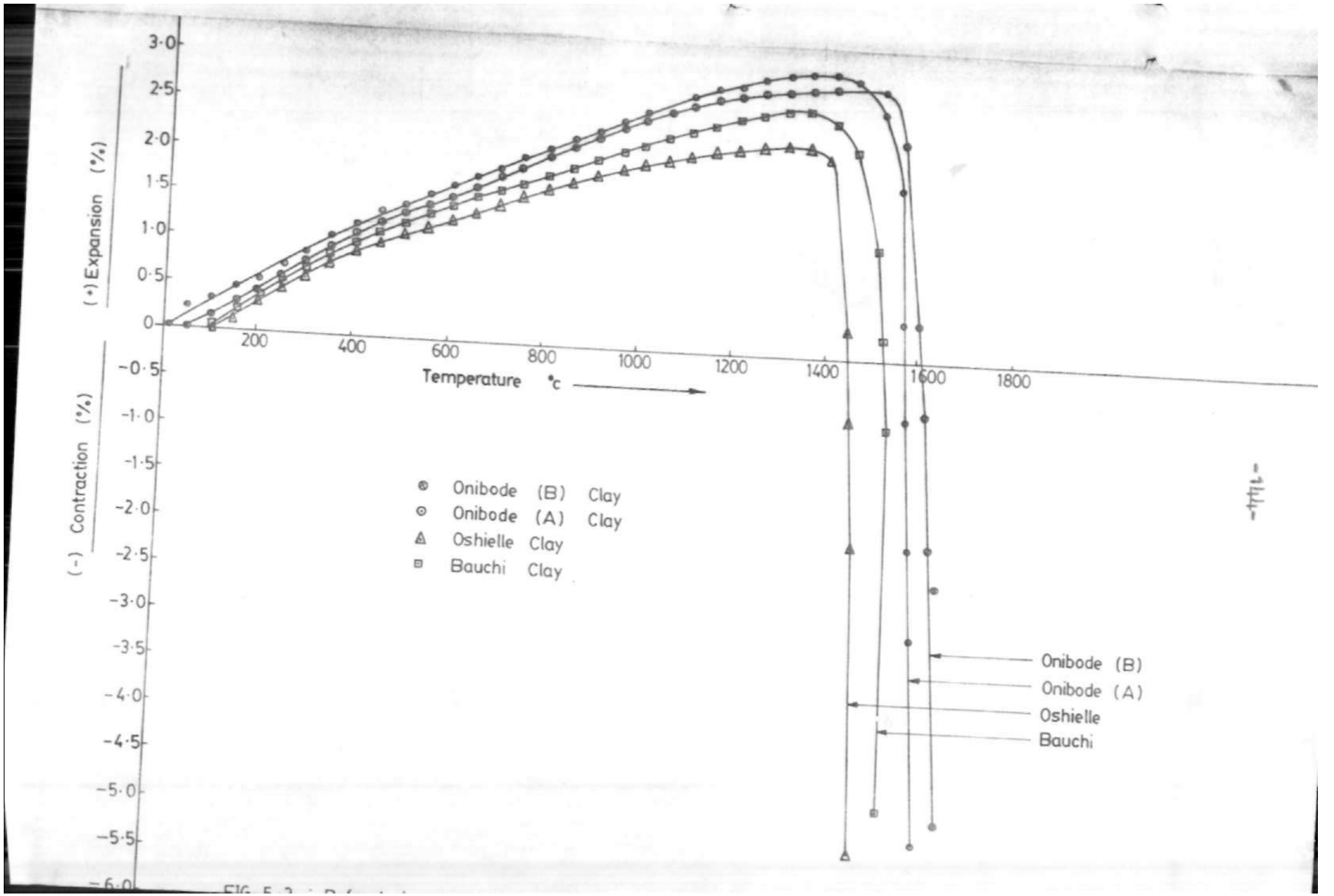


FIG . 5·1 (d) DTA Chart for Bauchi Clay .


(+) Expansion (%)
(-) Contraction (%)
3·0
2·5
2·0
1·5
1·0
0·5
0
-0·5
-1·0
-1·5
-2·0
-2·5
-3·0
-3·5
-4·0
-4·5
-5·0
-5·5
-6·0
200
400
600
800
1000
1200
1400
1600
1800
Temperature °C
Onibode (B) Clay
Onibode (A) Clay
Oshielle Clay
Bauchi Clay
Onibode (B)
Onibode (A)
Oshielle
Bauchi

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CHAPTER SIX

6.0 CONCLUSIONS

From the tests conducted on bricks made from Oshielle, Onibode and Bauchi clays, it was found that:

(1) Mouldability was good and agrees with the amount of water requirement of 18 - 25% by weight, even though it is on the low side of the range for the Oshielle and Onibode (A) clays.

(2) The two Onibode clays were found to be easily crushed into powder, however Oshielle and Bauchi clays were rather harder and more difficult to crush.

(3) All clay samples had clay content higher than 55% minimum. However, the Oshielle clay just barely had enough clay and kaolin content. Bauchi clay had the highest silica content of the four clays and this is reflected by the results of the sieve analysis. Oshielle clay seems to have the highest alumina content. Fe_2O_3 is found to be present in Oshielle, Onibode (A & B) clays and is reflected by their colour, while Bauchi which had none was pure white.

Fired appearance show the same as above. Cracks were found in the bricks made from Oshielle and Onibode (A) clays in the fired condition. This is indicative of lack of strong cohesion between clay

particles on firing due to high content free silica in Oshielle clay.

The physical properties of the bricks produced from the four clay samples are as follows:

(a) Shrinkage: Onibode (B) clay had fairly high shrinkage value outside the normal range of 7 - 9%. On the other hand, low shrinkage values were obtained for the Oshielle and Bauchi clays. Only Onibode (A) clay had shrinkage value within the normal range.

(b) Porosity: All have acceptable porosity values, though Bauchi clay was found to have slightly higher porosity value than normal while Oshielle clay was found to be very dense.

(c) Cold crushing strength: All have good cold crushing strength, though Oshielle clay was the weakest of them all, with cold crushing strength value only just above the minimum value. It is note worthy that the Onibode (B) clay produced very strong bricks.

(d) Refractoriness: All the clays have acceptable refractoriness, with sintering temperature greater than or equal to 1500^{o}C and refractoriness value greater than or equal to 1700^{o}C.

(e) Refractoriness Under Load: All have high refractoriness under load value results with Oshielle and Bauchi clays being capable of being used above 1500°C and Onibode clays above 1600°C.

(f) Thermal shock resistance: Only the Onibode clays have acceptable resistance to spalling. Oshielle and Bauchi clays have poor spalling characteristics especially Bauchi clays. This means that they may be unsuitable for use in the heat-treatment furnaces where rapid heating and cooling take place under load.

Based on the outcome of this investigation, the following suggestions can be made:

(i) The Onibode clays possess very good properties that make them suitable for the manufacturing of refractory brick for building furnaces for temperatures up to 1600°C.

(ii) The Oshielle clay with its low clay content, and being illitic in nature had inferior refractory properties especially with respect to thermal shock resistance, limits its use to areas where refractories with long operation life time are not required. However, it was to be the densiest of them all.

(iii) The Bauchi clay with its high porosity value and being illitic in nature had inferior refractory properties especially with respect to thermal spalling resistance, limits its application also to areas where refractories with long operation life are not required. However, Bauchi clay qualified to be used for insulating purposes.

(iv) In comparison to kankara clay, all the four clays had superior refractory properties than kankara clay. However, only Oshielle and Bauchi clays had thermal spalling resistance being inferior to kankara clay.

The production of refractory bricks from our local clay deposits, especially Onibode clays should commence, to meet our Iron and steel industry and other metallurgical and non-metallurgical industries needs. These clays possess all the useful refractory properties needed to assure the users.

The geological survey revealed that the four locations have vast reserve and aboundant clay deposits required to sustain well into further, the refractory bricks production in Nigeria. There will now be need for detailed geological mapping of these clay deposits.

CHAPTER SEVEN

7.0 RECOMMENDATIONS FOR FURTHER INVESTIGATION

Base on the outcome of this investigation, the following recommendations can therefore be made and further works needed to be done on Nigerian clays are suggested.

(i) Further investigation should be conducted to reduce the shrinkage values of Onibode(B) clay and to improve the apparent porosity of Bauchi clay, to make them improve on the requirement for refractory production.

(ii) There is need to further investigate into the refractory properties of the bricks produce from Oshielle and Bauchi clays at much higher firing temperatures. The temperature range that could be used may be between 1350^{o}C - 1500^{o}C where much improved properties are envisaged.

(iii) There are other valuable local clay deposits known, which are yet to be subjected to any form of investigation. More intensive investigations should be carried out on these clays to ascertain whether they possess adequate refractory properties needed to satisfy our metallurgical industries. Some of these deposits include Giru (Sokoto), Kano, Enugu and Ukpor clays etc.

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APPENDIX

TABLE A: COMPARISON OF THE RESULTS WITH TYPICAL PROPERTIES OF FIRECLAY REFRACTORIES

S/NO.	PROPERTIES	FIRECLAY	OSHIELLE CLAY	ONIBODE (A) CLAY	ONIBODE (B) CLAY	BAUCHI CLAY
(1)	Linear Shrinkage (%)	7 - 9	3.62	7.17	11.81	5.58
(2)	Bulk Density (g/cm^3)	1.90	1.83	1.94	2.21	1.50
(3)	Apparent Porosity (%)	20 - 30	16.67	20.00	23.25	33.33
(4)	Cold Crushing Strength (KN/m^2)					
	a.) Direction of forming	above 1,500	15,200	19,420	31,830	19,210
	b.) Normal to forming direction.	above 5,000	5,030	5,610	18,620	7,100
(5)	Thermal Spalling Resistance	30^+ cycles	18 cycles	30 cycles	28 cycles	6 cycles
(6)	Refractoriness (^oC)					
	a.) Seger cone number	26 - 34	31	33	33	32
	b.) Temperature Eqv.(^oC)	1580 - 1750	1700	1730	1730	1710
(7)	Refractoriness Underload (^oC)	1400 - 1600	1455	1575	1610	1530