

**CHARACTERIZATION OF CLAY FROM MARABAN RIDO KADUNA STATE
AND ITS APPLICATION IN THE PRODUCTION OF DENSE
REFRACTORY FIREBRICKS**

By

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DECLARATION

I declare that the work in this dissertation entitled, “Characterization of Clay from Maraban Rido Kaduna State and its Application in the Production of Dense Refractory Firebricks” has been carried out by me in the Department of Industrial Design. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

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CERTIFICATION

This dissertation entitled, “CHARACTERIZATION OF CLAY FROM MARABAN RIDO KADUNA STATE AND ITS APPLICATION IN THE PRODUCTION OF DENSE REFRACTORY FIREBRICKS,” by Sahabi SANI meets the standard and regulation governing the award of the Master of Science degree in Glass Technology of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This dissertation is dedicated to my parents, Alhaji Sani Sule and Hajiya Fatima Ishaq.

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ABSTRACT

The industries in Nigeria depend heavily on the use of refractories and their demands are presently being met, to a large extent by the importation of these refractories. Regrettably, about \$229 million is expended annually to import these materials into the country. Consequently, it leads to the draining of Nigeria's foreign reserve and these turns negatively affect the economic on the increase of capital expenses. Thus, it has become necessary to explore this clay for the production of refractories locally for blast furnaces in order to reduce their importation and meet the need of technological requirements of the country, and to conserve the much needed foreign exchange. The characterization of clay from Maraban Rido Kaduna State and its application in the production of dense refractory firebricks was investigated. The result shows that the clay was found to disintegrate into smaller angular particles after being mined with cream coloration, moderately hard with smooth texture and in lump sizes (ranging from 5cm to 15cm). Maraban Rido clay had a liquid limit of 41.5%, a plastic limit of 33.5% and a plasticity index of 8%. At firing temperature of 1280°C, the clay changed from cream colour to off-white. The off-white coloration might be due to the presence of low concentrations of iron oxides in the sample. The average firing shrinkage clay samples was 7.1% with little cracks. The X-ray fluorescence elemental analysis results showed Al₂O₃ and SiO₂ to be the dominant oxides at 44.0% and 51.8% respectively. The values of impurity oxides content for the clay sample such are K₂O (0.08%), CaO (0.16%), Fe₂O₃ (1.53%), TiO₂ (0.26%) etc. contents of 4.21% are all within the tolerable impurities associated to alumino-silicates group of refractories of about 2 to 5%, make the clay suitable for the production of superheat duty alumino-silicate refractory material. The dense firebricks produced from Maraban Rido clay showed little cracks as-formed, drying and firing at 1500°C with average firing shrinkage value of 7.1%, which

is within the recommended values of 7.0-10%. The apparent porosity assessment values for Maraban Rido dense firebricks averaged 33% which does not fall within the recommended values of 15-25%, while the bulk density on the average was 1.75g/cm^3 , does not fall within the acceptable level of fireclay brick of between $1.9\text{-}2.3\text{g/cm}^3$. This could be due to the inadequate compaction pressure during the pressing process, coupled with shapes of the particle of the grog, since the grog is manually crushed and the reaction occurring on firing. The cold crushing strength averaged 294.77kg/cm^2 meet the recommended standard of 150kg/cm^2 minimum for fireclay, the practical significance of this value will be strong enough to withstand handling, transportation and abrasion in services and the thermal shock resistance on the average gave a value of 30 cycles at temperature of 1200°C , term as an excellent thermal shock resistance. The Maraban Rido clay formed fireclay refractory firebrick which is among the alumino-silicates group of refractories. The Maraban Rido firebrick can be used in moderate heat treatment operation such as lining of regenerative chambers, recuperative chambers, chimney and annealing furnaces.

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LIST OF ABBREVIATIONS

%L _{FS} :	Percentage Linear Fired Shrinkage
AAS:	Atomic Absorption Spectrometry
ABU:	Ahmadu Bello University, Zaria, Nigeria
API:	Atterberg Plasticity Index
ASTM:	American Society for Testing Material
BD:	Bulk Density
BS:	British Standards
CCS:	Cold Crushing Strength
DTA:	Differential Thermal Analysis
EDXRF:	Energy Dispersive X-ray Fluorescence
FL:	Fired Length
GL:	Green Length
L _d :	Length when dried
LDS _f :	Linear Drying Shrinkage of as formed
L _{fd} :	Length as formed
LL:	Liquid Limit
LOI:	Loss on Ignition
Pa:	Apparent Porosity
PCE:	Pyrometric Cone Equivalent
PL:	Plastic Limit
PPI:	Pfefferkon Plasticity Index
RUL:	Refractoriness under Load
W ₁ :	Dry Weight
W ₂ :	Weight Deep in Mercury (Hg)

WDXRF: Wavelength Dispersive X-ray Fluorescence

XRD: X-ray Diffraction

XRF: X-ray Fluorescence

LIST OF NOTATIONS AND SYMBOLS

%	=	Percentage
<	=	Less than
>	=	Greater than
°C	=	Degree Celsius
°F	=	Degree Fahrenheit
μ	=	Micron (Micrometer)
μg	=	Microgram
n	=	Integer
ppm	=	Part per million
T	=	Temperature
V _b :	=	Bulk volume
V _o :	=	Volume of open pores
α	=	Alfa
β	=	Beta
ΔH	=	Enthalpy
ΔT	=	Temperature difference
θ	=	Theta
λ	=	Wavelength, Å
μm	=	Micrometer
π	=	Pi

DEFINITION OF TERMS

Aggregates: Calculated materials crushed into particles of classified size fractions to be collected together from the fractions for the formulations of batch.

Aluminosilicates: It is an inorganic compound ceramic material whose major constituents are alumina and silica. Examples include fireclay, kaolin, ball clay, etc.

Beneficiation: This is the systematic process of refining or treatment of raw materials to optimize their performance for higher manufacturing process in order to achieve grade products.

Chemico-mineralogical: This refers to the elemental oxide or chemical composition and the mineral phase present within the clay material.

Cold Crushing Strength: This measure the ability of bricks to withstand the structural load coming over them

Dense Refractory Brick: This is a refractory products made under high pressure by densification and compaction of refractory aggregates.

Fireclays: These are naturally occurring earthy materials having the chemical composition given by the formula $Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, whose alumina content is either above 25% or up to 45% of the weight, while the silica content is 50% to 80%.

Furnace: This is high temperature equipment used in the manufacturing or refining process where heat requirement is extreme. Examples of areas of application are the iron and steel, cement, glass and the petrochemical industries, etc.

Grog: This refers to pre-fired/calcined clay materials that are crushed into several particles sizes used for refractory production.

Porosity: This measure the percentage relationship between the volume of the open pore space and the total volume of a refractory.

Refractoriness: This measures the ability of bricks to withstand high temperatures over a long period of use without fusion or softening.

Thermal Shock Resistance: This measure the resistance of a refractory brick to sudden change in temperature as the result of alternate heating and cooling.

CHAPTER ONE

INTRODUCTION

The word "clay" has ambivalent definitions. On one hand it is used to define any soil particle smaller than $2\mu\text{m}$, but on the other hand it includes a large group of microcrystalline secondary minerals based on hydrous aluminium or magnesium silicates that have sheet like structures. Clay minerals have been part of human existence since antiquity and were used as natural nanomaterials along history for industrial and commercial uses. The first recorded applications were more than 5000 years ago, in Cyprus and Greece, for bleaching fleece and clothes, and removal of grease and stains from it (Rytwo, 2000).

This is an abundant fine earthy powder produced by the weathering and disintegration of granite and feldspathic rocks (Malu *et al.*, 2013). However, certain high grade types of clay deposits are limited in geographic occurrence and extent. Clays containing a preponderance of the clay mineral kaolinite are known as kaolinitic clays. Several commercial clays are composed predominantly of kaolinite. These are China clays, kaolins, ball clays, fireclays, and flint clays. The terms China clay and kaolin are used interchangeably in industry. The grinding action of clay particles in water, wind and ice results in very fine particle sizes (Mousharraf *et al.*, 2011).

Refractories are inorganic, non-metallic, porous and heterogeneous materials composed of thermally stable mineral aggregates, a binder phase and additives. The principal raw materials used in the production of refractories are: the oxides of silicon, aluminium, magnesium, calcium and zirconium and some non-oxide refractories like carbides, nitrides, borides, silicates and graphite (Bhatia, 2011).

1.1 Background of the Study

According to Chesters (1973) clay is a natural source of many industrial finished products. One of such products that have proved indispensable in the iron and steel industries and other non-ferrous industries is the refractory material. The raw materials for the production of various refractory products include kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), magnesite (MgCO_3), chromite (FeOCr_2O_3), and various types of clays. Aluminosilicate and magnesite refractory products are the major types of refractories used in the industries (Hassan and Aigbodion, 2014). There are vast deposits of clay spread across every region in the world, each differing from site to site on account of geological differences. Clay deposits are spread across the six geo-political zones of Nigeria.

There are several research records that have shown the vast abundance of clay deposits in Nigeria. The most extensively investigated clay deposits that mark the Nigerian landscape are the well-known Kankara kaolin deposit in Katsina State, Warram clay deposit in Enugu State, the Onibode in Ogun State and Majohota clay deposits in Plateau State. Earlier researchers such as Ahmed (1986), Garkida (1998), Fasuba *et al.* (2000), Sullayman (2006), Abdullahi (2009), Musa *et al.* (2012), and Hassan and Aigbodion (2014), have extensively worked on some of these clays in Nigeria.

In the past few years, there has been an increasing awareness on the scope, and the importance of refractory materials in the industrial development of Nigeria. With the revamped development of the iron and steel industry via the rehabilitation of various inland rolling mills and the envisaged completion and commissioning of the multi-billion dollar Ajaokuta Steel Company Limited to produce 1.3 million tonnes of liquid steel, there will be a great increase in consumption of refractory materials. Ajaokuta Steel Company Limited is estimated to require 36,000 tonnes of refractory bricks worth

over Sixty million naira just for furnace lining purposes only and more than 80% of the refractory bricks to be required are fired clay (Musa *et al.*, 2012).

The four refineries in Nigeria were recorded to have gulped about \$850 million for their turn around maintenance (TAM) between 1997 and 2002. The critical unit in the TAM process is the Fluid Catalytic Cracking (FCC). This unit is lined with enormous quantity of various grades of refractory line. Other demands for these products come from glass, chemical, hardware and cement industries. The refractory needs of these industries were well over 300,000 tonnes as at year 2000 (Musa *et al.*, 2012). Despite the huge amount of clay deposits available in Nigeria and the enormous research that have been carried out in the development of refractory products, refractory industries are yet to spring up in the country. Nigeria continues to depend on external sources of refractory materials for many of its industries (Ranti *et al.*, 2015).

Presently the clay from Maraban Rido deposit in Kaduna state has not been used as a refractory material for blast furnaces. The Kaduna brick industry located at Maraban Rido procures this clay raw material used for the production of insulating refractory brick A. Muhammad (personal communication, May 20, 2014). This research is however aimed at characterizing the clay deposit for its refractory properties and applications. Thus, this study will strive to evaluate both the physical and chemical properties of Maraban Rido clay deposit and to produce dense refractory bricks which will be subjected to some properties test.

1.2 Statement of the Problem

All over the world where energy is of paramount importance, high temperature operations continue to increase. The iron and steel, glass, ceramic, cement, refineries,

nuclear, chemicals and petro-chemicals and waste disposal industries are some of the industries where high temperature operations are unavoidable. In such industries, operating temperatures are as high as several hundreds to thousands of degrees. Refractory materials have been developed to accommodate and/or shield heat in the construction and maintenance for lining the interior walls of high temperature equipment like furnaces, flues, and chimneys thereby protecting the equipment shells usually made of steel or cast iron from breakouts and premature failure during process operations (Nurudeen, 2010).

The industries in Nigeria also depend heavily on the use of refractories and their demands are presently being met, to a large extent by the importation of these refractories. Regrettably, about \$229 million is expended annually to import these materials into the country. Consequently, it leads to the draining of Nigeria's foreign reserve and this turn negatively affect the economic on the increase of capital expenses on importation such as the Cost Insurance and Freight (CIF) price, Tariffs/Taxes and Subsidies, the Trade Margins of importers, and the costs of freight and transportation costs from the port to the warehouse (Esezober *et al.*, 2015).

Nigeria is endowed with large quantity of clay deposits all over the country, which are to be fully explored. One of such areas is Maraban Rido clay deposit. Thus, it has become necessary to explore this deposit for the production of refractories locally for blast furnaces in order to reduce their importation and meet the need of technological requirements of the country, and to conserve the much needed foreign exchange.

1.3 Aim of the Study

The aim of this study is to produce dense refractory firebricks from the Maraban Rido clay.

1.4 Objectives of the Study

The Objectives of the study are to:

- i. source and beneficiate the clay from Maraban Rido.
- ii. determine the physical and chemical composition of the clay samples.
- iii. produce grog aggregates, and develop a suitable body composition for the formulation of dense refractory firebricks.
- iv. produce dense refractory firebricks from the prepared clay/grog formulation and then firing of the bricks to the required sintering temperature.
- v. determine the refractory properties of the dense refractory bricks such as linear shrinkage, apparent porosity, bulk density, cold crushing strength, thermal shock resistance, and refractoriness.

1.5 Research Questions

- i. How will beneficiation of the clay samples have an effect in the brick production?
- ii. What will the physical and chemical composition of the clay be?
- iii. How will the production of grog aggregates and development of suitable body composition form the formulation for the dense refractory bricks?
- iv. How can the prepared grog and clay form the dense refractory firebricks which can be fired to the required sintering temperature?
- v. How can the dense refractory bricks be made to acquire properties which will meet the required standards?

1.6 Justification of the Study

Clay has served as an indispensable raw material for the production of products varying from bricks, electrical insulators, refractories, papers, paints, roofings and inks. Clays also find various applications in the manufacture of cement, plastics, building materials, fertilizers and insecticides. Clay products such as ceramic ware, refractory bricks, burnt bricks, roofing and floor tiles are cheaper and more durable than cement especially under tropical conditions (Abdullahi, 2009).

Dense refractory bricks find usage in the inner linings of high temperature equipment like kilns, blast furnaces, glass melting tanks, coke-ovens, foundries etc. used for industrial processing of materials as well as product development and manufacture, requiring high heat treatment (Sullayman, 2006). Ajaokuta Steel Company Limited is estimated to require 36,000 tonnes of refractory bricks worth over Sixty million naira just for furnace lining purposes only and more than 80% of the refractory bricks to be required are fired clay (Musa *et al.*, 2012), thus, the need for the current research.

1.7 Scope of the Study

The research covered the physical characterization of the clay sample from Maraban Rido such as its plasticity index, its chemical characterization to determine its elemental oxide composition by X-ray fluorescence method. The research also includes the production and sizing of grog aggregates from the raw clay and its use for the production of dense refractory firebricks. The dense firebricks produced were characterized for such properties as linear shrinkage, apparent porosity, bulk density, cold crushing strength and thermal shock resistance only.

1.8 Research Limitations

This study was restricted to certain areas due to the following:

- i. The inability compaction pressure of the hydraulic pressing machine to reach up to 400-500 KN, reduces the density of the firebricks.
- ii. The absence of furnace that fire above 1500°C, for 3-4days period in normal situations reduces the properties of the bricks. The firing temperature capacity of the furnace and time, determine the level of sintering that will be achieved during the actual firing process
- iii. The absence of standard Segar cones and inability to access a furnace that will give a firing temperature above 1500°C, led to inability to assess the pyrometric cone equivalent test (refractoriness test) of the brick.
- iv. There are no functional facilities within the proximity for conducting the refractoriness under load (RUL), resistance to slag attack, thermal conductivity and electrical conductivity tests.

1.9 Significance of the Study

This research study will contribute to meeting the industrial demand for fireclay refractory material used in the iron and steel, glass, ceramic, cement, refineries, nuclear, chemicals and petro-chemicals industries where high temperature operations are unavoidable.

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews available related literature relevant to the following areas: clay, properties and classification of clay, refractory materials, classification of refractory materials, alumino-silicates refractories, fireclay refractories, types of fireclay refractory bricks, development of dense refractory firebricks, properties of fireclay refractories and application of fireclay refractories.

2.1 Clay

The term "clay" refers to a naturally occurring material composed primarily of fine grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Folorunso *et al.*, 2012). Clay based materials occur both in the plain and river areas (Nweke and Ugwu, 2007). Clays are alumina-silicates, being composed of alumina (Al_2O_3) and silica (SiO_2) that contain chemically bound water. They have a broad range of physical characteristics, chemical compositions, and structures, common impurities include compounds (usually oxides) of barium, calcium, sodium, potassium, and iron, and also some organic matter. Crystal structures for the clay minerals are relatively complicated; however, one prevailing characteristic is a layered structure. The most common clay minerals that are of interest have what is called the kaolinite structure, Kaolinite clay. When water is added, the water molecules fit in between these layered sheets and form a thin film around the clay particles. The particles are free to move over one another which accounts for the resulting plasticity of the water-clay mixture (Callister, 1994).

2.2 Properties and Classification of Clay

Properties of the clays include plasticity, shrinkage under firing and under air drying, fineness of grain, color after firing, hardness, cohesion, and capacity of the surface to take decoration. On the basis of such qualities clays are variously divided into classes or groups; products are generally made from mixtures of clays and other substances. The purest clays are the china clays and kaolin's. "Ball clay" is a name for a group of plastic, refractory (high-temperature) clays used with other clays to improve their plasticity and to increase their strength. Bentonites are clays composed of very fine particles derived usually from volcanic ash. They are composed chiefly of the hydrous magnesium-calcium-aluminum silicate called montmorillonite (The Columbia Electronic Encyclopedia, 2012).

2.2.1 Particle size distribution in clays

Particle size distribution is affected by the starting powder characteristics and subsequent size reduction unit operations, such as milling and de-agglomeration. Therefore, it is often necessary to measure the size distribution at various stages of powder processing (ASM, 1995).

According to Ahmed (1986), the particle size distribution of clay is of importance in assessing its plasticity, cohesion and sinterability, as well as evaluating the extent to which it is contaminated with impurities. Particles of clay materials usually measure less than $1\mu\text{m}$ in diameter. Quartz (silica) particles on the other hand measure from $1\mu\text{m}$ upwards. Thus sieving clay minerals with Tyler mesh size $0.5\mu\text{m}$ will eliminate quartz from the bulk clay. Hydrometer analysis is a widely used method to obtain the distribution of particles sizes in the slit range ($<60\text{-}2\mu\text{m}$) and the percentage of clay minerals. The test is usually not performed if less than 10% of the material passes

through the 63µm (0.425mm) sieve. The hydrometer analysis utilizes the relationship among the velocity of fall of spheres in fluid, the diameter of the spheres, the specific weights of the sphere and of the fluid and the viscosity of the fluid as expressed by the stokes law.

The force due to the weight of each particle is given by:

$$F_1 = \frac{4\pi R^{3m}}{3} (d - d_0)g \dots\dots\dots (1)$$

This force is balanced by the force of viscosity:

$$F_2 = 6\pi nRV \dots\dots\dots (2)$$

Where F_1 is balanced by F_2 , the particle moves with constant velocity which is given by:

$$V = \frac{2g}{9n} (d - d_0) R^2 \dots\dots\dots (3)$$

Where: F_1 = the force due to viscosity, N

π = mathematical constant (22/7)

n = viscosity of water, Pascal Seconds

d = density of the clay particles, kg/m³

d_0 = density of water, kg/m³

g = acceleration due to gravity, m/s²

R = radius of the clay particles, m

V = velocity of sedimentation of the particles, m/s

Kaolinite is known to have bigger particle than montmorillonite. Table 2.1 shows the particle size distribution between kaolin and bentonite clay containing majority montmorillonite mineral crystals.

Table 2.1: Particle Size Distribution between Kaolin and Bentonite

Clay	Contents of Fractions Below		
	2 μ m	0.5 μ m	0.1 μ m
Kaolin	28-80	10-35	0-2
Bentonite	70-95	25-95	10-60

Source: Ahmed (1986).

2.2.2 Plasticity

Plasticity is the outstanding property of clay water systems. It is the property a substance has when deformed continuously under a finite force. When the force is removed or reduced, the shape is maintained. Mineralogical composition, particle size distribution, organic substances and additives can affect the plasticity of clays. Several measuring techniques and devices were proposed to determine the optimal water content in a clay body required to allow this body to be plastically deformed by shaping. The plasticity of clays is related to the morphology of the plate-like clay mineral particles that slide over the others when water is added, which acts as a lubricant. As the water content of clay is increased, plasticity increases up to a maximum, depending on the nature of the clay. Clay workers are accustomed to speak of “fat” or highly plastic clay such as ball clay or “lean”, relatively non-plastic clay such as kaolin, but it is very difficult to express these terms in measurable quantities. In the industry, plasticity is also referred to as extrudability, ductility, workability or consistency (Andrade *et al.*, 2011).

According to (Andrade *et al.*, 2011) uses the term consistency referring to states of ceramic raw materials, namely dry powder, granules, plastic body, paste and slip, which are dependent on the liquid content. Fig. 1 presents the apparent shear resistance as a

function of the water content for a typical clayish material. When water is added to dry clay, the first effect is an increase in cohesion, which tends to reach a maximum when water has nearly displaced all air from the pores between the particles. The minimum amount of water necessary to make clay plastic is commonly called the “plastic limit” (PL). Addition of water into the pores induces the formation of a fairly high yield-strength body that, however, may crack or rupture readily on deformation. A plastic clay body can withstand the addition of considerable amounts of water, passing through a stage in which it remains dry to the fingers and is easily molded. As the water content increases, the clay becomes a paste, in which the yield strength steadily diminishes. The clay becomes wet and sticky to the fingers and can no longer maintain a molded shape. The water content which corresponds to this state is called “liquid limit” (LL). With still higher water contents, the system becomes dispersion (slurry or slip). The difference in the water amounts at these two limiting points, related to the dry mass of the clay, is expressed as the “plasticity index” (PI).

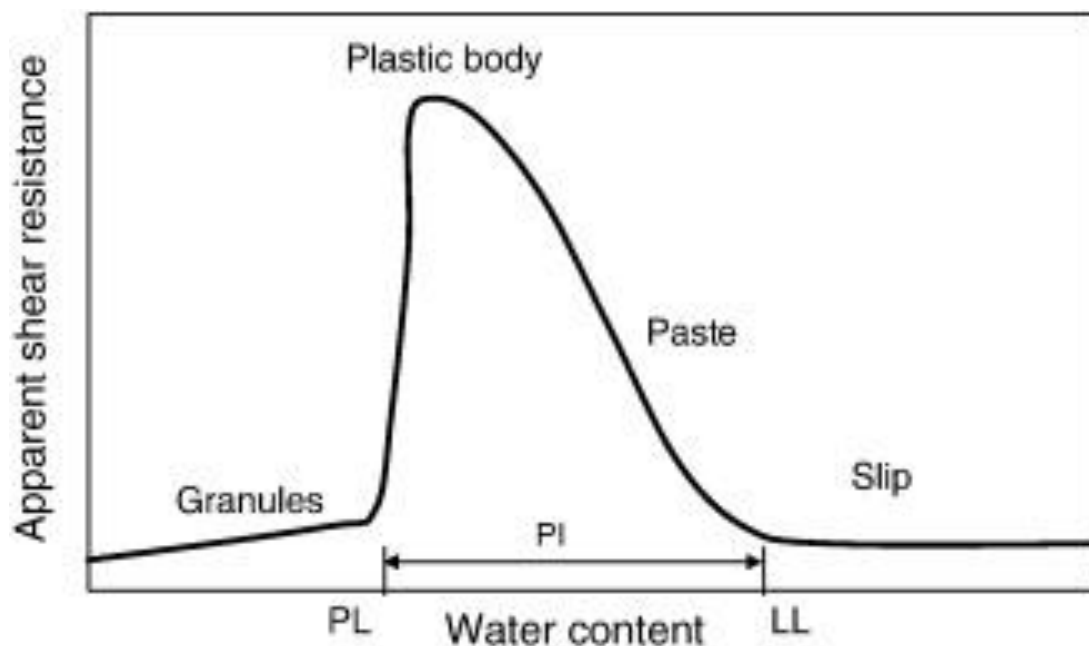


Figure 2.1: States of Consistency and Plasticity Limits of Clays
Source: Andrade *et al.* (2011)

There are several methods for measurement and characterization of the plasticity of a clay body. The experimental determination, in some cases, is operator dependent, which in turn may produce different results when different methods are compared. Among these methods, Atterberg, Pfefferkorn, stress/strain curves, indentation and rheological measurements are the most used techniques (See Table 2.2).

Table 2.2: Methods for Evaluating the Plasticity of Clays.

Method	Atterberg	Pfefferkorn	Penetrometer	Capillary rheometer	Brabender rheometer	Tension versus deformation
Measuring principle	Moulding	Impact deformation	Penetration	Pressure	Torque	Pressure
Parameters measured or calculated	PI (LL and PL)	Water content (mass percent)	Force	Viscosity, pressure extrusion, flow curve	Torque, shear stress, viscosity, extrusion head pressure	Tension, deformation
Speed	Low	Low	Average	Average	Average	Average
Reproducibility	Low	Average	Average/high	High	High	High
Cost	Low	Low	Average	High	High	Average
Standard	ASTM D4318 (2005)		BS 1377 (1990)			

Source: Andrade *et al.* (2011)

Atterberg plasticity index hinges on the principle that the more plastic a clay is the more water it can absorb without becoming fluid. This implies the range of water content over which it is plastic is very wide. When little water is intermittently added to dry clay, a point is first reached where the clay becomes plastic and cohesive. This corresponds to the minimum water requirement to form a stable film or consistency around each clay

particle. This is called the plastic limit (PL) of the clay, and is expressed as percentage weight of dry clay. The water content that brought about this state of clay is also, often denoted as P_w . Liquid limit (LL) is the second phase of the liquification process. Here, more water is added to the plastic clay and it becomes softer and eventually it reaches a stage where it flows under its own weight. The Liquid Limit (LL) is also often denoted as L_w . The Atterberg plasticity index (API) is thus given as: $API = L_w - P_w$ or $LL - PL$.

Test for clay plasticity using the Pfefferkon plasticity index also uses the principle of water tolerance. According to Abdullahi (2009) the plasticity index test is done by preparing a series of cylindrical test pieces of clay, of standard dimensions, covering a range of moisture. The test pieces are subjected to deformation through a standard compression by allowing a standard disc and a guide rod to fall on it from a fixed height. The deformation obtained in each test piece is calculated as the ratio of original length to deformed length. The deformation rate or ratio is plotted against the moisture content to give a smooth curve. The Pfefferkon index is the moisture content corresponding to a deformation ratio of 3:1. This test has been in widespread use in industries, and results correlate approximately with accepted values.

2.2.3 Chemical and mineralogical composition

The theoretical formula for clay is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, an alumino-silicate, but none are that pure and uncontaminated. There are many technical characteristics that define a material as a clay but, for ceramics, the primary characteristic beyond the alumina and silica content is the fact that they are composed of very small flat platelids with a resulting very large surface area with microscopic water between them so they slide on one another and additionally tend to hold their shape (Clay Planet, 2015).

A conventional full or complete chemical analysis of clays would normally comprise the determination of the loss on ignition (LOI), SiO₂, Al₂O₃, Fe₂O₃, TiO₂, K₂O, Na₂O, MgO, CaO, and other oxides. The Loss on Ignition measures the weight of the water of hydration (combined water), carbonates and carbonaceous matter. The parameter is rarely required but in practice it is determined as a pre-step to silica determination by heating a dried sample to 1000°C for 2 hours (Fasuba *et al.*, 2000 and Nnuka and Enejor, 2001).

According to Chesters (1973), Ahmed (1986), Chesti (1994), and Abdullahi (2009), all are in agreement that the following methods are essential in testing for the chemical and mineralogical properties of clay materials viz:

- i. Atomic Absorption Spectrometry (AAS).
- ii. Differential Thermal Analysis (DTA).
- iii. X-ray Fluorescence (XRF) and
- iv. X-ray Diffraction (XRD).

2.2.3.1 Atomic absorption spectrometry

According to (Royal Society of Chemistry, n.d) Atomic absorption spectrometry is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram ($\mu\text{g dm}^{-3}$) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atomic absorption spectrometry has many uses in different areas of chemistry.

- i. Clinical analysis - Analysing metals in biological fluids such as blood and urine.

- ii. Environmental analysis - Monitoring our environment e.g. finding out the levels of various elements in rivers, seawater, drinking water, air, petrol and drinks such as wine, beer and fruit drinks.
- iii. Pharmaceuticals - In some pharmaceutical manufacturing processes, minute quantities of a catalyst used in the process (usually a metal) are sometimes present in the final product. By using AAS the amount of catalyst present can be determined.
- iv. Industry - Many raw materials are examined and AAS is widely used to check that the major elements are present and that toxic impurities are lower than specified e.g. in concrete, where calcium is a major constituent, the lead level should be low because it is toxic.
- v. Mining - By using AAS the amount of metals such as gold in rocks can be determined to see whether it is worth mining the rocks to extract the gold.

Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. In AAS, the sample is atomised i.e. converted into ground state free atoms in the vapour state and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporised sample. Some of the radiation is absorbed by the lead atoms in the sample. The greater the number of atoms there is in the vapour, the more radiation is absorbed. The amount of light absorbed is proportional to the number of lead atoms (Royal Society of Chemistry, n.d).

A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample. Consequently an atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed (Royal Society of Chemistry, n.d).

2.2.3.2 *Differential thermal analysis*

The principal of 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 (Ahmed, 1986). Heat is absorbed (endothermic reaction) or released (exothermic reaction) whenever a chemical process result in a phase change. The amounts of heat exchanged (in calories per mole), usually expressed as ΔH or enthalpy, and the temperature at which the reaction occurs are fixed and characteristic for any material (ASM, 1995).

For purposes of phase identification, the most useful reactions are isothermal (that is, the temperature of the phase remains constant during the entire time the reaction is occurring). A change from a low temperature structure to a high temperature structure (polymorphic transformation), dissociation with loss of a volatile component (e.g. loss of H₂O or CO₂), reduction of oxidation state, and fusion are all endothermic isothermal processes that are detectable by thermal analysis. The reverse of all these processes is the exothermic isothermal process (ASM, 1995).

Differential Thermal Analysis (DTA) measures the temperature of a reference material and the temperature difference between the sample and the reference material. At the onset of a phase change during either heating or cooling, the temperature of the sample deviates from the reference temperature and remains constant until the reaction is complete. The temperature difference, ΔT , is negative and shown as a deviation from the base line, or peak on the thermogram (ASM, 1995).

2.2.3.3 *X-ray fluorescence*

X-ray fluorescence (XRF) analysis is one of the most common non-destructive methods for qualitative as well as quantitative determination of elemental composition of materials. It is suitable for solids, liquids as well as powders. There are two main methodological techniques that are wavelength dispersive analysis (WDXRF) and energy dispersive analysis (EDXRF) where the spectra are collected simultaneously in a wide energy range. In this case, the range of detectable materials covers all elements from Sodium (Na) to Uranium (U) and the concentration can range from 100% down to ppm. Detection limit depends upon the specific element and the sample matrix but in general heavier elements have higher detection limit (Areziki, 2014).

Fundamental principles of x-ray fluorescence:

The XRF method depends on fundamental principles that are common to several other instrumental methods involving interactions between electron beams and x-rays with samples, including: X-ray spectroscopy (e.g., SEM - EDS), X-ray diffraction (XRD), and wavelength dispersive spectroscopy (microprobe WDS). The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behaviour of atoms when they interact with radiation. When materials are excited with high energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the

energy of the radiation is sufficient to dislodge a tightly held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample (Wirth and Barth, 2015).

X-Ray fluorescence instrumentation - How does it work?

The analysis of major and trace elements in geological materials by XRF is made possible by the behaviour of atoms when they interact with X-radiation. An XRF spectrometer works because if a sample is illuminated by an intense X-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed within the sample in a manner that depends on its chemistry. The incident X-ray beam is typically produced from an Rh target, although W, Mo, Cr and others can also be used, depending on the application. When this primary X-ray beam illuminates the sample, it is said to be excited. The excited sample in turn emits X-rays along a spectrum of wavelengths characteristic of the types of atoms present in the sample. How does this happen? The atoms in the sample absorb X-ray energy by ionizing, ejecting electrons from the lower (usually K and L) energy levels.

The ejected electrons are replaced by electrons from an outer, higher energy orbital. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. This energy release is in the form of emission of characteristic X-rays indicating the type of atom present. If a sample has

many elements present, as is typical for most minerals and rocks, the use of a Wavelength Dispersive Spectrometer much like that in an electron microprobe (EPMA) allows the separation of a complex emitted X-ray spectrum into characteristic wavelengths for each element present. Various types of detectors (gas flow proportional and scintillation) are used to measure the intensity of the emitted beam. The flow counter is commonly utilized for measuring long wavelength (>0.15 nm) X-rays that are typical of K spectra from elements lighter than Zn (Wirth and Barth, 2015).

The scintillation detector is commonly used to analyze shorter wavelengths in the X-ray spectrum (K spectra of element from Nb to I; L spectra of Th and U). X-rays of intermediate wavelength (K spectra produced from Zn to Zr and L spectra from Ba and the rare earth elements) are generally measured by using both detectors in tandem. The intensity of the energy measured by these detectors is proportional to the abundance of the element in the sample. The exact value of this proportionality for each element is derived by comparison to mineral or rock standards whose composition is known from prior analyses by other techniques (Wirth and Barth, 2015)

Applications:

- i. X-Ray fluorescence is used in a wide range of applications, including
 - research in igneous, sedimentary, and metamorphic petrology
 - soil surveys
 - mining (e.g., measuring the grade of ore)
 - cement production
 - ceramic and glass manufacturing
 - metallurgy (e.g., quality control)
 - environmental studies (e.g., analyses of particulate matter on air filters)

- petroleum industry (e.g., sulfur content of crude oils and petroleum products)
 - field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers)
- ii. X-Ray fluorescence is particularly well-suited for investigations that involve
- bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment
 - bulk chemical analyses of trace elements (in abundances >1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment
 - detection limits for trace elements are typically on the order of a few parts per million
- iii. X-ray fluorescence is limited to analysis of
- relatively large samples, typically > 1 gram
 - materials that can be prepared in powder form and effectively homogenized
 - materials for which compositionally similar, well-characterized standards are available
 - materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood.

In most cases for rocks, ores, sediments and minerals, the sample is ground to a fine powder. At this point it may be analysed directly, especially in the case of trace element analyses. However, the very wide range in abundances of different elements, especially iron, and the wide range of sizes of grains in a powdered sample, makes the proportionality comparison to the standards particularly troublesome. For this reason, it is common practice to mix the powdered sample with a chemical flux and use a furnace or gas burner to melt the powdered sample. Melting creates a homogenous glass that can

be analyzed and the abundances of the (now somewhat diluted) elements calculated (Wirth and Barth, 2015).

2.2.3.4 X-ray diffraction

X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of x-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the x-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material (Evans Analytical Group, 2015).

Fundamental principles of x-ray powder diffraction:

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law.

$$n\lambda = 2d \sin \theta \dots\dots\dots (4)$$

Where λ is the wavelength of the rays and n is integer being the order of the diffraction. The angles θ are obtained from single crystal or powder diffraction methods using a camera or a diffractometer. Thus, the d values can be determined.

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d -spacing allows identification of the mineral because each mineral has a set of unique d -spacing. Typically, this is achieved by comparison of d -spacing with standard reference patterns. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this (Dutrow and Clark, 2015).

X-ray powder diffraction (XRD) instrumentation - How does it work?

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_{α} and K_{β} . K_{α} consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr).

Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_{α} radiation = 1.5418\AA . These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from 5° to 70° , angles that are preset in the X-ray scan (Dutrow and Clark, 2015).

Applications:

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

- characterization of crystalline materials

- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity (Dutrow and Clark, 2015).

2.2.4 Sinterability

Sintering is a densification process which implies a reduction in volume, i.e. shrinkage. During the sintering process, the surface energy decreases, because the incoherent particles are cohering together reducing the total surface. Sintering is the opposite of breaking the particles apart, which would require energy to break the chemical bonds. It is possible to say that sintering means forming bonds reducing the surface, so it does not require energy but evolves it, even if in a very little quantity (Ventureli and Paganelli, 2007).

According to Chesters (1973), Sullayman (2006) and Abdullahi (2009), absorbed water was removed during firing at just over 100°C and Kaolinite decomposed above 450°C, losing its hydroxyl groups as water. Thermogravimetry is a technique that measures the variation of mass of a sample subjected to a heating cycle, which may be associated to decompositions, dehydroxylations corrosions, etc. Also this kind of analysis provides no information in the sintering interval, because there are no mass variations. After this loss of water, no further mass variation takes place inside the material and the thermogravimetric curve remains flat. Traditional dilatometry measures the dimensional changes of a sample during a heating cycle, working in contact with the material to analyse. The mechanical contact is obtained with a small bar made of refractory material which is kept at a slight pressure on the sample. Due to this fact, the push rod dilatometer can follow the sample only as long as it is rigid enough not to be deformed

by the pressure of the rod. During the final stage of the sintering process, the material viscosity decreases and pressure of any kind applied to the sample alters its behaviour: the instrument measures a deformation which is not real. Furthermore, the analysis must be stopped in order to avoid damages for the measuring system (Ventureli and Paganelli, 2007).

2.3 Refractory Materials

The term refractory means hard to fuse (Chesti, 1994). Refractory materials are materials that are capable of withstanding high temperature both physically and chemically (Musa *et al.*, 2012). Refractories are materials that can retain their strengths at high temperature and withstand chemical attack in the severe conditions of working (Hassan, 2005). High quality refractory materials resist high temperature fluctuations between 1000°C and 1500°C and are also good thermal and electrical insulators. Refractory materials may be defined as materials that retain their physical and chemical identity when subjected to high operation temperatures (Musa *et al.*, 2012).

These materials are non-metallic compounds that can withstand temperatures above 1000°F (538°C). The ability to withstand exposure to heat above 538°C is the critical distinction separating refractory from other ceramics, fibres and coating application at only lower temperature. A refractory material is one which has the ability to withstand high temperature without breaking or deforming. Refractory products are used wherever high temperatures are required and include refractory bricks for furnace linings, tubes for electric furnaces, crucibles, thermocouple sheaths, refractory cements, among others (Musa *et al.*, 2012).

Refractories are heat-resistant materials that constitute the linings for high-temperature furnaces and reactors and other processing units. In addition to being resistant to thermal stress and other physical phenomena induced by heat, refractories must also withstand physical wear and corrosion by chemical agents. Refractories are more heat resistant than metals and are required for heating applications above 1000°F (538°C) (The Refractory Institute, 2014).

High temperature operations are involved in almost all the industries dealing with the treatment of ores and other materials for the manufacture of metallurgical, chemical and ceramic products. As such, equipment used for treatment of these materials must sustain the operating temperature and other working conditions such as corrosive, erosion and load conditions. Refractories are, therefore, class of materials which withstand high temperatures, resist the action of corrosive of liquids and dust-laden currents hot gases, etc. In technology these are generally referred to as the materials employed for the construction of furnaces, flues, crucibles, etc used in high temperature operations to make such equipment resistant to the corrosive action of gases and slag's present therein (Chesti, 1994). General requirements of a refractory material are:

- i. Withstand high temperatures
- ii. Withstand sudden changes of temperatures
- iii. Withstand action of molten metal slag, glass, hot gases, etc
- iv. Withstand load at service conditions
- v. Withstand load and abrasive forces
- vi. Conserve heat
- vii. Have low coefficient of thermal expansion

- viii. Should not contaminate the material with which it comes into contact (UNEP, 2006).

2.4 Classification of Refractory Materials

Refractories can be classified on the basis of chemical and mineralogical composition, methods of manufacture or physical form and their refractoriness.

2.4.1 Classification based on chemicominalogy

This classification is based on the chemical and mineralogical composition of the material (Ahmed, 1986 and Hubble, 1999). According to (Chesti, 1994), Refractory oxides of metals, non-metals or their mixture form the widely used group of refractory materials as they include some of the most stable in oxidizing atmospheres at high temperatures. The decreasing order of thermodynamic stability of these oxides at the standard reference temperature of 25.15°C is CaO, ThO₂, BeO, La₂O₃, SrO, Y₂O₃, BaO, HfO₂, Al₂O₃, ZrO₂, UO₂, CeO₂, TiO₂, SiO₂, V₂O₃, Ta₂O₃, MnO and NiO. According to their chemical behaviour refractory materials can be classified into three main types, namely acid, basic, and neutral. Acid refractories are refractories that are attacked by basic slag's (bases). Basic refractories are the refractories that are attacked by acid slag's (acids). Neutral refractories are the materials that are attacked neither by acids nor by bases. Such materials are also used to replace basic refractories where the corrosive action is strong. However, for various reasons, these rules are often violated; the chemical classification of refractories is largely academic and has an insignificant value as a guide to actual application (Hubble, 1999).

Table 2.3: Chemicominalogical Classification of Refractories

Acid Refractories	Basic Refractories	Neutral
Silica	Magnesite	Alumina
Aluminosilicates	Magnesite-Chrome	Carbon
Zirconia	Dolomite	Chrome
Zircon	Forsterite	Chrome-Magnesite

Source: Ahmed (1986)

2.4.2 Classification based on method of production

According to (Chesti, 1994), the method by which refractories are produced is commonly used to classify them. There are four main methods by which refractories are manufactured. These are pressing, ramming, extrusion and castables. Pressing process is classified into dry pressing and semi-dry pressing processes. In the dry pressing process, the batch material usually contains about 20-50% of grog (pre-fired material) in the case of fire clay, mixed with relatively small amount of moisture, 5-8%. In semi-dry pressing, about 8-9% moisture is used in the batch. The batch is charged into steel moulds and compacted by means of mechanically or hydraulically applied pressure of about 200kg/cm² or more. These are dried and fired to desired temperature. Lower moisture contents in mixtures require high press and higher moisture containing mixes increase the slumping changes at the time of release from the mould Thus a compaction pressure from 200kgf/cm² to 800kgf/cm² is suggested.

In ramming method of production, plastic consistency refractory batch are formed within male and female dies (mould) usually made of toughened resin or steel. Much of the water of plasticity is driven out in the compaction process. Batch containing high

percentage grog of coarse particles and optimum moisture contents (like in plastic pressing) need to have tapering mould walls and simultaneous top and bottom pressing cycle of long duration and longer retention time. In addition, maximum pressure is needed in order to ensure better and improved densification of the refractory product.

The extrusion production technique entails that the batch is mixed with about 10-15% moisture and is passed through a pug mill. It is then extruded through an auger system which normally has an in-built de-airing device to evacuate trapped air in the batch. It is also coupled with a cutting device which slices the pug roll into specified sizes for pre-pressing in the refractory production mould used essentially for the production of hollow wares.

Refractory Castables are dry mix hydraulic compositions of refractory aggregates with suitable bonding materials. On the addition of the required amounts of water to these compositions, a wet concrete-like mass is produced which forms useful castables. Ceramic bonding is developed in the cast shapes by heating to high temperatures. Refractory aggregates comprise grog of fireclay, bauxite, sillimanite and other alumina materials or chromite etc. which do not undergo structural changes on heating. Light weight insulating castables are also produced for use at temperatures of 1100-1800°C.

Refractory castables are used for producing monolithic linings besides patch work, etc. Castables can be used for getting both simple and complex linings quite easily. The use of castables avoids storage and inventories of large number of complicated shapes and minimizes the number of joints in structure which increases the life of the lining and reduces the maintenance jobs.

2.4.3 Classification based on refractoriness

Refractories are classified into following four types according to their refractoriness.

- i. Low heat duty refractories – These refractories have refractoriness in the range of 1520°C to 1630°C and have pyrometric cone equivalent (PCE) value in the range of 19 to 28. Example of these refractories is silica bricks.
- ii. Intermediate heat duty refractories – These refractories have refractoriness in the range of 1630°C to 1670°C and have pyrometric cone equivalent (PCE) value in the range of 28 to 30. Example of these refractories is fire clay bricks.
- iii. High heat duty refractories – These refractories have refractoriness in the range of 1670°C to 1730°C and have pyrometric cone equivalent (PCE) value in the range of 30 to 33. Example of these refractories is chromite bricks.
- iv. Super heat duty refractories – These refractories have refractoriness greater than 1730°C and have pyrometric cone equivalent (PCE) value greater than 33. Example of these refractories is magnesite bricks (Satyendra, 2013).

Table 2.4: Refractoriness Classification of Refractories

Type of Refractory	PCE (Segar Cones)	Refractoriness/Fusion Point (°C)
Low heat duty	19-28	1520-1630
Medium heat duty	28-30	1630-1670
High heat duty	30-33	1670-1730
Super duty	Greater than 33	Greater than 1730

Source: Gupta, (2008)

2.5 Aluminosilicate Refractories

The aluminosilicate refractories are materials consisting mainly alumina and silica. Fire clay and high alumina refractories form refractories form “Aluminosilicate” group of refractories comprising essentially of two basic oxides Al_2O_3 and SiO_2 associated with impurity oxides TiO_2 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , etc. to the tune of about 2 to 5% when put together (Chesti, 1994).

Table 2.5: Aluminosilicate Refractories Classification Based on Alumina Content

Refractory	Alumina Content (wt. %)
Fire Clay	25-45
Silliminite	45-65
Mullite	65-75
Bauxite-based	75-90
Corundum	90-100

Source: Ahmed (1986)

2.6 Fireclay Refractories

Fireclays are naturally occurring earthy materials having the chemically composition given by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Fireclays may be plastic, semi-plastic or non-plastic. Flint clays are very hard and non-plastic. Their plasticity is increased by adding of bond clays to them. Plastic clays may be less refractory and hence their refractoriness is increased by the addition of more refractory clay and thus desired properties of the fireclays are achieved by mixing different clays in proper proportions. The alumina content of fireclay generally ranges from 25-45% and they fuse between 1580°C - 1750°C . Presence of alkalies, sand, gravel, calcium carbonate, iron oxide, calcium

silicate, magnesium silicate, iron silicate, magnesium carbonate, iron sulphite, etc. in fireclays seriously lower their fusion temperatures and therefore should be free from them as far as possible (Chesti, 1994).

2.7 Types of Fireclay Refractory Bricks

According to (Satyendra, 2015) stated that the American Society of Testing Materials (ASTM), defined five standard classes of fireclay bricks. These classes are, super duty, high duty, medium duty, low duty and semi silica.

2.7.1 Super duty fireclay bricks

Super duty fireclay bricks have good strength and refractoriness. They have good volume stability at high temperatures and an alumina content of 40 % to 44 %. Super duty bricks have superior resistance to cracking or spalling when subjected to rapid changes of temperature. Their refractoriness, in terms of their PCE values, may not be less than 33. There are several possible modifications in the super duty fireclay bricks; including bricks fired at temperatures several hundred degrees higher than the usual product. The high temperature firing enhances the high temperature strength of the brick, stabilizes their volume and mineral composition, increases their resistance to fluxing, and renders them practically inert to disintegration by carbon deposition in atmospheres containing carbon monoxide gas.

2.7.2 High duty fireclay bricks

High duty fireclay bricks are used in large quantities and for a wide range of applications. Because of their greater resistance to thermal shock, high duty fireclay bricks can often be used with better economy than medium duty bricks for lining of furnaces operated at moderate temperatures over long periods of time but subject to

frequent shutdowns. The PCE value of the high duty brick may not be less than 31.5, and usually varies from 31.5 to 33.

2.7.3 Medium duty fireclay bricks

Medium duty fireclay bricks are appropriate in applications where they are exposed to conditions of moderate severity. These bricks, within their serviceable temperature ranges, can withstand abrasion better than many bricks of the high duty class. Medium duty fireclay bricks have PCE values in the range of 29 to 31.

2.7.4 Low duty fireclay bricks

These bricks find application as back up bricks for bricks with higher refractoriness. They are used for services where relatively moderate temperature prevails. The PCE values of low duty fireclay bricks cover the range 15 to 27-29

2.7.5 Semi silica fireclay bricks

These bricks contain 18 % to 25 % alumina and 72 % to 80 % silica, with a low content of alkalis and other impurities. With notable resistance to shrinkage, these refractories also have excellent load bearing strength and volume stability at relatively high temperatures.

2.8 Development of Dense Refractory Firebricks

According to (Chesti, 1994) clay got from the mines, is left in the open in thin layers for weeks or months. This causes the decaying of organic matter present in the clay due to heat, cold and atmospheric moisture. Some organic acids thus produced increase the plasticity of the clay. This treatment is called weathering or souring. Important factors that strongly affect the properties of dense refractory firebricks are beneficiation of the clay materials, particle size distribution, mixing and moulding, drying and firing

2.8.1 Beneficiation of clay raw materials

According to Abdullahi (2009), raw clay materials obtained directly from mines would usually require some purification treatment to separate the various impurities present. The most frequently used method is the sedimentation process which aims at separation of materials on a size basis, since no two materials are likely to have exactly the same size distribution. This method is often effective for separation of clay from sand, silt and quartz. Sieving is another method of purifying clay materials. Sieving also separates impurities on a size basis and is sometimes preferred to the sedimentation technique because it is much faster to accomplish. In sieving (wet sieving), the clay material is soaked in water, blunged and sieved through the appropriate sieve size.

2.8.2 Particle size distribution of grog aggregates

According to (Chesti, 1994), grog is a term used for fired clay particles. Good refractory clay is hard fired in rotary kilns and crushed to desired particle size. It is also made by crushing previously fired broken and scrap bricks. Grog is added to the clay mainly as an anti-shrinkage element in the form of angular particles of various sizes to achieve better interlocking of grains. Rounded particles are avoided for their decreased bonding capacity. Grog is added to clay for the following advantages: less shrinkage on heating, increased strength of the fired refractories, decreased apparent porosity and increased specific gravity, greater resistance to sudden changes in temperature and less addition of water to get a workable plasticity and lesser time required for drying the raw refractories and hence increased rate of production.

Particle size distribution of clay aggregates is the proportioning of the grog aggregates to be used in the brick manufacture. There are three basic considerations in material proportioning. These are the particle size distribution, maximum grains size and

composite proportioning (Ahmed, 1986 and Chesti, 1994). These authors maintained that both large and small grain materials are required in order to attain a close-packing grading such that intersects between the largest particles are filled by smaller grade. Thus the important working properties like low porosity, strength; thermal shock resistance and thermal conductivity are satisfied. In this process, coarse clay shapes are fired, crushed and sieved into suitable particle distribution. There exist several theories on grain size distribution but two of which are more widely used:

- i. Ainsworth theory of grain size packing; and
- ii. The Andreason's parameter.

The Ainsworth theory is in favour of the utilization of some specified grog sizes particles, leaving out others that are not within the range. On the other hand Andreason's parameter accommodates the use of all particles sizes in order to avoid wastages. Table 2.6 shows the hypothetical examples of minimum and maximum grain size (aperture openings) as well as their mean size values:

Table 2.6: Hypothetical Examples of Aperture Size and Mean Size

Aperture Size	Mean Size
(-2mm + 1mm)	1.5mm
(-1mm + 0.2mm)	0.6mm
(-0.2mm + 0.1mm)	0.15mm
(-0.1mm + 0.02mm)	0.06mm
(-0.02mm + 0.01mm)	0.015mm

Source: Sullayman (2006)

Andreason's equation has the following formula:

$$P = \left(\frac{d}{D}\right)^n \times 100$$

Where: P = Weight percentage fraction

d = Average size fraction

D = Maximum size of grain

n = Andreason's distribution parameter (n = 0.2 – 0.9)

In the Andreason's distribution parameter, it is believed that the maximum grain size of refractory must not be more than 20% of the smallest body thickness. For fireclay refractory, the industrial standard requires that the maximum grain size should be between 1mm and 3.28mm. For coarse grain refractory materials, n has been reported to have an optimum value of 0.7 (Ahmed and Hisham, n.d).

Theoretically coarse, medium and fine fractions are usually in the preferred ratio of 66:25:9 respectively. But factors such as the non-availability of desired mesh size and specific user requirement of a refractory product are tenable for adjustment of grog ratios. (Ahmed, 1986) while working on "phosphate bonded fire clay castables", adjusted the above ratio to 66:34 of coarse and medium fractions by adding the fine fractions to the medium fractions, based on the non-availability of sieve size 1.6µm.

In the study of "the effects of particle size distribution on physical properties of castables" (Samadi, 2003), adopted the following percentage as a range of grog fractions. They were 40% - 55% for coarse fraction, 20% - 33% for medium and 22% - 30% for fine fractions. Three formulations made from these percentages range of grog fractions according to (Samadi, 2003), had good performances in terms of strength, flow

ability, bulk density and apparent porosity. These therefore, portend justification for class adjustment of grain size distribution in a batch. Moreover, other exponents of refractory research and manufacture agree that a wider scale proportionate class aggregates in a refractory batch propels it for better performance while in use as well as meeting proper refractory properties.

Particle size distribution has a great deal of positive effects on the physical properties of refractories, as it helps to achieve better packing compared with using mono-sized particles (Samadi, 2003). This also has effect on the flow, apparent porosity and hence, strength in castables and other refractories. Tear and wear on the mould as well as thermal shock resistance are functions of maximum grain size of grogs. Particles cohesion also depends largely on the structure of the particles. These factors are crucial to the production of dense firebricks.

2.8.3 Mixing and moulding

Mixing which is done by finely crushed refractory clay is mixed with an appropriate quantity of the prepared grog and, if necessary, with the bond clay or calcined bauxite. Mixing is carried out either in dry state or by wet methods. In the former case different ingredients are taken in the requisite proportions, either on weight or volume basis, and mixed. In wet mixing the ingredients are mixed with water in a pug or pan mill. Before transferring to pug-mill, the mixture mat soaked in water for about 30-36 hours or more so that the water is absorbed by the clay and distributed uniformly throughout the mass. After thorough mixing, the mixture is ready for moulding into desired shapes.

Moulding is carried out either by hand moulding, pneumatic ramming or by mechanical pressing. About 7-9% water is used in hand moulding mixtures and 4-7% in case of

machine moulding mixtures. Lower moisture content containing mixtures requires high moulding pressures and higher moisture containing mixes increase the slumping chances at the time of release from mould. Hand-moulding refractories may not be of the appropriate size and may be less dense than those produced by machine-moulding processes. Larger size and complicated shapes are made by hand-moulding or pneumatic ramming using 10-12% and 7.5-9.5% moisture respectively in the moulding mixtures. Machine moulding gives a high rate of production (Chesti, 1994).

2.8.4 Drying

Drying of moulded refractories increases its green strength by removing moisture and thus making them safe for subsequent handling. Drying of the moulded shapes is done under shade or in well ventilated rooms and in absence of direct sunshine as faster rate drying will result in crack formations. Faster rate of drying results in uneven drying and development of strains in the refractory shapes making them liable to crack. Slow rate of drying ensures uniform drying both inside and outside the compact mass. Thus drying is carried out quite cautiously under predetermined conditions of temperature and humidity. Steam heated floors are used for final drying of green hand-moulded or extruded products after 1-4 days natural drying (Gupta, 2008).

2.8.5 Firing

Firing of dried fireclay refractories is carried out in batch or continuous type kilns. The kilns may be down-draught, up-draught or horizontal draught type. Tunnel kilns are used for mass production and chamber kilns are generally preferred for longer and complicated shapes. After burning, refractories are sorted and stored. Some of the bricks which are under-fired are fired again. Over-fired or other defective refractories, like Black-Heart formed due to insufficient supply of oxygen for combustion in the kiln, is

rejected (Chesti, 1994). The firing temperature of the bricks is dependent on the chemical quality of the brick rather than the nature of the forming technique but in any case must be sufficient to ensure the development of a ceramic bonding in order to maximize the potential corrosion resistance of the particular quality (Doyle, 1994).

2.9 Properties of Fireclay Refractories

A refractory must necessarily possess some required properties before it can be accepted use in service. However, requirements vary according to the refractory type. Generally, the primary considerations of users are:

- i. Rigidity and maintenance of size, shape and strength at the operating temperature.
- ii. Ability to withstand thermal shock as is met in heating and cooling of furnaces, or in fluctuations which occur during charging and normal operations
- iii. Resistance to chemical attack by whatever gas, slag or material likely to be encountered.

These qualities are determined by the properties of the refractories. The following are the more important properties of fireclay refractories; Drying and firing shrinkage, bulk density, apparent porosity, modulus of rupture, cold crushing strength, thermal shock resistance, refractoriness - under – load and non-destructive sonic testing

2.9.1 Drying shrinkage

Shrinkage resulting from drying or firing of refractories is more commonly expressed in linear than in volume. In reporting linear shrinkage, there could be two bases on which the calculation is made. If L_{fd} is the as – formed dimension and L_d is the dimension of

the dried unfired piece, percentage linear drying shrinkage on the as – formed basis is given by:

$$\%LDS_f = \frac{L_{fd} - L_d}{L_{fd}} \times 100 \dots\dots\dots (5)$$

Where: LDS_f = Linear Drying Shrinkage as formed

L_{fd} = Length as formed

L_d = Length when dried

On the other hand, percentage linear drying shrinkage on the dried basis is given by:

$$\%LDS_d = \frac{L_f - L_d}{L_d} \times 100 \dots\dots\dots (6)$$

Where: LDS_d = Linear Drying Shrinkage on the dried

L_f = Length as formed

L_d = Length of the dried

The greater the amounts water presents of water present in the formed piece, the greater the drying shrinkage. Excessive shrinkage may cause warping and possibly, cracking of the body. It is therefore desired to have drying shrinkage as small as possible.

2.9.2 Firing shrinkage

Firing Shrinkage of refractory is normally based on the desired green length or unfired dimension. If FL represents the fired dimension, percentage linear firing shrinkage is given in accordance with ASTM C179-14 (2014) as:

$$\%L_{FS} = \frac{GL - FL}{GL} \times 100 \dots\dots\dots (7)$$

Where, GL = Green length

FL = Fired length

$\%L_{FS}$ = Percentage Linear Fired Shrinkage

2.9.3 Bulk density

The bulk density of a refractory indicates the level of firing it has received and thus its degree of densification. This is determined by expression below

$$BD = \frac{W_1 d}{W_2} \dots\dots\dots (8)$$

Where, W_1 = Dry Weight

W_2 = Weight Deep in Mercury (Hg)

d = Density of Mercury

BD = Bulk Density

Apparent specific gravity, apparent solid density and True specific density are the other different density measurements used in testing. Apparent specific gravity equals apparent solid density if measured at room temperature. Apparent solid density measures the density without the open pores in the brick, while the True density measures the density without both closed and open pores. The difference between the two provides an indication of the proportion of closed pores present in the bricks. Bulk density is the most commonly used density measure for fireclay refractories (Sullayman, 2006). Typical bulk density of fireclay refractories is between the ranges of 1.9-2.3g/cm³ (ASTM, 1982).

2.9.4 Apparent porosity

When faced with a new refractory problem, it is the practice to start with a porosity test, as it provides useful background information, more so it is a sample and quick test. Apparent porosity measures the fraction of open void volume to the volume of the material. It is directly related to many other physical properties of a refractory including resistance to chemical attack. For a given class of refractory, those with the lowest

porosity have the greatest strength, thermal conductivity and heat capacity (Ahmed, 1986). However, such refractories have low resistance to thermal shock (Chester, 1973). If V_o is the volume of open pores of a refractory and V_b is bulk volume, its apparent porosity, P_a may be calculated from:

$$P_a = \frac{V_o}{V_b} \times 100 \dots\dots\dots (9)$$

OR

The apparent porosity (P_a) of the brick may also be determined from the relationship below in accordance with ASTM C20–00 (2015):

$$P_a = \frac{W - D}{W - S} \times 100 \dots\dots\dots (10)$$

Where, P_a = Apparent porosity

D = Dry Weight of Sample

W = Weight of Sample suspended in air including moisture in its open pores.

S = Weight of sample suspended in water.

The apparent porosity for a good dense fireclay refractory will range between 15-25% (ASTM, 1982).

2.9.5 Cold crushing strength (CCS)

The cold crushing strength, which is considered by some to be doubtful relevance as a useful property, other than it reveals little more than the ability to withstand the rigorous of transport. It can be seen as a useful indicator to the adequacy of firing and abrasion resistance in consonance with other properties such as bulk density and porosity, (Bhatia, 2011).

This is the ability of a refractory material to withstand the structural load coming over it. Dense and fine grained refractories generally possess good crushing strength whereas porous and coarse grained refractories have poor crushing strength. Cold crushing strength of refractories is carried out by placing a suitable refractory specimen on a flat surface followed by application of a uniform load to it through a bearing block in a standard mechanical or hydraulic compression testing machine. The load at which a crack appears in the refractory specimen represents the CCS of the specimen. According to ASTM C133-97 (2015) for refractory bricks, the cold crushing strength is calculated as:

$$\text{Cold Crushing Strength} = \frac{\text{Load applied (Kg)}}{\text{Area (cm}^2\text{)}} \dots\dots\dots (11)$$

2.9.6 Thermal shock resistance

Thermal shock resistance, also known as spalling resistance and is a measure of the resistance of a refractory to sudden changes in temperature. Refractories subjected to alternative cycles or heating and cooling must not spall or crack and crumble to pieces. On heating, the refractory grains expand and result in compression in the structure of the refractory which may be sufficient to cause shear failures (Chesti, 1994).

2.9.7 Refractoriness under load

Refractoriness points to the resistance of extreme conditions of heat (temperature > 1800 °F) and corrosion when hot and molten materials are contained while being transported and/or processed. The ability to withstand exposure to elevated temperatures without undergoing appreciable deformation is measured in terms of refractoriness. The refractoriness under load test (RUL test) gives an indication of the temperature at which the bricks will collapse, in service conditions with similar load. However, under actual

service where the bricks are heated only on one face, most of the load is carried by the relatively cooler rigid portion of the bricks. Hence the RUL, test gives only an index of the refractory quality, rather than a figure which can be used in a refractory design. Under service conditions, where the refractory used is heating from all sides such as checkers, partition walls, etc. the RUL test data is quite significant (Bhatia, 2011).

2.10 Application of fireclay Refractories

The application of fireclay bricks is influenced by several other properties in addition to the refractoriness. These properties are dimensional accuracy, crushing strength, porosity, and refractoriness under load. Machine pressed, fired fireclay refractories are used for many applications. The stress on the materials differs widely. For special applications, it is customary to manufacture bricks which are tailored to meet specific requirements (Satyendra, 2015). Fireclay refractories are mainly used for the construction of furnaces, kilns, ovens, fireplaces, regenerator's flues, boilers, and many other like structures in which heat is generated or through which hot gases pass (e.g. blast furnace stoves) (Gupta, 2008).

Because of its coefficient of thermal expansion, fireclay bricks are resistant to thermal fatigue. Coarse textured and high grog containing refractories have greater spalling resistance than those produced from fine textured and low grog mixtures. Other application of fireclay bricks include iron blast furnace lining, cupola, recuperators, annealing, roasting and reheating furnaces, chimney, beehive coke oven glass melting furnaces and other furnaces which allowed to cool frequently. They are also used in blast furnace runner, steel casting and pig iron handling ladles. Besides, pottery, petrochemical, fertiliser and cement plants also use them extensively (Gupta, 2008).

CHAPTER THREE

METHODOLOGY

This research study adopts experimental approach. This chapter details the materials, equipment, and experimental procedures followed in this research work.

3.1 Materials and Equipments

Some of the materials and equipments used in this research study includes the following; clay from Maraban Rido, water, lubricating oil, analytical weighing balance, ball milling machine, electric oven, electric furnace, Tyler mesh sieves, hydraulic press machine, hydraulic crushing machine, vernier calliper, hammer, wooden mould, steel mould, hot plate, mercury, beaker, plastic bucket, shovel and digger.

3.2 Experimental Procedure

The procedure includes sample preparation, beneficiation of sample, characterization of the clay sample, grog making, size reduction by crushing and milling, particle fractionation, mixing of batch for brick making, moulding of brick, drying and sintering of the bricks and analyses of the test brick samples.

3.2.1 Sample preparation

A trip was made to Maraba-Rido village in Chikun Local Government Area of Kaduna State. Clay samples were randomly collected after digging from different points at the deposit. The collected clay samples were later mixed thoroughly to obtain a representative locally homogeneous sample. The clay from Maraban Rido is shown in Plate I.



Plate I: Clay from Maraban Rido

3.2.2 Beneficiation of Maraban Rido clay sample raw material

The beneficiation of Maraban Rido clay sample was carried out at the Ceramics Section of the Department of Industrial Design, A.B.U., Zaria, Nigeria. The raw clay was soaked in water for 24 hours. It was stirred and sieved manually with Tyler mesh 200 corresponding to 75 μ m aperture size. The clay slurry obtained was allowed to sediment for 15 minutes and which was then decanted, ensuring that the bottom portion of the slurry was left behind. This was to eliminate any free silica particles which might be present. The particles in suspension were allowed to sediment by means of gravitational attraction within two days (48 hours). The water was decanted while the material was placed on plaster trough for further absorption of moisture hardening into plastic state.

3.2.3 Characterization of the clay sample raw materials

Testing the behaviour or nature of the raw material is very important in determining the properties of the refractory products and their quality controls for repetitive production.

There are two major classes of material characterization processes used in this study.

- i. Physical test to determine the plasticity index of the clay, the liquid limit and the plastic limit. Others are drying shrinkage and firing shrinkage tests on the clay.
- ii. The second material characterization test was conducted by X-ray Fluorescence (XRF) to determine the specific elemental oxide presence or chemical composition of the clay.

3.2.3.1 Determination of the plasticity index

The plasticity index test was carried at the Department of Civil Engineering A.B.U., Zaria, Nigeria. The plasticity of the clay was tested through the use of Atterberg plasticity index (API). Heckroodt (1994) described Atterberg plasticity index as the numerical difference between the moisture contents of the liquid limit and the plastic limit. The index expresses the range of moisture contents over which the clays will behave plastically. The value of plasticity index was expressed thus:

$$PI = LL - PL \dots\dots\dots (12)$$

Where LL = Liquid Limit

PL = Plastic Limit

PI = Plasticity Index

Determination of the liquid limits:

Liquid limit test BS1377 (1990) specifies two methods of determining the liquid limit of clay. They are the cone penetrometer method and the Casagrade apparatus method. The Casagrade apparatus method was adopted in this work. Liquid limit is the water content

at which the clay stops acting as a liquid and starts acting as plastic clay. About 200g of the clay sample was sieved through a 425 μ m sieve, air dried, and thoroughly mixed. The sample was placed on a glass sheet and mixed with a little distilled water. The cup of the apparatus was half filled with the wet clay and levelled off. A 2mm groove was then cut in the sample using the grooving tool. The handle of the apparatus was rotated at a steady rate, which actuates the cam, causing the cup to lift 10mm and then fall onto the base. The number of blows needed to close the gap over 13mm was recorded and a portion of the sample just tested was removed and placed in a container for water (moisture) content determination both before and after oven-drying at 105°C.

The groove was considered closed when two parts of the sample came into contact at the bottom of the groove; plastic flow caused the groove to close. The test was repeated two more times, employing a little more water for each test. To obtain the liquid limit, the water content (w), % was plotted vertically against the number of blows (N) horizontally. Therefore, the water content corresponding to 25 blows was taken as the liquid limit and expressed to the nearest whole number.

Determination of the plastic limit:

This is the limit between plastic and brittle failure. About 20g of the sample prepared as in the liquid limit test was used. A rod of about 80mm long and 3mm diameter was used here. The sample was mixed on the glass plate with just enough water to make it sufficiently plastic for rolling into a ball, which was then rolled out between the hand and the glass to form a thread. When small cracks began to appear, the thread was divided into two parts. One part was formed into a thread, rolled until the diameter of the thread was reduced from 6mm to 3mm. The rod diameter assisted in determining the thread diameter. The sample is said to be at its plastic limit when it just crumbled at a

thread diameter of 3mm. At this stage, a section of the thread was removed, placed in a container for water content determination both before and after oven-drying at 105°C. The test was repeated one more time.

3.2.3.2 Linear shrinkage

The linear shrinkage was carried out at the section of Ceramics Design of the Department of Industrial Design, A.B.U., Zaria, Nigeria. Five clay test bars of 14cm dimensions were prepared, with an indented 10cm line along its length. The test bars were subjected to gradual drying process under ambient condition for 7days. They were then dried in a Gallenkamp oven, type ov-420 at 110°C for 24 hours, burned in a down-draught kerosene fired kiln to about 1280°C and soaked at that temperature for 3 hours. At the end of the drying and firing operation each of the test bars was observed for shrinkage. The shrinkage values were evaluated using these equations below:

(a) Drying Shrinkage

$$DS = \frac{WL - DL}{WL} \times 100 \dots\dots\dots (13)$$

Where: WL = Wet Length

DL = Dry Length

DS = Dry Shrinkage

(b) Firing Shrinkage Test

$$\%L_{FS} = \frac{DL - FL}{DL} \times 100 \dots\dots\dots (14)$$

Where: DL = Dry Length FS

FL = Firing Length

$\%L_{FS}$ = Percentage Firing Shrinkage

3.2.3.3 Chemical analysis of Maraban-Rido clay sample

The chemical analysis test was carried out at the Department of Research and Development Centre of Defence Industry Corporation of Nigeria, Kaduna-Nigeria. Chemical analysis was carried out on the clay sample in order to ascertain its oxide composition. The modern techniques typically adopted for the determination of the chemical composition are the X-ray fluorescence spectrometer (XRF) and Atomic Absorption Spectrometer (AAS) (Chesti, 1994). However, the XRF process is regarded as having the “advantage of high level of chemical specificity and reliability of its element presence”. Thus the XRF technique was adopted by this researcher for the determination of the elemental composition of Maraban-Rido clay sample.

The sample analysed was first grounded into a powder in agate mortar to grain sizes <125µm. Pellets of size 19mm was prepared from 0.5g of powder. The powder was mixed with three drops of organic liquid binder (epoxy glue) and pressed afterwards to 10 tons with hydraulic press. The sample was placed on the specimen chamber. Radiation emerging from the X-ray tube window excites secondary X-ray Spectra of elements within the sample. These secondary X-ray emissions which are characteristic of the elements analysed are intercepted by the detector. This is transformed into voltage signals and fed into the analyser for processing.

3.2.3.4 Loss on ignition

The water content percentage (%) of the clay was determined by measuring the weight loss of a known mass of the sample of 1gram in a porcelain crucible was pre-heated at 100°C for 2hours in an oven. It was then ignited to a constant weight. The crucible was then placed in a muffle furnace and the temperature was gradually increased form 320°C to 1000°C and maintained for 2 hours. The crucible was allowed to cool in a desiccator.

Weights were taken until constant values were obtained. Loss on ignition, (LOI) was calculated using this relation:

$$\text{L.O.I} = \frac{M - m}{M} \times 100 \dots\dots\dots (15)$$

Where: M = Mass of sample (g)

m = Mass of sample after ignition (g)

3.3 Preparation of Maraban Rido Clay Sample for Grog Production

After beneficiation, the resulting plastic clay was worked into a plastic mass of stiff consistency and moulded into shapes using a rectangular wooden mould of (26 x 14 x 8) cm dimension lubricated with engine oil. The clay blocks was dried in ambient air for seven days and then in an oven at 105°C for 72 hours. The bricks were charge into kerosene fired down-draught kiln and burnt to about 1280°C under oxidizing atmosphere. Pre-heating was done for 2 hours before full firing for about 8 hours. The kiln was left to cool at ambient temperature for 24 hours. The calcined clay, referred to as grog or chamotte was crushed manually with hammer into larger and smaller particle size fractions and it was sieve to this sieve grain sizes 2.6mm, 1.18mm, 0.600mm, 0.300, 0.15, and 0.075mm. This is to ensure that the coarse and fine grog ratio of 55:45 is obtained as suggested by (Chesters, 1973 and Chesti, 1994). The grog preparation process is shown in Figure 3.1.

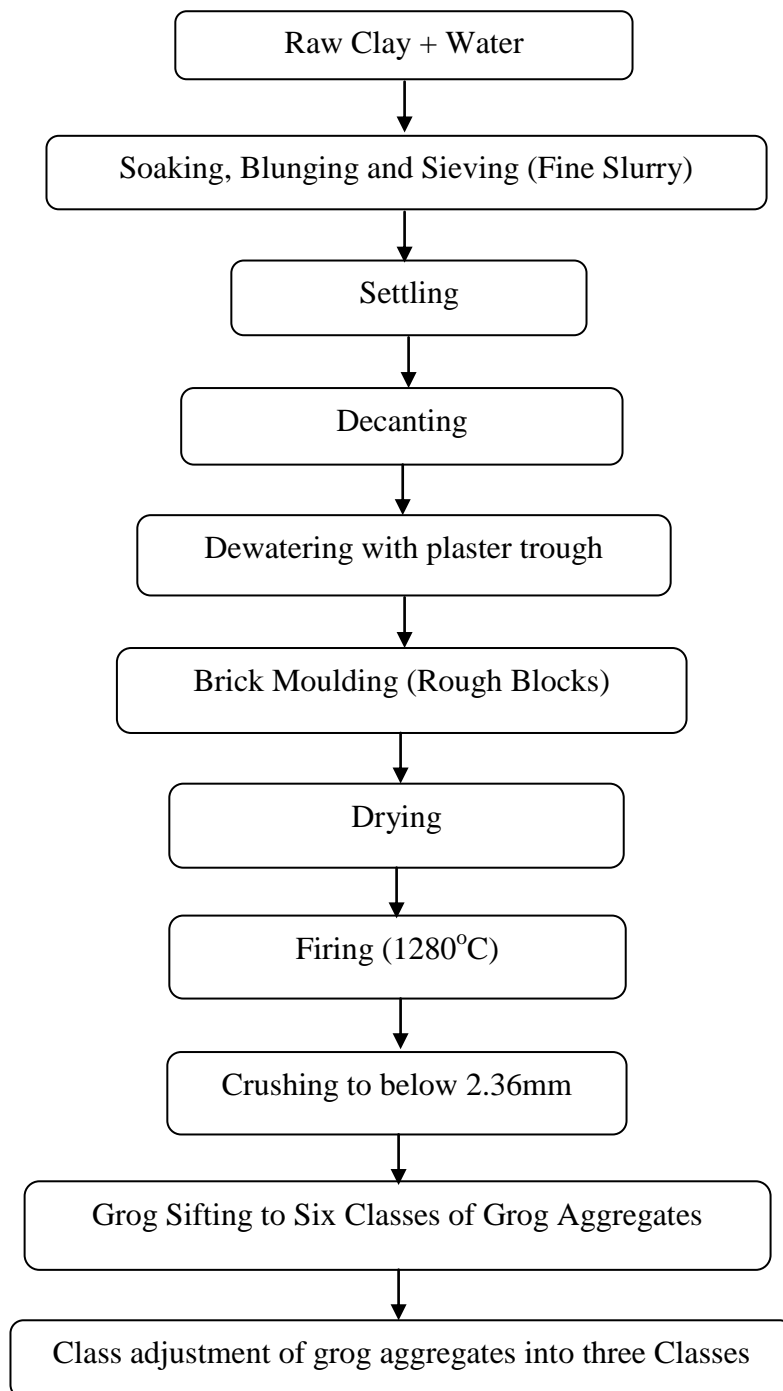


Figure 3.1: Grog Preparation Process

3.4 Production of Dense Refractory Firebricks

The production of the dense brick was carried out at the Refractory Section of National Metallurgical Development Centre Jos, Nigeria. The dense refractory bricks were

produced from crushed grog based on Andreason parameter equation methods. This started from the selection of batch composition, through pressing of test samples to drying and firing of bricks. The production of dense refractory firebrick process is shown in Figure 3.2.

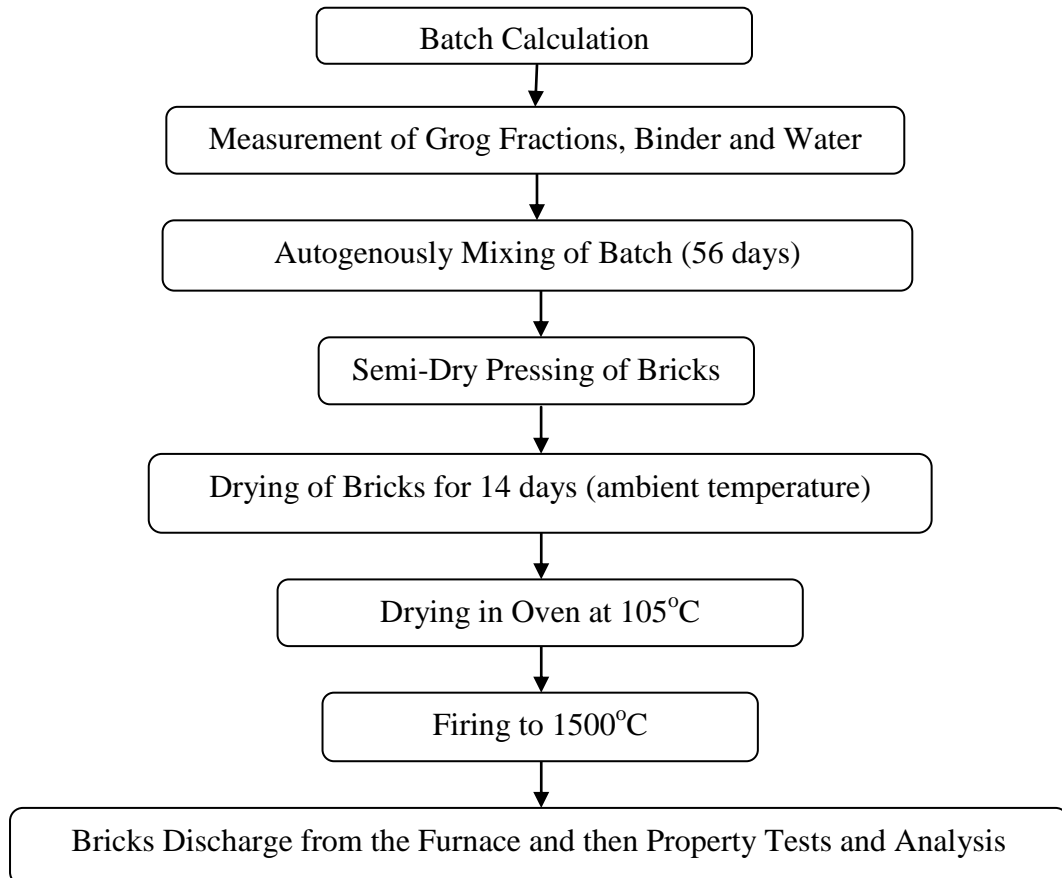


Figure 3.2: Production of Dense Refractory Firebrick Process

3.4.1 Batch composition using Andreason parameter equation

Two factors were taken into consideration in making the composition for the dense firebricks; the size fractions of grog and the proportion of the fractions to be blended. In this research work, Andreason Parameter Equation was used to achieve these set objectives.

The Andreason Equation describes the volume or weight ratio of the grain size classes of the media used in a refractory production. It represents the ratios of the three particle size classifications in a refractory batching such as coarse, medium and fine fractions necessary for the desired dense packing. This ensures that all particle size was taken care of in the batch thereby allowing for adequate packing density within the brick.

However, weighing and packing of a batch should be so ordered that all particle classes are adequately and proportionally taken care of in the batch composition. Theoretically coarse, medium and fine fractions are usually in the preferred ratio of 66:25:9 respectively. But factors such as the non-availability of desired mesh size and specific user requirement of a refractory product are tenable for adjustment of grog ratios. (Ahmed, 1986), while working on “phosphate bonded fireclay castables”, adjusted the above ratio to 66:34 of coarse and medium fractions by adding the fine fractions to the medium fractions, based on the non-availability of sieve size 1.6 μ m.

In the study of “the effects of particle size distribution on physical properties of castables” (Samadi, 2003), adopted the following percentage as a range of grog fractions. They were 40% - 55% for coarse fraction, 20% - 33% for medium and 22% - 30% for fine fractions. Three formulations made from these percentage range of grog fractions according to (Samadi, 2003), had good performances in terms of strength, flow ability, bulk density and apparent porosity. These therefore, portend justification for class adjustment of grain size distribution in a batch. Moreover, other exponents of refractory research and manufacture agree that a wider scale proportionate class aggregates in a refractory batch propels it for better performance while in use as well as meeting proper refractory properties.

Based on the factors enumerated above, this research adopt (- 2.36mm + 1.18mm) as coarse grain size (- 1.18 + 0.600mm) as medium grain size, (- 0.600mm + 0.300mm) (- 0.300mm + 0.150mm) (- 0.150mm + 0.075mm) as fine particle size fractions. After sieving, the content on each sieve was weighed and the total weighed obtained from the sieve was used as the total grog fractions in the batch.

The raw clay from Maraban Rido deposit was adopted as the bond material for this research. According to (Chesti, 1994) a bond material of about 10wt% of the total grog quantities is recommended. Thus, 10wt% of the total weight of the grog fractions of the refractory brick was computed for the brick samples produced.

For a semi-dry press method of refractory production which is the method adopted for this research work, various literatures have recommended a minimum of 10 wt.% moisture per weight of particles or clay used (Chesti, 1994), but 15wt% was used due to improper mixture at 10wt% moisture content.

The resulting fractions obtained from Andreason parameter calculations, the bonding fractions and moisture or water content was mixed for brick composition in a porcelain ball mill (without balls) for 30 minutes. This was to ensure a product of uniform composition and uniform distribution of fine and coarse grains and bond materials. It also ensures uniform moisture distribution within the particles for easy moulding and development of best possible properties in the fired refractories. The mixed batches were allowed to mature for 56 days to increase the plasticity of the bond materials for adhesive properties.

3.4.2 Mathematical calculation of Andreason parameter equation

Each of the six grain size used in this research (as stated in Section 3.3) was classified in grog fraction groups as indicated in section 3.4.1. These values were carefully used to calculate the weight percentages (wt. %) of grog fraction in each group, using Andreason Parameter Equation in the following sieve sizes: 2.36mm, 1.18mm, 0.600mm, 0.300mm, 0.150mm and 0.075mm.

The Adreasion parameter equation:

$$P = 100 \times \left(\frac{d}{D} \right)^n \dots\dots\dots (16)$$

Where: P = Weight proportion of fraction

D = Maximum size of grain in the distribution (2.36mm)

d = Average grain size of the fraction

n = Andreasons distribution parameter. (n = 0.2 – 0.9)

3.4.3 Semi-dry pressing of refractory bricks using hydraulic press machine

The pressing of the bricks was carried out at the refractory section of National Metallurgical Development Centre Jos, Nigeria. The moulds used for forming the sample bricks was made from mild steel with internal cross section of (10 x 5.3 x 2.3) cm and external dimension of (20.1 x 15.4 x 2.5) cm. The pressing machine (Paul Weber hydraulic press) available to this researcher had a maximum pressure capacity of 300 KN. The batch for each brick was charged into the mould and the piston or plunger lowered to compress the mixture. A compaction pressure of 300 KN was applied on each brick. The semi-dry pressing of the brick samples with hydraulic pressing machine is shown in Plate II.



Plate II: Semi-Dry Pressing of the Brick Samples with Hydraulic Pressing Machine

3.4.4 Drying of the bricks

The pressed bricks were allowed to dry on the laboratory table for 14 days under ambient temperature conditions. They were later dried in an oven at 105°C for 24 hours to expel any moisture left in the bricks and to avoid crack during firing. The drying of the brick sample is shown in Plate III.



Plate III: Drying of the Brick Samples

3.4.5 Firing of refractory bricks

Firing was carried out in electric heating furnace (Carbolite furnace with serial no. 8/01/195, type RHF 16/15) pre-set at heating rate of 7°C/min. The absence of furnace that fire for 3-4days period in normal situation, this firing procedure was used, which involved heating and soaking the samples at various temperatures 250°C for 1 h; 650°C for 1 h; 950°C for 1 h; 1100°C for 2 h and 1500°C for 3 h. The bricks were then allowed to cool in the furnace at a cooling rate of 1°C /minute immediately after firing to avoid sudden cracks. The cooling rate was achieved with a digital pre-set furnace and this was done to avoid sudden cooling that may result to cracking of the bricks after firing.

3.5 Fired Refractory Brick Analysis

The fired refractory brick analysis of the bricks was carried out at the Refractory Section of National Metallurgical Development Centre Jos, Nigeria. The surface quality of the refractory brick was observed after furnace annealing. Also properties like linear shrinkage, apparent porosity, bulk density, cold crushing strength, and thermal shock resistance were investigated.

3.5.1 Determination of the percentage linear shrinkage

The green weight of the brick was taken after moulding with an indented diagonal line of 10 cm across the length; air dried and fired in the furnace for 1500°C. The green and fired dimensions of the bricks were measured using the Vernier calliper. The linear shrinkage was calculated as a percentage of the original wet length as shown below in accordance with ASTM C179-14 (2014):

$$\%L_{FS} = \frac{GL - FL}{GL} \times 100 \dots\dots\dots (17)$$

Where, GL = Green length

FL = Fired length

%L_{FS} = Percentage Linear Fired Shrinkage

3.5.2 Determination of the apparent porosity

Apparent porosity is very important in refractories as it affects other properties, it can be determined by boiling point method or evacuation method. The boiling point method was used for this investigation. Test specimens measuring 2.3cm x 2.3cm x 2.3cm were cut in a cubic form from the already sintered refractory brick by a cut off wheel from within the centre of the refractory brick. All the particles adhering to the surface of the cut specimens were cleaned off.

The specimens were oven-dried at 110°C to a constant weight (D) with accuracy of 0.1gram and the dry specimen brick was then suspended in distilled water with an asbestos as barriers between the specimen and the bottom of the container (beaker of 300ml) and boiled on a hot plate to 100°C for 2 hours, after boiling, while still in hot water, the water was now displaced with cold water and the weight (W) was measured on a spring balance hinged on the a tripod stand (Mettler AE 200 Top load balance).

The test samples were removed from the water and extra water wiped off from the surface by lightly blotting the sample with wet towel and the weight (S) in air was measured, the apparent porosity (Pa) of the bricks was determined from the relationship below in accordance with ASTM C20–00 (2015):

$$Pa = \frac{W - D}{W - S} \times 100 \dots\dots\dots (18)$$

Where, Pa = Apparent porosity

D = Dry Weight of Sample

W = Weight of Sample suspended in air including moisture in its open pores

S = Weight of sample suspended in water.

3.5.3 Determination of the bulk density

Bulk density can be defined as the weight per unit volume of the refractory including the volume of open pore space. In essence the property helps to ascertain the strength of the refractory to compacting pressure and thus the volume stability of the refractory. The test specimen is cut from the core of the sintered refractory brick. Wipe off all the adhering particles and dusts and weigh on a balance (W_1). Approximately 1000g of clear

mercury was poured into a 100 ml beaker and placed on the balance pan centrally under the saddle. The balance was adjusted until the gramme-scale read zero.

The saddle was lowered into the mercury by means of the hand wheel and locked with the bridge locking screw. The micrometre was adjusted until the pointer touched the surface of the mercury. The balance was tared back to zero. The saddle was then raised by means of the hand wheel and the sample brick which was cut to a cubic size was placed on the surface of the mercury using a tong. The saddle was lowered immersing the specimen and the bridge locking screw was locked. The micrometre was adjusted until the pointer just touched the surface of the mercury. The balance was read and terms the weight, W_2 . The saddle was raised and specimen removed from the surface of the mercury using a tong. The volume of the specimen is given as $V = W_2/d$. The temperature of the mercury was 26°C corresponding to density of 13.5312.

The bulk density is calculated from the expression below

$$BD = \frac{W_1 d}{W_2} \dots\dots\dots (19)$$

Where, W_1 = Dry Weight

W_2 = Weight Deep in Mercury (Hg)

d = Density of Mercury

BD = Bulk Density

3.5.4 Determination of the cold crushing strength

The fired bricks were cut in cubic form with different dimensions were tested for crushing strength, using hydraulic machine. The cut samples were placed on a flat block surface. A uniform load was applied axially by turning the hand wheel at a uniform rate until fracture occurs. The loads at which cracks appeared in the samples were recorded

and the crushing strength was then calculated using the relationship below in accordance with ASTM C133-97 (2015):

$$\text{Cold Crushing Strength} = \frac{\text{Load applied (Kg)}}{\text{Area (cm}^2\text{)}} \dots\dots\dots (20)$$

3.5.5 Determination of the thermal shock resistance

The fired bricks of test sample cubic size of 2.3cmx2.26cmx2.26cm were used. The thermal shock was carried out using the test rig according with ASTM-C16-03 (2012). The test rig consists of a sample holding table which is designed so that the heat transfer due to conduction is reduced to its minimum value. Stainless steel sheathed K-type insulated junction thermocouples of 0.5 mm in diameter and 150 mm long were used to measure the surface and the centre temperatures. These thermocouples can measure temperatures ranging from 0 to 1100°C. The sample was placed in the test rig and maintained at about 1100°C and soaked for 15 minutes, after which, it was air cooled and observed for any cracks. If none was observed, it was returned to the furnace and the same process repeated until the sample cracked.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Sample Description

Maraban Rido clay disintegrates into smaller angular particles after mined in a lumpy form. The clay varies in physical characteristics such as the cream coloration, moderately hard with smooth texture and in lump sizes that vary between 5cm to 15 cm (See Table 4.1). When the sample is wetted with water it becomes a little plastic indicating it to be clay. The Maraban Rido clay falls within the range of some selected clays in Nigeria.

Table 4.1: Physical Characteristics of Clay from Maraban Rido Compared with some other Local Clays

Clay	Colour	Physical Form	Lump Sizes
Maraban Rido	Cream	Moderately hard with smooth texture	5 - 15cm
Ahoko*	Light grey	Moderately hard with smooth touch	5 – 20Cm
Onibode**	Light grey	Hard lumps with smooth touch	30 – 40Cm
Kankara**	White	Soft, smooth powdery lumps	Less-than 5cm
Manjahota**	Cream	Moderately hard, with soft touch	10 – 20Cm
Warram**	Ash grey	Very hard lumps with smooth touch	20 – 40Cm
Nafuta**	Cream with brown stains	Hard lumps of coarse texture	5 -15cm

Source: *Abdullahi (2009) and **Ahmed (1986)

4.2 Linear Shrinkage of the Clay Samples

Maraban Rido clay showed a fired shrinkage value of 7.1% as shown in Table 4.2, which falls within the common range for refractory clays of 7-10% (Chesters, 1973).

The drying shrinkage is of little significance, since the value changes with moisture content during casting. Maraban Rido clay fired at 1280°C developed little cracks. The off white coloration of the fired clay samples indicates the presence of small concentrations of iron oxide impurities. The little cracks observed in the fired clay sample could be due to the differential thermal expansion between the clay particles and the constituent quartz grains.

Table 4.2: Drying and Firing behaviour of Maraban Rido Clay

Dried (110°C) for 24 hours			Fired (1280°C) for 8 hours		
Colour	Crack Formation	Linear Shrinkage (%)	Colour	Crack Formation	Linear Shrinkage (%)
Cream	Cracked	2	Off white	Little Cracks	7.1

4.3 Plasticity Index

Results of the liquid limit (LL) and plastic limit (PL) tests conducted on the Maraban Rido clay sample showed that the liquid limit was 41.5% and its plastic limit was 33.5% as shown in Figure 4.1 and 4.2 respectively. Figure 4.1 shows the plot of moisture/water content (w) as a function of number of blows (N) from which the LL was determined. Plasticity index derived from LL and PL is shown in Table 4.3. Maraban Rido clay gave a plasticity index value of 8%. The plasticity index value obtained indicates that the clay sample from Maraban Rido was low in plasticity level. This could be attributed to the presence of low organic matter in the clay. The plasticity index of the Maraban Rido clay sample is shown in Figure 4.3.

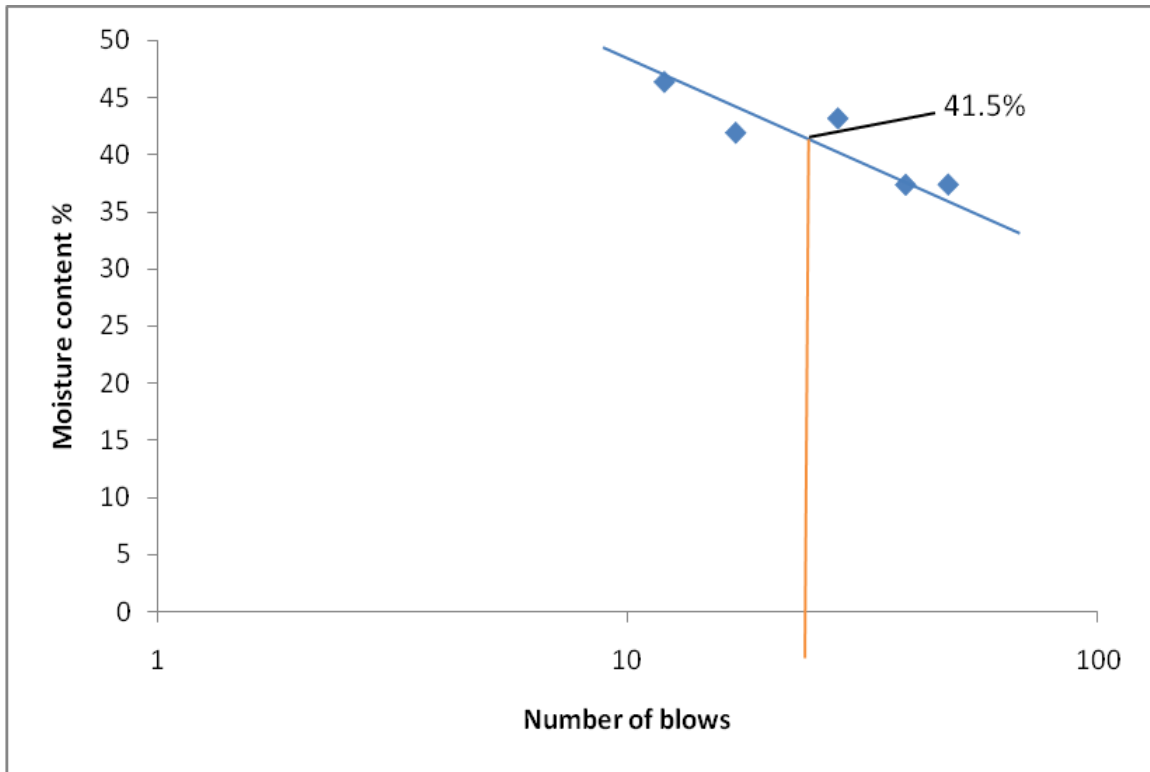


Figure 4.1: Water Content (w) as a Function of Number of Blows (N) and Liquid Limit

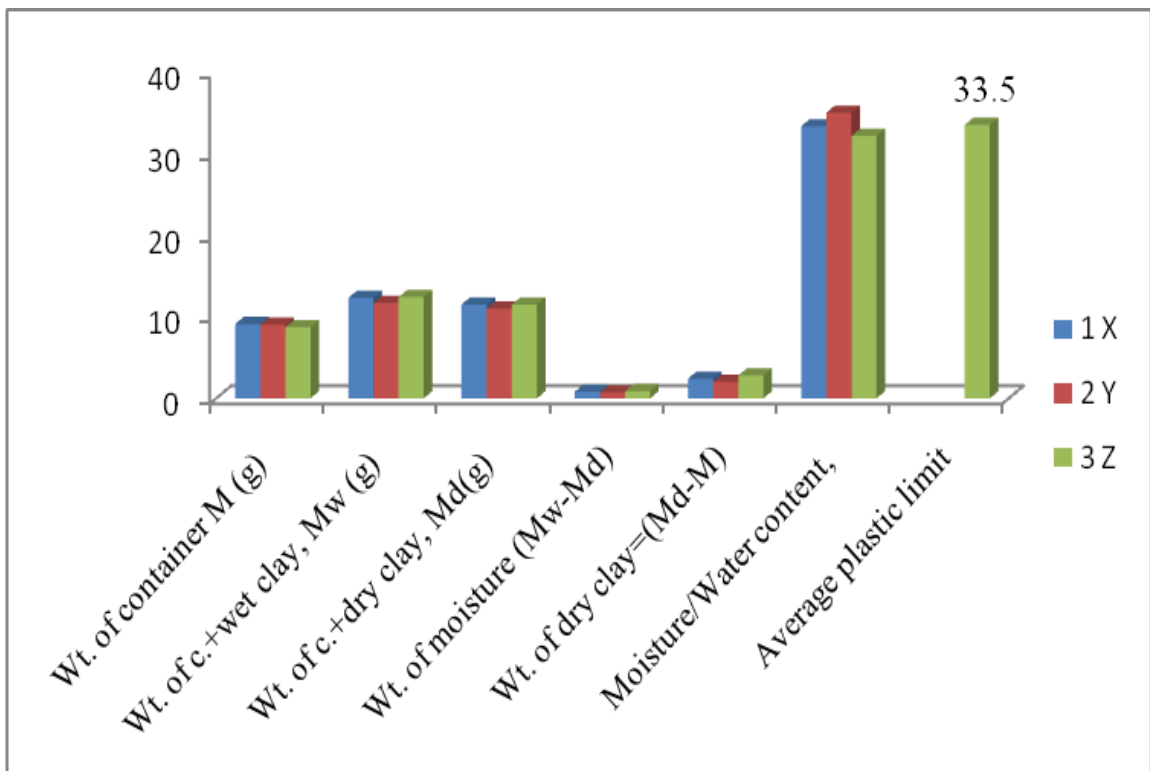


Figure 4.2: Plastic Limit of the Maraban Rido Clay Samples

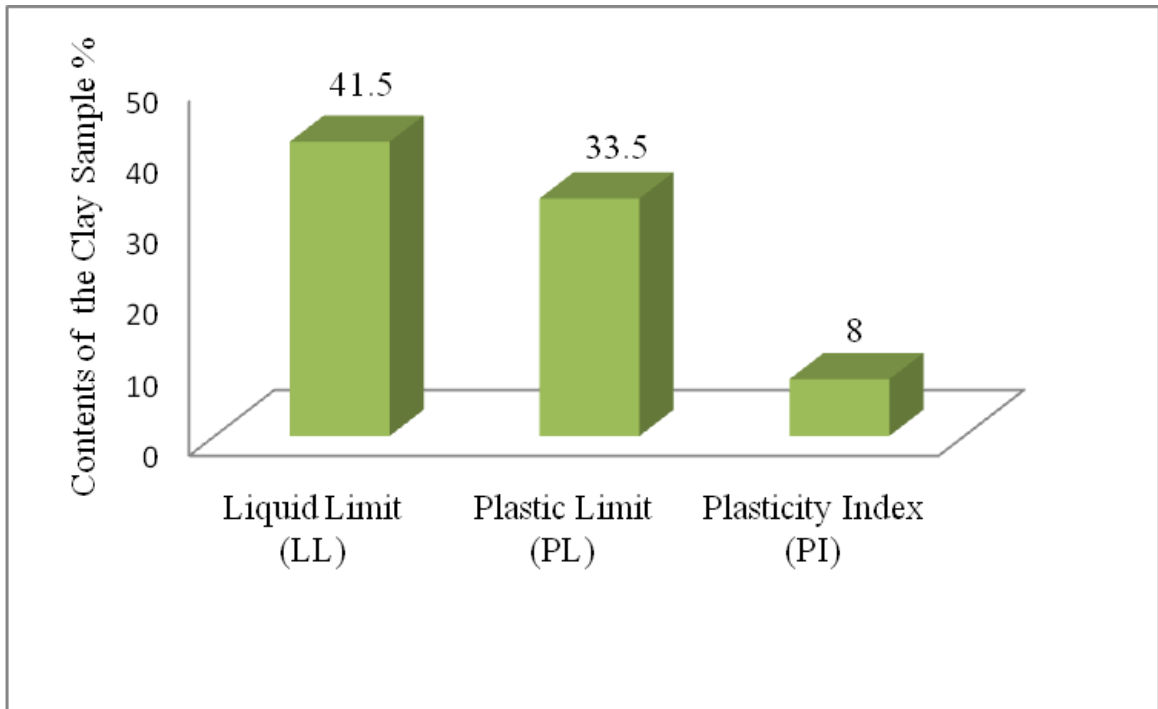


Figure 4.3: Plasticity Index of the Maraban Rido Clay Sample

4.4 Chemical Composition

The result obtained from X-ray fluorescence analysis of the beneficiated clay sample from Maraban Rido indicates that the principal oxides present to be alumina (Al_2O_3) and silica (SiO_2). The tested clay samples showed that the alumina (Al_2O_3) content was 44.0% and the silica (SiO_2) content was 51.8% (See Table 4.3). These values for alumina and silica make Maraban Rido clay suitable as a fireclay refractory material. The values of impurity oxides content for the clay sample such are K_2O (0.08%), CaO (0.16%), Fe_2O_3 (1.53%), TiO_2 (0.26%) etc. contents of 4.21% are all within the tolerable impurities associated to aluminosilicates group of refractories of about 2 to 5%. The averagely high content values for alumina (44.0%) coupled with the relatively low impurity contents (4.21%) make Maraban Rido clay suitable for the production of super-heat duty aluminosilicate refractory material (Chesti, 1994).

Table 4.3: Elemental (XRF) Analysis of Raw Clay Samples

Composition	Maraban Rido Clay (%)
Al ₂ O ₃	44.00
SiO ₂	51.80
Fe ₂ O ₃	1.53
K ₂ O	0.08
CaO	0.16
TiO ₂	0.26
V ₂ O ₅	0.03
Cr ₂ O ₃	0.02
MnO	0.02
CuO	0.01
SeO ₂	0.08
Ga ₂ O ₃	0.02
Ag ₂ O	1.61
BaO	0.11
WO ₃	0.03
Au	0.09
HgO	0.16
Na ₂ O	ND
L.O.I

4.5 Surface Appearance

The as-formed bricks appeared light cream except for the brown patches at the sides due to the steel mould contact during the pressing process. After firing, the bricks appeared

off-white. The physical appearance of the bricks as-formed, drying and firing revealed that there was a little crack in all the bricks. This means that the grog and the clays did not bond very well during pressing due to low plasticity of the bonding clay, with relatively low compaction pressure of 300 KN (See Table 4.4). The final brick samples in the furnace are shown in Plate IV.

Table 4.4: The Surface Appearance of the Bricks

Sample	As-formed	After Drying	After Firing	Colour
Maraban Rido Bricks	Little Crack	Little Crack	Little Crack	Off White



Plate IV: Final Brick Samples in the Furnace

4.6 Linear Shrinkage

The average percentage linear firing shrinkage of Maraban Rido clay was found to be 7.1%, as reflected in Figure 4.4. The clay is within the recommended values of fireclay bricks which have values from 7.0-10% (ASTM, 1982). This value is satisfactory, because higher shrinkage value may result in warping and cracking of the brick that will cause loss of heat in the furnace. The low shrinkage is attributed to the fact that about 90% of the compositions of the bricks are grog with about 15wt% moisture content. The firing shrinkage of the brick samples is shown in Figure 4.4.

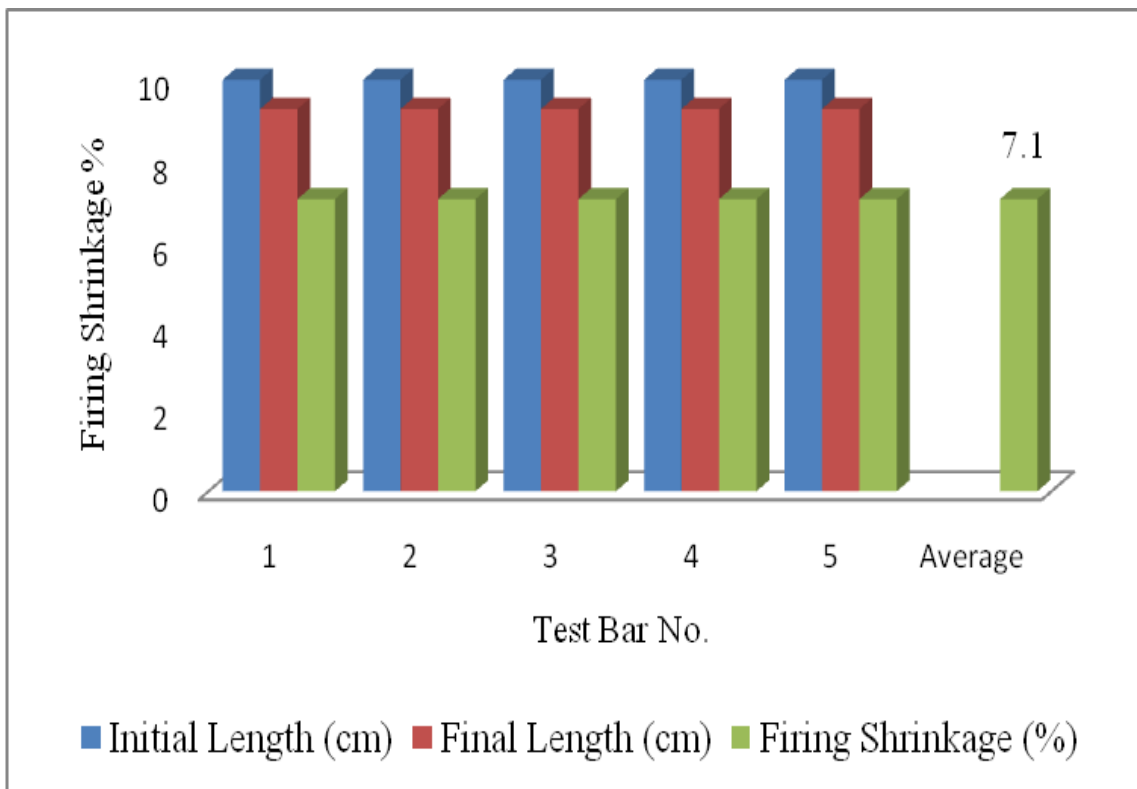


Figure 4.4: Firing Shrinkage of the Brick Samples

4.7 Apparent Porosity

The average apparent porosity value of the bricks was 33% (Figure 4.5) for the Maraban Rido clay sample. Hence the porosity of the clays does not fall within the acceptable level as recommended for fireclay bricks of 15-25% (ASTM, 1982). The very high

porosity value of the refractory brick could be due to the fact that the plasticity of the clay bonding is low, inadequate compaction pressure during the pressing process, coupled with shapes of the particle of the grog, since the grog is manually crushed and the reaction occurring on firing. Thus firing Maraban Rido bricks to higher temperatures above 1500°C would allow for proper sintering and densification to take place. This could enhance achieving the recommended maximum porosity level of 25%. The apparent porosity of the brick samples is shown in Figure 4.5.

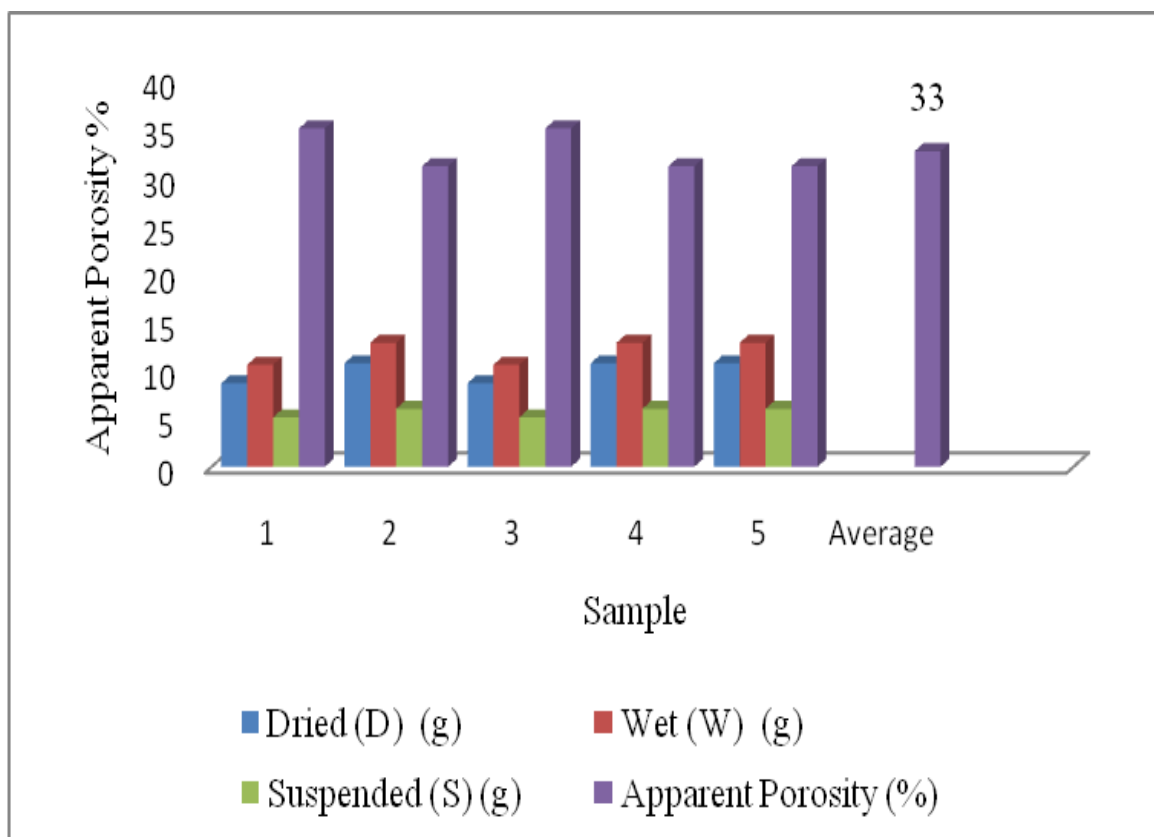


Figure 4.5: Apparent Porosity of the Brick Samples

4.8 Bulk Density

The average bulk density value of the bricks was 1.75g/cm³ for the Maraban Rido clay sample. Hence the bulk density of the clays does not fall within the acceptable level as recommended value for fireclay bricks of 1.9-2.3g/cm³ (ASTM, 1982). The very low bulk density value of the refractory brick could be due to the fact that the plasticity of the

clay bonding is low, inadequate compaction pressure during the pressing process, coupled with shapes of the particle of the grog, since the grog is manually crushed and the reaction occurring on firing. Thus firing Maraban Rido bricks to higher temperatures above 1500°C would allow for proper sintering and densification to take place. This could enhance achieving the recommended bulk density level of 1.9g/cm³. The bulk density of the brick samples is shown in Figure 4.6.

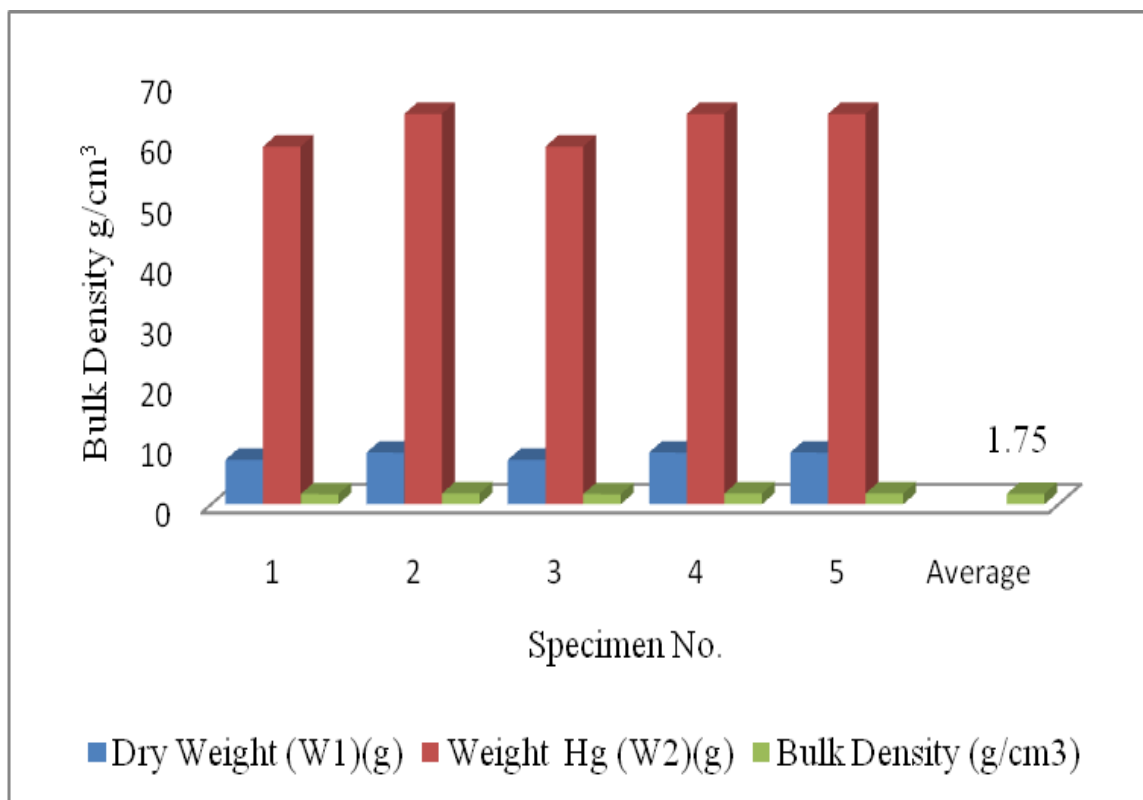


Figure 4.6: Bulk Density of the Brick Samples

4.9 Cold Crushing Strength (CCS)

The average cold crushing strength value obtained was 294.77kg/cm² for Maraban Rido clay as presented in Figure 4.7. The clay meets the recommended standard of cold crushing strength of 150kg/cm² minimum for fireclay (ASTM, 1982). The practical significance of this value is that the brick will be strong enough to withstand handling, transportation and abrasion in services. The cold crushing strength of the brick samples is shown in Figure 4.7.

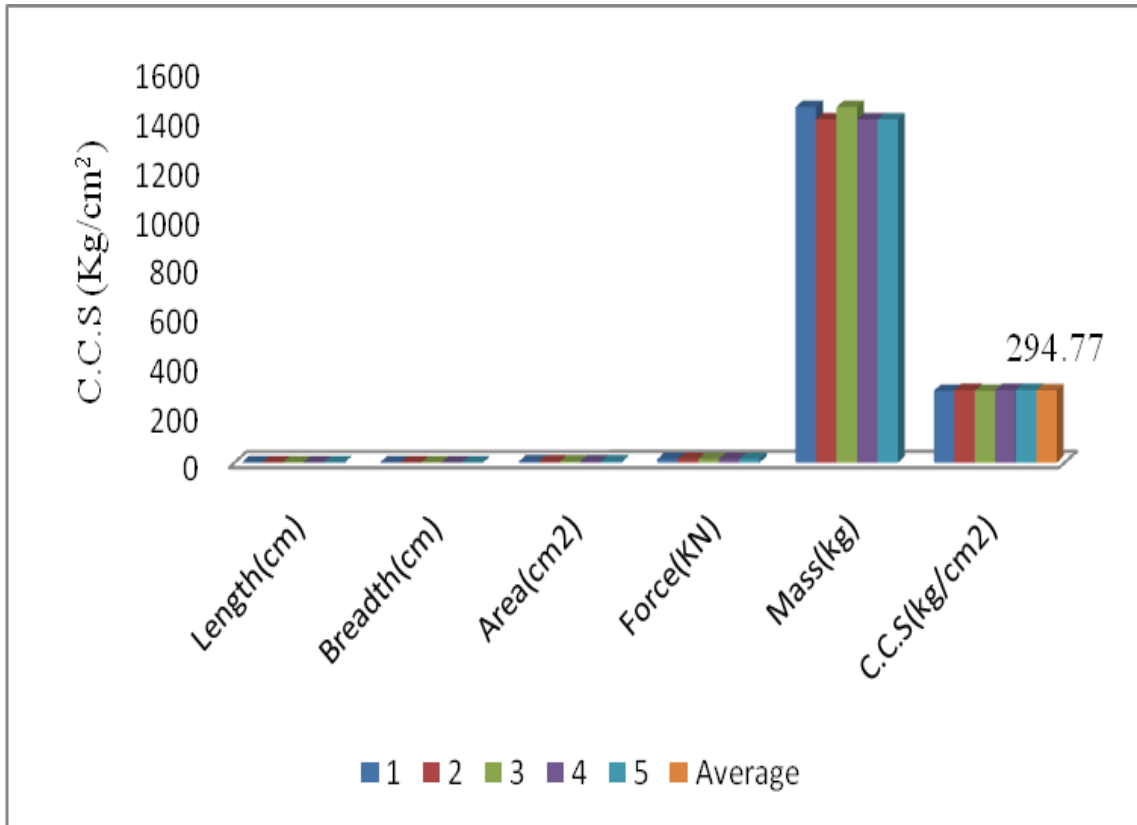


Figure 4.7: Cold Crushing Strength of the Brick Samples

4.10 Thermal Shock Resistance

The average thermal shock resistance value was 30 cycles from the bricks made from Maraban Rido clay as presented in Table 4.5. The Bricks produced fall within the acceptable ranges of 20-30 cycles for fireclay brick (ASTM, 1982) which is rated as an excellent thermal shock resistance. An excellent rating of thermal shock resistant test implies that Maraban Rido firebricks will have a long operational lifespan. This is due to the fact that no degree of fusion have taken place that may further transformed the brick, which will result to low thermal shock resistance.

Table 4.5: Thermal Shock Resistance of Brick Samples

Fired Temperature (°C)	Thermal Shock Resistance Category	No. of Thermal Cycles
1200	Excellent	30, 30, 30, 30, 30
Average		30

4.11 Findings

- i. Maraban Rido clay had a plasticity index of 8%. The plasticity index value showed that the Maraban Rido clay had low plasticity. This enhances its use for the production of refractory materials.
- ii. The chemical composition of beneficiated Maraban Rido clay showed that the main elemental oxides to be Al₂O₃ (44.0%) and SiO₂ (51.8%), implying that the clay material can be used in the production of super heat duty class of refractory bricks and it had a low level of impurity oxides contents of 4.21%.
- iii. The off white colouration of the clay material after firing at a temperature of 1280°C indicates the presence of low organic content and relatively low ferrous oxide content.
- iv. The dense fireclay refractory bricks showed little cracks as-formed, drying and firing at 1500°C due to the low plasticity of the clay used as the bonding material and compaction pressure, with an average firing shrinkage of 7.1%.
- v. The Maraban Rido refractory brick had an average apparent porosity of 33% and an average bulk density of 1.75g/cm³. This could be due to the inadequate compaction pressure during the pressing process, coupled with shapes of the particle of the grog, since the grog is manually crushed and the reaction occurring on firing. Thus firing Maraban Rido bricks to higher

temperatures above 1500°C would allow proper sintering and densification to take place.

- vi. The average cold crushing strengths value of 294.77kg/cm² of the bricks meet standard values of 150kg/cm² minimum for fireclay. This means that high strength bricks can be made from this clay.
- vii. The average thermal shock resistance value of 30 cycles at 1200°C fall into the excellent classification of 30 cycles. This makes it suitable for heat treatment furnaces application.
- viii. The application of 300 KN pressure for the production of the dense bricks was grossly inadequate. This was reflected in the lower density of 1.75g/cm³, and the very high porosity of 33%.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

This chapter entails the conclusions drawn from the investigation results and discussions and general recommendations made by the researcher.

5.1 Conclusions

The present research was centred on the development and characterization of clay from Maraban Rido as refractory materials. From the investigation results and discussions, the Maraban Rido clay formed fireclay refractory firebrick which is among the aluminosilicates group of refractories, the most commonly used refractories because of their cheapness, but because they are slightly acidic in nature; their use in basic conditions is avoided. The Maraban Rido firebrick can be used in moderate heat treatment operation such as lining of regenerative chambers, recuperative chambers, chimney, annealing furnaces.

5.2 Recommendations

The research results obtained has produced some important information on the characterization and suitability of Maraban Rido clay deposit as refractory materials and thus, the following recommendations are proposed for further investigation on the characterization of Maraban Rido clay.

- i. Maraban Rido clay should be further investigated to ascertain its refractoriness and refractoriness under load.
- ii. Maraban Rido clay should further be investigated by using ball clay with less iron impurities oxides or any firebrick bonding materials such as sodium silicates for proper adhesive bonding in order to ascertain its properties and application.

- iii. Maraban Rido clay should further be investigated by firing refractory brick made from the clay above 1500°C in order to ascertain its properties and find the suitability of these clays for refractory use.
- iv. It is recommended that further investigation on the micro structural analysis of these bricks be carried out, so as to ascertain the particles spacing and interfacial bonding of the clay.

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APPENDIX A

DATA OBTAINED FROM BATCHING

Mathematical Calculation of Batch for Brick Using Andreason Parameter Equation

Each of the six grain size used in this research was classified in grog fraction groups as indicated in section 3.4.1. These values were carefully used to calculate the weight percentages (wt. %) of grog fraction in each group, using Andreason Parameter Equation in the following sieve sizes:

- i. 2.36mm,
- ii. 1.18mm,
- iii. 0.600mm,
- iv. 0.300mm,
- v. 0.150mm, and
- vi. 0.075mm.

The Adreason Formula:

$$P = 100 \times \left(\frac{d}{D} \right)^n$$

Where: P = Weight proportion of fraction

D = Maximum size of grain in the distribution (2.36mm)

d = Average grain size of the fraction

n = Andreasons distribution parameter. (n = 0.2 – 0.9)

Therefore, the average sizes of fractions used for this research work were obtained as shown in Table A1.

Table A1: Average Size of Fractions Used in the Work

Grog Fraction	Sieve Size (mm)	Average Size of Fraction (mm)
P1	-2.36 + 1.18	$d1 = 3.54/2 = 1.77$
P2	-1.18 + 0.600	$d2 = 1.78/2 = 0.89$
P3	-0.600 + 0.300	$d3 = 0.90/2 = 0.45$
P4	-0.300 + 0.075	$d4 = 0.45/2 = 0.225$
P5	0.075	$d5 = 0.075/2 = 0.0375$

Therefore, Andreason parameter for P1 – P5, using 0.7 as the adopted value for the “n” is as follows:

$$P = 100 (d/D)^n$$

$$P1 = 100 (1.77/2.36)^{0.7} = 81.76$$

$$P2 = 100 (0.89/2.36)^{0.7} = 50.52$$

$$P3 = 100 (0.45/2.36)^{0.7} = 31.35$$

$$P4 = 100 (0.225/2.36)^{0.7} = 19.29$$

$$P5 = 100 (0.0375/2.36)^{0.7} = 5.51$$

The sum total of all proportions representing each of the grog fractions i.e. P1 + P2 + P3 + P4 + P5, is as presented in Table A2.

Table A2: Sum Total of Grog Fractions Proportions

Grog Fraction	Proportion
P1	81.71
P2	50.52
P3	31.35
P4	19.29
P5	5.51
Total	188.43

The percentages of grog fractions adopted for the batch using the above values as the reference point was evolved as follows:

$$P1 = (81.76/188.43) \times 100 = 43.39\%$$

$$P2 = (50.52/188.43) \times 100 = 26.81\%$$

$$P3 = (31.35/188.43) \times 100 = 16.64\%$$

$$P4 = (19.29/188.43) \times 100 = 10.24\%$$

$$P5 = (5.51/188.43) \times 100 = 2.92\%$$

The total batch aggregates by particle size classification are presented in the Table A3.

Table A3: Batch Aggregates Particle Classification

Grog Fraction	Proportion (%)
P1	43.39
P2	26.81
P3	16.64
P4	10.24
P5	2.92
Total	100

Calculation for Grog Fraction Weight Proportion of each Classification Based on Total Weight of 15.0kg Obtained from Maraban Rido Grog for the Batch in Brick Production.

$$P1 = \frac{43.39}{100} \times 15\text{kg} = 6.51\text{kg}$$

$$P2 = \frac{26.81}{100} \times 15\text{kg} = 4.02\text{kg}$$

$$P3 = \frac{16.64}{100} \times 15\text{kg} = 2.41\text{kg}$$

$$P4 = \frac{10.24}{100} \times 15\text{kg} = 1.54\text{kg}$$

$$P5 = \frac{2.92}{100} \times 15\text{kg} = 0.44\text{kg}$$

Table A4: Batch Grog Particle Size by Weight for Each Classification

Grog Fraction	Weight of Grog Particle (kg)	Particle Size Classification
P1	6.51	Coarse
P2	4.02	Medium
P3	2.41	Fine
P4	1.54	Fine
P5	0.44	Fine

Calculation for Bond Materials

Total Grog x 10% of the Bond Materials

$$\text{i.e. } 15\text{kg} \times \frac{10}{100} = 1.5\text{kg}$$

Calculation for Moisture Content

(Total weight of grog fraction + Weight of bond materials) x 15% of moisture content

$$\text{i.e. } (15\text{kg} + 1.5\text{kg}) \times \frac{15}{100} = 2.48\text{kg}$$

Conversion to (ml): $2.48 \times 1000 = 2480\text{ml}$

Table A5: Standard Sieve Designation Used and Classification

Grog Fraction	Sieve Size (mm)	Tyler Type (No.) (U.S.)	Class Adjustment
P1	2.36	8	Coarse
P2	1.18	16	Medium
P3	0.600	30	Fine
P4	0.300	50	Fine
P5	0.075	200	Fine

APPENDIX B

DATA OBTAINED FROM PHYSICAL TEST

Table B1: Liquid Limit of Maraban Rido Clay Sample

Test	1	2	3	4	5
Container number	C1	C2	C3	C4	C5
Number of blows, N	48	39	28	17	12
Wt. of container M (g)	8.7	9.1	8.7	8.8	8.7
Wt. of c. plus wet clay, Mw (g)	19	18.3	21.3	28.1	27
Wt. of c. plus dry clay, Md(g)	16.2	15.8	17.5	22.4	21.2
Wt. of moisture loss,(Mw-Md)	2.8	2.5	3.8	5.7	5.8
Wt. of dry clay=(Md-M)	7.5	6.7	8.8	13.6	12.5
Moisture/Water content,	37.3	37.3	43.2	41.9	46.4
Final liquid limit on the plot of graph					41.5

Table B2: Plastic Limit of Maraban Rido Clay Sample

Test	1	2	3
Container number	X	Y	Z
Wt. of container M (g)	9.1	9.0	8.7
Wt. of container plus wet clay, Mw (g)	12.3	11.7	12.4
Wt. of container plus dry clay, Md(g)	11.5	11.0	11.5
Wt. of moisture/Water loss,(Mw-Md)	0.8	0.7	0.9
Wt. of dry clay=(Md-M)	2.4	2.0	2.8
Moisture/Water content,	33.33	35.00	32.14
Average plastic limit			33.5

Table B3: Plasticity Index of Maraban Rido Clay Sample

Details	Contents of the Clay Sample %
Liquid Limit (LL)	41.5
Plastic Limit (PL)	33.5
Plasticity Index (PI)	8

APPENDIX C

DATA OBTAINED FROM LINEAR FIRING SHRINKAGE

Calculation of Linear Firing Shrinkage

Using Equation (7) where L is in cm, the percentage linear firing shrinkage was calculated are given below:

For Sample 1:

$$\text{Green Length} = 10$$

$$\text{Fired Length} = 9.29$$

$$\%L_{\text{FS}} = \frac{10 - 9.29}{10} \times 100 = 7.1\%$$

For Sample 2:

$$\text{Green Length} = 10$$

$$\text{Fired Length} = 9.29$$

$$\%L_{\text{FS}} = \frac{10 - 9.29}{10} \times 100 = 7.1\%$$

For Sample 3:

$$\text{Green Length} = 10$$

$$\text{Fired Length} = 9.29$$

$$\%L_{\text{FS}} = \frac{10 - 9.29}{10} \times 100 = 7.1\%$$

For Sample 4:

$$\text{Green Length} = 10$$

$$\text{Fired Length} = 9.29$$

$$\%L_{\text{FS}} = \frac{10 - 9.29}{10} \times 100 = 7.1\%$$

For Sample 5:

Green Length = 10

Fired Length = 9.29

$$\%L_{FS} = \frac{10 - 9.29}{10} \times 100 = 7.1\%$$

$$\text{Average} = \frac{7.1 + 7.1 + 7.1 + 7.1 + 7.1}{5} = 7.1\%$$

Table C1: Firing Shrinkage of the Bricks Samples

Test Bar No.	Initial Length (cm)	Final Length (cm)	Firing Shrinkage (%)
1	10	9.29	7.1
2	10	9.29	7.1
3	10	9.29	7.1
4	10	9.29	7.1
5	10	9.29	7.1
Average			7.1

APPENDIX D

DATA OBTAINED FROM APPARENT POROSITY

Calculation of Apparent Porosity

The apparent porosity was calculated using Equation (10) is given below:

For Sample 1:

$$\text{Dried weight } D \text{ (g)} = 8.66,$$

$$\text{Wet weight } W \text{ (g)} = 10.57$$

$$\text{Suspended weight } S \text{ (g)} = 5.12$$

$$\%Pa = \frac{10.57 - 8.66}{10.57 - 5.12} = 35.05\%$$

For Sample 2:

$$\text{Dried weight } D \text{ (g)} = 10.72$$

$$\text{Wet weight } W \text{ (g)} = 12.85$$

$$\text{Suspended weight } S \text{ (g)} = 6.01$$

$$\%Pa = \frac{12.85 - 10.72}{12.85 - 6.01} = 31.14\%$$

For Sample 3:

$$\text{Dried weight } D \text{ (g)} = 8.66,$$

$$\text{Wet weight } W \text{ (g)} = 10.57$$

$$\text{Suspended weight } S \text{ (g)} = 5.12$$

$$\%Pa = \frac{10.57 - 8.66}{10.57 - 5.12} = 35.05\%$$

For Sample 4:

$$\text{Dried weight } D \text{ (g)} = 10.72$$

$$\text{Wet weight } W \text{ (g)} = 12.85$$

$$\text{Suspended weight } S \text{ (g)} = 6.01$$

$$\%Pa = \frac{12.85 - 10.72}{12.85 - 6.01} = 31.14\%$$

For Sample 5:

Dried weight D (g) = 10.72

Wet weight W (g) = 12.85

Suspended weight S (g) = 6.01

$$\%Pa = \frac{12.85 - 10.72}{12.85 - 6.01} = 31.14\%$$

$$\text{Average} = \frac{35.05 + 31.14 + 35.05 + 31.14 + 31.14}{5} = 33\%$$

Table D1: Apparent Porosity of Brick Samples

Specimen No.	Weight of Specimen in gram (g)			Apparent Porosity (%)
	Dried (D)	Wet (W)	Suspended (S)	
1	8.66	10.57	5.12	35.05
2	10.72	12.85	6.01	31.14
3	8.66	10.57	5.12	35.05
4	10.72	12.85	6.01	31.14
5	10.72	12.85	6.01	31.14
Average				33.00

APPENDIX E

DATA OBTAINED FROM BULK DENSITY

Calculation of Bulk Density

The bulk density was calculated using Equation (8) is given below:

For Sample 1:

$$\text{Dried weight } W_1 \text{ (g)} = 7.37$$

$$\text{Weight deep in mercury Hg } W_2 \text{ (g)} = 59.43$$

$$\text{Density of mercury } d \text{ at } 26^\circ\text{C} = 13.5312$$

$$\text{B.D} = \frac{7.37 \times 13.5312}{59.43} = 1.68$$

For Sample 2:

$$\text{Dried weight } W_1 \text{ (g)} = 8.59$$

$$\text{Weight deep in mercury Hg } W_2 \text{ (g)} = 64.85$$

$$\text{Density of mercury } d \text{ at } 26^\circ\text{C} = 13.5312$$

$$\text{B.D} = \frac{8.59 \times 13.5312}{64.85} = 1.79$$

For Sample 3:

$$\text{Dried weight } W_1 \text{ (g)} = 7.37$$

$$\text{Weight deep in mercury Hg } W_2 \text{ (g)} = 59.43$$

$$\text{Density of mercury } d \text{ at } 26^\circ\text{C} = 13.5312$$

$$\text{B.D} = \frac{7.37 \times 13.5312}{59.43} = 1.68$$

For Sample 4:

$$\text{Dried weight } W_1 \text{ (g)} = 8.59$$

$$\text{Weight deep in mercury Hg } W_2 \text{ (g)} = 64.85$$

$$\text{Density of mercury } d \text{ at } 26^\circ\text{C} = 13.5312$$

$$\text{B.D} = \frac{8.59 \times 13.5312}{64.85} = 1.79$$

For Sample 5:

Dried weight W1 (g) = 8.59

Weight deep in mercury Hg W2 (g) = 64.85

Density of mercury d at 26°C = 13.5312

$$\text{B.D} = \frac{8.59 \times 13.5312}{64.85} = 1.79$$

$$\text{Average B.D} = \frac{1.68 + 1.79 + 1.68 + 1.79 + 1.79}{5} = 1.75$$

Table E1: Bulk Density of Brick Samples

Specimen No.	Dry Weight (W ₁) (g)	Weight Hg (W ₂) (g)	Bulk Density (g/cm ³)
1	7.37	59.43	1.68
2	8.59	64.85	1.79
3	7.37	59.43	1.68
4	8.59	64.85	1.79
5	8.59	64.85	1.79
Average			1.75

APPENDIX F

DATA OBTAINED FROM COLD CRUSHING STRENGTH

Calculation of Cold Crushing Strength (C.C.S)

The cold crushing strength was calculated using Equation (11) is given below:

For Sample 1:

$$\text{Length L (cm)} = 2.3$$

$$\text{Breath B (cm)} = 2.15$$

$$\text{Area A (cm}^2\text{)} = 4.95$$

$$\text{Force F (KN)} = 14.5$$

$$\text{Mass M (kg)} = 1450$$

$$\text{C.C.S} = \frac{1450}{4.95} = 292.93\text{kg/cm}^2$$

For Sample 2:

$$\text{Length L (cm)} = 2.2$$

$$\text{Breath B (cm)} = 2.15$$

$$\text{Area A (cm}^2\text{)} = 4.73$$

$$\text{Force F (KN)} = 14.0$$

$$\text{Mass M (kg)} = 1400$$

$$\text{C.C.S} = \frac{1400}{4.73} = 295.99\text{kg/cm}^2$$

For Sample 3:

$$\text{Length L (cm)} = 2.3$$

$$\text{Breath B (cm)} = 2.15$$

$$\text{Area A (cm}^2\text{)} = 4.95$$

$$\text{Force F (KN)} = 14.5$$

$$\text{Mass M (kg)} = 1450$$

$$\text{C.C.S} = \frac{1450}{4.95} = 292.93\text{kg/cm}^2$$

For Sample 4:

$$\text{Length L (cm)} = 2.2$$

$$\text{Breath B (cm)} = 2.15$$

$$\text{Area A (cm}^2\text{)} = 4.73$$

$$\text{Force F (KN)} = 14.0$$

$$\text{Mass M (kg)} = 1400$$

$$\text{C.C.S} = \frac{1400}{4.73} = 295.99\text{kg/cm}^2$$

For Sample 5:

$$\text{Length L (cm)} = 2.2$$

$$\text{Breath B (cm)} = 2.15$$

$$\text{Area A (cm}^2\text{)} = 4.73$$

$$\text{Force F (KN)} = 14.0$$

$$\text{Mass M (kg)} = 1400$$

$$\text{C.C.S} = \frac{1400}{4.73} = 295.99\text{kg/cm}^2$$

$$\text{Average C.C.S} = \frac{292.93 + 295.99 + 292.93 + 295.99 + 295.99}{5} = 294.77\text{kg/cm}^2$$

Table F1: Cold Crushing Strength of Brick Samples

Specimen	Length (cm)	Breadth (cm)	Area (cm ²)	Force (KN)	Mass (kg)	C.C.S (kg/cm ²)
1	2.30	2.15	4.95	14.50	1450	292.93
2	2.20	2.15	4.73	14.00	1400	295.99
3	2.30	2.15	4.95	14.50	1450	292.93
4	2.20	2.15	4.73	14.00	1400	295.99
5	2.20	2.15	4.73	14.00	1400	295.99
Average						294.77