A STUDY ON THERMAL CONDUCTIVITY OF SIX UNEXPLORED NIGERIAN CLAYS FOR POSSIBLE REFRACTORY AND INSULATING MATERIALS

AMKPA JOB AJALA

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

A STUDY ON THERMAL CONDUCTIVITY OF SIX UNEXPLORED NIGERIAN CLAYS FOR POSSIBLE REFRACTORY AND INSULATING MATERIALS

AMKPA JOB AJALA

A thesis submitted in fulfilment of the requirement for the award of the
Doctor of Philosophy

Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

July, 2017

DEDICATION

This thesis is dedicated to my beloved family; in loving memory of my late father late Engr. Festus Abara Amkpa and my late mother Mama Rakiya Rabecca Amkpa for their prayers. The thesis is also dedicated to my dearly wife Blessing Jummai Amkpa and my children Victor Akamsoko Amkpa, Victoria Rakiya Amkpa and Vincent Ayetum Amkpa for their prayers, patience, sacrifices and most of all their understanding throughout this academic journey.

ACKNOWLEDGEMENT

First, I hereby acknowledge my profound gratitude to Almighty God for giving me the health, mental and physical strength to undertake this research work.

Second, my special thanks go to my supervisor Dr. Nur Azam Badarulzaman for his professional guidance, constructive criticisms, observation, suggestions, thoughtful comments, advice and for making this thesis work eventful, invaluable learning experience and most of all support, encouragement, patience and understanding throughout this academic journey, which had resulted into success after lots of sacrifices.

Third, I would like to thank and appreciate all the educators, the dean of Faculty of Mechanical and Manufacturing Engineering, Head of Department of materials and design engineering, PM. Dr. Hamimah, PM. Dr. Hassan Zuhudi, PM. Dr. Saidin, the dean center for graduate studies (CGS), Director Office for Research, Innovation, Commercialization and Consultancy Management (ORICC), director International Office and the entire academic staff of Faculty of Mechanical and Manufacturing Engineering may Allah bless you all. Dr. Suzi Salwah Bint. Jikan, Faculty of Science, Technology and Human Development.

Fourth, I appreciate the technical assistance accorded me during my laboratory exercises by Mr. Fazlan and Mr. Sharul of the Polymer and ceramic Lab., Mr. Tamizi and Mr. Anuaris of material Lab., all of Faculty of Mechanical and manufacturing Engineering. Also, I thank Mr. Yemi Olowolafe of the Nigeria Metallurgical Development Centre (NMDC) Jos, Pleteau State, Nigeria.

Fifth, I honestly do recognize and appreciated the research units of the Universiti Tun Hussein Onn Malaysia for supporting this research under Postgraduate Incentive Grant.

Finally, I also wish to thank my own senior brothers Assc. Prof. Samuel Amkpa, Prof. Awam David Amkpa, Dr. Mrs. Blessing Jummai Amkpa, Late Prof.

Ndanumsa Egila & family, Prof. Adamu Baikie, Late pastor Yusuf Jibo, Alh. Karimu Musa, the registrar FPI, Matthew Ojo the rector FPI, Bishop Emmanuel Egbunu, Baba Eri, Abraham Amkpa, Mama Angela Akpan (mama Calaba), Sylvanus Akpama, Zakariya Egbunu, Aaron Aye, Tijjani Abdullahi, Friday Omagu, Mohammed Umar Bello, Sunday Olajide, Kennedy Dapel, Yohanna Garba Bundot, Hajiya Asebe Musa, Onalo Ugbede, Engr Idris Ali, Felicia Bala, Abegil Ali, St James Anglican church, Batu Pahat, Johor, Malaysia, and all my other dear friends in both Malaysia and Nigeria for their prayers, encouragement and discouragement which have created the positive desire to finish this research within the time table schedule. There are many more personalities who deserve my appreciation for supporting me to reach this stage of my life.

.

ABSTRACT

Refractories are mineral and chemical based materials, with high heat resistance properties. Refractory manufacturing typically uses clay as the main raw material. The study aims to investigate six unexplored Nigerian clay based on the suitability of their chemical, physical, mechanical and thermal properties as refractories. Six clay deposit locations in Nigeria were selected namely Kpata, Riyom, Gombe, Aloji, Barkin-lade and Quan'pan. The samples were obtained through a two meters depth excavation method. Experimental specimens were produced from these samples through dry-pressing methods followed by firing at 900-1200°C. All specimens were tested to identify the chemical, physical, mechanical and thermal properties of ASTM standards. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis show that all specimens contain alumino-silicates as the dominant composition, with 10% loss on ignition. Through the Archimedes test, the percentage of porosity is found in the range of 20-30%, with bulk densities about 1.7-2.3g/cm^3. Cold crushing strength (CCS) and modulus of rupture (MOR) give readings of 15-59 MPa and 6.2-9MPa respectively. Meanwhile, the analysis on thermal properties found specimens having thermal shock resistance on a 20-30 scale cycle, pyrometric cone equivalence (PCE) at a temperature range of 1500-1700°C and thermal conductivity at a range of 0.01-0.9W/m.K. The overall experiment results are within the range of ASTM standards and this illustrates that all of the clay is potentially a refractory material.

ABSTRAK

Refraktori adalah bahan-bahan berasaskan mineral dan kimia, dengan sifat kerintangan haba yang amat tinggi. Pembuatan refraktori lazimnya menggunakan tanah liat sebagai bahan mentah utama. Kajian ini bertujuan menyelidik enam tanah liat Nigeria yang belum diterokai berdasarkan kesesuaian sifat kimia, fizikal, mekanik dan terma masing-masing sebagai refraktori. Enam lokasi deposit tanah liat di Nigeria telah dipilih iaitu Kpata, Riyom, Gombe, Aloji, Barkin-lade and Quan’pan. Sampel-sampel tersebut diperolehi menerusi kaedah penggalian sedalam dua meter. Spesimen ujikaji telah dihasilkan daripada sampel-sampel tersebut menerusi kaedah penekanan kering dan disusuli dengan pembakaran pada suhu 900-1200°C. Kesemua sampel ini diuji bagi mengenalpasti ciri-ciri kimia, fizikal, mekanik dan terma berasaskan piawaian ASTM. Analisis pendafluor sinar-X (XRF) dan pembelauan sinar-X (XRD) menunjukkan bahawa kesemua spesimen mengandungi alumino-silikat sebagai komposisi dominan, dengan 10% kehilangan pada nyalaan. Menerusi ujian Archimedes, peratus keliangan pula didapati dalam julat 20-30%, dengan ketumpatan pukal sekitar 1.7-2.3g/cm^3. Ujian kekuatan hancur sejuk (CCS) dan modulus pecah (MOR) masing-masing memberikan bacaan 15-59 MPa dan 6.2-9MPa. Sementara itu, analisis ke atas sifat terma mendapati spesimen mempunyai rintangan kejutan terma pada skala 20-30 kitaran, kesetaraan kon pirometrik (PCE) pada julat suhu 1500-1700°C dan kekonduksian terma pada julat 0.01-0.9W/m.K. Keseluruhan keputusan ujikaji adalah di dalam julat piawaian ASTM dan ini menggambarkan bahawa semua tanah liat tersebut berpotensi sebagai bahan refraktori.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

A (m^2)	Cross section area of heat flow in a material
AP	Apparent porosity
ASTM	American Society for Testing and Materials
AU	Gold
Avg	Average
B	Breadth
BD	Bulk density
CCS	Cold crushing strength
CTE	Coefficient of Thermal Expansion
D (m)	Diameter
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
E	Total energy
EDX	Energy Dispersive Spectroscopy
F	Force (N)
J	Joules
j/g°C	Specific heat
kg	Kilogram
L	Length
m	Mass of the of the clay brick
MOR	Modulus of rupture
MPa	Mega Pascal
PCE	Plyometric Cone Equivalent
PFS	Percentage firing shrinkage
Q/A	Heat flux
q	Heat flow

S	Soaked weight
SEM	Scanning Electron Microscopy
SG	Specific gravity
STA	Simultaneous Thermal Apparatus
T	Temperature (°C)
TES	Thermal energy storage
TGA	Thermogravimetric Analysis
TPS	Transient plane source
W	Width (mm)
W/mk	Thermal conductivity
PWA	Percentage Water absorption
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
$\Delta T/\Delta L$	Thermal gradient
μm	Micrometer
ΔL	Change in Length
ΔT	Change in Temperature
ρ	Density, g/cm^3

CHAPTER 1

INTRODUCTION

1.1 Background

Heat recovery systems in the early human endeavors used water as a storage medium (Abhat *et al*., 1978). Therefore, solar energy source and household demands for it in general, did not match each other at any given time. This trend, have necessitated the use of thermal energy storage (TES) systems to resolve the mismatch so as to provide energy requirements (Abhat, 1983). Obviously, the potentials are huge for the application of thermal energy storage systems for our homes and industries. TES systems can facilitate an important role, as they provide great potential for facilitating energy savings and reduce environmental impact (Ibrahim and Rosen, 2002). These systems of thermal energy storage were not used as it should and was due to many reasons. Most of these systems are not yet economically competitive with fossil fuels and their long term reliability is not yet ascertained.

It is very necessary to search for an alternative means by the use of thermal insulators around such storage systems in order to maintain high temperatures inside by preventing heat losses to the surroundings (Turner and Malloy, 1988). There are different insulating materials which come in various forms like loose fill rigid boards, pipe and insulating form. Proper and adequate selection of the insulating materials to be used is based on the thermal properties which include the thermal conductivity, specific heat capacity and thermal diffusivity.

The thermal insulation is provided by embedding insulation materials at least on the roof top areas of the furnace and vertical walls of the storage system (Novo *et al.*, 2010). When thermal insulation of the heat storage system is poorly done, it leads to high heat losses (Bauer *et al.*, 2010). Currently fibre glass and rock wool are used as thermal insulation materials for the storage systems. Basically it is due to their low thermal conductivity values leading to good thermal insulation. These thermal insulators however contained siliceous and hazardous dust whose inhalation will increases the danger for the development of lung disease Gilham *et al*. (2016) and are expensive and also dangerous to human health as a result of exposure during handling especially those in fibrous form (Bardelli *et al.,* 2017).

Previous studies have shown that people who manufacture fibre glass have sixty percent more fibre glass material in their lungs than those who had not been exposed (Merler *et al.,* 2017). There is the need for finding alternative thermal insulating materials which are processed from clay which are cheap, reliable and do not pose a risk to human health, for example, kaolin fabricated into aluminium silicates (Al-Malah and Abu-Jdayil, 2007).

Thermal insulators are materials or combination of materials which are used in order to retard the flow of heat energy. The effective installation of thermal insulation can significantly reduce the thermal energy lost from thermal heat storage system surfaces. The energy lost for an insulating material depends largely on the thermal properties and thicknesses of the insulation. The choice of the type and form of the proper insulation materials depends on where the insulation is to be applied as well as the desired material's physical and thermal properties (Al-Homoud, 2005).

The basic requirement for thermal insulation is to provide a significant resistance path to the flow of heat through the insulation material. In accomplishing this, the insulating material must reduce the rate of heat transfer by conduction. In the experimental determination of the thermal conductivity of solids, a number of different methods of measurement are required for the different ranges of temperature and for various classes of materials having different ranges of thermal conductivity values (Aksoz *et al.*, 2012).

The knowledge and concept of heat transfer in insulating material or porous media has increasingly found relevance in science and engineering (Akinyemi *et al*., 2011). Similarly, Sauer *et al.* (2003), have expressed that thermal properties of porous insulating material as of great importance to environmental sciences, agriculture and engineering, especially in relation to temperature and energy transfer which is better understood in the study of thermal conductivity of materials, its measurement and predicting how much heat can be stored is a key to its utilization by the industries.

The increasing demand for high refractory materials to work on other at high temperatures coupled with the over reliance on the imported refractory has presented a rethink for the technological and industrial development of Nigeria. It is either Nigeria discontinue importation of these refractory bricks and develops its own technology or become import dependence with retrogressive economic implication. The raw materials for the manufacture of fireclay refractory largely contained alumina, silica and impurities. These raw materials deposits are found in very large commercial quantities all over the six geopolitical zones of Nigeria. The clay specimen used in this research were collected from two geopolitical zones that comprises of three states of Gombe, Plateau and Kogi as presented in Figure 3.2 Nigerian Map indicating the clay samples deposit sites.

At the moment, the country depends largely on foreign insulating and refractory bricks even though, reviewed literatures have shown that these raw materials are dominate in its location and ground. Literatures have indicated some scanty works on Nigerian clays in an attempt to understand their properties, but it was not sufficient enough. The investigation of differient clays without their knowledge of thermal characteristics leave so much to be desired. The clay raw specimen when properly studied or investigated, the results can be utilized in manufacturing refractories, other engineering products and by so doing encourage local industrial development in Nigeria (Obadinma, 2003; Yakubu and Abdulrahim 2014).

Table 1.1: Clay deposits and District

Description	Deposit	District	Local Geology	Reference
A	Kpata	Bassa local government area, Kogi East (Kogi State)	Tropical in nature with dry and we seasons. Primary deposits of kaolin are generally formed by the alteration of alumino- silicate rich parent rock such as granite by weathering. Rocks which comprises of the various grouping of coarse grained granites	Odigi, (2000); Imasuen *et al.* (2009), Imasuen *et al.* (2013)
B	Riyom	Riyom local government area, Jos south (Plateau State)	The Jos Plateau state has the highest mineral deposits in Nigeria which are in large quantity and among which are tin, coal, dolomite, kaolin, feldspar, calcium, iron ore, bauxite, tantalite and barite. The Riyom town is situated in the tropical zone.	Hassan *et al.* (2015)
C	Gombe	Gombe local government area, Gombe (Gombe State)	Gombe is blessed with minerals in commercial quantity which includes uranium, gemstone, clay, feldspar, gypsum, kaolin, mica and limestone. It belongs to the tropical zone with wet and dry seasons.	Mbaya *et al.*(2012)
D	Aloji	Ofu local government area Kogi East (Kogi State)	The soil within the clay deposit site is generally loamy having composed of silt, sand and clay. Kaolin deposits are generally located in this site as either primary (residual) or secondary (sedimentary). The mode of formation of the kaolin may have considerable influence on the mineralogy. Tropical	Odigi, (2000); Imasuen *et al.* (2009), Imasuen *et al.* (2013)
E	Barkin-ladi	Barkin-ladi local government area Plateau South (Plateau State)	There are also sizeable pockets of loamy soil of volcanic origin in the high Plateau. Currently in Barikin-ladi, minerals that are mined and processed in commercial quantity are the kaolin, tin, coal, dolomite, tantalite, clay, quartz and calcium. It temperate climate.	Hassan *et al.* (2015)
F	Quan'Pan	Plateau South (Plateau State)	It has a temperate weather with temperature between 18-22 °C. Dolomite, coal, quartz, kaolin, clay and tin is still mined in large commercial quantity and processed on the plateau.	Hassan *et al.* (2015)

According to Manukaji (2013) and Abuh *et al*. (2014) that there is no state in Nigeria without a clay deposit and not many of them have been thoroughly evaluated thermally and utilized for industrial purposes. The thermal conductivity measurement and other thermal properties analysis of refractory materials from Nigeria raw clay will promote but also enhance further studies of the clay abundance and help not to relay on importation of refractories Atanda *et al*. (2013) and this will certainly bring the much needed local industrial development.

Thermal conductivity is simply the measure of a material to conduct heat through its mass. Different insulating materials and other type of material have specific thermal conductivity values that can be used to measure their insulating effectiveness. Li *et al.* (2012) defined thermal conductivity as the amount of heat or energy (K) that can be conducted in unit time through unit area of unit thickness of material, when there is a unit temperature difference.

As indicated by Tiwari *et al.* (2013), there has been an increased awareness of the importance of accurately calculating the thermal conductivity of refractory and heat-insulating materials for furnace design, these values fluctuate considerably depending on the method and the measurement conditions. In their submission, Katsube *et al.* (2006), said that recent urgent demands for reduced energy consumption and efficient energy usage require high performance thermal insulation materials. Such demands have been made in the field of refractory materials. Conventional insulating brick and refractory bricks have good heat-resistance performance and can be produced at low cost (Shimizu *et al.*, 2013) relatively with poor thermal insulating performance.

Schulle and Schlegel (1991) opined that research towards a better understanding of the physical properties of heterogeneous solids has both scientific and technological importance. Similarly, Kingery (1960) discussed that physical properties that determine much of the utility of ceramic (refractories) materials are those properties directly related to temperature changes. Litovsky *et al.* (1996) posited that particular class of these solids is constituted by materials containing a large volume fraction of porosity which are used in situations requiring very good thermal insulation.

Grandjean *et al.* (2005), expressed that prediction of their thermal properties and especially the effective conductivity by analytical or computer calculation is therefore of strong interest. A specific investigation by Aksoz *et al.* (2012) indicated that thermal conductivity using the transient method is calculated from the thermal diffusivity with a further knowledge of the density and specific heat of the materials. This research seeks to investigate the methods of measuring thermal conductivity using the steady state method of the selected clay specimen from Nigeria and their thermal properties in an attempt to encourage its uses in the engineering practices in Nigeria. The properties with which the research was mainly concerned about are the chemical composition; physical (porosity, bulk density, firing shrinkage, water absorption, and specific gravity of the refractory material), mechanical (cold crushing strength and modulus of rupture), thermal (thermal conductivity, heat capacity, coefficient of thermal expansion at room temperature of all the clay deposits specimen. This was further collaborated by Kingery (1960), that a theory and practice to arrive at the heat capacity and thermal conductivity to determine the temperature changes in a refractory/insulating material should be a welcome idea.

1.2 Problem statement

Recent urgent demands for reduced energy consumption and efficient energy usage require high performance thermal insulation materials (Katsube *et al.*, 2006). Such demands have been made in the field of insulating materials and refractories. At the moment it is often not enough getting approximate data from textbooks, but thermal measurements of materials are necessary and the rapid technology development for decades have generated an increasing effort to expand our knowledge of thermal properties (Papadopoulos, 2005). The uses of refractory and insulating materials that can withstand high temperature without deformation and for the prevention of heat losses (escape) respectively, in exchangers, boilers, reactors, ovens, and furnaces in industries where there application are required like in Nigeria and other parts of the world is the main concern. The results are analyzed using scientific methods. The findings are presented in an overview of the thermal properties and their performance characteristics. The main features of measurement and analysis of thermal conductivity of the clay and its applications in thermal energy storage should be studied to match the requirement of the industries because of its low thermal conductivity.

The usage of refractory bricks as well as thermal insulating material requires prior knowledge of all their thermal properties (Laaroussi *et al.*, 2013). As indicated by Xaman *et al*. (2009) the common methods used for measuring and determining the thermal conductivity of insulating materials are based on steady state one-dimensional measurements. Cengel and Ghajar. (2015) stated that there are two basic types of steady state measurements: the absolute and the comparison. The absolute method (accurate result) determines the thermal conductivity through a specimen directly by the electrical powered input measurement instrument. The comparison method uses a reference material of known thermal conductivity or heat flow meter. This modern thermal properties measurement equipment are not readily available in Nigeria and where they are available, it is absolete.

The in-depth assessment and evaluation of thermal properties of Nigerian clays for the production of insulating materials and refractories will enhance further studies of the abundance clay deposits and not depending on importation of insulating materials (Chukwudi, 2008; Aremu *et al*., 2013). Insulating refractories are very useful and play a very crucial role in the industrial development of any nation.

Virtually all the refractories requirements in all the pyro-metallurgical industries in Nigeria are imported, while the raw material for the production of these refractories materials are available in large quantity in Nigeria (Aderibigbe, 1989; Atanda *et al*., 2012). In Nigeria, kaolin clay deposits are available but they remained under-utilized (Omowumi, 2001; Manukaji, 2013).

Almost all Nigerian clays previously studied, showed inadequacy in terms of application of thermal properties measurement and methods. There was an evidence of some findings carried out but mainly on their chemical and physical characterization. The in-depth investigation of their thermal characteristics and critical areas of material clay behaviour like reaction and interaction with heat were not ascertained. Hence, the Nigerian clay thermal properties were not ascertained especially in the measurement of thermal conductivity (TC), energy absorption through use of differential scanning calorimeter (DSC), thermal expansion using coefficient of thermal expansion (CTE), weight loss using thermogravimetry analysis (TGA) and reaction by use of differential thermal analysis (DTA) methods.

The submission of Aremu *et al*. (2013) that clay is abundant in Nigeria and the deposits are in commercial quantities can be upheld that for a prospective industrial nation and that the clay deposit includes magnesite, dolomite and Kaolin. As expressed by Yakubu and Abdulrahim (2014); Hassan (2000), there is large reserves of silica, fireclay and kaolin clays in Nigeria that can be used for refractory materials if adequate investigation on the abundant natural resources were carried out. Similarly, Atanda *et al*. (2012) expressed that there are vast reserves of untapped clay mineral materials in Nigeria. The indication by Nigerian raw material research development council RMRDC (2010) emphasized that there were considerable data on Nigeria clays showing the deposits and locations in all the regions of the country for industrial and economic sustainability.

In view of these re-echoing of the clay availability, inadequacies in terms of any strong research group to undertake this researchable area, coupled with Nigerian's high dependance on imported refractory products, the enormous cost of importing refractories annually according to Hassan *et al*. (2014) and Yakubu and Abdulrahim (2014) was to the tune of $2.9 billion USA dollars, the under-utilized abundance of clay (refractories raw materials) deposits can be used for production of refractory. All these have necessitated, motivated and justified this study.

These six clay specimen were chosen because of their geographical locations which means their closeness to the prospective end users; ceramic companies, metallurgical industry and largely, the specimen were unexplored clay deposits in Nigeria specifically for refractory application.

1.3 Research objectives

The aim of this research is to investigate, evaluate and analyze the physical, mechanical and thermal properties of the unexplored Nigerian clays for their uses as refractory and insulating materials. To achieve this, these are the objectives:

i. To determine the chemical composition of all clay deposits specimen for their suitability for production of insulating and refractory material.
ii. To determine the best physical properties of the clay specimen through apparent porosity, bulk density, firing shrinkage, water absorption at firing temperatures of 900°C, 1000°C, 1100°C and 1200°C.

iii. To evaluate the best mechanical strength properties of the specimens at varied firing temperatures for their suitability as thermal insulator and refractory fireclay bricks.
iv. To determine the thermal properties of the clay specimen.
v. To propose the potential application for the clay specimen as refractory or thermal insulators.

1.4 Research scope

The scope of the study is in the following areas:

i. Removal of top soil and digging 2 meters beneath the earth surface using the digger and were collected into plastic containers.
ii. Crushing and grinding of clay deposits carried out using the ball-mill and mono-mill respectively.
iii. Performed sieve shaking process for the clay deposits ASTM E11-500 (2015) using sieve sizes of 70, 63, 50 (μm) and a pan. All the clay that passed sieve 50 μm used for the entire tests procedure in the study.
iv. Particle sizes analysis of the clay deposits performed according to Analysette 22 techniques.
v. Performed the chemical composition (XRF) test using the of all clay deposits and ascertain their suitability for production of insulating and refractory materials.
vi. Firing of all specimens was done at varied firing temperatures of 900°C, 1000°C, 1100°C and 1200°C at the heating rate of 2.5°C/min.
vii. Physical properties of firing shrinkage, water absorption, apparent porosity, bulk density of all fired specimens according to ASTM C20-00.
viii. Preparation and production of test specimens according to ASTM standards.
ix. Evaluate the mechanical properties of the fired specimen through cold crushing strength (CCS) and modulus of rupture (MOR) according to ASTM C133-97.

x. The unfired raw material specimen and fired specimen for phase and phase changes respectively were analyzed and characterized.

xi. EDX test carried out using SEM method for surface morphology and characterized.

xii. The steady state technique for thermal conductivity measurement at room temperature was performed using the hot guided plate apparatus technique according to ASTM 203-93.

xiii. Investigation and analysis of thermal properties of all clay deposits was conducted according to engineering standards such as:

   a. Performed refractoriness test for the specimens using PCE techniques to ascertain their fusion temperatures and their suitability for refractory application and insulating materials.
   b. Evaluated the thermal shock resistance of the specimen and the effects of sudden changes in temperature during service.
   c. Measured the thermal conductivity of the clay specimen, analyzed the specimen and established their suitability for production of refractory fireclay bricks.
   d. Differential scanning calorimeter (DSC) for energy absorption.
   e. Evaluate the clay specimen specific heat capacity (C_P) that will rise it temperature.
   f. Thermogravimetry analysis (TGA) to study the weight loss.
   g. Differential thermal analysis (DTA) for exothermic and endothermic reactions in the clay specimen.
   h. Investigate and evaluate the thermal expansion (CTE) rate against temperature of the clay specimen.

1.5 Summary

This chapter presented the background information. It expressed the problem statement that motivated the study. Despite the abundance of the raw materials in Nigeria for refractory manufacture, Nigeria still imports all her refractory from Germany, China and Great Britain. The research aim was to investigate and ascertained the suitability of the six selected unexplored Nigerian clays for production of refractory. The objectives were achieved through the performance of these experimental procedures and tests for the chemical, physical, mechanical and thermal properties of the specimens. The scopes were limited to the performance of the various tests as stated in the objectives of the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discussed the literature as relating to theories of thermal conductivity of refractories; standard terminology relating to refractories, definition of clays, types and their uses, physical properties of fireclay bricks, the standard values for apparent porosity, water absorption, specific gravity, firing shrinkage, and bulk density, mechanical properties of fireclay bricks using cold crushing strength (CCS), modulus of rupture (MOR) methods for refractory and the standard values; thermal properties of refractory fireclay bricks using thermal shock resistance, refractoriness (PCE), thermal conductivity (K), energy absorption using DSC technique, specific heat capacity (C_P), coefficient of thermal expansion (CTE), thermogravimetry (TGA), differential thermal analysis (DTA) and clay deposits characterization through using SEM for morphology, the use of EDX study the dominate elements and finger prints or phase changes using XRD techniques.

2.2 Thermal transport and methods

The thermal transport and methods of thermal conductivity measurement for solid materials are key issues to achieve optimum performance for a particular thermal application These instruments are the special types of guarded hot-plate apparatus, guarded heat-flow meter, transient hot-wire and hot-plane instruments as well as laser flash devices (Hammerschmidt *et al*., 2015; Lype *et al*., 2016). Zhang *et al.* (2010) that thermal conductivity is the key property of film specimen, such as proton exchange membrane, gas diffusion and refractories. The steady state method and transient method are developed to measure the thermal conductivity of powder and other substances but may differ greatly from bulk specimen because of the phonon scattering at the surface and different manufacturing process (Zhang *et al.,* 2014). As outlined by Hammerschmidt *et al.* (2015) that over the years a number of measurement techniques have been developed for this purpose and collaborated by Cengel and Ghajar (2012) submitted that the earliest group of measurement techniques is the steady state techniques.

The technique is based on establishing a temperature gradient over a known thickness of a specimen and controlling the heat flux from one side to the other (Xaman *et al.,* 2009). The Steady-state techniques are primarily suitable for analyzing materials with low or average thermal conductivity at moderate temperature (Cengel and Ghajar (2012). The transient techniques measure temperature-time response of the specimen when a signal is sent out to create heat in the body. These methods can be used for measuring thermal conductivity for broader range of temperatures and thermal properties (Kubicar, 1990). As the temperature decreases the situation worsen since the thermal conductivity of most materials decreases rapidly. A low thermal conductivity is essential for materials used as thermal insulators (Rajput, 2010).

2.3 Background theory

In heat transfer, we are primarily interested in heat, which is the form of energy that can be transferred from one system to another as a result of temperature difference. According to Cengel (2012) heat transfer is the science that deals with the determination of the rates of energy transfer in a substance or body. One of the most fundamental laws of nature is the conservation of energy principle. It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant. That is, energy cannot be created or destroyed. The conservation of energy principle also forms the backbone of all the engineering fields. A person who has a greater energy input (food) than energy output (exercise) will gain weight (store energy in the form of fat) and a person who has a smaller energy input than output will lose weight. The change in the energy content of a body or any other system is equal to the difference between the energy input and the energy output and the energy balanced. Askeland *et al.* (2011) expressed that the energy gap in insulating ceramic materials is too large for many electrons to be excited into the conduction band except at very high temperatures.

Thus, the theory is that the transfer of heat in ceramics occurs primarily by lattice vibrations (phonons). Since the electronic contribution is absent, the thermal conductivity of most ceramics is much lower than that of metals. The main reason why the experimentally observed conductivity of ceramics is low, however, is the level of porosity. Porosity increases scattering. The best insulating brick, for example, contains a large porosity fraction. Effective firing reduces porosity (and therefore increases thermal conductivity). Consequently, the transfer of heat in ceramics occurs primarily by lattice vibrations (phonons). Materials with a close-packed structure and high modulus of elasticity produce high energy phonons that encourage high thermal conductivities.

Askeland *et al.* (2011) agreed that the absence of electrons contribution in heat transfer in refractory material make it suitable for use as energy storage material. These authors also emphasized that glasses have low thermal conductivity. The amorphous loosely packed structure minimizes the points at which silica chains contact one another, making it more difficult for the phonons to be transferred. However, the thermal conductivity increases as the temperature increases; higher temperatures produce more energy phonons and more rapid transfer of heat. The uses of different coatings on glass to make buildings and cars more energy efficient are all engineering achievement. Some ceramics have thermal conductivities approaching that of metals. The fundamental mechanisms of thermal conduction are lattice waves (phonons) and the emission and absorption of radiant energy (photons) within the bulk of the material. These processes and their temperature dependence are examined and the expected thermal conductivity for insulating and refractory materials is approximated over the desired temperature range. Methods for determining the thermal conductivity of similar materials at elevated temperatures are evaluated to determine the most suitable for measuring the thermal conductivity of materials (Askeland *et al.*, 2016).

2.4 Phonon contribution to thermal conductivity

Phonon contribution is the quantized lattice waves that are indication of the presence of Phonons in a material. There are four different modes or phonon waveforms: longitudinal optical, transverse optical, longitudinal acoustic and transverse acoustic. Longitudinal phonons are quantized compression waves and transverse phonons are quantized shear waves (Regner *et al*., 2013; Zhou *et al*., 2015). Phonons are lattice vibrations in which the atoms in the unit cell oscillate relative to each other with the phonon contribution to a material's thermal conductivity (Cengel and Ghajar, 2015). The transfer of energy by phonons depends on three variables; the specific heat, the average phonon velocity and the mean free path of the phonon. In the temperature range to be tested, the specific heat and the average phonon velocity are essentially constant (Zhou *et al*., 2015). The mean free path of the phonons may change slightly over the desired temperature range. The mean free path refers to the distance the phonons can travel without being scattered.

2.5 Scattering of phonons

The scattering of phonons in ceramic causes a vibrations and excitations that help to store energy than conducting heat. In terms of scattering phonons, the excitations of principle concern are other phonons, specifically anharmonic phonon-phonon scattering. There are two types of anharmonic phonon-phonon scattering: N-type or normal processes, scattering with no net change in phonon momentum, and U-type or umklapp processes, scattering that results in a change in momentum. In both of these processes energy must be conserved. Anharmonic phonon-phonon scattering can be explained in terms of the interaction of two phonons thus, a phonon passing through a crystal lattice displaces the atoms of the lattice from their equilibrium positions, thereby introducing strain fields locally around these atoms. A second phonon passing through this region experiences a periodic variation of the elastic properties, in effect, a periodic variation in the material's refractive index. As a result a third phonon is produced. Anharmonic phonon-phonon scattering and scattering by defects are sources of thermal resistance that lead to the establishment of thermal gradients in materials. While the mean free path of both normal and umklapp process change with temperature, only umklapp processes contribute to the thermal resistance of a lattice (Cengel and Ghajar, 2015). The disordered structure increases the mean path of the phonons and therefore reduces the amount of energy transported by the phonons. The thermal conductivity contribution of phonons in a porous material is much less than it is in crystalline materials. The expected thermal conductivity of ceramic base porous materials (CBPIM) should be similar to the values obtained for clear fused silica (Tiwari *et al*., 2013). The thermal conductivity of fused silica over the temperature range of 50 to 1100°C depends on two modes of conduction, the sum of the phonon and photon contributions to thermal conductivity. The thermal conductivity near the low end of the temperature range is primarily due to phonon conduction. The phonon contribution to thermal conductivity increases slightly as the temperature increases, but it does not change significantly.

2.6 Thermal conductivity

Thermal conductivity is the amount of heat conducted in a unit time through a unit area normal to the direction of heat flow (Budinski and Budinski, 2010). Refractories are non-metallic materials capable of enduring high temperatures and suitable as construction materials for industrial furnaces (Aramide and Seidu, 2013). Heat flows through solids due to elastic vibration of atoms or molecules or due to transfer of energy by the free electrons. Insulators have lower conductivities as they depend entirely on the lattice vibration of atoms and molecules. In dielectrics (thermal insulators) thermal conductivity is caused alone by the atomic or molecular vibration of the lattice representing a certain type of crystal structure. Budinski and Budinski (2010) explained that the rate of heat flow per unit time in a homogeneous material under steady-state conditions per unit area, per unit temperature gradient in a direction perpendicular to area. The thermal conductivity K is therefore, a measure of the rate at which heat is transferred through a material (Askeland *et al*., 2011).

$$Q/A = K \quad = \quad \Delta T/\Delta X \qquad (2.1)$$

The heat flux has to be uniaxial in all these methods and hence radial heat loss or gain must be minimized by methods such as insulation. Consider a specimen of cross bar section A across which a thermal gradient exists. T_2 and T_1 are the temperature measured over a length. Let Q be the quantity of heat flowing through A as shown in Figure 2.1. Thermal conductivity K is given by the ratio of the heat flux Q/A to the thermal gradient ΔT/ΔL. The measurement of heat flux can be directly or indirectly.

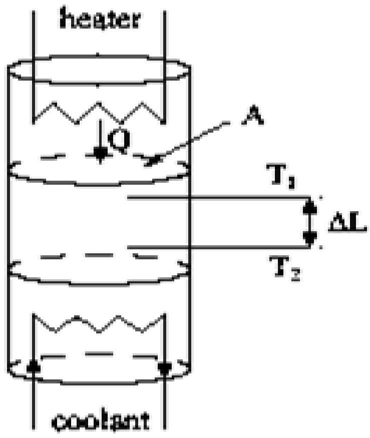

Figure 2.1: Heat Flux in calorimeter (Cengel and Ghajar, 2015)

2.7 Thermal conductivity measurement techniques

Thermal conductivity measurement methods are of steady state and transient methods (Hammerschmidt *et al.,* 2015). Conventionally, steady state techniques were most widely used as they are mathematically simpler. Steady state is frequently used for materials of low thermal conductivity but can be time consuming and requires expensive equipment (apparatus) but the result of the measurement is usually accurate and widely acceptable (Cengel and Ghajar, 2015).

The methods of transient have an advantage of experimental procedure in which once the difficult mathematical processes or treatment has been sorted out, the application becomes easier. The transient method has the potential of determining the thermal diffusivity directly. The result of thermal conductivity measurement using this technique comes with a lot of errors and as such not accurate as in the cases of steady state techniques especially with dry materials. The level of error can affect the sense of its acceptability. Lype *et al.* (2016) gave the two methods as transient and steady state methods. Highlighted by Cengel (2012) these methods are used for measurement of thermal conductivity for solids, liquids and gases. Hammerschmidt *et al.* (2015) further reiterated that the steady-state techniques of measurements of thermal conductivity by the guarded-hot-plate typically employed specimens as much as one hundred times larger than the transient method, although it is time consuming because of the time required to establish steady-state conditions at each test temperature. Tiwari *et al*. (2013) stated that there are two major methods for determining the thermal conductivity of solids, liquid and gas materials. The most suitable method for a given material depends largely on the properties of the material and the conditions under which the measurements are performed experimentally. The standard values expected for thermal conductivity of the ceramic base porous insulating material is within the range of 0.03-3.5W/mK for thermal insulators (Tiwari *et al*., 2014). Alumina clay is a hard material and as such, specimen with complex shapes that require a lot of machining are practically not easy but can be produced. The process required to manufacture the alumina fireclay bricks, restricts the thickness of the test specimen to less than 0.5mm. The alumina brick is rigid and electrically non-conducting. It is desired to have thermal conductivity data over a temperature range of 50-1100 °C when carrying out the experiment (Tiwari *et al*., 2013; Lype *et al*. (2016). The main mode of thermal conductivity at the lower temperatures would be by phonons. As the temperature is increased, the thermal conductivity would depend on the combined effects of phonons and photons. A method to obtain accurate thermal conductivity data at a reasonable cost is desirable. The hardware required for this method should easily be obtainable and inexpensive to manufacturers which should be an attempt to further understand in detailed the experimental approach for measurement of thermal conductivity in insulating and refractory bricks.

2.8 Steady-state method

Steady-state methods use Fourier's Law to directly measure the thermal conductivity of the test materials. In their research, Cengel and Ghajar (2015) stated that in Fourier’s law, the heat flux is equal to the negative temperature gradient multiplied by a constant of proportionality, the thermal conductivity of the medium; the negative sign is indicative of the fact that the heat flow is in the opposite direction to the temperature gradient. In this method, the heat flux crosses a specific cross-sectional area in the volume element of a clay specimen material which is usually determined and the temperature gradient across this volume element is measured. Steady state thermal analysis requires only the thermal conductivity (Schacht, 2004). Thermal conductivity is then calculated using Fourier's Law. Steady-state methods include the envelop method, the radial heat flow method, the calorimeter, the guarded hot plate method (Cengel and Ghajar, 2015).

2.8.1 Envelop method

In the envelope method, a specimen is made around a heater in a shape similar to the heater as presented in Figure 2.2. Thermal conductivity is determined using envelope methods (Adams and Loeb, 1954; McQuarrie, 1954). The immediately steady state has been achieved, the heat flow via the envelope is equivalent to the power P dissipated by the heater. The temperature gradient ΔT is measured using thermocouples situated on diverse isothermal layers, and the shape factor B is determined by the shape of the envelope. There are different shapes used in the envelope method. The spheroidal method uses the mathematically simplest shape factor. Specimens are not easily formed for the cylindrical envelope method, it is rarely being used but it is appropriate for measuring the thermal conductivity of pipes and tubes insulation (Adams, 1954; Kingery, 1954, McQuarrie, 1954).

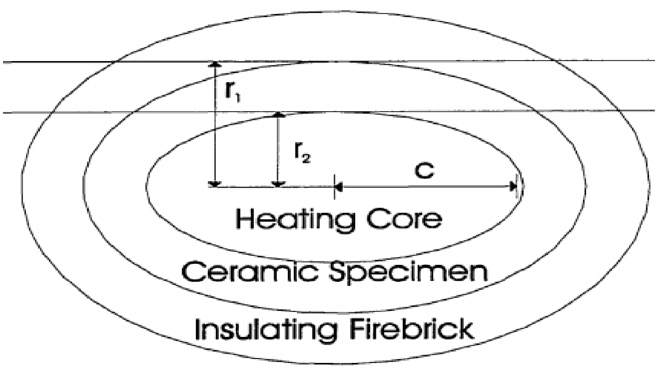

Figure 2.2: Schematic diagram of envelop technique (Adams, 1954)

2.8.2 Radial heat flow technique

The radial heat flow method is a steady state technique. The method necessitates the fabrication of hollow cylinder-shaped test specimen. An elongated heater is placed beside the axis of the specimen and thermocouples are placed at two radial positions syrnmetrically around the specimen usually at 120 degree intervals. The simpIest locations are the inner and outer exteriors of the specimen. The area between the specimen and the heater is packed with a granular or bubbled insulation. This material is placed between the outside of the specimen and the furnace case. Heaters are placed along the outside of the case to heat the whole furnace environment. A draft of this furnace is shown in Figure 2.3. The longer the specimen being tested the more the heat flow is limited to purely radial. Guard heaters at the ends can be used to restrict any axial heat flow that may be present. The thermocouple arrangement is repeated at intervals along the axis to measure the temperature gradient and discover any axial heat flow that may be present (Speyer, 1994; Cengel and Ghajar, 2015).

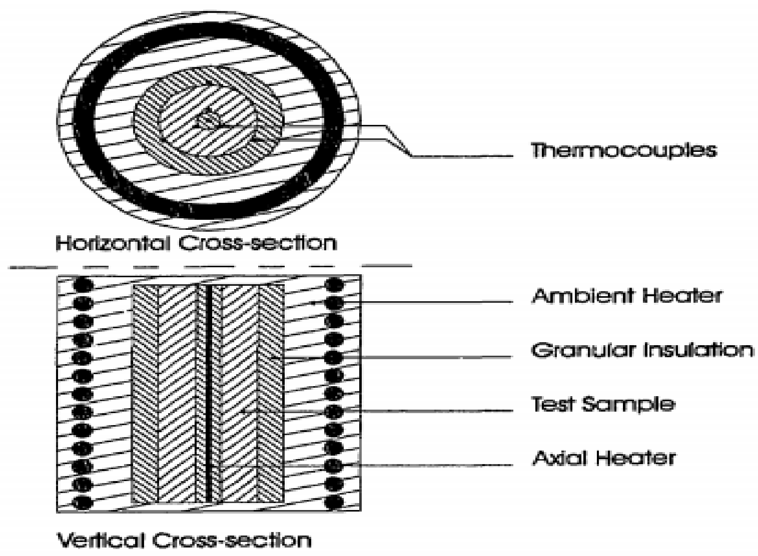

Figure 2.3: Schematic diagram of Radial heat flow method (Speyer, 1994)

2.8.3 Calorimeter technique

The calorimeter method has been a standard test method since 1945 and was designated (Speyer, 1994; ASTM C201-93, 1996). The steady state method uses the principle of Fourier's law to directly determine the thermal conductivity of materials. The equipment consists of specimen brick surrounded by guard bricks of the same material as presented in Figure 2.4. They are situated in between the calorimeter and the heating elements. The heat flows from the heaters into a SiC slab positioned over the guard bricks to normalize the temperature gradient. The bricks are arranged on water Calorimeter cooled base with separated water cooling for the calorimeter, internal guards and external guards. The test specimen sits on top of the calorimeter, overlying onto the internal guards. The temperature of the calorirneter and internal guards are maintained in steady state at a constant temperature.

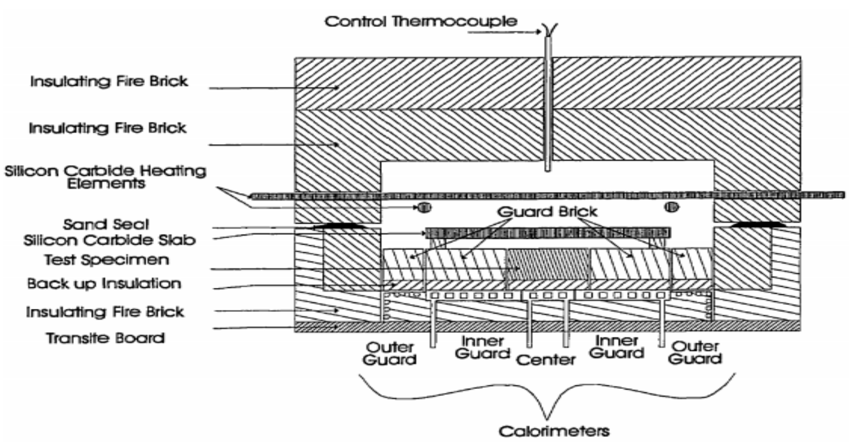

Figure 2.4: Schematic working principle of calorimeter method (Speyer, 1994)

2.8.4 Guarded hot plate technique

The guarded hot plate is a steady state method used to measure the thermal conductivity of ceramic materials that can be formed into a disk shape (Cengel and Ghajar, 2015). The furnace is design according to ASTM Cl77-85 (1996) and ASTM C202-93 (2013) is shown in Figure 2.5. A single or two specimens can be placed above and below a smaller disk shaped heater in the middle of a cylindrical guard heater whose temperature is matched to that of the heater. During the measuring, the temperature changes the specimen and thermocouples are located above and below positions. The heaters are placed to regulate the amount of the gradient through the specimen. Heat irons are placed at the top of the stack to assist in axial heat flow. The temperature difference across specimen can be used to determine the heat flux through the specimen and verify the thermal conductivity of specimen. When large uniform specimen is being produced, the guarded hot plate method is an excellent method for determining the thermal conductivity of a material. It is necessary that any heat flow through the specimen is axial, hence the control and monitoring of the guard heaters is important (Francl and Kingery, 1954; Vasilos and Kingery, 1954, Sheffield and Schorr, 1991).

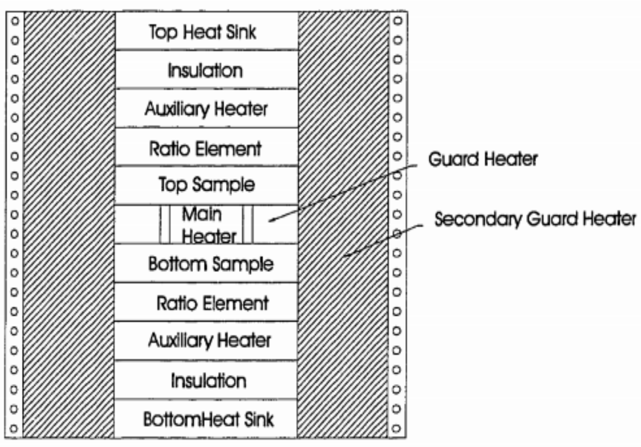

Figure 2.5: Schematic diagram of guarded hot plate (Sheffield and Schorr, 1991)

2.9 Transient method

Generally, transient techniques are mathematically complex when measuring the thermal diffusivity. They require advanced mathematical approaches such as Bessel functions, Fourier series analysis, Laplace transforms, and other graphical or numerical (finite element or finite difference) computational methods. With regard to transient thermal analysis, the required thermal material properties include the density, specific heat and thermal conductivity (Schacht, 2004). The clay specimen material has no tabulated specific heat or density data. Both would have to be determined, in addition to the diffusivity, over the complete temperature range. Under these conditions, the transient methods for measuring thermal conductivity can be used for ceramic based porous materials (Brodkey and Hershey, 1988). The transient methods: hot wire method, laser flash technique and hot-disk transient plane source (TPS).

2.9.1 Hot wire technique

The hot wire method involves placing an electrically heated wire into a specimen material as demonstrated in Figure 2.6. This intrusive method is inadequate to testing fluids, melted plastics and foams. The temperature of the wire is measured as heat flows out radially from the wire into the specimen. Plotting the temperature of the wire versus the logarithm of time, thermal conductivity can be calculated. In general the technique is restricted to lower temperature range and the minimum accurate of techniques mentioned (Murshed *et al.*, 2005; Hwang *et al.*, 2006).

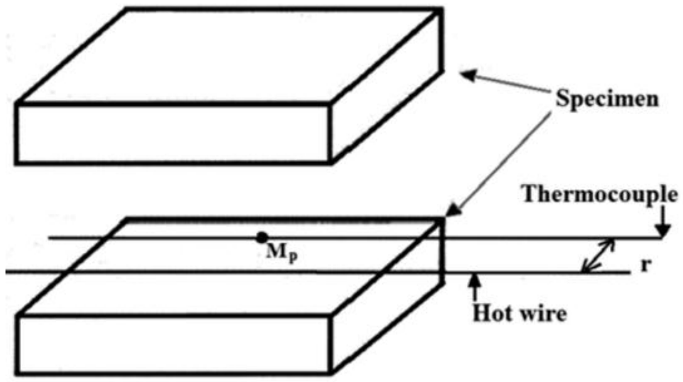

Figure 2.6: Schematic and principle of Hot wire method (Murshed *et al.*, 2005)

2.9.2 Laser flash technique

The laser flash method is that in which a short pulse of heat, given by a laser flash, is applied to the front surface of a specimen. On the back surface of the specimen, an infrared (IR) detector is used to measure the change in temperature as displayed in Figure 2.7. The monitored temperature data, which act as a function of time are used to determine thermal diffusivity (Dos Santos *et al*., 2005; Lin *et al.*, 2012). If the heat capacity and density of the specimen are known, the thermal conductivity can be calculated. The method is usually conducted according to ASTM E1461.

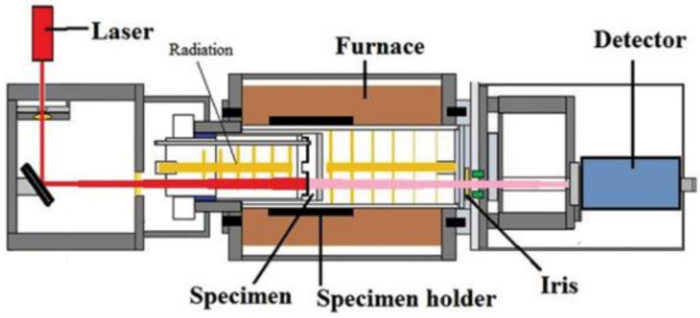

Figure 2.7: Schematic and principle of laser flash method (Lin *et al.*, 2012)

2.9.3 Transient plane source (TPS)

The hot disk is referred to as transient plane source (TPS) technique that utilizes a hot disc sensor and a patented mathematical model of Gustafson in the year 1991 (Al-Ajlan *et al.*, 2006; Solorzano *et al.*, 2008). He combined electronics to derive the thermal conductivity. This method requires two identical specimens which sandwich the sensor, pressing heavily the specimen in the process as revealed in Figure 2.8. The operator is responsible for developing the necessary timing, power parameters and selecting the appropriate data consequently building a linear regression in satisfying the model's requirements.

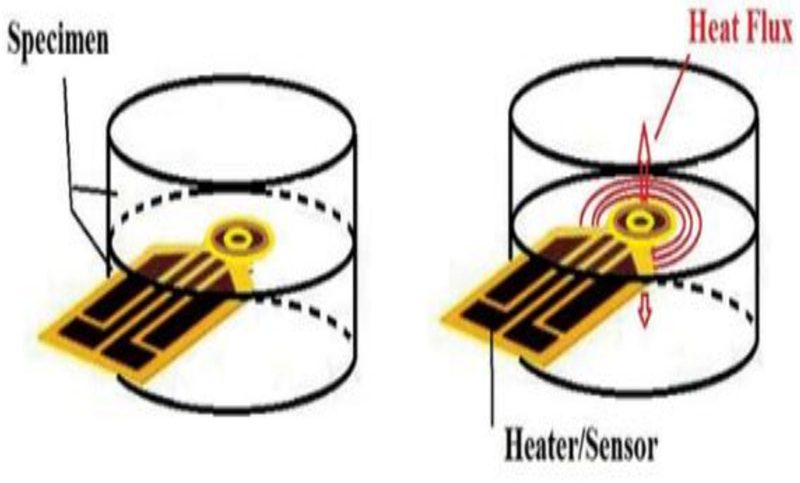

Figure 2.8: Schematic principle of transient plane source (Solorzano *et al.*, 2008)

REFERENCES

Abdullahi, M. Y., and Sumaila, U. (2007). Characterization of Some Nigeria Clays as Refractory Materials for Furnace Lining. *Continental Journal of Engineering Sciences 2*, 30-35.

Abhat, A. (1983). Low Temperature Latent Heat Thermal Energy Storage : Heat Storage Materials. *Solar Energy, 30*(4), 313-332.

Abhat, A., DeWinter, F., and Cox, M. (1978). *Performance Studies of Heat Pipes Latent Heat Thermal Energy Storage System. Sun, Mankind's Future Source Energy*. (Vol. 2). New York, USA: Pergamon Press.

Abolarin, M. S., Olugboji, O. A., and Ugwuoke. I. O. (2006). Determination of Moulding Properties of Locally Available Clays for Casting Operations. *Annual Engineering Conference (FUTA)* , 238-242.

Abuh, M. A., Abia-Bassey, N., Udeinya, T. C., Nwannewulhe, H. U., Abong, A. A., and Akpomie, K. G. (2014). Industrial Potentials of Adiabo Clay in Calaba Municipal Cross Rivers State, South-South Nigeria. *The Pacific Journal of Science and Technology, 15*(1), 63-75.

Adams, M and Loeb, A. L. (1954). Thermal Conductivity: II, Development of a Thermal Conductivity Expression of the Special Case of Prolate Spheroids. *Journal of the American Ceramic Society, 37*(2), 73-74.

Adams, M. (1954). Thermal Conductivity: III, Prolate Spheroidal Envelope Method (Data for Al_2O_3, BeO, MgO, ThO_2, ZrO_2). *Journal of the American Ceramic Society, 37*(2), 74-79.

Aderibigbe, D. A. (1989). Local Sourcing of Raw Materials and Consumables for Iron and Steel Industries in Nigeria-Challenges for the Future. *Raw Materials Research and Development Council of Nigeria (RMRDC), 55*.

Adindu, C. I., Ekenyem, C. S., Okafor, G., Moses, J., Nwokedi, N. P., and Nnachi, B. (2016). Influence of Grog Size on the Performance of NSU Clay-Based

Dense Refractory Bricks. *American Journal of Materials Science and Engineering, 4*(1), 7-12.

Agbo, A. O, Idenyi, N. E., and Mbah, C. M. (2015). Characterization of Nkalagu Obukpa Clay Deposits for Industrial Uses. *International Journal of Multidisciplinary Research and Development, 2*(8), 689-692.

Agrawai, P., Misra, S. N., and Sharma, T. (2013). Correlation Between Chromophore Impurity Content and Fired Colour Date of Kaolin Clay. *International Journal of Mondern Physics, 22*, 51-61.

Akinyemi, O. A., Sauer, T. J., and Onifade, Y. S. (2011). Revisiting the Block Method for Evaluating Thermal Conductivities of Clay and Granite. *International Communications in Heat and Mass Transfer, 38. 1014-1018*.

Aksoz, S., Ozturk, E., and Marash, N. (2013). The Measurement of Thermal Conductivity Variation with Temperature for Solid Materials. *Measurement, 46*(1), 161-170.

Al-Ajlan, S. A. (2006). Measurements of Thermal Properties of Insulation Materials by Using Transient Plane Source Technique. *Applied Thermal Engineering, 26*(17), 2184-2191.

Al-Homoud, M. S. (2005). Performance Characteristics and Practical Applications of Common Building Thermal Insulation Materials. *Building and Environment, 40*, 351-364.

Aliyu, A. M., Umaru, M., Aris, M. I., and Munri, S. M. (2012). A Comparative Study on the Refractory Properties of Selected Clays in North Central Nigeria. *Academic Research International, 3*(1), 393-398.

Al-Malah, K., and Abu-Jdayil, B. (2007). Clay-Based Heat Insulator Composites: Thermal and Water Retention Properties. *Applied Clay Science, 37*, 90-96.

Amrane, B., Ouedraogo, E., Mamen, B., Djaknoun, S., and Mesrati, N. (2011). Experimental Study of the Thermo-mechanical Behaviour of Alumina-silicate Refractory Materials based on a Mixture of Algerian Kaolinitic Clays. *Ceramics International, 37*(8), 3217-3227.

Anand, K. B., Vasudevan., and Ramamurthy, K. (2003). Water Permeability of Alternative Masonry Systems. *Built Environment, 38*, 947-957.

Aramide, F. O. (2012). Effect of Firing Temperature on Mechanical Properties of Fired Masonry Bricks Produced from Ipetumodu Clay. *Leonando Journal of Sciences, 21*, 70-82.

Aramide, F. O., Alaneme, K. K., Olubambi, P. A., and Borode, J. O. (2014). Characterization of some Clay Deposits in South West Nigeria. *Leonardo Electronic Journal of Practices and Technologies, 25*, 46-57.

Aramide, F.O., and Seidu, S. O. (2013). Production of Refractory Lining for Diesel Fired Rotory Furnace from Locally Sourced Kaolin and Potter's Clay. *Journal of Minerals and Materials Characterization and Engineering, 1*, 75-79.

Aremu, D. A., Aremu, J. O., and Ibrahim, U. M. (2013). Analysis of Mubi Clay Deposit as a Furnace Lining. *International Journal of Science & Technology Research, 2*(12), 182-186.

Aroke, U. O., El-Nafaty, U. A., and Osha,.A. (2013). Properties and Characterization of Kaolin Clay from Alkaleri, North Easthern Nigeria. *International Journal of Emerging Technology and Advanced Engineering, 3*(1), 387-392.

Askeland, D. R, Pulay, P. P., and Wright, W.J. (2011). *The Science and Engineering of Materials* (Sixth ed.). Stamford, CT 06902, USA: Cengage Learning.

Askeland, D. R., and Wright, W. J. (2016). *The Science and Engineering of Materials* (Seventh ed.). Cengage Learning.

ASTM C1100-88. (2005). *Standard Test Method for Ribbon Thermal Shock Testing Refractory Materials* (Vol. 15.01). ASTM, International.

ASTM C133-97. (2015). *Standard Test Methods for Cold Crushing Strength and Modulus of Rupture of Refractories* (Vol. 15.01). ASTM, International.

ASTM C20-00. (2015). *Standard Test Method for Apparent Porosity, Water Absorption, Specific Gravity, Firing Shrinkage, and Bulk Density* (Vol. 15.01). ASTM, International.

ASTM C201-93. (1996). Standard Test Method for Thermal Conductivity of Refractories. ASTM, International.

ASTM C202-93. (2013). *Standard Test Method for Thermal Conductivity of Refractory Brick* (Vol. 15.01). ASTM, International.

ASTM C24-09. (2013). *Standard Test Method for Pyrometric Cone Equivalent (PCE) of Fireclays and High Alumina Refractory Materials* (Vol. 15.01). ASTM, International.

ASTM C242-01. (2007). *Standard Terminology Ceramic Whiteware and Related Products* (Vol. 15.01). ASTM, International.

ASTM C27-98. (2013). *Standard Classification of Fireclay and High Alumina Refractory Brick* (Vol. 15.01). ASTM, International.

ASTM C493-98. (2002). *Standard Test Method for Bulk Density and Porosity of Granular Refractory Materials by Mercury Displacement* (Vol. 15.01). ASTM, International.

ASTM C71-12. (2012). *Standard Terminology Relating to Refractories* (Vol. 15.01). ASTM, International.

ASTM C832-00. (2015). *Standard Test Method of Measuring Thermal Expansion and Creep of Refractories Under Load* (Vol. 15.01). ASTM, International.

ASTM D4220/D4220M-14. (2014). *Standard Practices for Preserving and Transporting Soil Samples* (Vol. 15.01). ASTM, International.

ASTM D7348. (2013). Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion residues. *(Vol. 15.01).*

ASTM E11-15. (2015). *Standard Specification for Woven Wire Test Sieve Cloth and Test Sieves* (Vol. 15.01). ASTM, International.

ASTM E1249. (2011). *Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry* (Vol. 14.05). ASTM, International.

ASTM E473-11. (2016). *Standard Terminology Relating to Thermal Analysis and Rheology* (Vol. 15.01). ASTM, International.

Atanda, P., Adeiji, O., and Oluwole, O. (2012). Development of Heat Treatment Refractory Bricks Using Local Nigeria Clay. *International Journal of Materials and Chemistry, 2*(5), 185-191.

Athar, T., Vishwakarma, S. K., Bardia, A., Alabass, R., Alqarlosy, A., and Khan, A. A. (2016). Green Approach for the Synthesis and Characterization of $ZrSnO_4$ Nanopowder. *Applied Nanoscience, 1*(11), 767-777.

Austin, J. B. (1931). The Thermal Expansion of some Refractory Oxides. *Journal of the American Ceramic Society, 14*(11), 795-810.

Aye, A. E., and Oyetunji, A. (2013). Metallurgical Analysis of Ugunoda Clay Deposit, Nigeria for Use as a Refractory. *International Journal of Science and Advanced Technology, 3*(10), 25-29.

Bam, S. A, Gundu, D, T., and Edeoja, A. O. (2015). Evaluation of thermo-Mechanical Behaviour of Clay-Silica Sand Blends for Bricks Production. *International Journal of Research in Engineering and Science, 3*(5), 61-66.

Bardelli, F., Veronesi, G., Capella, S., Bellis, D., Charlet, L., Cedola, A., and Belluso, E. (2017). New Insights on the Biomineralisation Process Developing in Human Lungs around in Haled Abestros Fibres. *Scientific Reports, 7*, 44862.

Barnett, W. K., and Hoopes, J. W. (1995). *The Emergence of Pottery: Technology and Innovation in Ancient Society*. Washington: Smithsonian Institution Press.

Bauer, D., Marx , R., Nubbicker-Lux, J., Ochs, F., Heidemann, W., and Muller-Steinhagen, H. (2010). German Central Solar Heating Plants with Seasonal Heat Storage. *Solar Energy, 84*, 612-623.

Beeley, P. (2001). *Foundry Technology*. UK: Butterworth-Heinemann.

Bergaya, F., Theng, B. K. G., and Lagaly, G. (2006). *Handbook of Clay Science* (First ed.). UK: Elsevier.

Boettinger, W.J., Kattner, U.R, Moon, K. W., and Perepezko, J. H. (2006). DTA and Heat-flux DSC Measurements of Alloys Melting and Freezing. 960-15.

Bolton, W., and Higgins, R. A. (2015). *Materials for Engineers and Technicians* (Sixth ed.). Uk: Routledge Taylor and Francis Group.

Bordeepong, S., Bhongsuwan, D., Pungrassami, T., and Bhongsuwan. (2012). Mineralogy, Chemical Composition and Ceramic Properties of Clay Deposits in Southern Thailand. *Kasetsart Journal of Natural Science, 46*, 485-500.

Bories, C., Vedrenne, E., Paulhe-Massol, A., Vilarem, G., and Sablayrolles, C. (2016). Development of Porous Fire Clay Bricks with Bio-based Additive: Study of the Environmental Impacts by Life Cycle Assessment (LCA). *Construction and Building Materials, 125*, 1142-1151.

Brady, G. S., Clauser, H. R., and Vaccari, J. A. (2002). *Materials Handbook* (fifteenth ed.). New York: McGraw-Hill.

Brodkey, R. S., and Hershey, H. C. (1988). *Transport Phenomena, A Unified Approach.* McGraw-Hill Inc.

Brown, M. E. (1998). *Introduction to Thermal Analysis, Techniques and Applications.* New York: Chapman and Hall.

Budinski, K. G., and Budinski. M. K. (2010). *Engineering Materials: Properties and Selection* (Ninth ed.). New Jersey, USA: Pearson Prentice Hall.

Buhrke, V. E., Jenkins, R., and Smith, D. K. (1998). *A Practical Guide for the Preparation of Specimens for X-Ray Fluorescence and X-Ray Diffraction Analysis*. John Wiley & Son, Inc.

Burdge, J., and Overby. (2015). *Chemistry: Atoms First* (Second ed.). McGraw Hill education.

Cairn-Smith. (1988). *Clay Mineral and the Origin of Life.* London, UK: Pergamon Press.

Callister, W. D., and Rethwisch, D. G. (2013). *Fundamentals of Materials Science and Engineering.* (fourth, Ed.) Singapore: John Wily and Sons.

Carretero, M. I., Pozo, M., Lagido, J. L., Femandez-Gonzalez, M.V., Dalgado, R., Gomez, L., Armijo, F., and Maraver, F. (2014). Assessment of Three Spanish Clays for Their Use in Pelotherapy. *Applied Clay Science, 99*, 131-143.

Cengel, Y. A. (2008). *Introduction to Thermodynamics and Heat Transfer* (Second ed.). New York: McGraw-Hill.

Cengel, Y. A., and Boles, M. A. (2015). *Thermodynamics: An Engineering Approach, (eight edition).* New York: McGraw Hill Education.

Cengel, Y. A., and Ghajar, A. J. (2012). *Heat and Mass Transfer: Fundamentals & Applications (Fourth edition).* McGraw Hill Education.

Cengel, Y. A., and Ghajar, A. J. (2015). *Heat and Mass Transfer: Fundamentals & Applications (Fifth Edition in SI Units).* McGraw Hill Education.

Chen, H., Rogalski, M. R., and Anker, J. N. (2014). Advances in Functional X-rays Imaging Techniques and Contrast Agents. *Physical Chemistry Chemical Physics, 14*(39), 13469-13486.

Chester, J. H. (1973). *Refractories, Production and Properties.* London, UK: The Iron and Steel Institute.

Chesti, A. R. (1986). *Refractories: Manufacture, Properties and Applications* (First ed.). New Delhi: Prentice-Hall of India Private Limited.

Chukwudi, B. C. (2008). Characterization and Evaluation of the Refractory Properties of Nsu Clay Deposit in Imo State Nigeria. *Pacific Journal of Science and Technology, 9 (2) 487-494*.

Cila, M. S., Demelo Cartaxo, J., Menezes, R.R., Debina Santana, L. N., and Dearaujo Neves, G. (2016). Production of Fire Clay Porous Structure with no aligned Macro Porosity from Water -based Slurry by Freeze Casting Process: A New Approach. *Ceramics International, 42*(1), 9278-9282.

David, H., Robert, R., and Jearl, W. (2010). *Fundamentals of Physics.* John Wiley and Sons.

Deer, W. A., Howie, R. A., and Zussman, J. (1992). An Introduction to the Rock-forming Minerals. London: Longman.

Dincer, I., and Rosen, M. A. (2002). *Thermal Energy Storage: Systems and Applications.* Sussex, UK: John Wiley and Sons, Ltd.

Dos Santos, W. N., Mummery, P., and Wallwork, A. (2005). Thermal Diffusivity of Polymers by the Laser Flash Technique. *Polymer Testing, 24*(5), 628-634.

Elmaghraby, M. S., and Ismail, A. I. M. (2016). Utilization of some Egyptian Waste Kaolinitic Sand as Grog for Bricks and Concrete. *Silicon, 8*(2), 299-307.

Elngar, M. A. G., Mohamed, F. M., Asrar, G., Carmen, M. S., and Shalabi, M. E. H. (2010). Effect of Additives on the Performance of the Fire-Clay Refractory Bricks. *Eurasian Chemico-Technological Journal, 12*(2), 171-179.

Euan, G. (2007, November Friday,16). *Euan the Potter: How to build a kiln*. Retrieved May 4, 2016, from euancraig.blogsport.my/search: http://www.euancraig.com

Evbuomwan, B. O., Ifebbor, I., and Atuka, M. M. (2013). Characterization of Omoku and Ogoni Clay in Rivers State Nigeria for Use as Industrial Raw Materials. *International Journal of Science and Engineering Investigations, 2*(18), 72-76.

Fakolujo, O. S., Olokode, O. S., Aiyedun, P. O., Oyeleke, Y. T., Anyanwu, B. U., and Lee, W. E. (2012). Studies on the Five (5) Selected Clays in Abeokuta, Nigeria. *The Pacific Journal of Science and Technology, 13*(1), 83-90.

Feather Jr, R. M., Snyder, S. L., and Zike, D. (2002). *Earth Science: National Geographic Society* (Teacher Wraparound ed.). Glencoe/McGraw Hill.

Fleischmann, A., Hao, H. Y., Neumann, M., and Enss, C. (2003). A New Technique for Measuring Thermal Conductivity at Low Temperature. *Physica B: Condensed Matter, 329*, 1525-1526.

Foldvari, M. (2011). *Handbook of Thermogravimetric System of Minerals and its use in Geological Practice* (Vol. 213). Budapest: Geological Institute of Hungary.

Folorunso, D. O., Aribo, S., and Olaniran, O. (2015). Performance Evaluation of Insulating Firebricks Produced from Hydrometallurgically Purified Termite Hill Clay Reinforced with Alumina. *American Journal of Engineering Research*, *4*(5), 1-7.

Fourier, J. B. (1955). *The Analytical Theory of Heat.* New York, USA: Dover Publication.

Gabbott, P. (2007). *The Principles and Applications of Thermal Analysis.* London: Wily-Blackwell.

Gaied, M. E., and Gallata, W. (2015). Beneficiation of Feldspar Ore for application in the Ceramic Industry: Influence of Composition on the Physical Characteristics. *Arabian Journal of Chemistry, 8*(2), 186-190.

Garzon, E. Sanchez-Soto, P. J., and Romero, E. (2010). Physical and Geotechnical Properties of Clay Phyllites. *Applied Clay Science, 48*(3), 307-318.

Geiger, G. H., and Poirier, D. R. (1973). *Transport Phenomena in Metallurgy*. Addison-Wesley Publishing Company, Inc.

Gilham, C., Rake, C., Burdett, G., Nicholson, A. G., Davison, L., Franchini, A., Carpenter, J., Hodgson, J., Darnton, A., and Peto, J. (2016). Pleural Mesothelioma and Lung Cancer Risks in Relation to Occupational History and Asbestors Lung Burden. *Occupational Environment Medicine, 73*, 290-299.

Gilmore, C. M. (2013). *Materials Science and Engineering Properties.* Cengage Learning.

Goldstein, G.I., Newbury, D. E., Echin, P., Joy, D.C., Fiori, C., and Lifshin, E. (1981). *Scanning Electron Microscopy and X-ray Microanalysis.* New York: Plenum Press.

Googlemap. (2016). *Nigerian Map Showing Clay deposit sites*. Retrieved from www.googlemap.com

Grandjean, S., Absi, J., and Smith, D. S. (2005). Numerical Calculation of the Thermal Conductivity of Porous Ceramics Based on Micrographs. *Journal of European Ceramic Society, 07*, 061.

Gupta, O. P. (1997). *Elements of Fuels, Furnaces and Refractories.* New Delhi: Khanna Publishers.

Hall, C., and Hoff, W. D. (2012). *Water Transport in Brick, Stone and Concrete* (Second ed.). New York, USA: Spone Press.

Hall, P. L. (1987). *Clays: Their Significance, Properties, Origin and Uses. A Handbook of Determinative Methods in Clay Mineralogy.* (M.J, Ed.) Glasgow and London, UK: Blackie, Wilson Inc.

Hammerschmidt, U., Hameury, J., Strned, R., Turzo-Andras, E., and Wu, J. (2015). Critical Review of Industrial Techniques for Thermal Conductivity Measurements of Thermal Insulation Methods. *International Journal of Thermophysics*, *36*(7), 1530-1544.

Hassan, A. M., Raji, B.A., Malgwi, W. B., and Agbenin, J.O. (2015). The Basaltic Soils of Plateau State, Nigeria: Properties, Classification and Management Practices. *Journal of Soil Science and Environment Management, 6*(1), 1-8.

Hassan, S. B. (2000). Refractory Properties of Bauchi and Onibode Clay of Nigeria for Furnace Lining. *African Journal of Science Technology, 1*, 56-60.

Hatakeyama, T., and Liu, Z. (1998). Handbook of Thermal Analysis.

Hawkins, A. B., Lawrence, M. S., and Privett, K. D. (1986). Clay Mineralogy and Plasticity of the Fuller's Earth Formation. *Clay Mineral, 21*, 293-310.

Heindl, R. A. (1933). Thermal Expansion of Refractories to 1800 C. *Bur Stand J Res*, 715-735.

Hwang, Y. J., Ahn, Y. C., Shin, H. S., Lee, C. G., Kim, G. T., Park, H. S., and Lee, J. K. (2006). Investigation on Characteristics of Thermal Conductivity Enhancement of Nanofluids. *Current Applied Physics, 6*(6), 1068-1071.

Ibitoye, S., and Alo, O. (2014). Adaptation of Odolewu Clay for Use as Refractory Material. *International Journal of Scientific & Engineering Research, 5*(4), 837-843.

Ibrahim, D., and Rosen, M. (2002.). *Thermal Energy Storage: Systems and Applications.* (First ed.). John Wiley and Sons Inc.

Imasuen, O. I., Akah, F. A., and Ibrahim, I. (2009). Petrographic, Sedimentlogical and Geochemical Attributes of the Rock settings in Agada and Environs, South East of Lokoja, Kogi State, Nigeria. *Journal of Science and Industrial Policy, 2*(1), 51-65.

Imasuen, O. I., Asuen, G. O., and Aibuki, O.O. (2009). Petrological and Geochemical Investigations of Metamorphosed Rocks Northwest Ekido, Bassa Local Government Area, South East of Lokoja, Kogi State, Nigeria. *International Journal of Environmental Science*, *5*(2), 70-75.

Imasuen, O. I., Olatunji, J. A., and Onyeobi, T. U. S. (2013). Geological Observations of Basement Rocks, around Ganaja, Kogi State, Nigeria. *Journal of Geology and Mining, 3*(2), 57-66.

Jain, P. L. (2009). *Principles of Foundry Technology* (Fifth ed.). New Delhi: Tata McGraw Hill Education Private Limited.

Johari, I., Said, S., Hisham, B., Bakar, A., and Ahmad, Z. A. (2010). Effect of the Change of Firing Temperature on Microstructure and Physical Properties of Clay Bricks from Beruas (Malaysia). *Science of Sintering, 42,* 245-254.

Jozanikohan, G., Sahabi, F., Novouzi, G. H., and Memarian, H. (2015). Thermal Analysis: A Complementary Method of Study of the Shurijeh Clay Minerals. *International Journal of Mining & Geo-Engineering, 49*(1), 33-45.

Katsube, K., Hashida, M., and Tenra, T. (2006). Development of High-Performance Vacuum Insulation Panel. *Matsushita Technical Journal, 52*, 482-485.

Kausik, D., Somnath, S., Himansu, S. T., and Arup, G. (2015). Refractories of Alumina-Silica System. *Transactions of the Indian Ceramic Society, 73*(1), 1-13.

Kehinde, M. A. O., and Aliyu, A. (1989). *Technologies and Machinary for Processing Mineral Base Draw Materials in Nigeria. Task Force Committee Report.* Lagos: Nigerian Material Society.

Khandelwal, M., and Mench, M. M. (2006). Direct Measurement of Through-Plane Thermal Conductivity and Contact Resistance in Fuel Cell Materials. *Journal of Power Sources, 161*, 1106-1115.

Khanna, O. P. (2009). *A Test Book of Material Science and Metallurgy*. India: Dhanput Rai Publication.

Kingery, W. D. (1954). Thermal Conductivity: VI, Determination of Conductivity of Al_2O_3 by Spherical Envelop and Cylinder Methods. *Journal of the American Ceramic Society, 37*(2), 88-90.

Kingery, W. D. (1960). *Introduction to Ceramics.* New York, USA: John Willey Publishing.

Kirillin, V. A., Sychev, V. V., and Shoindlin, A. E. (1976). *Engineering Thermodynamics.* Moscow: Mir Publishers.

Kitouni, S., and Harabi, A. (2011). Sintering and Mechanical Properties of Porcelains Prepared from Algerian Raw Materials. *Ceramica, 57*, 453-460.

Klancnik, G., Medved, J., and Mrvar, P. (2010). Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) as a Method of Material Investigation. *Materials and Geoenvironment, 57*(1), 127-142.

Klein, C., and Dutrow, B. (2008). *Mineral Science.* John Wiley & Sons, Inc.

Klockenkamper, R. (1997). *Total Reflection X-Ray Fluorescence Analysis.* John Wiley & Son, Inc.

Kubicar, L. (1990). *Pulse Method Measuring Basic Thermophysical Parameters.* Amsterdam: Elsevier Publishing.

Kubicar, L., and Bohac, C. (2000). A Step-Wise Method for Measuring Thermophysical parameters of Materials. *Measurement Science and Technology, 11*, 252-258.

Kubicki, B. (1995). *Sintered Machine Elements.* Hertfordshire, Britain: Ellis Horwood Limited.

Kubiliute, R., and Kaminskas, R. (2013). The Pozzolanic Activity of Calcined Clay-Silica Gel Composites. *Materials Science (Medziagotyra), 19*(4), 453-460.

Kunzel, H. M., and Kiessl, K. (1997). Calculation of Heat and Moisture Transfer in Exposed Building Components. *International Journal of Heat Mass Transfer, 40*(1), 159-167.

Laaroussi, N., Cherki, A., Garoum, M., Khabbazi, A., and Feiz, A. (2013). Thermal Properties of a Sample Prepared using Mixtures of Clay Bricks. *Energy Procedia, 42*, 337-346.

Lawal, A. O., and Abdullahi, Y. (2010). Evaluation of Industrial Potentials of Alluvial Clays from the Confluence of River Niger and Mimi. *Science World Journal, 5*(3), 213-221.

Leng, Y. (2008). *Materials Characterization: An Introduction to Microscopic and Spectroscopic Method.* Hong Kong: John Wiley & Sons.

Li, H., Nagano, K., and Lai, Y. (2012). Heat Transfer of a Horizontal Spiral Heat Exchanger Under Ground Water Advection. *International Journal of Heat Mass Transfer, 55 (23-24) 6819-6831.*

Lin, W., Shang, J., Gu, W., and Wong, C. P. (2012). Parametric Study of Intrinsic Thermal Transport in Vertically Aligned Multi-walled Carbon Nanotubes Using a Laser Flash Technique. *Carbon, 50*(4), 1591-1603.

Litovsky, E., Shapiro, M., and Shavit, A. (1996). Gas Pressure and Temperature Dependance of Thermal Conductivity of Porous Materials: Part 2. Refractories and Ceramics with Porosity Exceeding 30%. *Journal of the American Ceramic Society, 79*, 1366-1376.

Liu, X., and Yu, W. (2006). Evaluating the Thermal Stability of High Performance Fibers by TGA. *Journal of Applied Polymer Science, 99*, 937-944.

Lotha, G. (2007). *Fuller's Earth Encyclopedia.* Britannia.

Lum, L. S., Malghan, S. G., and Schiller, S. B. (1996). Standard Reference Materials for Particle Size Analysis of Ceramic Powders by Gravity Sedimentation. *Powder Technology, 87*(3), 233-238.

Lype, E. F., Eichom, R., and Masi, J. F. (2016). *Progress in International Research on Thermodynamic and Transport Properties.* New York, USA: Academic Press.

Mangonon, P. L. (1999). *The Principles of Materials Selection for Engineering Design. PART 1 and 11.* New Jersey: Prentice Hall.

Manoharan, C., Sutharsan, P., Dhanapandian, S., and Venkatachalapathy, R. (2012). Characteristic of some Clay Materials from Tamilnadu, India, and their Possible Ceramic uses. *Ceramics, 58*, 412-418.

Manukaji, J. U. (2013). Chemical and Mechanical Characteristic of Clay Samples from Kaduna State Nigeria. *International Journal of Engineering Inventions, 2*(7), 20-26.

Mbaya, L. A., Ayuba, H. K., and Abdullai, J. (2012). An Assessment of Gully Erosion in Gombe Town, Gombe State, Nigeria. *Journal of Geography and Geology, 4*(3), 110-121.

McQuarrie. (1954). Thermal Conductivity Verses High-Temperature Method and Results for Alumina, Magnesia and Beryllia from 1000°C to 1800°C. *Journal of the American Ceramic Society, 37*(2), 83-89.

Merler, E., Somigliana, A., Girardi, P., and Barbieri, P. G. (2017). Residual Fibre Lung Burden among Patients with Pleural Mesothelioma who have been Occupationally Exposed to Asbestors. *Occupational and Environmental Medicine, 74*, 218-227.

Moukhina, E. (2012). Determination of Kinetic Mechanisms for Reactions Measured with Thermo-analytical Instruments. *Journal of Thermal Analysis Calorimetry, 100*(3), 1203-1214.

M-Tebandeke, L., Sebuwufu, P. J. M., Nyanzi, S. A., Schumann, A., Nyakairu, G. W. A., Ntale, M., and Lugolobi, F. (2015). The Elemental Mineralogical, IR, DTA and XRD Analysis Characterized Clays and Clay Minerals of Central and Easthern Uganda. *Advances in Materials, Physics and Chemistry, 05*(2), 67-86.

Mu, B., Wang, Q., and Wang, A. (2015). Effect of Different Clay Minerals and Calcination Temperature on the Morphology and Color of Clay $CoAl_2O_4$ Hybrid Pigments. *RSC Advances, 5*(124), 102674-102681.

Mukasa-Tebandeke, Z., Ssebuwufu, P. J. M., Nyanzi, S. A., Schumann, A., Nyakairu, G.W.A., Ntale, M., and Lugolobi, F. (2015). The Elemental, Mineralogical, IR, DTA and XRD Analysis Characterized Clays and Clay Minerals of Central and Easthern Uganda. *5*(2), 67-86.

Murray, H. H. (1963). Mining and Processing Industrial Kaolin. *Ge Miner News, 16*, 3-11.

Murshed, S. M. S., Leong, K.C., and Yang, C. (2005). Enhanced Thermal Conductivity of TiO_2-Water Based Nanofluids. *International Journal of Thermal Science, 44*(4), 367-373.

Murthy, V. S R , Jena, A. K , Gupta, K. P and Murty, G. S. (2003). *Structure and Properties of Engineering Materials.* New Delhi: Tata McGraw-Hill Publishing Company Limited.

Nait-Ali, B., Haberko, K., Vesteghem, H., Absi, J., and Smith, D. S. (2007). Preparation and Thermal Conductivity Characterization of Highly Porous Ceramics Comparison between Experimental Results: Analytical

Calculations and Numerical Simulations. *Journal of European Ceramic Society, 27. 1345-1350*.

Nath, S. K., Kumar, S., and Kumar, R. (2014). Effect of Mechanical Activation on Cordierite Synthesis Through Solid-state Sintering Method. *Building Materials Science, 37*(6), 1221-1226.

Nawi, A. M., and Badarulzaman, N.A. (2015). Effect of Plaster of Paris Water and Sintering Temperatures on Physical Properties of Pottery. *ScienceDirect, 26*, 752-755.

Nigerian Metallurgical Development Center. (2015). *NMDC Jos, Technical unit.* Federal Ministry of Mines and Steel Development, Abuja, Nigeria.

Novo, A.V., Bayon, J. R., Castro-Fresno, D., and Rodriguez-Hernandez, J. (2010). Review of Seasonal Heat Storage in Large Basins: Water Tanks and Gravel Water Pits. *Applied Energy, 87*(1), 390-397,.

Nwannenna, O., Apeh, F., Ogunro, A., and Fabiyi, M. (2014). Characterization of Ibamajo, Mowe and Nkwo-Alaike Fireclays for use as Refractory Materials in Foundry Industry. *Chemical and Process Engineering Research, 24*(1), 1-8.

Oaikhinan, E. P. (1999). Raw Material Development in Nigeria in the next Millennium. *Intercom, 46*(6), 10-14.

Obadinma, F. (2003). Development of Refractory Bricks for Heat Treatment Facilities. *Journal of Science and Technology Research, 2*(2), 13-17.

Odewale, I. O., Obika, B. M., and Tse, D. T. (2015). Production and Characterization of Aluminosilicate Refractory Brick Using Uwana Beach Silica Sand, Ekebedi and Unwana Clay. *British Journal of Applied Science & Technology, 5*(5), 461-471.

Odigi, M. I. (2000). Geochemical and Geotectonic Setting of Migmatitic Gneiss and Amphibolites in the Okene-Lokoja Area South Western Nigeria. *Journal of Mineral Geology, 38*, 81-89.

Olupot, W., Jonsson, S., and Byaruhanga, K. (2013). Effects of Sintering Process on Properties of Triaxial Electrical Porcelain from Ugandan Ceramic Minerals. *World Academy of Science, Engineering and Technology, 7*, 05-20.

Omowunmi, O. J. (2001). Characterization of some Nigerian Clays as Refractory Materials for Furnance Lining. *Nigerian Journal of Engineering Management, 2*(3), 1-4.

Onyeji, A. (2010). Analysis and Characterization of Nyikangbe Clay, Chanchaga LGA, Niger State. *Journal of Metallurgy and Materials Engineering, 5*(2), 55-62.

Osarenmwinda, J., and Abel, C.P. (2014). Performance Evaluation of Refractory Bricks Produced Local Sourced Clay Materials. *Journal of Applied Science, Environment and Management, 18*(2), 151-157.

Oumarou, N., and Kocaefe, Y. (2016). Investigation on the Refractory Bricks used for the Flue Wall of the Horizontal Anode Baking Ring Furnace. *Ceramics International, 42*(16), 18436-18442.

Pal, A. R., Bharati, S., Krisha, N. V. S., Das, G. C., and Pal, P. G. (2012). The Effects of Sintering Behaviour and Phase Transformations on Strength and Thermal Conductivity of Disposable Tundish Lining with Varying Compositions. *Ceramic International, 38*, 3383-3389.

Panda, A. K., Mishra, B. G., Mishra, D. K., and Singh. (2010). Effect of Sulphuric Acid Treatment on Physico-chemical Characteristic of Kaolin Clay. *Colloids Surfaces A, 363*, 98-104.

Papadopoulos, A. (2005). State of the Art in Thermal Insulation Materials and Aims for Future Developments. *Energy Building, 37*(1), 77-86.

Pappas Adlerburg, N. (2013). Unwrapping Past: A Chemical Analysis of Context Lacking Artifacts from Ptolemaic and Roman Egypt In Correlation with the Process of Mummication.http://chemwiki.ucdavis.edu/@api/deki/files /232/xrd. png?size= bestfit&width=32 3&height-237& revision=1.

Peretz, L., and Bradt, R. C. (1983). Linear Thermal Expansion Coefficients of Mullite-Matrix Alumino-Silicate Refractory Bodies. *Journal of the American Ceramic Society, 66*(12), 823-829.

Ptacek, P., Kubatova, D., Havlica, J., Brandstetr, J., Soukal, F., and Opravil, T. (2010). Isothermal Kinetic Analysis of the Thermal Decomposition of Kaolinite: The Thermogravimetric Study. *Thermochimica Acta, 501*(1-2), 24-29.

Rajput, R. K. (2004). *Material Science and Engineering* (Third ed.). Daryaganj Delhi, India: S.K Kataria & Sons.

Ramaswamy, S., and Raghavan, P. (2011). Signification of Impurity Mineral Identification in the Value Addition of Kaolin: A Case Study with Reference to an Acidic Kaolin from India. *Journal of Minerals and Materials Characterization and Engineering*, *10*(11), 1007.

Raut, A. N., Comez, C. P. (2016). Thermal and Mechanical Performance of Oil Palm Fiber Reinforced Mortar Utilizing Palm Oil Ash as Complementary Binder. *Construction and Building Materials, 126*, 476-483.

Raw Materials Research and Development Center. (2010). Guide to the Non-metallic Mineral Industrial Potential in Nigeria. 1-85. Nigeria: RMRDC Publication.

Reed, S. J. (1996). *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*. (First ed.). New York, USA: The Press Syndicate of the University of Cambridge.

Regner, K. T., Sellan, D. P., Su, Z. A., Amon, C. H., McGaugheg, A. J. H., and Malen, J.A. (2013). Broadband Phonon Mean Free Path Contributions to Thermal Conductivity Measured Using Frequency Domain Thermoreflectance. *Nature Communications*, *4*, 1640.

Rhodes, D. (1973). *Clays and Glazes for the Potters.* London, UK: Pitman Publisher.

Rice, P. M. (2015). *Pottery Analysis: A Sourchbook* (Second ed.). London, UK: The University of Chicago Press Ltd.

Rosenberg, D., Ntelson, D., and Osheroff, D. D. (2000). Low Temperature. *Journal of Low Temperature Physics, 120*(3-4), 259-268.

Sadik, C., Albizane, A., and El Amrani, I. (2013). Production of Porous Firebrick from Mixtures of Clay and Recycled Refractory Waste with Expanded Perlite Addition. *Journal of Materials and Environmental Science, 4*(6), 981-986.

Sanjay, G., and Sugunan, S. (2007). Glucoamylase Immobilized on Montmorillonite: Influence of Nature of Binding on Surface Properties of Clay-Support and Activity of Enzyme. *Journal of Porous Materials, 14*(2), 127-136.

Sarge, S. M., Gmelin, E., Hohne, G. W., Cammenga, H. K., Hemminger, W., and Eysel, W. (1994). The Caloric Calibration of Scanning Calorimeters. *Therochimica Acta*, *247*(2), 129-168.

Sauer, T. J., Meek, D. W., Ochsner, T. E., Harris, A. R., and Horton, R. (2003). Errors in Heat Flux Measurement by Flux Plates of Contrasting Design and Thermal Conductivity. *Vadoze Zone Journal, 2*(4), 580-588.

Schacht, C. A. (1995). *Refractory Linings: Thermomechanical Design and Applications.* New York, USA: Marcel Dekker, Inc.

Schacht, C. A. (Ed.). (2004). *Refractories Handbook.* New York, USA: Marcel Dekker, Inc.

Schulle, W., and Schlegel, E. (1991). Fundamentals and Properties of Refractory Thermal Insulating Materials (High-temperature Insulating Materials): Ceramic Monographs-Handbook of Ceramics. *Supplement to Interceram, 40*(7), 1-12.

Sears, F. W., and Zemanisky, M. W. (1977). *University Physics* (Fourth ed.). Readings, Massachusetts, USA: Addison-Wesley Publishing Co.

Sheffield, G. S., and Schorr, J.R. (1991). Comparision of Thermal Diffusiivity and Thermal Conductivity Methods. *American Society Bulletin, 70*(1), 102-106.

Shimizu, T., Matsuura, K., Furue, H., and Matsuzak, K. (2013). Thermal Conductivity of High Porosity Alumina Refractory Bricks Made by a Slurry Gelation and Forming Method. *Journal of the European Ceramic Society, 33. 3429-3435*.

Sites, N. M. (2016).

Smally, D. (1985). U.S Patent No 4,525,665. *Washington, DC: U.S Patent and Trademark Office*.

Smith, W. F., and Hashemi, J. (2006). *Foundations of Materials Science and Engineering* (Fourth ed.). McGraw-Hill, Inc.

Solorzano, E., Reglero, J. A., Rodriquez-Perez, M. A., Lehmhus, D., Michmann, M., and De Saja. (2008). An Experimental Study on Thermal Conductivity of Aluminium Foams by Using the Transient Plane Source Method. *International Journal of Heat and Mass Transfer, 51*(25), 6259-6267.

Somiya, S. (2013). *Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties.* Academic Press.

Speyer, R. F. (1994). *Thermal Analysis of Materials.* Marcel Dekker Inc.

Stubna, I., Trnik, A., Podoba, R., Ondruska, J., and Vozar, L. (2014). The Influence of Thermal Expression and Mass Loss on the Young's Modulus of Ceramics during Firing. *International Journal of Thermophysics, 35*(9-10), 1879-1887.

Subrata, B. (2014). Refractories: A Comprehensive Report. *Transactions of the Indian Ceramic Society, 65*(2), 81-95.

Sujith, S.S., Kumar, S. A., Mangalaraja, R. V., Mohamed, A. P., and Ananthakumar, S. (2014). Porous to Dense $LaPO_4$ Sintered Ceramics for Advanced Refractories. *Ceramic International, 40*(9), 15121-15129.

Sutcu, M., Akkurt, S., Bayram, A., and Uluca. (2012). Production of Anorthite Refractory Insulating Firebrick from Mixtures of Clay and Recycled Paper Waste with Sawdust addition. *Ceramics International, 38*, 1033-1041.

Ten, J. G., Orts, M. J., Saburit, A., and Silva, G. (2010). Thermal conductivity of Traditional Ceramics. Part 1: Influence of Bulk Density and Firing Temperature. *Ceramics International*, *36*(6), 1951-1959.

Tikhonov, V. A., Arkhangelsky, I. V., Belyaev, S. S., and Matveev, A. T. (2009). Carbonization of Polymeric Nonwoven Materials. *Thermochimica Acta 486*, 66-70.

Titiladunayo, L. F., and Fapetu, O. P. (2011). Selection of Appropriate Clay for Furnace Lining in a Pyrolysis Process. *Journal of Emerging Trends in Engineering and Applied Sciences, 2*(6), 938-945.

Tiwari, N., Singh, S., Parihar, A. S., and Tripathi, D. N. (2013). Measurements and Analysis of Thermal Conductivity of Insulating Material. *International Journal of Application, 2*(7), 550-556.

Tonkov, E. Y., and Ponyatovsky, E. G. (2005). *Bismuth, in Phase Transformations of Elements under High Pressure.* Boca Raton, Florida, USA: CRC Press.

Turner, W. C., and Malloy, J. K. (1988.). *Thermal Insulation Handbook.* New York,: McGraw-Hill Book Company.

Tutic, E., Jovanovic, M., and Mujkanovic, A. (2016). Preparation of Mullite Ceramics from Bayer Electrofilter Fines and Low Kaolinite Clay. *Science of Sintering, 48*(2), 247-257.

Tuttle, R. B. (2012). *Foundry Engineering: The Metallurgy and Design of Castings.* CreateSpace.

Ugheoke, B. I., Mamat, O., and Ari-wahjoedi, B. (2013). Thermal Expansion Behavior, Phase Transitions and some Physico-mechanical Characteristics of Fired Doped Rich Husk Silica Refractory. *Journal of Advanced Ceramics, 2*(1), 79-86.

UNEP. (2006). Thermal Energy Equipment: Furnace and Refractories. *Energy Efficiency Guide for Asia: United Nations Environmental Programme*.

Vaculikova, L., Plevova, E., Vollova, S., and Koutnik, I. (2011). Characterization and Differentiation of Kaolinites from Selected Czech Deposits Using Infrared Spectroscopy and Differential Thermal Analysis. *Acta Geodynamic et Geomasteralia, 8*(1), 59-67.

Valaskova, M. (2015). Clays, Clay Minerals and Cordierite Ceramics: A Review. *Ceramics-Silikaty, 59*(4), 331-340.

Vasilos, T., and Kingery, W. D. (1954). Thermal Conductivity: XI, Conductivity of Some Refractory Carbides Nitrides. *Journal of the America Ceramic Society, 37*(9), 409-414.

Vishnevskii, I.I., Aselrod, E, I., Talyanskaya, N.D., Melentev, N.D., and Glushkova, D.B. (1975). The Thermal conductivity of Refractory Fiber Products. *Journal of Refractories and Industrial Ceramics, 16*, 408-413.

Wagner, W. (1975). Modern Industry Structure: Materials Process, Products and Careers. Library of Congress, American Technical Society.

Wesley, L. R. (2014). *Clays and Clay Minerals: Geological Origin, Mechanical Properties and Industrial Applications.* New York, USA: Nova Science Publishers, Inc.

Westman, A. (2007). The Thermal Expansion of Fireclay Bricks. *The Engineering Experiment Station, 1106*(1), 5-24.

Whitten, K.W., Davis, R.E., LarryPeck, M., and Stanley, G. G. (2014). *Chemistry* (Tenth ed.). Mary Finch.

Wolfe, D. H. (1988). *Introduction to College Chemistry* (Second ed.). McGraw-Hill, Inc.

Yakubu, S. O., and Abdulrahim, M. Y. (2015). Suitability of Birinin Gwari and Maraban Rido Clays as Refractory Materials. *American Journal of Engineering Research, 3*(3), 8-15.

Yan, W., Li, N., Li, Y., Liu, G., Han, B., and Xu, J. (2011). Effect of Particle Size on Microstructure and Strength by Porous Spinel Ceramics Prepared by Pore-forming in Situ Technique. *Bulletin of Materials Science, 34*(5), 1109-1112.

Zhang, H., Li, M., Fang, W., Dan, D., Li, Z., and Tao, W. (2014). A Numerical Study on the Theoretical Accuracy of Film Thermal Conductivity using Transient Plane Source Method. *Applied Thermal Engineering, 72. 62-69.*

Zhang, J. S., Yang, J. Y., Zhu, W., Xiao, C. J., Zhang, H., and Peng, J. Y. (2010). Research Advancers in the Measurement for the Thermal Conductivity of Thin Solid Films. *Material Review, 24. 105-107.*

Zhou,Y., Zhang, X., and Hu, M. (2015). Quantitatively Analyzing Phonon Spectral Contribution of Thermal Conductivity Based on NonequilibriumMolecular Dynamics Simulations. 1. From Space Fourier Transform. *Physical Review B, 92*(19), 195204.