

**CHARACTERIZATION AND MODIFICATION OF CLAYS FROM SELECTED
SITES IN MURANG'A AND NYERI COUNTIES KENYA FOR ASSESSING
REFRACTORY APPLICATIONS**

LOMERTWALA MNANGAT HASSAN

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DECLARATION

This Thesis is my original work and has not been presented for a degree in any other university or any other award.

Signature 

Date ...18/11/2020

Name: LOMERTWALA M. HASSAN

Reg. No. AS401/5142/2017

SUPERVISORS

We confirm that the student under our supervision carried out the work reported in this Thesis.


Signature 

Date 18/11/2020

Dr. Peter W. Njoroge (Ph.D.)

Department of Physical and Biological Sciences

Murang'a University of Technology

Signature 

Date 18/11/2020

Dr. Sylvia A. Opiyo (Ph.D.)

Department of Physical and Biological Sciences

Murang'a University of Technology

Signature 

Date 18/11/2020

Dr. Brian M. Ptoton (Ph.D.)

Department of Chemistry

Kisii University

DEDICATION

This research study is dedicated to my parents Mr. Yusuf Sengo and Mrs. Zainabu Sengo. This thesis is also dedicated to my brothers and sisters.

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ABBREVIATIONS AND ACRONYMS

AAS – Atomic Absorption Spectroscopy

API – American Petroleum Institute

BD-Bulk Density

CEC- Cation Exchange Capacity

CCS- Cold Crushing Strength

IR- Infra-Red

KNBS- Kenya National Bureau of Statistics

LOI- Loss On Ignition

PA-Apparent Porosity

PVC-Polyvinyl Chloride

TSR-Thermal Shock Resistance

SPSS- Statistical Package for Social Sciences

XRD- X-Ray Diffraction

ABSTRACT

Clay is a stony or earthy mineral aggregate composed of fine-grained minerals, which are plastic at appropriate water content and hardens up when fired. Uses of clay include manufacture of cement, ceramics, bricks, drilling clays, paints, fillers in paper industry and for refractory production. Refractories are materials that withstand high temperatures and are comprised of oxides with high melting temperature such as Al_2O_3 , SiO_2 , ZrO , Cr_2O_3 , and MgO . Clay deposits have been reported in Kenya in areas such as Kano plains, Mwea, Chavakali and Ilesi. Murang'a and Nyeri counties are also two of such areas with clay deposits. Despite the abundance of clay, Kenya still imports both clay products and raw clays for industrial use, clay worth 3 billion Kenya shillings was imported in 2013. This project intended to determine the elemental and mineralogical composition of clays from Murang'a and Nyeri counties to determine whether they can be used for refractory applications. Furthermore, the study determined the effect of acid washing and addition of CaO on the refractory properties of clays. Most of Kenyan clays are used for ceramics and cement manufacture. The samples of clays used in this study were obtained from Githima ($0^\circ 46' 40''$ S and $37^\circ 6' 31''$ E), Kimathi Sampling site ($0^\circ 40' 0''$ S and $37^\circ 10' 28''$ E) and Ithanje Sampling site ($0^\circ 36' 30''$ S and $37^\circ 6' 46''$ E). Elemental and mineralogical composition were determined using Atomic Absorption Spectrophotometer and X-Ray Diffraction respectively. The clays were leached using hydrochloric and oxalic acid separately at concentration of 0.0, 0.1, 0.25, 0.5, 1, and 2 M. The clay was blended with 0, 1, 2, 5, 15 and 30 % of CaO . The raw, acid-treated and clays containing CaO were moulded into blocks (8x4x4 cm) followed by air and oven drying then fired in a furnace at 1000°C . The fired bricks were tested for apparent porosity, bulk density, linear shrinkage, and refractoriness. The major components of the raw clays when expressed as oxides were 40.80-55.40 % SiO_2 , 16.27-30.33 % Al_2O_3 , 0.62-7.62 % TiO_2 , 0.84-2.65 % K_2O , 0.02-1.82% MgO . Elemental composition of the acid treated clays, in oxide form were in the ranges of 40.80-65.16 % SiO_2 , 7.16 -30.33 % Al_2O_3 , 0.33-7.62 % TiO_2 , 0.24-2.65 % K_2O , 0.01-1.82 % MgO . Refractory properties of the raw clays were in the ranges 26.31-31.33 % apparent porosity, 1.56-1.68 g/cm^3 bulk density, 1-3 % linear shrinkage, and 1609-1686 $^\circ\text{C}$ refractoriness. Refractory properties of the acid treated clays were in the ranges of 21.65-35.1 % apparent porosity, 1.32-1.76 g/cm^3 bulk density, 1-3.62 % linear shrinkage, and 1575-1686 $^\circ\text{C}$ refractoriness. Refractory properties of CaO added clays were in the ranges of 22.16-31.33 % apparent porosity, 1.56-2.8 g/cm^3 bulk density, 0.8-3.3 % linear shrinkage, and 1579-1686 $^\circ\text{C}$ refractoriness. These clays meet certain aspects of refractory materials. However, they require enhancement through acid treatment and CaO addition to meet requirements for refractory application. Proper utilization of findings from this study would improve Kenya's industrialization and economic diversification.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Clay is a stony or earthy mineral aggregate composed of fine-grained minerals, which are plastic at appropriate water content and hardens up when fired (Deer *et al.*, 1992; Murray, 2004). Clays have variable chemical composition that largely depends on parent rock from which they originated and the physical and chemical changes in the environment where they are found (Eze *et al.*, 2012). Clay minerals consisting of hydrous silicates of aluminum and or magnesium with significant amounts of iron, nickel, chromium and other cations in their crystalline structure (Rodrigues, 2003). The silicates exist in form of thin sheets and therefore belong to the family of phyllosilicates (Bakker, 1993).

Clay mineral groups have unique properties that promote their industrial applications. Some of these minerals include palygorskite-sepiolite, smectites, illites, and kaolins (Murray, 2004). Kaolins have been extensively used in ceramic, paper and paint industries and many other plants such as oil refinery as a cracking catalyst and water treatment plants (Belver *et al.*, 2002; Caulcante *et al.*, 2005; Salawudeen, 2007; Vaga, 2007). Smectites have high cation exchange capacity, swelling ability, and high surface area. These properties make smectites to be used largely in various branches of industry. Smectites have found applications in agriculture (for seed coating and as carrier material for fertilizers, pesticides), drilling fluids, paints, papermaking, pharmaceuticals, cosmetics, plastics, adhesives, bonding foundry sands, iron ore pelletizing, decolorization and ceramics (Christidis, 1998). Palygorskite-sepiolite

minerals have industrial applications such as making oil-well drilling fluids that help in removing rock cuttings from the hole, making adhesives in the production of corrugated paper, and making liquid suspension fertilizers among others (Wachira, 2014).

Refractory bricks are ceramic materials that withstand high temperatures while maintaining their structural properties as well as resist destructive influences such as abrasion, rapid changes in temperature and pressure, corrosion by slags and fluxes, erosion by molten slags (Chlup *et al.*, 2006). They are also expected to withstand load at service conditions, resist contamination of the material with which it comes into contact, maintain sufficient dimensional stability at high temperature after or during repeated thermal cycling, and conserve heat (Chukwudu, 2008). Refractories are comprised of naturally occurring oxides with high melting temperature such as Al_2O_3 , SiO_2 , ZrO , Cr_2O_3 , MgO (Jock *et al.*, 2013; Owoeye and Olufunke, 2016).

Refractory materials are utilized in huge quantities in the chemical industries, metallurgical industries, glassmaking, ceramics industries, petrochemical industries, steam boilers, and hot stoves where they are molded into various types of shapes used to line the interiors of heat exchangers, furnaces, glass melting devices, kilns, and other devices that process materials at very high temperatures (Sani *et al.*, 2011; Jock *et al.*, 2013). The high strengths shown by primary chemical bonds in refractory materials make them to be chemically inert with high thermal stability (Gustave and Christian, 2017). Most common clay based refractories are the fireclay materials, which are made using aluminosilicate mineral-kaolinite ($\text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4$)

plus other impurities such as iron oxides and alkalis. The alumina (Al_2O_3) content ranges from 25 to 45 % (Chukwudu, 2008). Classification of refractories is based on alumina-to-silica ratio (Al_2O_3) and on the impurity content. Refractory bricks are crucial and play a vital role in industrial development of any nation. However, despite Kenya having abundant sources of raw material and suitable technology advancement, it spends approximately 3 billion Kenya Shillings annually to import refractories mostly from India and China for its manufacturing sector (KIPPRA, 2013). According to Central Bureau of Statistics report of 2014, Kenya has a potential of cutting down refractories imports to 20 % and increase exports by 15 % in 10 years (Makokha, 2015). The main consumers of refractory materials are cement and extractive industries, which are on the rise (Makokha, 2015). In general, the demand of refractory bricks is bound to increase tremendously owing to the increased growth of Kenya's manufacturing sector (World Bank, 2013). The boom in the building and construction industry in Kenya has led to increased volume of utilization of cement, leading to high number of new cement manufacturing industries and consequently increasing demand on refractory bricks.

Presence of built-in impurities in clays has a huge impact on the utility of clays. Most clays contain high levels of iron oxides, acid treatment help improve properties and applications of clay (Belver *et al.*, 2002; Xavier *et al.*, 2014). Reduction of iron content is of great importance for the usability of clay in many of its applications especially where purity requirements are specifically high, in order to make high quality ceramic products clay with low iron content, preferably less than 1% is desirable (Karoki, 2009).

Approaches of minimizing iron in clays include froth floatation, gravity and magnetic separation, reductive roasting, size separation by hydrocyclone, selective flocculation and acid treatment/leaching (Barrios *et al.*, 2001; Ajayi and Adefila, 2012; Ajemba, 2016; Muriithi *et al.*, 2012; Wachira, 2014; Oswago, 2016;). Chemical treatment methods such as acid activation improve surface and catalytic properties of clay by inducing changes in crystal structures of aluminosilicate minerals because of the dissolution of ions and/or structural rearrangement (Coma *et al.*, 1990; Barrios *et al.*, 2001; Belver *et al.*, 2002; Xavier *et al.*, 2014).

Hydrochloric acid is preferentially used because of the ease of titration of its slurry, ease of removal of the iron matrix and titanium oxide insolubility, which is present in many types of clay (Al-Zahrani and Majid, 2009). However, other inorganic acids used include sulfuric acid (Muriithi *et al.*, 2012; Wachira, 2014; Ajemba, 2016). Among the organic acids, Oxalic acid has shown the best efficiency in kaolin whitening with iron removals of 45-80% having been obtained (Calderon *et al.*, 2005). Wachira (2014) studied iron removal from clays by acid treatment and reported that plasticity property of the acid treated clays was restored by base treatment of the acid treated samples. In a study by Oswago (2016) on elemental and mineralogical composition of raw and acid washed clays from Kano plains, the findings of this study revealed that iron oxides levels were reduced by acid treatment and the second finding was that acid treatment alters mineralogical composition of clays and results to clay minerals interconversion (Oswago, 2016).

Effects of additives such as MgO, CaO, B₂O₃, TiO₂, V₂O₅, V₂O₃ have been studied with the aim of improving the properties and the applications of clays (Skels *et al.*, 2011; Vodora *et al.*, 2014; Sarmad *et al.*, 2018). Effect of silicon carbide addition on Kankara clay revealed that apparent porosity and linear shrinkage of the refractory bricks made from the blend decreased with Silicon carbide addition. However, thermal shock resistance and cold crushing strength of the refractory brick increased with Silicon carbide addition (Hassan, 2005).

Various studies have been carried out in Kenya on clays, Murriithi *et al.*, (2012) assessed chemical and mineral composition of Mwea clays for their potential as a source of aluminium and aluminium compounds. Wachira (2014) studied iron removal from clays by acid treatment and reversal of the clay's plasticity. Ujeneza (2014) studied on optimization of acid activation and bleaching performance of local bentonite clay (Bentonite clays obtained from Thika and Athi River). The results obtained established that acid activation is an effective method of improving adsorption performance of Athi River bentonite clay (Ujeneza, 2014). Ombaka *et al.*, (2015) assessed the potential of Tharaka Nithi clays for industrial and agricultural applications, the results obtained from this study established that clays from Tharaka Nithi could be used in agriculture as agro mineral additive to enhance soil fertility for crop production, a fluxing agent in ceramics and glass applications. Lusambili (2016) investigated physico-chemical characteristics of raw clays used in pottery in Ileshi, Kakamega county Kenya (Lusambili, 2016). Kipsanai *et al.*, (2017) studied Kenyan anthill clays for refractory materials production. Makokha *et al.*, (2018) studied on characterization of Kenyan ceramics for

firebrick incinerator linings production (Clays were obtained from Eburru and Mukurwe-ini), results obtained revealed that Mukurwe-ini clays had good structural properties at high temperatures and were comparable with commercial products in the market and were therefore suitable for manufacture of incinerator linings.

Murang'a and Nyeri Counties are located in the central part of Kenya. The clays in the region are currently, used in ceramic industries and cement industries for cement manufacture by Simba cement Company. There is no data available to show whether the clays from the selected sites from the two counties can be used for refractory applications. There is dearth of information regarding their elemental and mineralogical composition. The chemical and mineralogical composition of the clays explains properties, which in turn determine industrial and other economic uses. Clay industries in Kenya import clay products and raw clays for industrial use yet Kenya has clay deposits in areas such as Kano plains, Mwea, Tharaka Nithi, and Chavakali. Murang'a and Nyeri Counties are also two of such areas. However, there is no information on whether acid activation and use of additive can improve refractory properties of clays from selected sites in Murang'a and Nyeri Counties.

1.2 Statement of the Problem

Industrial applications of clays is determined by their chemical composition which dictates it's resistant to a changing process or insulating properties. Clays for refractories are mostly comprised of naturally occurring oxides with high melting temperature such as Al_2O_3 , SiO_2 , ZrO , Cr_2O_3 , and MgO . There is no data available on mineralogical, elemental composition and refractory properties of clays from the selected sites in Murang'a and Nyeri Counties

which is currently used by ceramic industries to make tiles, pots, and building bricks and used for cement manufacture only. There is no documented information if the clays from those sites can be exploited for refractory applications. To fully exploit the potential of the clays for industrial application, there is a need to characterize the clays. Acid treatment and use of additives such as calcium oxide and magnesium oxide have been reported to enhance quality and upgrade properties of clay for industrial application. However, there is no information on whether refractory properties of clays from selected sites in Murang'a and Nyeri Counties can be enhanced through acid treatment and use of additives.

1.3 Objectives of the Study

1.3.1 General Objectives

To characterize and modify clays from selected sites in Murang'a and Nyeri Counties for assessing refractory applications.

1.3.2 Specific Objectives

- i) To determine elemental and mineralogical composition of clays from selected sites in Murang'a and Nyeri counties.
- ii) To determine the effect of acid (HCl and oxalic acid) treatment on elemental composition of clays from selected sites in Murang'a and Nyeri counties.
- iii) To determine effect of acid treatment on refractory properties of clays from selected sites in Murang'a and Nyeri Counties.
- iv) To determine effect of addition of calcium oxide (CaO) on refractory properties of clays from selected sites in Murang'a and Nyeri Counties.

v) To determine effects of acid treatment and calcium oxide (CaO) addition on refractory properties of clays from selected sites in Murang'a and Nyeri counties.

1.4 Hypotheses of the Study

- i) The elemental and mineralogical composition of clays from Murang'a and Nyeri counties vary with site of collection.
- ii) The elemental composition of clays from selected sites in Murang'a and Nyeri counties are affected by acid-treatment.
- iii) Refractory properties of clays from selected sites in Murang'a and Nyeri counties are affected by acid-treatment.
- iv) Refractory properties of clays from selected sites in Murang'a and Nyeri counties are affected by addition of calcium oxide (CaO).
- v) Refractory properties of clays from selected sites in Murang'a and Nyeri counties are affected by acid treatment and calcium oxide (CaO) addition.

1.5 Justification of the Study

The main consumers of the refractories are cement and extractive industries, which are on the rise. In general, the demand of refractory firebricks is bound to increase tremendously owing to the increased growth of Kenya's manufacturing sector (World Bank, 2013). The boom in the building and construction industry in Kenya has led to increased volume of utilization of cement, leading to high number of new cement manufacturing factories and consequently increasing demand on firebricks.

Kenya's metal, process industries and small industries that use kilns where elevated temperatures are used have considerable needs for refractories. Currently, the country imports clay related products including refractories despite the presence of vast deposits of clay in the country. There is evidence suggesting that demand for high quality clay is high. Kenya spent

over 340 million Kenyan shillings between 2007 and 2011 to import about 15,000 tonnes of clays and clay related minerals (KNBS, 2012). A study of the elemental and mineralogical composition of Kenya's clays would reveal their composition and properties hence their suitability for use as raw materials in clay product industries.

Most Kenyan clays are unsuitable for ceramic and many industrial applications because they have intolerable high levels of impurities such as iron oxides. Therefore, beneficiation of these locally available raw materials in view of upgrading their properties to that of standard commercial clay of various type is of paramount importance. There is need to explore different methods of improving and upgrading the materials through acid-treatment and use of additives. In order to determine the profitability of utilizing clays for any application, it is important to examine the microstructural morphology, determine the mineralogical composition and analyze the various phases in clay deposits. However, since most of the clays in the country (Kenya) have not been characterized they are deemed unsuitable in terms of meeting requisite requirements for industrial applications. The ever-increasing demand of clays for industrial application calls for modification (use of additives, acid-treatment) of the locally sourced clays to meet the technological and local consumption. Modification of clays will aid enhance clay properties to meet the requisite requirements for industrial applications hence compete excellently with imported ones.

Clays from selected sites in Murang'a and Nyeri Counties have not been harnessed and developed to their full potential and there are no reports regarding their elemental and

mineralogical composition. Characterization of Murang'a and Nyeri Counties clays would reveal their elemental and mineralogical composition, which will help in deciding their suitability for various industrial applications. Successful modification of the clays for refractory applications will serve as source of refractory materials to the local industries and this may trigger establishment of small industries for making refractory bricks, which will create jobs for the locals and help improve the economy. This is in line with Kenya's development agenda "Vision 2030" and government Big 4 Agenda.

1.6 Significance of the Study

This study ensured that clay minerals in the region are documented and their suitability for various applications including making refractory bricks and this will contribute to the clay literature in the country. The characterization revealed what else the clays are suitable for and possibly spur diversification of products produced. Successful modification of the clays will help bridge the importation cost since refractory materials will be sourced locally. Possibility of small industry establishment to process valuable resource (Clay) into finished products such as refractory bricks, high quality ceramics. This will promote job creation to the locals hence will help improve the economy. The results will also inform policy issues.

1.7 Scope and Limitation

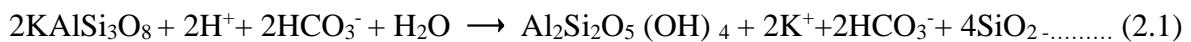
The study only considered two acids hydrochloric and oxalic acid at concentration of 0.0 M, 0.1 M, 0.25 M, 0.5 M, 1 M and 2 M. Refractory properties studied were limited to apparent porosity, bulk density, linear shrinkage and refractoriness. The percentages of calcium oxide (CaO) additive used were limited to 0 %, 1 %, 2 %, 5 %, 15 % and 30 % of CaO. This study considered only oxides in the clays that affect refractory properties of clays such as SiO₂, Al₂O₃, MgO, CaO, TiO₂, Fe₂O₃.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Geology and Formation of Clays

Clay deposits are widespread all over the world and have been used by nearly all civilizations for varied purposes. According to Geologists, the earth was formed from cooling of the molten materials into separate layers; the surface layer formed from the cooling of the molten material is made of igneous rock composed chiefly of silica and alumina (Nigrosh, 1986). Clays are formed mainly as a result of weathering process, which changes rocks composition at or near the earth's surface (McGregory and Plummer, 1985). Weathering being both a mechanical and chemical process, it ensures that particles sizes of the rocks are reduced mechanically via mechanical weathering and change in chemical composition to new chemical combinations via chemical weathering (Eze *et al.*, 2012). Clay minerals formation from hydrothermal weathering of feldspar involves displacement of cations from feldspar by the hydrogen ion (H^+) from carbonic acid as shown below in equation 2.1 (McGregory and Plummer, 1985).



Feldspar

Kaolinite

Vegetation cover significantly affects the composition of clay minerals on the surface of soil horizons especially for magnesium-based chlorites such as amesite $(Mg,Fe)_4Al_4Si_2O_{10}(OH)_8$ and chamosite $(Fe,Mg)_3Fe_3AlSiO_3O_{10}(OH)_8$ (Velde and Barre, 2V010).

2.2 Properties of Clay

Clays contain particles that are fine-grained which yield large surface area that are chemically surface-active and physically sorptive. Most of the clay minerals have a negative charge as a result of substitution of Si^{4+} by cations of lower valence hence causing an increase in chemical

reactivity in ion exchange and chemical combination. These are some of the attributes that add to clay properties, which contributes to its technical utilization (Murray, 2004).

2.2.1 Shrinkage

Shrinkage refers to volume loss in clay due to firing or drying hence there is drying and firing shrinkage. Shrinkage caused by drying depends on clay minerals character, water content and particle size of the clay constituent. Plastic clays have high drying shrinkage, which results in cracking and warping of clay materials. Sandy clays have a low drying shrinkage resulting to the production of the weak porous body. Shrinkage due to firing depends largely on crystalline phase changes that occur during firing, clay minerals dehydration characteristics and volatile materials available in clay (Mc Graw-Hill, 1992).

2.2.2 Strength

Strength refers to the capacity to cope up with stress of forming without collapsing. Strength property of clay is affected by clay body chemistry, particle size differentiation and thixotropy (Zakin, 2001). There are two types of strengths of clay i.e green and dry strengths of clay. Green strength of clay is measured as traverse breaking strength that prevails while plasticizing water is present. Green strength of clays increases continuously with water addition to a maximum. However, green strength varies with the type of minerals and the composition of exchangeable cations in the clays. Montmorillonites clays green strengths are the greatest whereas illites, chlorites and kaolinites green strengths are slightly lower (Murray, 1979). Dry strength of clay is usually measured as a traverse breaking strength of a test piece after drying

for long (usually at 105 °C) to expel all pore and adsorbed water. Dry strength is greatly reduced by the presence of non-clay mineral composition in clay. However, it increases with decrease in particle size and presence of organic materials in clays. Dry strength is generally higher when Na is the adsorbed cation (Murray, 1979). Dry strength relies on the proportion of fine particles present such that the larger the proportion, the greater the dry strength. Some of the other factors that have an impact on dry strength of clays are the extent of drying, the method of forming the ware and the degree of colloidal fraction (McGraw-Hill, 1992).

2.2.3 Colour

The natural colour of clays may be grey, black, tan, white, brown, green or red. The brown, grey, yellow or red clays have iron in different forms (Glen *et al.*, 2002). Clays containing iron turn brown, red or tan when fired. White or light coloured clays are considered to have low quantities of iron (Glen *et al.*, 2002). Colour interferes with aesthetic value of clay, which is critical in most structural clay products. The colour of clay products is affected by a number of factors including the state of division of iron minerals, the firing temperature, the degree of vitrification, the oxidation state of iron, the firing temperature, lime, magnesia in the clay material, and composition of fire gases used during the burning process. The red burning clays contain 5 % and more Fe₂O₃, white burning clays contain less than 1 % Fe₂O₃ while buff burning clays contain Fe₂O₃ in the ranges of 1-5 % (McGraw-Hill, 1992).

2.2.4 Vitrification

This refers essentially to formation of glass, which ensue because of the gradual fusion of the more easily melted constituents, which makes up the glass bonding material in the fired product. The temperature range over which fusion of a material occurs is referred as vitrification range. Clay minerals having short vitrification ranges include montmorillonites, illites, and chlorites whereas kaolinites have long vitrification ranges. Impurities such as calcite and feldspar, which act as fluxes, have a tendency of lowering vitrification. The extent of vitrification relies on the duration of firing and temperature attained (Mc Graw-Hill, 1992).

2.2.5 Plasticity

This is the ability of a material to be deformed under stress without rupturing and to retain the shape produced under stress (Murray, 1979). Plasticity enables the material to undergo permanent deformation in any direction without rupture under a stress beyond that of elastic yielding. A number of factors affect plasticity of clays including particle size and shape, type of clay mineral, soluble salts, adsorbed ions, the quantities and type of non-clay minerals, and organic matter content (McGraw-Hill, 1992). However, plasticity of clays is enhanced by the presence of fine particles in clays (Zakin, 2001). Plasticity of clays depends on;

- i) The quantity of Water of plasticity- the requisite amount of water needed to develop optimum plasticity or the range of water content in which plasticity is demonstrated.
- ii) The amount of penetration of an object into the formed plastic mass of clay, which is frequently done by use of a needle or some special plunger.

- iii) The amount of stress required to deform the clay and the maximum deformation the clay will undergo before rupture at different moisture contents and with varying degrees of stress application (Murray, 2004).

2.2.6 Firing

Firing property of clay is fusion and hardening of clays on heating at elevated temperatures. At a temperature, range of 100-105 °C loss of pore waters and shrinkage occurs with attendant dimensional changes. Sulphides oxidation occurs in temperatures of between 400-500 °C, and loss of hydroxyl waters from clay minerals occur between 500-900 °C. Modification of clay mineral structure but not destruction of the structure is associated with the loss of hydroxyl water. Shrinkage in the two-layer minerals (Kaolinites and halloysites) is usually observed but not in the three-layer minerals (Murray, 1979). In the temperature range of 800-950 °C, clay minerals structure is lost and major firing shrinkage develops. At temperatures above 900 °C, new crystalline phases develop in all the clay minerals except those containing large amounts of Fe, alkalis, alkaline earths, for which case fusion may result after the loss of structure without any intervening crystalline phase (Mc Graw-Hill, 1992).

2.3 Clay minerals

Clay minerals formation depends on either of the following processes; metamorphism process, weathering process and diagenesis (Grimshaw, 1971; Weaver and Pollard, 1973). Clay minerals are found either as pure concentrates in nature or as mixture of clay minerals. Smectites, illites, palygorskite-sepiolite and kaolin groups are among the four major clay minerals groups having differing physical structures, crystal orientation, chemical and mineral composition and more often occur as pure concentrates of the mineral (Hans and

Andrei, 2004). Some of the other mineral groups such as vermiculates and chlorites occur alongside non-clay minerals such as shales (Murray, 2004).

2.3.1 Kaolin Group

Clay minerals under kaolin group include; halloysite, dickite, kaolinite and nacrite. Kaolin group minerals all have a 1:1 lattice whereby silica layer and alumina layer are stacked in alternating fashion. Kaolinite formation occurs under acidic conditions through hydrothermal changes of feldspar or weathering processes (Miranda and Coles, 2003). The chemical composition of Kaolinite is $Al_2Si_2O_5(OH)_4$ (Belver *et al.*, 2002; Vaga, 2007). High molecular stability associated with Kaolinite causes its low isomorphous substitution and low surface area, consequently, this results to it having lower cation exchange capacity (CEC) compared to montmorillonite and this plays a role in it having low cohesion, plasticity, swelling, and shrinkage (Murray, 1999; Aroke *et al.*, 2013). Some of kaolin group industrial applications include; ceramic manufacture, papermaking, rubber making, cosmetics and base pigment, plastic and pharmaceutical products, catalyst for auto-emission control devices and for petroleum cracking (Olaremu, 2015).

Manufacture of fertilizer prills requires incorporation of Kaolin as an anti-cracking agent, Kaolin is also used as a carrier for pesticides, Kaolin is used to provide alumina without iron in white cement manufacture, and in glass fiber production as a low alkali and low iron source of alumina. Kaolin stained with ferric results to the deep red or red color observed in ceramic products after firing in a sufficiently oxidizing condition. Clays stained with iron find

applications in colored clay products but are unsuitable for high-quality ceramics applications. In most high-value applications of kaolin, brightness is an important property (Chandrasekhar *et al.*, 2006). Ordinarily, kaolin occurs alongside other minerals considered as impurities such as shales, feldspar, quartz, mica, and clay stones.

2.3.2 The Smectites Group

Smectites refers to a group of Ca, Mg, Na, Li and Fe aluminum silicates. Some of smectites minerals include saponite, nontronite, montmorillonites, hectorite, and beidellite. Smectites have 2:1 lattice having three layers consisting of a central alumina octahedron sheet with two silica tetrahedron sheets (Moore and Reynolds, 1989). High surface area, high cation exchange and swelling ability associated with smectites promote their extensive applications in various branches of industry. Smectites are chiefly sourced from bentonite rocks. Sodium montmorillonite usually has higher swelling capacity compared to bentonite having calcium as the major mineral component (Murray and Elzea, 1994). Smectites are used in the industry for synthesis of foundry binders (Grim and Guven, 1978). Smectites are also used in making drilling mud, sealants in ponds, absorbents for insecticides and pesticides to protect crops and humans, cosmetic and fertilizer industries to effect uniform spread of chemical, vegetable and animal oils, bleaching clays to decolourise mineral (Murray, 2004). Smectites is used as well to make strong heat-resistant composites utilized in food wrappings, packaging and automobiles (Beall, 1996).

2.3.3 The Palygorskite-Sepiolite Groups

Palygorskite-sepiolite groups are hydrated magnesium aluminum silicates having an elongated shape. Since palygorskite-sepiolite have large surface area hence they are commonly referred as fuller's earth or sorptive clays (Murray, 2004). Although palygorskite and sepiolite are similar palygorskite contains higher aluminium content whereas sepiolite contains higher magnesium content. Palygorskite-sepiolite differs regarding crystal structures with palygorskite having a chain-like crystalline structure made of inverted ribbons of silica tetrahedron connected by aluminium and magnesium octahedral to form a 2:1 layer structure. Palygorskite-sepiolite minerals are utilized in adhesives making for corrugated paper production, synthesis of liquid suspension fertilizers, used in synthesis of oil well drilling fluids that aids in rock cuttings removal from the hole (Wachira, 2014).

2.4 Clay Structure and Composition

Clays are composed of hydrous aluminosilicates that have phyllosilicate structure with grain size of less than 4 μm . Having three of the four oxygens in SiO_4 tetrahedral linked to form sheets of a pseudo hexagonal network is the basis of a phyllosilicate structure (Mason, 1968). Clay minerals consist of sheet structures that are made up of fine-grained alumina octahedron layers and silica-tetrahedral layers (Figures 2.1 and 2.2)

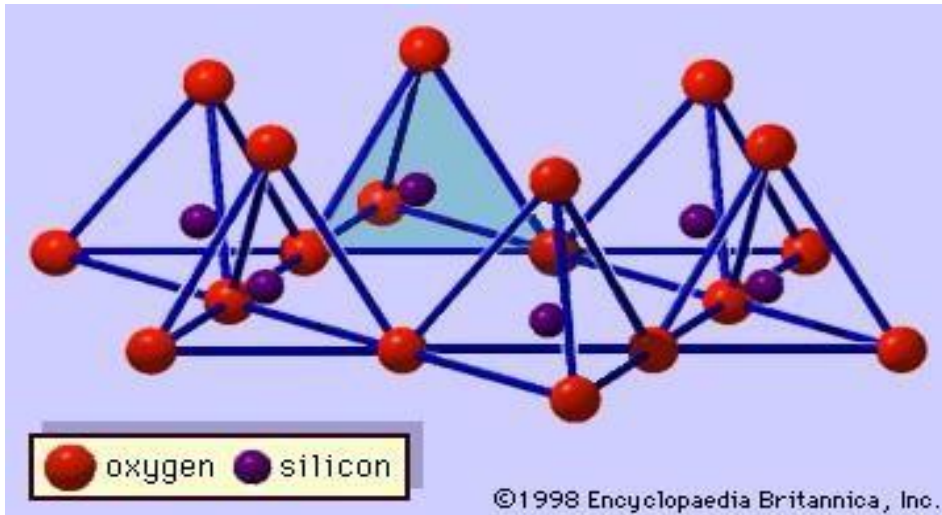


Figure 2. 1 Showing Silica tetrahedral layers (Encyclopaedia Britannica, 1998)

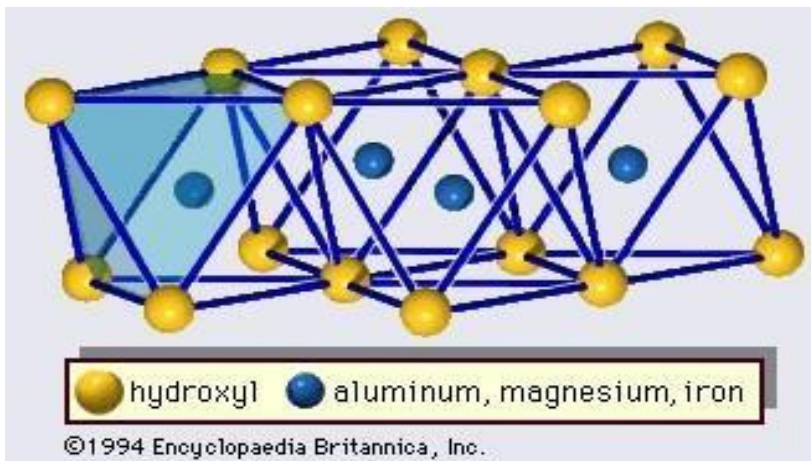


Figure 2. 2 Showing alumina octahedron layer, (Encyclopaedia Britannica, 1994)

The slippery property of clays results from the plate-shaped grains that slide over each other's surface (Zakin, 2001). Different combinations of the alumina-octahedron and silica-tetrahedron layers in each clay mineral forms the basis of their identification and differentiation by X-ray diffraction.

2.5 Uses of Clay

Differences in clay minerals applications result from their varying silica tetrahedral and alumina octahedral sheets, which results in differences in chemical and physical properties. Some of factors that determine clay properties and uses include plasticity, PH, surface chemistry, area, and charge, green, fired and dry strength, Particle size, shape and distribution, refractoriness, fired color, color brightness and color (Murray, 2006). Chemical inertness, white or near white color, softness and non-abrasion, low viscosity and ability to flow and disperse readily, good covering and binding power are some of the additional properties that qualify Kaolin for industrial applications.

2.5.1 Use of Clay for Ceramics

Ceramics are inorganic, heat-resistant, non-metallic solids comprising of metallic and non-metallic elements. Despite having different types of ceramics, they are generally hard, but brittle and corrosion-resistant. They can withstand high temperatures hence can serve as a good insulator. Some of these properties have contributed to their widespread application in modern life (Barsoum and Michael, 1996). The thin layers of water between the tiny flat plates of clay play a crucial role in holding the tiny plates together and lubricates the plates thus allowing the plates to slide past one another. This permits clay to be easily molded into various shapes. High temperatures expel water and allow bond formation between plates, holding them together and promoting hard solid formation. Bone ash has shown ability to form strong bonds when added to clay; this makes ceramics difficult to break. White ceramics are made from white clays, primarily Kaolin whereas the commonly utilized clay for making roof tiles

and flowerpots are usually stained with iron-oxides (red-orange) (Ball, 1997). Ceramic products such as sanitary ware, white ware and tiles are made using clay.

2.5.2 Use of Clay in Paper Industry

In paper industry, clay is used for paper coating and as a paper filler. When used as a filler, clay helps improve paper opacity, smoothness, and replaces some of the costly pulp fibers.

When clay is used as a coating, it helps impart brightness, opacity, smoothness, improves printing quality of the paper and give it a gloss finish (Murray, 2004).

2.5.3 Use of Clay in Paints

Paint refers to a fluid system in which pigments are suspended (Grim, 1962). Clays find applications in both oil and water based paints where it helps extend the titanium oxide opacifying pigment, regulates viscosity to prevent pigment from settling during storage, provides thixotropy crucial for secure applications of paint without sagging or running after application, promotes film strength, aid in tint retention and helps improve gloss (Murray, 2004)

2.5.4 Use of Clay in Plastic and Rubber Industries

In plastic and rubber industries, kaolin clay mineral is used as a functional filler and as an extender. Use of a calcined metal-kaolin as insulator in PVC wire helps improve electrical resistivity of the wire coating (Sekutowski, 1992).

2.5.6 Use of Clay in Inks

The mainly used clay minerals in printing inks is kaolins which is used to improve adhesion, limit ink penetration into paper, improve color intensity, control rheology and act as an extender of the polymer present in the ink (Murray, 2004).

2.5.7 Use of Clay as Cracking Catalyst

Zeolites and Aluminium silicates used commonly as catalysts in petroleum refining are made using kaolins (Murray, 1994). Petroleum cracking catalyst is manufactured using halloysites (Murray, 2004).

2.5.8 Clay as a Chemical Raw Material

Air-floated kaolin is used to synthesize fiberglass. Kaolin finds applications in cement plants as it serves as a source of alumina and silica, strengthen cement and give it a white color. Kaolin serves as a raw material in zeolites production; zeolites being essential ingredients in detergents (Murray, 2006).

2.5.9 Use of Clay as Drilling Mud

Sodium montmorillonite high swelling ability qualifies it as a key ingredient in freshwater drilling muds worldwide. A small amount of the high swelling clay is required to contribute the high viscosity, thixotropic fluid with low filter cake permeability necessary to comply with the American Petroleum Institute (API) drilling fluid specifications (Murray, 2004).

2.5.10 Use of Clay in Pencil Leads

Kaolin clay is added to graphite to make pencil leads. Kaolin clay fine particle and plasticity play a crucial role of extruding the graphite-kaolin mixtures (Murray, 1961).

2.5.11 Use of Clays in Suspensions and Diluents

Kaolins are used as suspending agents in pharmaceuticals, cosmetics, enamels and medicines.

Some pills use kaolin as a diluents and a binder in pressing pills (Murray, 2004).

2.5.12 Use of Clays in Fertilizers, Desiccants and Insecticides

Kaolin clay is utilized in agriculture as a carrier for fertilizers and insecticides. Kaolin when mixed with highly deliquescent materials is used as a desiccant to promote flow (Murray, 2004)

2.5.13 Use of Clay in Roofing Granules and Polishing Compounds

White kaolin is used to synthesis roofing granules by calcining its coarse granular particles.

Fine particle calcined kaolin of 3 μm is as well utilized in polishing compounds for silver, automobiles, copper, brass and other metals (Murray, 2004).

2.6 Refractory Materials

Refractory materials are inorganic materials composed of mixture of high melting temperatures oxides. They do this without change in composition, undue deformation or failure (Kudrin, 1985). Chemical inertness and thermal shock resistance are required for refractory materials (Atanda and Imasogei, 2009). Having these properties make refractory materials suitable in the production of high-temperature devices and equipment like furnaces, incinerators, crucibles, insulation and other metallurgical furnaces linings where high resistant to high temperature is required (Markov and Krivandin, 2004). These devices and equipment play a crucial role in the processing of raw materials to finished goods in industries. About 80 % of the total refractory materials are used in industries dealing with metals for constructing kilns, furnaces, reactor vessels and boilers. The remaining 20 % are used in industries dealing with non-metals such as glass, hardware and cement industries (Hassan and Adewara, 1994).

Abu - Hamattech *et al.*, (2003) studied on improvement of chemical composition and heat treatment of original materials made of kaolinite clay for manufacturing of refractory bricks, by adding Al_2O_3 to the original materials and then carrying out heat treatment to obtain satisfactory chamotte to manufacture refractory bricks. Abolarin *et al.*, (2004) studied on the applications of clays from Kuru, Barkin-ladi, Alkaleri, and Buachi (Nigeria) for refractory applications. The results obtained established the clays were suitable for refractory production because they had high thermal shock resistance (TSR), cold crushing strength (CCS), and bulk density (They had good refractory properties). Elnagar *et al.*, (2009) studied on manufacturing of refractory bricks from available materials in Egypt such as ceramic powder, bentonite and clay. The results showed that if increasing over 1.5 % of ceramic powder, bentonite and clay, the shrinkage, porosity and water absorption of refractory bricks decreased, while volumetric mass and strength upon compression increased. In 2012, Jordanian authors applied the manufacturing of chamotte refractory bricks from clay with refractory capacity of 1180 – 1450 °C (Fayyad *et al.*, 2012).

Atanda *et al.*, (2012) studied on the heat treatment of original materials made of clay and ceramic powder to manufacture refractory bricks. The results obtained from 20-30 % of ceramic powder and 70-80 % of clay met the physico-chemical and technical requirements to produce refractory bricks (Atanda *et al.*, 2012). Jock *et al.*, (2013) studied on the manufacturing of chamotte refractory bricks from clay, which were used in furnaces, incinerators and reactors. As a result, refractory bricks had a refractory capacity of 1600 °C and satisfied the physico-chemical criteria of refractory bricks. Osarenmwinda *et al.*, (2014) studied on the application of clay sources in Nigeria to produce chamotte refractory bricks for furnaces and stoves with the refractory capacity of bricks higher than 1600 °C and good insulation. Olufunke and Owoeye (2016) studied on the application of Abaji clays for

refractory production. The results obtained revealed that Abaji clay deposits met the standard requirements to be utilized as a refractory clay.

Bello *et al.*, (2016) studied on application of Ujogba clay for refractory production. The results obtained established that Ujogba clay meet the standard requirements to be used as refractory raw material. Kipsanai *et al.*, (2017) studied on the possibility of using Kenyan anthill clay, as a major raw material in the production of refractory linings. The results obtained established that anthill clay can serve as a substitute to the imported refractory raw material. Kipsanai (2018) studied on the application of Chavakali clay for refractory production. Results showed that Chavakali clay can be utilized as refractory raw material. Chikwelu *et al.*, (2018) studied on the applications of Mbaukwu clay (Nigeria). The results obtained established that Mbaukwu clay could be useful for manufacture of ceramics such as tableware, tiles and other ceramic wares production. Shuaib-Babata *et al.*, (2018) studied on the applications of clays from Kwara state (Nigeria) for refractory production. The results obtained revealed that Kwara state clays meet the standard requirements for refractory applications and could suitably offer an alternative source of refractory clays to the imported clays in some refractory applications. Clays from Kuru, Barkin-ladi, Alkaleri, and Bauchi locations of Nigeria were found to be suitable for refractory application because of their high thermal shock resistance, bulk density, cold crushing strength, and refractory properties (Abolarin *et al.*, 2004). However, there is no documented information if clays from selected sites in Murang'a and Nyeri counties can be exploited for refractory applications.

2.7 Effects of Acids on Clays

Iron exists in clays in two forms, it exists in form of hydrated oxides. Iron oxides are normally found adsorbed on the surface of clay particles where iron plays the role of a compensating cation pillar between the silicate layers (Stucki, 2006). In this role, iron affects significantly the cation-exchange capacity of the clay minerals and consequently their physico-chemical

properties. In the second form, iron exists in the crystal structure of clay minerals because of isomorphic substitution of cations in the tetrahedral and octahedral sites of the clay minerals. Structural and colloidal iron in clays notoriously affects colour of clays when they are fired. Confinement of iron in structural form and in low concentration is more often than not tolerable. Raw materials with high iron oxides concentration reduce whiteness of clay minerals, giving them a brown-yellow colouration and therefore limiting their use in high-grade ceramics applications (Calderon *et al.*, 2005). In colloidal form, physical methods are in most cases adequate in the reduction of hematite and goethite by magnetic separation. Removal of structural iron presents a difficult challenge, because the process is more often than not difficult and an arduous task (Stucki *et al.*, 1984).

Iron impurities in clay can be reduced using physical and chemical methods. Most chemical methods use leaching agents such as mineral or organic acids. Studies available in literature indicate that treating clays with acid dissolves impurities such as calcite and replaces the exchangeable cations with hydrogen ions. Acid treatment also opens the edges of the platelets and consequently their surface area and pore diameters increase (Valenzuela and Souza, 2011). Chlorination use in extractive metallurgy is gaining popularity in impurities removal mainly of titanium and iron from kaolin clay minerals. This method has produced exceptional results (Ruiz and Gonzalez, 2006). Chemical treatment of clays does alter their natural properties. Treatment of clay with acids, for instance will adversely affect its plasticity. This property is of utmost importance in ceramic making and structural engineering. It is a well-established fact that at high acid-clay ratios, the layered crystal structure of most clay minerals is destroyed and a non-crystalline silica phase is created (Jones and Kooli, 1996).

Iron stained clays can be cleaned significantly by acids, however it is noteworthy that it is difficult to remove the structural iron, ferrous or ferric (Fysh *et al.*, 1983). However, studies undertaken in past works have found that structural iron is removable from clays by using

thermochemical treatment methods (Eze *et al.*, 2012). Acid treatment for instance, normally proceeds by removing cations adsorbed on the surfaces, those in the interlamella layer and then the structural cations. The dissolution of cations in clay minerals depends on acid concentration, composition of the clay minerals, temperature, acid-clay ratio and time of treatment. Acid treatment of clay minerals results in increase of surface area of the clay particles due to destruction of the clay mineral structure and its eventual conversion to free form of SiO₂ (Kang and Giselle, 2001; Ruiz and Gonzalez, 2006).

Chemical treatment methods such as acid activation help improve catalytic and surface properties of fibrous clays (Belver *et al.*, 2002) by inducing changes in the crystal structure of aluminosilicate minerals as a result of rearrangement of the structure or dissolution of structural ions (Coma *et al.*, 1990). An acid action on clays is enhanced, especially when it has an anion of comparable size and geometry as a clay component and this allows even weak acids to dissolve clay under some conditions. Studies have suggested that the concentration of acid and temperature of leaching affect significantly the percentage of iron and rate of leaching from clays (Chiarizia and Horwitz, 1991; Muriithi *et al.*, 2012; Wachira, 2014). Hydrochloric acid is preferred because of the ease of titration of its slurry, ease with which iron matrix is removed and titanium oxide insolubility, which occurs more often in clays (Al-Zahrani and Majid, 2009). Studies have suggested that oxalic acid has the best efficiency in Iron removal especially from kaolin clay, with iron removals of 45-80 % having been obtained (Calderon *et al.*, 2005). Barrios *et al.*, (2001) studied on improvement of structure and texture of saponite clay by acid treatment. The results obtained established that acid attack progressively destroyed saponite

and caused partial dissolution of the octahedral Mg (II) cations. However, surface area was doubled with respect to that of natural saponite. Panda *et al.*, (2010) reported that leaching and disintegration of clay sheet occurs on treatment with different concentration of acid. The results obtained further established that as acid strength increased metallic oxides content such as MgO, CaO, Al₂O₃, ZnO, and TiO₂ decreased progressively. However, this causes an increase in Silica SiO₂ content. The results obtained from XRD assessment revealed that pure clay crystalline structure was significantly affected with acid treatment since the structure of the clay treated at high acid strength is amorphous (Panda *et al.*, 2010). Boudriche *et al.*, (2011) reported that the structure and morphology of attapulgite clay are not affected at low concentration of hydrochloric (HCl) (≤ 1 M). However, at high concentration of hydrochloric (HCl) (≥ 3 M), Al and Mg cations from the octahedral and tetrahedral sheets are dissolved resulting to destruction of the chemical structure leading to formation of amorphous silica, which maintains the original fibrous morphology.

Eze *et al.*, (2012) studied on improvement of physicochemical properties of kaolin clay by acid treatment and reported that iron oxides and other metallic compounds are removed from the surface of kaolin clay by acid treatment (hydrochloric acid). Xavier *et al.*, (2014) studied on improvement of physicochemical characteristics of palygorskite clay by acid treatment (hydrochloric acid) and documented that surface area of the sample treated with hydrochloric (HCl) acid at concentration of 6 mol/L was significantly increased. Ajemba *et al.*, (2016) reported that surface area and adsorption capacity of the treated samples increased to

approximately four times that of natural sample. The results further revealed that bentonite clay could be modified by acid activation to improve its application as sorbent in the vegetable oil industry. Amari *et al.*, (2018) studied effect of acid activation on clay minerals. The results obtained established that deep interlayer modification occurs even at low concentration of H₂SO₄. Results from spectroscopy analysis by Infra-red (IR), X-Ray Diffraction (XRD) and chemical analysis showed that the chemical analysis showed that the chemical structure of clay from a partially crystallized state to amorphous silica at a great extent of acid activation (H₂SO₄). It is not known whether clays from selected sites in Murang'a and Nyeri counties are affected by acid-treatment.

2.8 Effect of Additives on Clays

Additives such as MgO and CaO affects significantly the refractory properties of clays. Magnesium oxide high melting point (2800 °C) and excellent resistance to attack by iron oxides, alkalis and high lime content of flakes formed at the working temperature of steel melting furnaces makes them an attractive choice for use as an additive (Smith and Fahrenholtz, 2008). Increasing the percentage of additives (MgO) increases the apparent porosity and decreases the bulk density (Sarmad *et al.*, 2018). Calcium oxide occurs in nature as a relatively pure limestone (CaCO₃). The successful application of this highly refractory CaO material with a melting point (about 2600 °C) would bring about an economical solution of the shortage of other raw materials that may have better refractory properties. An advantage of CaO addition is a small irreversible contraction of the fired body (Vodova *et al.*, 2014).

Hassan *et al.*, (2014) reported that based on the percentage Al₂O₃ content of both the clay samples with sawdust and rice husk additives, and they are not very good candidate materials for the production of refractory bricks. Ameh *et al.* (2018) studied potential of rice husk and Luffa sponge as an additive to Nkpologu clay for industrial applications, the results showed that the bricks have good refractory properties. Therefore, the bricks are suitable for insulating refractories, making linings of ovens, kilns, heating furnaces and ladles.

It is not known whether use of additives can enhance refractory properties of clays from selected sites in Murang'a and Nyeri counties.

2.9 Methods of Analysis

2.9.1 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption spectroscopy applies absorption spectrometry to determine the quantity of analyte present in a sample. Normally standards whose concentration are known are required to establish relation between concentration and absorbance, this therefore depends on Beer-Lambert law to establish the relationship as shown in equation 2.2;

$$T = \frac{I}{I_0} = 10^{-\alpha l} \dots\dots\dots (2.2)$$

(Where T is Transmittance, α is Absorption Coefficient, L is Path Length).

The advantages of using this method is that it is free from radiation and spectral interferences, and this is brought about by the fact that every element (metal) has its characteristic absorption wavelength. However, depending on different environmental matrices, Information like dissolved metals, total metals, total recoverable metals, and suspended metals can easily be obtained (Mendham *et al.*, 2000).

2.9.1.1 Atomic Absorption Instrumentation

For a sample constituents to be analyzed it must be atomized first. Electrothermal, flames and hydride generation atomizers are some of the most commonly used atomizers for atomization of the sample constituents. An element specific line radiation source is used to irradiate the atoms and monochromator is used to filter the element specific radiation from any other radiation emitted. Air/acetylene or nitrous oxide/acetylene flame are the commonly used source of energy necessary for free atom production (Nielsen, 2010). Nebulizer converts sample solution into fine aerosols, which are transferred to spray chamber. In the spray chamber the finest aerosol droplets ($< 10 \mu\text{m}$) are mixed with the flame gases, approximately 1-2 % of the aspirated sample solution reaches the flame. On top of the spray chamber is a burner head that produces a flame that is laterally long (usually 5–10 cm) and only a few millimeters deep. The radiation beam passes through this flame at its longest axis, and the gas flow-rates may be adjusted to produce the highest concentration of free atoms. The burner height may also be adjusted, so that the radiation beam passes through the zone of highest atom cloud density in the flame, resulting in the highest sensitivity (Gary, 2004).

A schematic diagram of an AAS instrument is shown in figure 2.3.

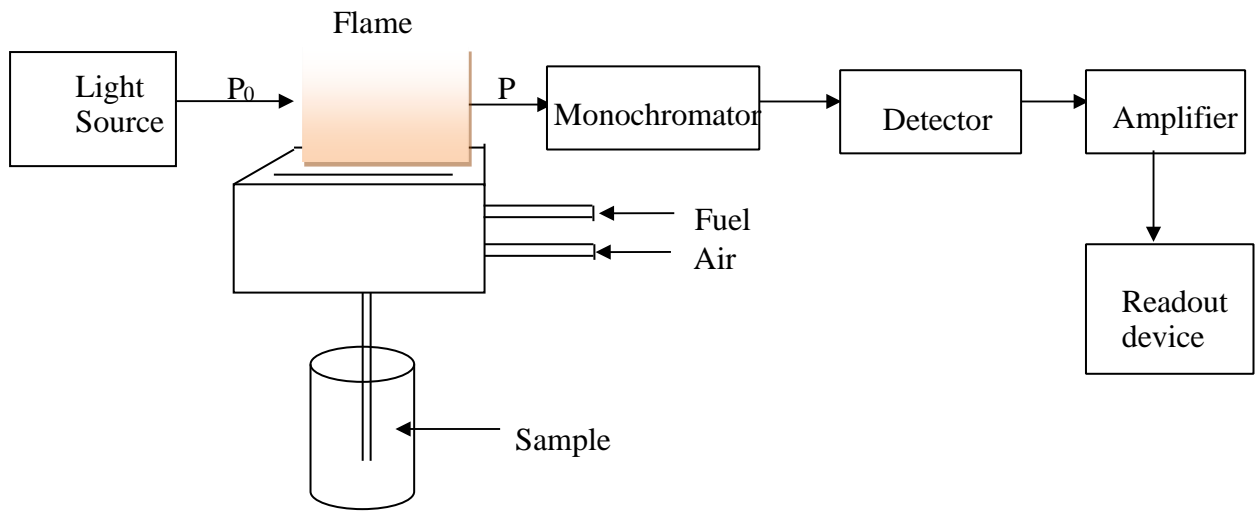


Figure 2. 3 Block diagram of a flame atomic absorption spectrometer (Skoog et al., 2008)

2.9.2 X-Ray Diffraction (XRD)

XRD analysis involves the use of X-rays of a known wavelength to radiate sample for crystal structure identification. Wave nature of X-rays causes their diffraction by the lattice of the crystal, this gives a characteristic pattern of the peak at different angles and of different intensity. This is expressed by Bragg equation (Myers, 2002), as shown in the relation below.

$$2d \sin \theta = n\lambda \dots \dots \dots (2.3)$$

(Where *d* is the spacing between diffracting planes, *λ* is the wavelength of the beam, *θ* is the incident angle, *n* is an integral, which is a multiple of the wavelengths for the phases of *n*th number of beams that strikes the layers of atoms in a mineral). Every mineral has a set of unique *d* spacing. Therefore, the X - ray detector moves around the sample and measures the intensity of these peaks and the position of these peaks (diffraction angle *2 θ*). XRD measurement is achieved by comparing of *d* spacing obtained with standard referencing pattern (Moore and Reynolds, 1997). By confirming from a handbook of mineral diffraction

patterns, the sample can be easily identified (Jones and Childers, 1993). X-rays intensity is measured on the Y-axis, and increasing values of the 2θ are shown on the X-axis. The height of the peaks (intensity) depends upon the number of crystallites present in the sample diffracting the X-Rays, thus more finely ground sample will give higher but narrower peaks than the same coarsely ground sample. For the area under the graph measuring crystallinity, it gives the same result in each case whether the sample is finely or coarsely ground (Moore and Reynolds, 1997).

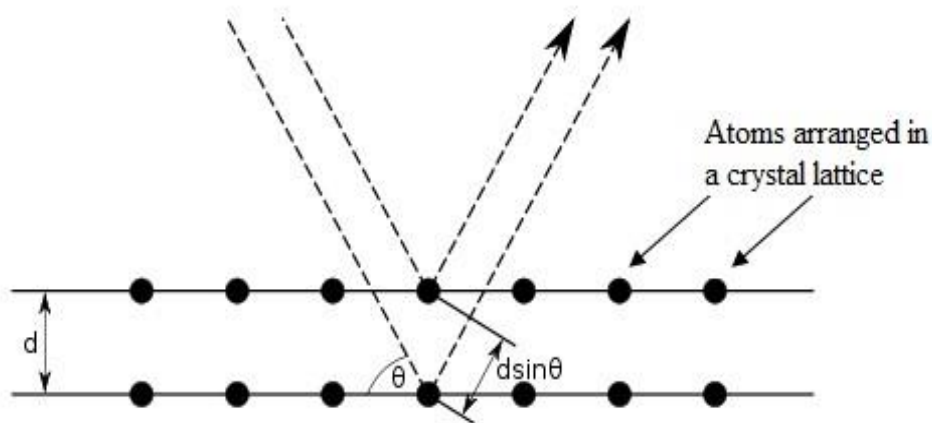


Figure 2. 4: Shows scattering off of two beams of X-Rays (Source; Harris and White, 2007)

Bragg diffraction occurs when two beams of X-rays with identical wavelength and phase approach a crystalline solid and are scattered off by two different atoms within it (Myers, 2002). The lower beam traverses an extra length of $2d \sin \theta$. Constructive interference occurs when this length is equal to an integral multiple of the wavelength of the radiation (Myers, 2002). Copper metal X-ray is one of the most

commonly used X-rays , with a wavelength of 1.54056×10^{-10} m. Copper is commonly used because of its high thermal conductivity and it can be cooled easily, which produces strong K_{α} and K_{β} lines (Jeruzalmi, 2006). The K_{β} line is sometimes suppressed with a thin ($\sim 10\text{-}\mu\text{m}$) nickel foil. Simple and cheap variety of sealed X-ray tube has a stationary anode (the Crookes tube) and produces ~ 2 kW of X-ray radiation. The more expensive variety has a rotating-anode type source that produces ~ 14 kW of X-ray radiation (Jeruzalmi, 2006).

Plate 2.1 below shows the basic components of the D2 phaser X-Ray Diffractometer used at Geology and Mines department. The D2 Phaser is the most compact and fastest, all-in-one crystalline phase analysis tool available. The instrument is low power operation XRD where the X-ray tube has a long life.

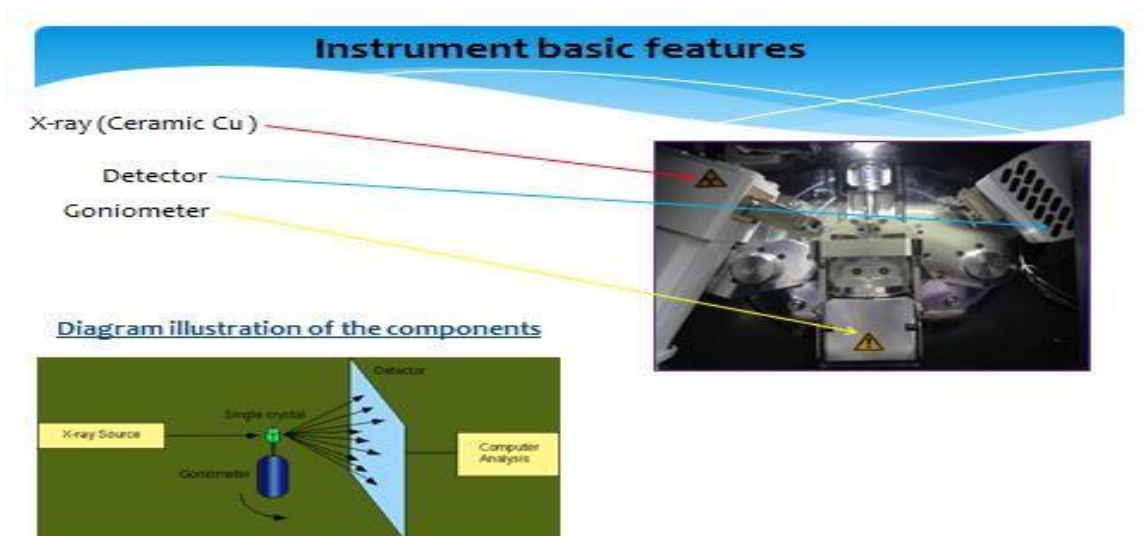


Plate 2.1: Showings some components of the D2 phaser diffractometer

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Research Design

Purposive non-probability sampling design was used to select sampling sites. Samples were obtained from sites whose clays are currently used by commercial enterprises and the locals for commercial purposes.

3.2 Study Area

Clays used in this study were obtained from selected sites in Murang'a and Nyeri Counties located in the former Central province, Kenya which lies in the coordinates Githima sampling site ($0^{\circ} 46' 40''$ S and $37^{\circ} 6' 31''$ E), Kimathi Sampling site ($0^{\circ} 40' 0''$ S and $37^{\circ} 10' 28''$ E) and Ithanje Sampling site ($0^{\circ} 36' 30''$ S and $37^{\circ} 6' 46''$ E)



Plate 3.1 Githima sampling site ($0^{\circ} 46' 40''$ S and $37^{\circ} 6' 31''$ E) **Plate 3.2:** Kimathi Sampling site ($0^{\circ} 40' 0''$ S and $37^{\circ} 10' 28''$ E)



Plate 3.3: Ithanje Sampling site ($0^{\circ}36'30''S$ and $37^{\circ}6'46''E$)

3.3 Sampling

The clay samples were collected at two depths that is 0.5 and 1.0 meter. In each site, the clay samples were obtained from three (3) sampling points at each sampling site that were at least 100 meters apart. From each sampling point/depth, 10 kg samples were collected and packed in new cleaned plastic buckets, which were then covered with their lids (Christian, 2005).

3.4 Sample Preparation and Analysis

Characteristic samples for each sampling site were placed in glass beakers and dried in an oven at a set temperature of $105^{\circ}C$ for three (3) hours, and then allowed to cool in a desiccator. The dried samples were crushed and ground into powder fit for use in XRD instrument and acid digestion (Norton, 1974; Richerson, 1992; Wachira, 2014; Oswago, 2016).

3.4.1 Sample Preparation for Atomic Absorption Spectroscopy (AAS) Analysis

Weighed 0.1 g of the characteristic sample for each site were placed in a 125-mL plastic beaker, 1.0 mL of aqua-regia were added then 3.0 mL of hydrofluoric acid were added and left to digest for 8 hours. 50 mL boric acid was added to allow further digestion for one hour.

This solution was topped to the 100 mL mark using distilled water. Samples were analyzed alongside the standards (Muriithi *et al.*, 2012; Mutembei *et al.*, 2013; Oswago, 2016).

3.4.2 Sample Analysis for X-Ray Diffraction (XRD)

XRD analysis was performed using a D2 Phaser diffractometer. The sample was placed on sample holder and tapped on the bench for proper sample packing to avoid peak shifts. A sharp razor blade was used to level the sample on the sample holder. The sample was then placed into the XRD machine for mineral analysis (Muriithi *et al.*, 2012; Wachira, 2014; Oswago, 2016).

3.4.3 Sample Preparation of the Modified Clay

Finely ground clay was blended and thoroughly mixed with calcium oxide (CaO) in the following proportions CaO/Clay; KA(30+70) %, KB(15+85) %, KC(5+95) %, KD (2+98) %, and KE (1+99) % (Sarmad *et al.*, 2018).

3.4.4 Leaching Clays with Acids

Weighed 1000 g of each sample was put in a bucket and 2000 mL of hydrochloric acid of different molarities was added to each clay sample and the reaction allowed to proceed for 24 hours. The same procedure was followed using oxalic acid. Each of the mixtures obtained was subjected to filtration and the residue washed using distilled water to remove any acid-matrix. Rinsed residues were oven dried then later cooled. The cooled samples were prepared as in 3.4.1 for AAS analysis (Eze *et al.*, 2012; Muriithi *et al.*, 2012; Xavier *et al.*, 2013; Wachira, 2014; Oswago, 2016).

3.5 Development of Refractory Bricks

Test refractory brick was shaped using wooden box mold having internal dimensions of 8.0 cm long, 4.0 cm wide, and 4.0 cm high. The test refractory brick was air-dried and then oven

dried at 105 °C for 12 hours to expel moisture from the test refractory brick. Dried test brick was fired in a furnace at a temperature of 1000 °C for six hours (Kipsanai, 2018).

3.6 Testing of the Brick Samples

3.6.1 Apparent Porosity

Apparent porosity refers to the ratio of pore volume to the bulk volume. Apparent porosity determines interconnected or open pores in a refractory. Apparent porosity was determined by volume of the liquid absorbed by the pores when refractory brick is immersed in water overnight. According Harbison-Walker, (2005), apparent porosity affect a refractory's capability of resisting penetration by slags, fluxes and metals, generally higher values of apparent porosity means greater insulating effect of the refractory material.

Test brick was dried in an oven set at 105 °C until it achieves a constant mass. The brick was cooled and weighed and weight recorded as W1. The test brick was completely soaked in water for 24 hours, it was then taken and wiped and the weight recorded as W2. Dimensions of the test brick was measured and used to calculate the volume of the test brick. Percent apparent porosity of the test brick after 24 hours soaking in water was given by the relation,

$$\text{Apparent porosity, } PA = \{(W2 - W1) / V * 100\}$$

Where: W1= Weight of dry test brick, W2= Weight of test brick after soaking in water overnight, V= is the volume of the test brick cm³ (Shaw, 1972; Kipsanai, 2018).

3.6.2 Bulk Density

Bulk density refers to the amount of the refractory material within a given volume. An increase in bulk density of a refractory material tends to increases its heat capacity, volume stability and

resistance to slag penetration. Bulk density is the ratio mass or weight to volume and it is expressed in pounds per cubic foot or kilograms per cubic meter (Aggarwal, 2001).

According to Berger, (2010) report, the simplest way of measuring Bulk Density for uniform rectangular refractory shapes was by dividing Dry Weight by Bulk Volume, which was calculated from measured dimensions. Apparent porosity, permeability and density measurements show whether a body is fully dense and whether therefore it could be expected to stand up to aggressive slag attack and penetration by process gases.

Air-dried test brick was oven dried at 105 °C, cooled and weighed. Dimensions of the test brick was obtained and used to calculate test brick volume, bulk density was obtained by calculation using the equation:

Bulk density, $BD = DW/V \text{ g/cm}^3$ (Ekwere, 2009).

Where, DW=Weight of the dry brick, V= Volume of the dry test brick (Kipsanai, 2018).

3.6.3 Firing Shrinkage Test

Linear shrinkage refers to the permanent change that refractory materials undergo on heating under a given conditions. Clay drying is usually accompanied by shrinkage, this because water film between clay particles is expelled during evaporation thus drawing the particles closer together to close up the interstices. The effect of this action is the shrinkage of the entire mass of clay.

To determine the fitness of a particular brick for service, it is often tested for shrinkage under temperature conditions equivalent to those, which it would receive in use. This was done by

first determining the length or volume of the brick by measurement and then subjecting it to a prolonged heating at the desired temperature. After the brick has cooled, it is again measured and the length, volume and shrinkage determined.

Measurement of dimensional changes that take place between dried sample brick at 105 °C and fired test brick at 1000 °C (Jock *et al.*, 2013) gives the firing shrinkage property of the test brick, this was calculated using the following relation:

$$\text{Firing shrinkage} = (LD-LF)/LD$$

Where LD= Length of test brick dried at 105 °C.

LF=Length of test brick fired at 1000 °C (Olufunke and Owoeye, 2016; Kipsanai, 2018)

3.6.4 Loss On Ignition (LOI)

Powdered samples two grams were put in crucibles and weighed. The crucible and its contents were fired at 1000 °C in a furnace for three hours, and then cooled in a desiccator before weighing.

Loss on Ignition was calculated and given as percentage using the relation below:

$$\text{Loss on ignition} = \{(W_1-W_2)/W_1\} 100$$

where W_1 = weight of the crucible + weight of the sample before firing and W_2 = weight of the crucible + weight of the sample after firing (Muriithi *et al.*, 2012; Wachira, 2014; Olufunke and Owoeye, 2016; Kipsanai, 2018).

3.7 Data Analysis

The results of this study were subjected to data analysis using SPSS software and the statistics used are descriptive statistics and cross-tabulation. ANOVA was used to compare effectiveness of the two acids (Hydrochloric acid and Oxalic acid).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

The elemental and mineralogical composition of raw clays from the three sampling sites were determined using AAS and XRD respectively. The findings of the elemental and mineralogical analysis are presented in tables and charts. The elemental composition is expressed as percentages of oxides of the respective elements for raw and acid-washed clays from the selected sites. For mineralogical composition, the XRD spectra of peaks of identified minerals are provided together with a summary of percentage composition. The findings of refractory properties of refractory bricks made using raw, acid-treated and additive added clays are presented in charts and tables.

4.2 The Elemental Composition of Raw Clays

4.2.1 Elemental composition of raw clay samples

Samples from the three sites were analyzed for the various elemental oxide composition. Elemental analysis was done in form of a full assay of the elemental oxides and was done using AAS and the results are presented in Table 4.1.

Table 4. 1 Elemental composition of clays from selected sites in Murang'a and Nyeri counties, Kenya

Composition	Githima	Kimathi	Ithanje	Standard for refractory bricks ³
SiO ₂	40.80±0.06	55.40±0.20	44.03±0.03	46-62
Al ₂ O ₃	16.27±0.05	22.40±0.02	30.33±0.15	25-44
CaO	0.56±0.04	0.67±0.05	0.53±0.03	0.1-2.0
MgO	0.02±0.01	1.82±0.02	0.02±0.01	-
K ₂ O	0.96±0.03	2.65±0.03	0.84±0.02	-
TiO ₂	7.62±0.03	0.62±0.03	3.49±0.03	-
MnO	0.08±0.02	0.06±0.02	0.23±0.15	-
Fe ₂ O ₃	20.53±0.15	3.90±0.02	10.40±0.20	0.5-2.4
LOI	11.47	12.2	10.84	8-18

- Not specified

Source: ³Standard for refractory bricks (Chester, 1973).

From Table 4.1 the major elements present in clay from the selected sites (Githima, Kimathi, and Ithanje) are silica (SiO₂), alumina (Al₂O₃), iron (III) oxide (Fe₂O₃). The other elements present in appreciable levels are potassium oxide (K₂O), titanium oxide (TiO₂), and magnesium oxide (MgO), while those present in trace amounts are calcium oxide (CaO) and manganese oxide (MnO). The clays were found to have percentage range composition of 40.80-55.40 % SiO₂, 16.27-30.33 % Al₂O₃, 0.53-0.67 % CaO, 0.02-1.82 % MgO, 0.84-2.65 % K₂O, 0.62-7.62 % TiO₂, 0.06-0.23 % MnO and 3.90-20.53 % Fe₂O₃.

Kimathi sample was found to be the highest silicate clay (55.40±0.20); its value fell within the standard range of 46-62 % SiO₂ that is required for the production of good refractory (Yami and Umaru, 2007). Ithanje sample SiO₂ value (44.03 %) was slightly lower than the standard

range of 46-62 % for refractory bricks production (Yami and Umaru, 2007). Githima sample also had silica value (40.80 %) that does not meet the requirement of 46-62 % SiO_2 for refractory bricks production (Yami and Umaru, 2007). The levels were in agreement with previous reports, which showed that levels of SiO_2 in clay samples varies with the site of collection (Muriithi *et al.*, 2012; Kipsanai, 2018).

Ithanje sample had the highest alumina (Al_2O_3) content of 30.33 % followed by the Kimathi sample which had 22.40 % Al_2O_3 . Githima sample had the least Al_2O_3 content of 16.27 %. These clays can be described as moderate alumina clays and show appreciable consistency within the value of 13-30 % Al_2O_3 for typical refractory materials (Aye *et al.*, 2008). alumina (Al_2O_3) levels of clays from Githima, Kimathi, and Ithanje are in agreement with previous reports, which showed that levels of alumina (Al_2O_3) clay samples vary with the site of collection (Muriithi *et al.*, 2012; Kipsanai, 2018). Alumina (Al_2O_3) content for the Ithanje sample fell within the standard range of 25-44 % Al_2O_3 for refractory bricks production (Chester, 1973). However, alumina content for Githima and Kimathi sample does not meet the standard requirement for refractory bricks manufacture.

The composition of calcium oxide (CaO) in the clay samples ranged between 0.53-0.67 % CaO. Kimathi sample had 0.67 % CaO, Githima sample had 0.56 % CaO while the Ithanje sample had 0.53 % CaO. Calcium oxide content of all the three clay samples meet the requirement of 0.1-2.0 % CaO for refractory bricks manufacture (Chester, 1973). Loss On Ignition (LOI) values in the clay samples ranged between 10.84-12.20 % LOI. Kimathi sample had the highest

LOI value of 12.20 % followed by the Githima sample with 11.47 % and the Ithanje sample had the least LOI value of 10.84 %. The three clay samples LOI values fell within the acceptable range of 8-18.0 % LOI for refractory bricks production (Chester, 1973).

The composition of iron oxides (Fe_2O_3) in the clay samples ranged between 3.90-20.53 % Fe_2O_3 . Githima sample had the highest Fe_2O_3 content of 20.53 % while the Ithanje sample had 10.40 % Fe_2O_3 and Kimathi had the least Fe_2O_3 content of 3.90 %. The clay samples' iron content does not fall within the standard range of 0.5-2.4 % Fe_2O_3 for refractory bricks (Chester, 1973).

From the results in Table 4.1, the levels of elemental oxides were in agreement with previous reports, which showed that levels of elemental oxides (SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 , MnO , K_2O) in the clay samples vary with the site of collection (Muriithi *et al.*, 2012; Kipsanai, 2018)

Results of the elemental composition of clays from the three selected sites (Table 4.1) shows that the elemental composition varies with the site of collection, therefore this justifies the hypothesis that the elemental composition of clays from selected sites in Murang'a and Nyeri Counties vary with the site of collection.

However, the levels of iron oxides (3.90, 10.40, and 20.53 %) were relatively higher; Therefore these clays cannot be utilized in refractory production and other clay products that require clays with less than 1% iron content in its current state (Karoki, 2009).

4.2.2 Mineralogical composition of raw clay samples from selected sites in Murang'a and Nyeri counties, Kenya.

The mineralogical composition of clay samples collected from Githima, Kimathi, and Ithanje in Murang'a and Nyeri counties was determined using XRD and the results were as presented in Figures 4.1, 4.2 & 4.3 and Table 4.2.

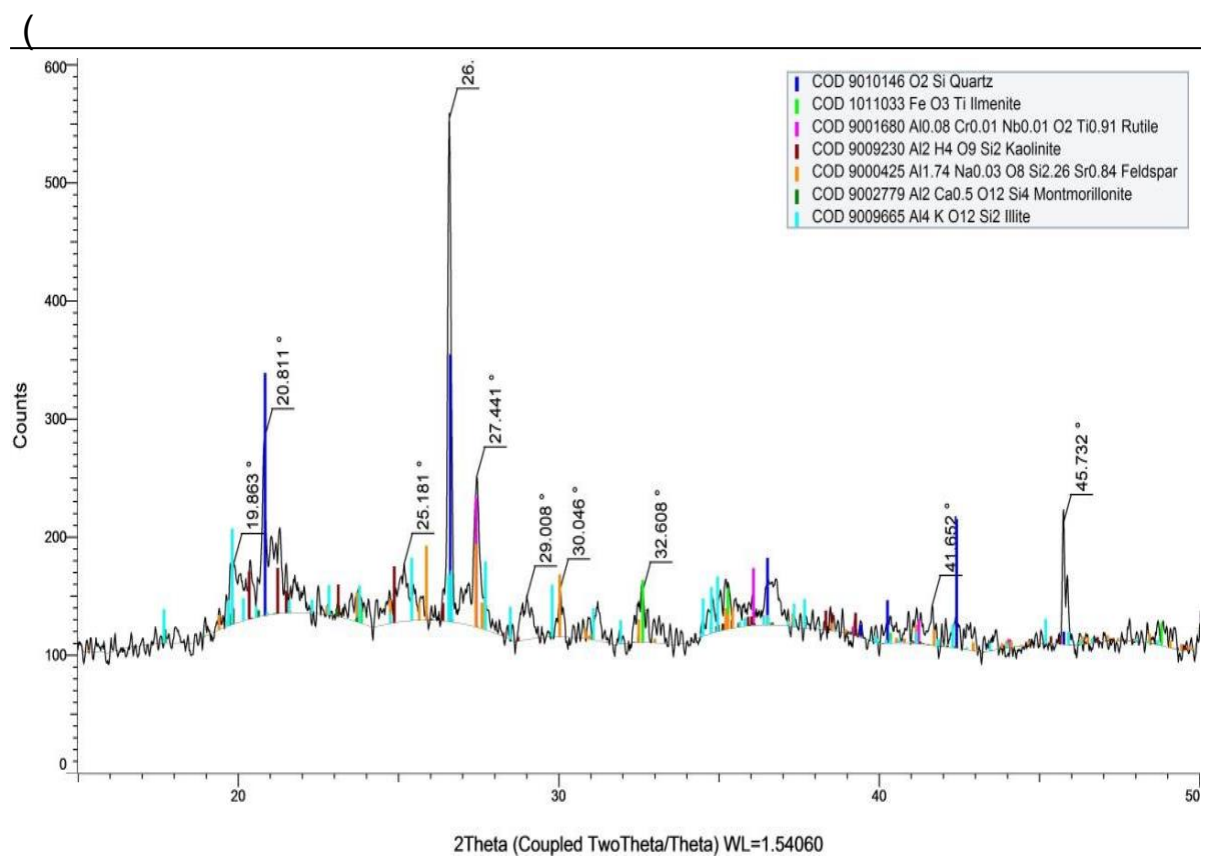


Figure 4. 1: XRD spectrum of Githima clay

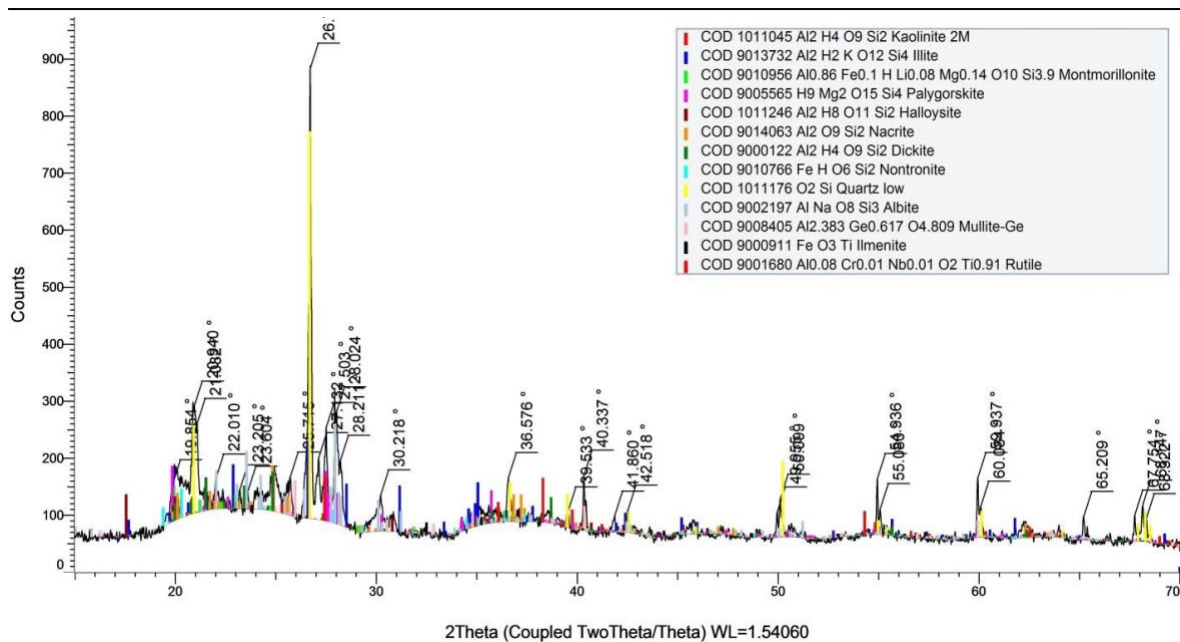


Figure 4. 2: XRD spectrum of Kimathi clay

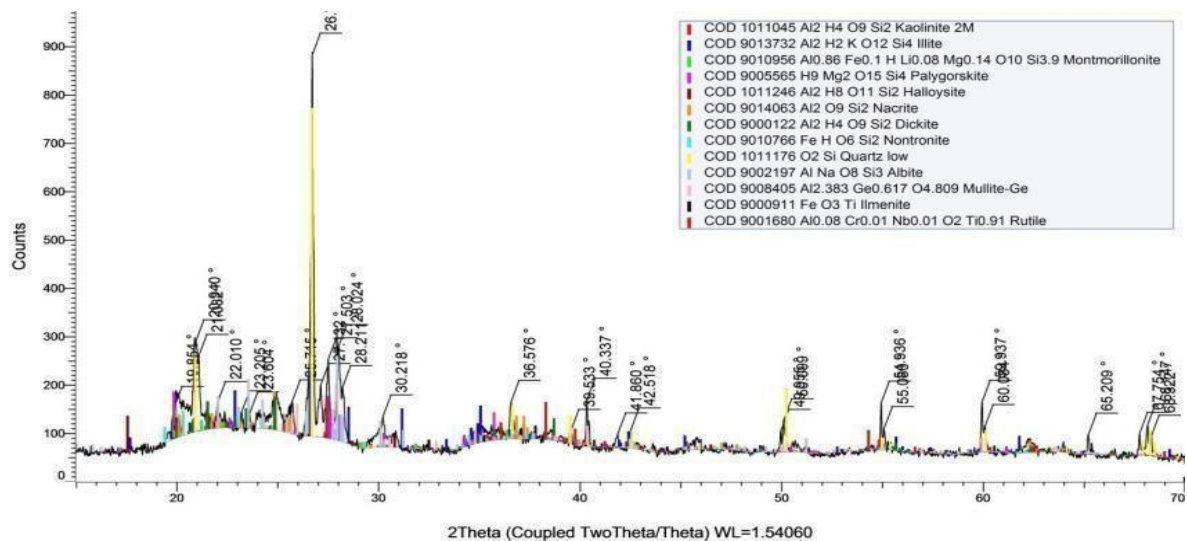


Figure 4. 3: XRD spectrum of Ithanje clay

Table 4. 2: Mineralogical composition of clays from Selected Sites in Murang'a and Nyeri counties, Kenya.

The mineralogical composition of the clay samples was determined using XRD. Table 4.2 provides the findings of mineralogical composition.

Mineral/Site	Githima	Kimathi	Ithanje
Kaolinite	15.0 %	8.3 %	17.0 %
Quartz	17.6 %	11.6 %	4.8 %
Illite	37.9 %	15 %	13.9 %
Nacrite	6.2 %	10.3 %	16.8 %
Dickite	5.8 %	7.4 %	16.4 %
Montmorillonite	2.8 %	4.8 %	3.7 %
Ilmenite	1.8 %	0.5 %	2.3 %

From Table 4.2 the major minerals in the clays samples were kaolinite and illite. The other clay minerals present in appreciable levels were dickite, nacrite, montmorillonite, halloysite, palygorskite, and sepiolite. Some of the minerals present in the clay samples were non-clay minerals including ilmenite, rutile, quartz, feldspar, and albite. The analysis showed that raw clay samples from Githima contained illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, quartz (SiO_2) , kaolinite $Al_2Si_2O_5(OH)_4$, feldspar $(KAlSi_3O_8)$, rutile (TiO_2) , montmorillonite $(Ca,Na)_{0.3}Al_2(Si, Al)_4O_{10}(OH)_{2.x}$, and ilmenite $(FeTiO_3)$. Kimathi clay sample contained kaolinite, illite, palygorskite $(Mg,Al)_2Si_4O_{10}(OH).4(H_2O)$, sepiolite $Mg_4Si_6O_{15}(OH)_{2.6}H_2O$, quartz, nacrite $Al_2Si_2O_5(OH)_4$, halloysite $Al_2Si_2O_5(OH)_4$, albite $Na(AlSi_3O_8)$, montmorillonite and dickite $Al_2(Si_2O_5(OH)_4)$. Ithanje clay sample contained kaolinite, dickite, illite, nacrite, albite, and montmorillonite. Kaolinite was responsible for imparting plasticity on clays thus allowing molding of the bricks easily (Wachira, 2014).

From the results in Table 4.2 above and XRD spectrum, it is evident that the mineralogical composition of the samples differs from the site of collection i.e mineralogical composition varies with the site of collection. The results of the mineralogical analysis of these clays

samples compared that of raw clays obtained from Mukurwe-ini, the latter were found to contain kaolinite, quartz, albite and Microline. However, since quartz, Microline, and albite are non-clay minerals hence kaolinite was the only clay mineral present in Mukurwe-ini clays (Wachira, 2014). The mineralogical analysis of raw clays samples are in agreement with results from a previous study, raw clays obtained from Kano plains, Kenya was also found to contain kaolinite, albite, quartz, montmorillonite, and dickite (Oswago, 2016).

Results of the mineralogical composition of clays from the three selected sites (Table 4.2) shows that the mineralogical composition varies with the site of collection, therefore this justifies the hypothesis that the mineralogical composition of clays from selected sites in Murang'a and Nyeri counties vary with the site of collection.

4.3 Effects of Acid Treatment on the Elemental Composition of Clays samples

Table 4.3 below shows the variation in concentration of the various elements when the clays samples were treated with different concentrations of hydrochloric and oxalic acid.

Table 4. 3: Variation of elemental composition of clays from selected sites with acid treatment

Acid used	Site	Acid conc	*Elemental composition (%)								LOI
			SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	
HCl acid	Githima	0.0 M	40.80±0.06	16.27±0.05	0.56±0.04	0.02±0.01	0.96±0.03	7.62±0.03	0.08±0.02	20.53±0.15	11.47
		0.1M	42.34±0.44	16.01±0.24	0.55±0.08	0.02±0.01	0.94±0.14	7.59±0.59	0.08±0.03	19.56±0.62	12.24
		0.25M	44.27±0.56	14.56±0.23	0.42±0.04	0.02±0.01	0.86±0.12	7.18±0.20	0.07±0.02	18.14±0.45	13.17
		0.5M	47.08±0.32	13.03±0.51	0.38±0.03	0.01±0.01	0.82±0.17	6.04±0.86	0.05±0.01	13.12±0.38	14.36
		1M	50.12±0.62	12.87±0.33	0.33±0.05	0.01±0.01	0.78±0.19	5.96±0.54	0.04±0.01	10.14±0.41	15.35
		2M	52.14±0.85	11.86±0.40	0.28±0.01	ND	0.72±0.22	5.82±0.33	0.02±0.01	8.54±0.31	16.45
	Kimathi	0.0 M	55.40±0.20	22.40±0.02	0.67±0.05	1.82±0.02	2.65±0.03	0.62±0.03	0.06±0.02	3.90±0.02	12.2
		0.1M	56.46±0.83	21.37±0.37	0.65±0.06	1.8±0.05	2.45±0.04	0.61±0.08	0.05±0.02	3.85±0.52	13.11
		0.25M	58.16±0.73	20.89±0.54	0.62±0.05	1.66±0.03	2.39±0.03	0.58±0.04	0.04±0.01	3.78±0.48	13.98
		0.5M	61.04±0.63	18.87±0.09	0.6±0.04	1.57±0.02	2.29±0.02	0.51±0.02	0.03±0.01	3.66±0.08	14.16
		1M	63.14±0.47	18.14±0.08	0.54±0.02	1.5±0.04	2.21±0.01	0.48±0.06	0.03±0.01	3.61±0.04	14.98
		2M	65.16±0.76	17.45±0.07	0.45±0.02	1.43±0.02	2.16±0.01	0.43±0.04	0.02±0.01	3.57±0.05	15.02
	lthanje	0.0 M	44.03±0.03	30.33±0.15	0.53±0.03	0.02±0.01	0.84±0.02	3.49±0.03	0.23±0.15	10.40±0.20	10.84
		0.1M	46.05±0.59	29.09±0.24	0.51±0.06	0.02±0.01	0.81±0.07	3.42±0.11	0.21±0.03	10.13±0.32	10.98
		0.25M	52.92±0.69	28.12±0.46	0.42±0.08	0.02±0.01	0.77±0.04	3.36±0.08	0.17±0.04	9.98±0.25	11.06
		0.5M	54.18±0.58	26.16±0.64	0.33±0.05	0.01±0.01	0.72±0.06	3.27±0.06	0.14±0.03	8.45±0.81	11.99
		1M	55.87±0.38	25.13±0.18	0.27±0.03	ND	0.68±0.02	3.22±0.04	0.12±0.02	8.41±0.63	12.47
		2M	59.45±0.26	21.35±0.34	0.22±0.01	ND	0.63±0.02	3.16±0.02	0.09±0.01	7.42±0.15	13.87

Oxalic acid	Githima	0.0 M	40.80±0.06	16.27±0.05	0.56±0.04	0.02±0.01	0.96±0.03	7.62±0.03	0.08±0.02	20.53±0.15	11.47
		0.1M	47.06±0.73	14±0.16	0.52±0.06	0.02±0.01	0.92±0.01	7.42±0.56	0.07±0.02	15±0.57	13.00
		0.25M	50.46±0.58	12.42±0.09	0.41±0.03	0.01±0.01	0.72±0.06	7.31±0.52	0.05±0.02	9.16±0.52	16.18
		0.5M	54±0.38	10±0.39	0.39±0.04	0.01±0.01	0.32±0.07	7.24±0.34	0.03±0.01	8.2±0.67	17.62
		1M	56±0.45	9.04±0.21	0.32±0.08	ND	0.27±0.03	7.21±0.59	0.02±0.01	8.01±0.89	19.04
		2M	59.02±0.32	7.16±0.52	0.28±0.04	ND	0.24±0.02	7.16±0.65	0.01±0.01	7.56±0.92	20.42
	Kimathi	0.0 M	55.40±0.20	22.40±0.02	0.67±0.05	1.82±0.02	2.65±0.03	0.62±0.03	0.06±0.02	3.90±0.02	12.2
		0.1M	56.02±0.84	19.62±0.48	0.62±0.08	1.42±0.08	2.34±0.05	0.44±0.04	0.05±0.02	3.62±0.08	13.02
		0.25M	57.02±0.63	18.04±0.42	0.58±0.06	1.12±0.04	2.1±0.04	0.42±0.03	0.04±0.01	3.11±0.07	14.12
		0.5M	61.11±0.83	15.54±0.27	0.54±0.03	0.84±0.05	1.96±0.06	0.4±0.01	0.02±0.01	2.84±0.04	16.02
		1M	63.07±0.45	13.08±0.09	0.51±0.03	0.78±0.03	1.92±0.02	0.37±0.02	0.01±0.01	2.81±0.03	17.72
		2M	65±0.55	12.92±0.28	0.46±0.04	0.73±0.03	1.88±0.04	0.33±0.03	0.01±0.01	2.77±0.05	18.02
	lthanje	0.0 M	44.03±0.03	30.33±0.15	0.53±0.03	0.02±0.01	0.84±0.02	3.49±0.03	0.23±0.15	10.40±0.20	10.84
		0.1M	45.02±0.53	24.96±0.28	0.41±0.08	0.02±0.01	0.83±0.07	2.84±0.09	0.09±0.03	9.94±0.52	15.02
		0.25M	46.22±0.41	22.92±0.36	0.33±0.06	0.02±0.01	0.82±0.03	2.83±0.06	0.07±0.02	9.12±0.62	16.41
		0.5M	47.91±0.38	20.66±0.52	0.27±0.01	0.01±0.01	0.72±0.06	2.8±0.04	0.04±0.02	8.02±0.48	19.83
		1M	48.34±0.66	17.09±0.22	0.21±0.04	0.01±0.01	0.68±0.03	2.75±0.01	0.03±0.01	7.95±0.64	20.04
		2M	49.42±0.32	14.78±0.08	0.18±0.04	ND	0.62±0.02	2.71±0.08	0.02±0.01	7.91±0.78	20.98

*Values are means ± SD (n=3)

From Table 4.3 the SiO₂ content of Githima clay increased from 40.80 to 52.14 % as HCl acid strength increased from 0.0 M to 2 M. However, silica (SiO₂) content for the Githima sample treated with HCl acid fell within the standard range of 46-62 % SiO₂ content that is required for the production of good refractory materials (Yami and Umaru, 2007). LOI increased as well from 11.47 % to 16.45 % as HCl acid strength increased from 0.0 M to 2 M, LOI values for all Githima sample treated clays were within the acceptable range of 8-18 % LOI for refractory bricks (Chester, 1973). Alumina composition in the Githima sample treated with HCl decreased from 16.27 % to 11.86 % as HCl acid concentration increased from 0.0 M to 2 M. However, the values of alumina (Al₂O₃) content did not meet the requirement of 25-44 % Al₂O₃ for refractory bricks (Chester, 1973).

The composition of iron oxides in the Githima sample treated with HCl decreased from 20.53 % to 8.54 % as acid concentration increased from 0.0 M to 2 M. However, all the samples treated with HCl have higher iron content that did not fall within the standard range of 0.5-2.4 % Fe₂O₃ for refractory bricks (Chester, 1973). Magnesium oxide (MgO) content decreased with an increase in HCl acid concentration (0.0 M to 2 M) from 0.02 to below detectable levels. Potassium oxide (K₂O) content decreased from 0.96 to 0.72 % as acid strength increased from 0.0 M to 2 M HCl. Titanium oxide (TiO₂) content decreased from 7.62 to 5.82 % as acid strength increased from 0.0 M to 2 M HCl. Manganese oxide (MnO) content decreased from 0.08 to 0.01 % as acid strength increased from 0.0 M to 2 M. It is clear from the results in Table 4.3 that as the acid strength increased from 0.0 M to 2 M, the levels of MgO, Al₂O₃, CaO,

K₂O, and TiO₂ decreased progressively. However, the levels of SiO₂ and LOI increased as acid strength increased. This is in line with a report by Panda *et al.*, (2010) while studying the effect of acid treatment on the Kaolin clay structure and chemical properties.

The silica content in the Githima clay sample treated with oxalic acid increased from 40.80 % to 59.02 % as the acid concentration increased from 0.0 M to 2 M. However, all the values of the Githima sample treated with oxalic acid fell within the standard range of 46-62 % SiO₂ content that is required for the production of good refractory materials (Yami and Umaru, 2007). LOI values of Githima samples treated with oxalic acid increased from 11.47 % to 20.42 % as the acid concentration increased from 0.0 M to 2 M. However, most of the LOI values for Githima samples treated with oxalic acid are within the standard range of 8-18 % LOI for refractory bricks (Chester, 1973). The composition of iron oxide content decreases from 20.53 to 7.56 % with an increase in oxalic acid concentration from 0.0 M to 2 M. However, iron oxides content was high and did not fall within the acceptable range of 0.5-2.4 % Fe₂O₃ for refractory bricks (Chester, 1973). The composition of alumina (Al₂O₃) as well decreased from 16.27 to 7.16 % as oxalic acid concentration increased from 0.0 M to 2 M. However, alumina content for all the samples are below the acceptable range of 25-44 % Al₂O₃ for refractory bricks (Chester, 1973). Titanium oxide (TiO₂) levels decreased from 7.62 to 7.16 % as oxalic acid concentration increased from 0.0 M to 2 M. Potassium oxide (K₂O) content reduced from 0.96 to 0.24 % as oxalic acid concentration increased from 0.0 M to 2 M. Manganese oxide (MnO) content reduced from 0.08 to 0.01 % as oxalic

acid concentration increased from 0.0 M to 2 M. Magnesium oxide (MgO) content was reduced from 0.02 % to below detectable levels. Calcium oxide (CaO) content was reduced from 0.52 to 0.28 %. From the results in Table 4.3, it is clear that the elemental composition of the Githima clay is significantly affected with acid treatment (oxalic acid), the levels of SiO₂ and LOI increase as oxalic acid concentration increases. However, Fe₂O₃, Al₂O₃, MnO, CaO, MnO, TiO₂, and K₂O decrease with an increase in oxalic acid concentration.

The SiO₂ content of the Kimathi sample treated with HCl increased from 55.40 to 65.16 % as acid concentration increased from 0.0 M to 2 M HCl. However, most of the SiO₂ values fell within the acceptable range of 46-62 % for the production of good refractory materials (Yami and Umaru, 2007). The LOI of the Kimathi sample treated with HCl increased as well from 12.20 to 15.02 % as acid concentration increased from 0.0 M to 2 M HCl. However, all LOI values for Kimathi acid-treated samples were within the standard range of 8-18 % LOI for refractory bricks (Chester, 1973). The composition of iron oxides (Fe₂O₃) content decreased progressively from 3.90 to 3.57 % as acid concentration increased from 0.0 M to 2 M HCl. However, iron oxides content was high and therefore did not fall within the standard range of 0.5-2.4 % Fe₂O₃ for refractory bricks (Chester, 1973).

The composition of alumina (Al₂O₃) was reduced significantly from 22.40 % to 17.45 % as HCl concentration increased from 0.0 M to 2 M. However, no alumina (Al₂O₃) content values fell within the standard range of 25-44 % Al₂O₃ for refractory bricks (Chester, 1973). Potassium oxide (K₂O) content was reduced from 2.65 to 2.16 % as HCl concentration

increased from 0.0 M to 2 M. Magnesium oxide (MgO) content decreased as well from 1.82 to 1.43 % as HCl concentration increased from 0.0 M to 2 M. Calcium oxide (CaO) content decreased from 0.67 to 0.45 % as HCl concentration increased from 0.0 M to 2 M. Titanium oxide (TiO₂) content decreased from 0.62 to 0.43 % as HCl concentration increased from 0.0 M to 2 M. Manganese oxide (MnO) content decreased from 0.06 to 0.02 % as HCl concentration increased from 0.0 M to 2 M. From Table 4.3 above, it is evident that Kimathi clay elemental composition is affected by treating with hydrochloric acid. The levels of most soluble metal oxides decreased with an increase in the concentration of the acid. Levels of Al₂O₃, CaO, MgO, K₂O, TiO₂, MnO, and Fe₂O₃ decreased progressively with an increase in HCl concentration. These findings are in agreement with findings by Eze *et al.*, (2012) while investigating the effect of acid treatment on the physicochemical properties of Kaolin clay obtained from a mine in Abia state, Nigeria.

The silica content of Kimathi clay increased from 55.40 to 65.00 % as oxalic acid concentration increases from 0.0 M to 2 M. However, most of the silica content values fell within the standard range of 46-62 % for refractory bricks (Yami and Umaru, 2007). Loss On Ignition (LOI) increased as well from 12.20 to 18.02 % with an increase in oxalic acid concentration from 0.0 M to 2 M. However, most of the LOI values fell within the standard range of 8-18 % LOI for refractory bricks. The composition of iron oxide (Fe₂O₃) reduced from 3.90 to 2.77 % as oxalic acid concentration increased from 0.0 M to 2 M. However, iron content values are higher than the recommended range of 0.5-2.4 % Fe₂O₃ for refractory bricks

(Chester, 1973). Alumina (Al_2O_3) content decreased from 22.40 to 12.92 % as oxalic acid concentration increased from 0.0 M to 2 M. However, alumina composition does not fall within the recommended range of 25-44 % for refractory bricks (Chester, 1973).

Potassium oxide (K_2O) content decreased from 2.65 to 1.88 % as oxalic acid concentration increased. Magnesium oxide (MgO) content was reduced from 1.82 to 0.73 %. Manganese oxide (MnO) was reduced as well from 0.06 to 0.01 %. Titanium oxide (TiO_2) was reduced from 0.62 to 0.33 %. Generally, most of the metallic oxides in Kimathi clay samples are leached with oxalic acid, some of those oxides include Fe_2O_3 , Al_2O_3 , MnO , CaO , K_2O , MgO , and TiO_2 , these oxides decrease with an increase in oxalic acid concentration. However, SiO_2 and LOI levels increase with an increase in acid strength.

The composition of silica (SiO_2) increased from 44.03 to 59.45 % as HCl concentration increased from 0.0 M to 2 M. However, most silica composition values fell within the recommended range of 46-62 % SiO_2 for production of good refractory materials (Yami and Umaru, 2007). Loss On Ignition (LOI) increased as well from 10.84 to 13.87 % as Hydrochloric (HCl) acid concentration increased from 0.0 M to 2 M. However, all LOI values fall within the acceptable range of 8-18 % LOI for refractory bricks (Chester, 1973). Iron oxide (Fe_2O_3) composition decreased from 10.84 to 7.42 % as HCl concentration increased from 0.0 M to 2 M. However, iron oxide content does not fall within the acceptable range of 0.5-2.4 % for refractory bricks (Chester, 1973). Alumina (Al_2O_3) was reduced from 30.33 to 21.35 % with hydrochloric (HCl) acid increase from 0.0 M to 2 M. However, most alumina content values

fell within the acceptable range of 25-44 % Al_2O_3 for refractory bricks (Chester, 1973). Titanium oxide (TiO_2) was reduced from 3.42 to 3.16 % as HCl concentration increased from 0.0 M to 2 M. Calcium oxide (CaO) was reduced from 0.51 to 0.22 % as HCl concentration increased from 0.0 M to 2 M. Potassium oxide (K_2O) decreased from 0.81 to 0.63 % as HCl concentration increased from 0.0 M to 2 M. Manganese oxide (MgO) levels was reduced from 0.21 to 0.09 % as hydrochloric acid (HCl) concentration increased. Magnesium oxide (MgO) levels were reduced from 0.02 to below detectable levels.

The elemental composition of clays from Ithanje was significantly affected with treatment with hydrochloric acid, levels of SiO_2 , and LOI increased with an increase in HCl concentration as shown in Table 4.3 above. However, some of the metallic oxides were reduced by HCl treatment, metallic oxides decreased by acid treatment include; Fe_2O_3 , Al_2O_3 , MnO , K_2O , MgO and CaO . These results are similar to one found by Xavier *et al.*, (2014) while investigating the effect of acid treatment on clay palygorskite clay obtained from Guadalupe.

The composition of silica increased from 44.03 to 49.42 % as oxalic acid concentration increased from 0.0 M to 2 M. However, most silica content values fell within the recommended range of 46-62 % SiO_2 for production of good refractory materials (Yami and Umaru, 2007). Loss On Ignition (LOI) increased as well from 10.84 to 20.98 % as oxalic acid concentration increased from 0.0 M to 2 M. However, most of the LOI values fell within the acceptable range of 8-18 % Al_2O_3 for refractory bricks (Chester, 1973). Alumina (Al_2O_3) composition decreased from 30.33 to 14.78 % as oxalic acid concentration increased from 0.0

M to 2 M. However, most of the alumina content values fell within the acceptable range of 25-44 % Al_2O_3 for refractory bricks (Chester, 1973). Iron oxide (Fe_2O_3) composition reduced from 10.40 to 7.91 % as oxalic acid concentration increased from 0.0 M to 2 M.

Titanium oxide (TiO_2) content decreased from 3.49 to 2.71 % as oxalic acid concentration increased from 0.0 M to 2 M. Potassium oxide (K_2O) content decreased from 0.84 to 0.62 % as oxalic acid concentration increased from 0.0 M to 2 M. Manganese oxide (MnO) content decreased as well from 0.14 to 0.02 % as oxalic acid concentration increased from 0.0 M to 2 M. Magnesium oxide (MgO) was reduced from 0.02 % to below detectable levels. Treating Ithanje clay samples with oxalic acid shows that some of its metallic oxides are adversely affected. From the results in Table 4.3, it is evident that oxalic acid leached some of the soluble metallic oxides such as Fe_2O_3 , Al_2O_3 , MgO , CaO , and TiO_2 ; their levels were reduced with an increase in acid strength. However, SiO_2 and LOI levels increased with an increase in acid strength.

The results of acid treatment indicate that the chemical composition of the clays changed substantially. As the concentration of the acid increased, there was a marked increase in the dissolution of all soluble cations (Xavier *et al.*, 2014). Acid-treatment causes a reduction in the composition of most elements with a higher reduction being achieved at a higher concentration as shown in Table 4.3. Wachira, (2014) did a study on the effects of acids (sulphuric, hydrochloric, and oxalic acid) treatment on the iron composition of clays from Murkurwe-ini and found that the levels of SiO_2 and LOI increased after acid treatment while

there was a reduction of Fe_2O_3 , MgO , Na_2O , Al_2O_3 , TiO_2 , and CaO , these findings are in agreement with the results in Table 4.3.

Loss On Ignition (LOI) of the clays increased after acid treatment. This is due to an increase in amorphous silica that made water adsorption higher (Panda *et al.*, 2010). Figure 4.4 gives a more simplified but comprehensive summary of the comparison of iron removal from the clay samples from the selected sites between the two acids (hydrochloric and oxalic acid). Oxalic acid was found to be more effective at the same acid concentration than hydrochloric acid and this was in agreement with a previous report by Calderon *et al.*, (2005). The findings were in line with report by Wachira (2014) while studying iron removal of clays and restoration of clays' plasticity. Figure 4.4 shows the percentage of iron oxides remaining after acid treatment. Lower values of Iron oxides were observed on clays treated using oxalic acid showing that oxalic acid is more effective on iron oxides reduction.

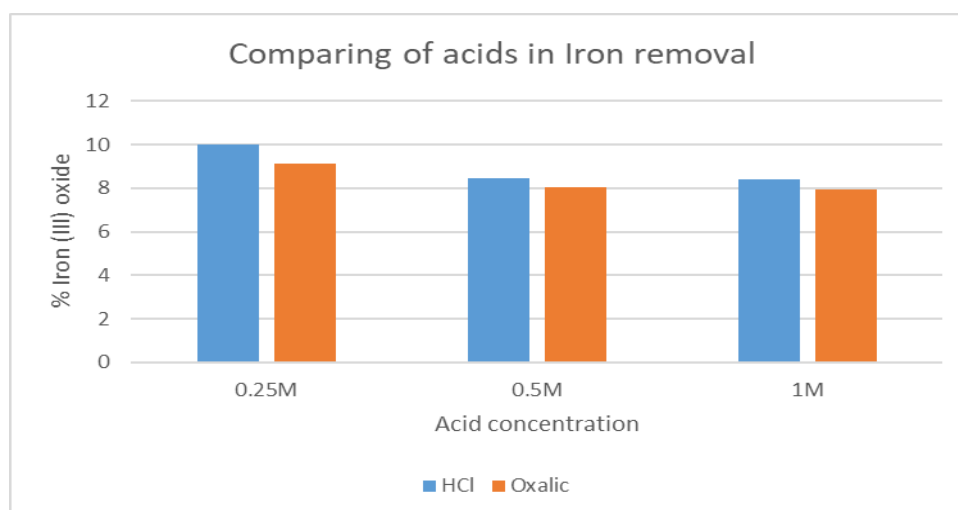


Figure 4. 4: Comparison of the effect of acids treatment on the iron composition of clay sample

Results of the elemental composition of clays from the three selected sites (Table 4.3 above) show that the clays are affected significantly by acid treatment, therefore this justifies the hypothesis that the elemental composition of clays from selected sites in Murang’a and Nyeri counties are affected by acid treatment.

4.4 Refractory Properties of Clays

4.4.1 Refractory Properties of Raw Clays from Selected Sites.

Table 4.4 below shows the refractory properties of refractory bricks made using raw clay.

Table 4. 4: Refractory properties of clays from selected sites in Murang’a and Nyeri counties, Kenya.

Property	Githima	Kimathi	Ithanje	*Standard clay for refractory bricks
Fried Linear Shrinkage	1	3	3	2-10
Apparent porosity %	26.31	26.72	31.33	20-30
Bulk density g/cm ³	1.56	1.68	1.56	2.2-2.8
Refractoriness, °C	1609	1655	1686	1500-1750
Loss On Ignition	11.47	12.2	10.84	

*Thermal and physical properties international standard (Chester, 1973)

Githima sample apparent porosity value of (26.31 %) is within the recommended range of 20-30 % as stated by Ugwuoke and Amalu (2017). Githima sample linear shrinkage value (1%) is slightly lower than the acceptable value of 2-10 % for refractory bricks as reported by Kipsanai (2018). Bulk density value (1.56 g/cm³) for the Githima sample does not fall within the standard range of 2.2-2.8 g/cm³ for refractory bricks as reported by Chester (1973). Githima sample has

good thermal shock resistance that meets the requirement of 20-30 cycles as reported by Yami and Umaru (2007). Refractoriness value (1609 °C) for the Githima sample meets the requirement of 1500-1700 °C for refractory bricks as reported by Chester (1973).

Apparent porosity value for the Kimathi sample (26.72 %) meets the requirement of 20-30 % for refractory bricks as stated by Ugwuoke and Amalu (2017). Bulk density value (1.68 g/cm³) for the Kimathi sample does not meet the requirement of 2.2-2.8 g/cm³ as stated by Chester (1973). Kimathi sample linear shrinkage value (3 %) fell within the acceptable range of 2-10 % for refractory bricks as reported by Chester (1973). Kimathi sample refractoriness value (1655 °C) meets the requirement of 1500-1700 °C for refractory bricks as stated by Chester (1973).

Apparent porosity of the Ithanje sample (31.33 %) was slightly above the standard range of 20-30 % for refractory bricks as reported by Ugwuoke and Amalu (2017). Bulk density value (1.56 g/cm³) for the Ithanje sample fell below the standard range of 2.2-2.8 g/cm³ for refractory bricks as stated by Chester (1973). Linear shrinkage value (3 %) for the Ithanje sample meets the requirement of 2-10 % for refractory bricks as reported by Chester (1973). Ithanje sample refractoriness value (1686 °C) fell within the standard range of 1500-1700 °C for refractory according to Chester (1973).

Generally, the clays had a range of 26.31-31.33 % apparent porosity, 1-3 linear shrinkage, 1.56-1.68 g/cm³ bulk density, 1609-1686 °C refractoriness. The refractoriness of clays from selected sites was within the standard limits. The Ithanje clay apparent porosity was slightly above the

standard limit whereas Githima and Kimathi clay apparent porosity is within the acceptable range. However, bulk densities of the clays were below the standard values for refractory materials.

A comparison of the results of the refractoriness values of clay samples from the three selected sites in Table showed that the Ithanje clay sample possesses the highest refractoriness value of 1686 °C while the Githima clay sample had the lowest refractoriness value of 1609 °C (Figure 4.5). This is because the Ithanje clay sample possesses higher alumina (Al_2O_3) content hence the higher refractoriness necessary to form the glass-ceramic bonding material, which characterizes ceramic products as reported by Omotoyinbo and Oluwole (2008). Figure 4.5 shows the variation of refractoriness with the site. Ithanje sample has the highest refractoriness value.

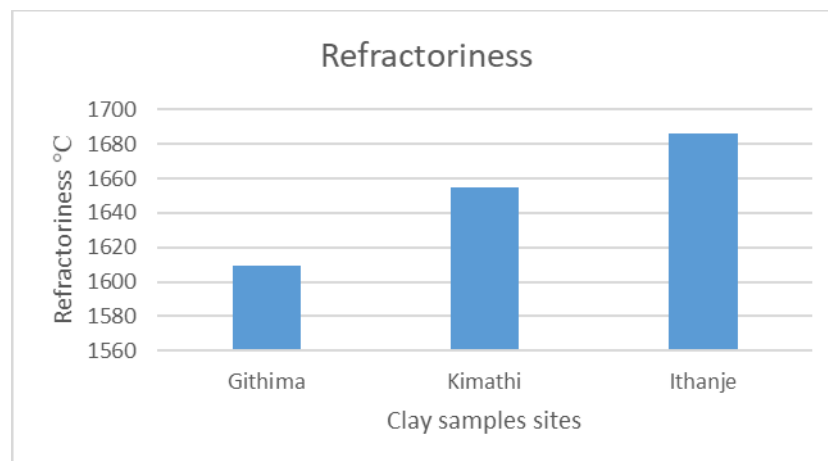


Figure 4. 5: Variation of refractoriness with sites

4.4.2 Effects of acid treatment on refractory properties of clays from selected sites

The results of the refractory properties of clays samples treated with different concentrations of acids were presented in Table 4.5. Table 4.5 below shows variation in refractory properties of refractory bricks made using acid-treated clays.

Table 4. 5: Effects of acid treatment on refractory properties of clays from selected Sites

Table 4.5 presents the findings of effects of acid treatment (Hydrochloric acid) on refractory properties of clays from selected sites.

Githima	Acid	Conc.	Apparent porosity (%)	Bulk density (g/cm ³)	Linear shrinkage (%)	Refractoriness (°C)
	HCl	0.0 M	26.31	1.56	1.00	1609
		0.1 M	32.18	1.80	1.20	1603
		0.25 M	33.76	1.77	1.30	1600
		0.5 M	34.22	1.75	1.36	1589
		1 M	34.80	1.72	1.40	1584
		2 M	35.10	1.64	1.52	1575
Kimathi		0.0 M	26.72	1.68	3.00	1655
		0.1 M	27.68	1.68	3.10	1643
		0.25 M	28.03	1.64	3.22	1637
		0.5 M	29.34	1.59	3.28	1624
		1 M	29.31	1.55	3.32	1612
		2 M	30.02	1.44	3.41	1611
Ithanje		0.0 M	31.33	1.56	3.00	1686
		0.1 M	23.76	1.76	3.14	1659
		0.25 M	24.17	1.65	3.19	1650
		0.5 M	24.92	1.52	3.25	1638
		1 M	25.27	1.45	3.29	1622
		2 M	25.86	1.32	3.31	1611

Table 4. 6: Effects of acid treatment (oxalic acid) on refractory properties of clays from selected sites

Table 4.6 presents the findings of effects of acid treatment (oxalic acid) on refractory properties of clays from selected sites.

Site	Acid	Conc.	Apparent porosity (%)	Bulk density (g/cm ³)	Linear shrinkage (%)	Refractoriness (°C)
Githima	Oxalic acid	0.0 M	26.31	1.56	1.00	1609
		0.1 M	23.69	1.69	1.40	1608
		0.25 M	28.19	1.67	1.70	1603
		0.5 M	30.42	1.62	1.80	1601
		1 M	33.68	1.55	1.90	1603
		2 M	34.57	1.53	2.2	1599
Kimathi		0.0 M	26.72	1.68	3.00	1655
		0.1 M	22.16	1.71	3.30	1650
		0.25 M	24.76	1.62	3.35	1648
		0.5 M	26.44	1.73	3.42	1639
		1 M	31.90	1.59	3.58	1635
		2 M	34.15	1.45	3.62	1632
Ithanje		0.0 M	31.33	1.56	3.00	1686
		0.1 M	21.65	1.65	3.16	1680
		0.25 M	22.14	1.53	3.22	1677
		0.5 M	24.18	1.47	3.41	1669
		1 M	26.67	1.42	3.49	1664
		2 M	33.14	1.36	3.52	1647

Treatment of Githima clay sample with different concentrations of HCl acid causes an increase in its apparent porosity (from 26.31 to 35.1 %) as the acid concentration increases from 0.0 M to 2 M. However, the values of apparent porosity of Githima samples treated with the acid were within the recommended values of 20-30 % for refractory bricks according to Chester (1973). Bulk density values (1.56, 1.80, 1.77, 1.75, 1.72, 1.64 g/cm³) of Githima samples treated with hydrochloric (HCl) acid does not fall within the recommended range of 2.2-2.8 g/cm³ for refractory bricks. Linear shrinkage values are lower than the recommended values for refractory bricks. All refractoriness values (1609, 1603, 1600, 1589, 1584, and 1575 °C) are within the acceptable range of 1500-1700 °C for refractory bricks. From the results in Table

4.5 and 4.6 (Githima sample treated with different concentrations of oxalic acid), the values of apparent porosity (26.31, 23.69, 28.19, 30.42, 33.68, and 34.57 %) are well within the standard range of 20-30 % for refractory bricks as stated by Ugwuoke and Amalu (2017). All bulk density values for Githima samples treated with oxalic acid are below the recommended value for refractory bricks. Most of the linear shrinkage values (1, 1.4, 1.7, 1.8, 1.9, and 2.2 %) are below the acceptable range for refractory bricks. Refractoriness values (1609, 1608, 1603, 1601, 1603, and 1599 °C) are well within the acceptable range of 1500-1700 °C for refractory bricks as reported by Chester (1973).

Treatment of Kimathi sample with different concentrations of HCl causes an increase in its apparent porosity (26.72 to 30.02 %) as hydrochloric (HCl) acid concentration increases from 0.0 M to 2 M. However, the values of the apparent porosity of Kimathi samples are within the recommended levels for refractory bricks. Bulk density values (1.68, 1.68, 1.64, 1.59, 1.55, and 1.44 g/cm³) for Kimathi samples treated with hydrochloric (HCl) acid are lower than the acceptable values for refractory bricks. Linear shrinkage values (3, 3.1, 3.22, 3.28, 3.32, and 3.41 %) for Kimathi samples are well within the standard range of 2-10 % for refractory bricks according to Chester (1973). Refractoriness values for all Kimathi samples are within the recommended range for refractory bricks.

Kimathi samples treated with different concentrations of oxalic acid have their values of apparent porosity (26.72, 22.16, 24.76, 26.44, 31.90, and 34.15 %) within the recommended values of 20-30 % for refractory bricks as stated by Ugwuoke and Amalu (2017). Bulk density values

(1.68, 1.71, 1.62, 1.73, 1.59, and 1.45 g/cm³) for Kimathi samples treated with oxalic acid are below the recommended values for refractory bricks. Linear shrinkage values (3, 3.3, 3.35, 3.42, 3.58, and 3.62 %) for Kimathi samples treated with different concentrations of oxalic acid are within the standard range of 2-10 % for refractory bricks as stated by Kipsanai (2018). All refractoriness values (1655, 1650, 1648, 1639, 1635, and 1632 °C) are within the acceptable range of 1500-1700 °C for refractory bricks as reported by Chester (1973).

Ithanje samples treated with different concentrations of hydrochloric (HCl) acid have its apparent porosity values within the recommended value of 20-30 % for refractory bricks as stated by Ugwuoke and Amalu (2017). However, its bulk density values (1.56, 1.76, 1.65, 1.52, 1.45, and 1.32 g/cm³) are lower than the standard range of 2.2-2.8 g/cm³ for refractory bricks as reported by Chester (1973). Linear shrinkage values (3, 3.14, 3.19, 3.25, 3.27, and 3.31 %) for Ithanje samples treated with hydrochloric (HCl) acid are within the recommended range of 2-10 % for refractory bricks. Refractoriness values (1686, 1659, 1650, 1638, 1622, and 1611 °C) for Ithanje samples treated with hydrochloric (HCl) acid are well within the recommended values of 1500-1700 °C for refractory bricks as stated by Chester (1973).

Ithanje samples treated with different concentrations of oxalic acid have their values of apparent porosity (31.33, 21.65, 22.14, 24.18, 26.67, and 33.14 %) are well within the standard range of 20-30 % for refractory bricks according to Chester (1973). Their bulk density values (1.56, 1.65, 1.53, 1.47, 1.42, and 1.36 g/cm³) are lower than the recommended values of 2.2-2.8 g/cm³ as stated by Chester (1973). Linear shrinkage values (3, 3.16, 3.22, 3.41, 3.49, and

3.52 %) are within the standard range of 2-10 % for refractory bricks according to Chester (1973). Refractoriness values (1686, 1680, 1677, 1669, 1664, and 1647 °C) fell within the standard range of 1500-1700 °C for refractory bricks according to Chester (1973).

Generally, Refractory bricks made using acid-treated clays were found to have their refractory properties in the following ranges apparent porosity (21.65-35.1) %, bulk density (1.42-1.81) g/cm³, linear shrinkage (1.2-3.62) %, and refractoriness (1575-1680) °C. Refractoriness of clays decreases as the acid strength increases, this is attributed to the fact that some of the metallic oxides responsible for improving refractoriness are in the process of trying to reduce iron oxides, which has deleterious effects on refractory properties of clay, are washed by the acids. However, linear shrinkage and apparent porosity are enhanced by the actions of acid treatment. Linear shrinkage is an indicator of the firing efficiency of the clay samples. Omowumi (2000) in his work quoted a recommended value of the range of 4-10 %. Abolarin *et al.*, (2004) in their work advised that lower values were more desirable so that the clay will be less susceptible to volume change. Clays from selected sites treated with acid improved their linear shrinkage values to fall within the recommended range. The apparent porosity seeks to measure the open or interconnected pores in a refractory; the results show the apparent porosity of acid-treated clays fell within the standard range of 20-30% according to Chester, (1973).

The variation of the refractoriness of the clay samples with acid treatment is shown in Table 4.5 and 4.6, 0.0 M treated clay sample (Raw clays) possess the highest refractoriness values (1655 and 1686 °C) while the 2 M treated clay samples had the lowest refractoriness (1575 and

1599 °C). This is because the higher proportion of alumina (Al_2O_3) in the raw clay causes the higher refractoriness necessary to form the glass-ceramic material while in the acid-treated clay samples, acid treatment lowers alumina (Al_2O_3) content hence lowering the refractoriness as stated by Omotoyinbo and Oluwole (2008). However, the values of refractoriness of all clay samples treated with acids fell within the standard range of 1500-1700 °C).

Figure 4.6 shows the variation of refractoriness with HCl acid concentration. Refractoriness decreases with an increase in HCl acid concentration.

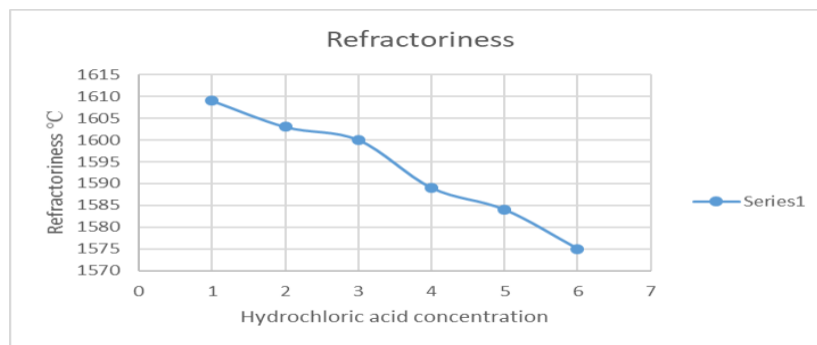


Figure 4. 6: Variation in refractoriness with HCl acid concentration

Figure 4.7 shows the variation of apparent porosity with HCl concentration. Apparent porosity increases with HCl acid concentration.

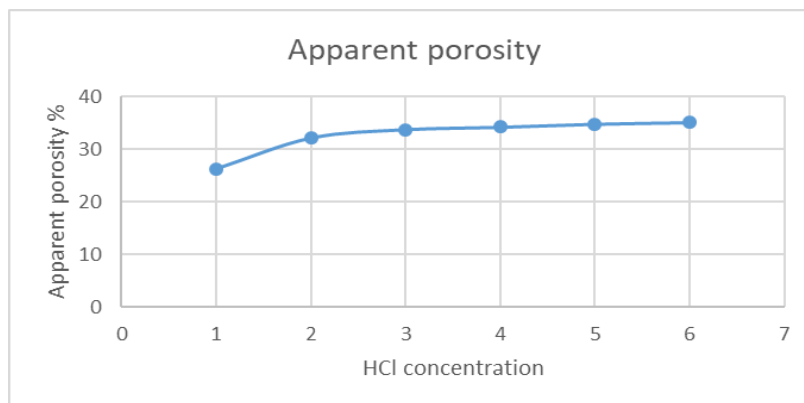


Figure 4. 7: Variation of apparent porosity with HCl concentration

Figure 4.8 shows variation of linear shrinkage with HCl acid concentration. Linear shrinkage increases with an increase in HCl concentration.

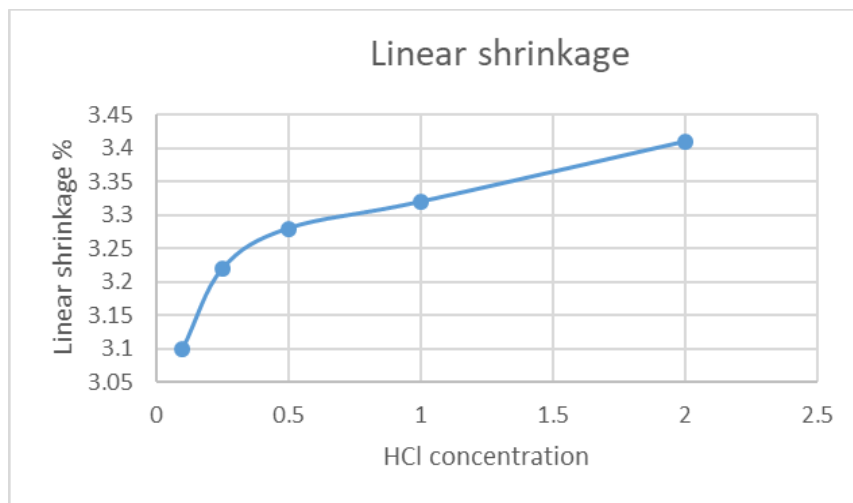


Figure 4. 8: Variation of linear shrinkage with HCl concentration

Figure 4.9 shows the variation of bulk density with HCl acid concentration. Bulk density decreases with an increase in HCl acid concentration.

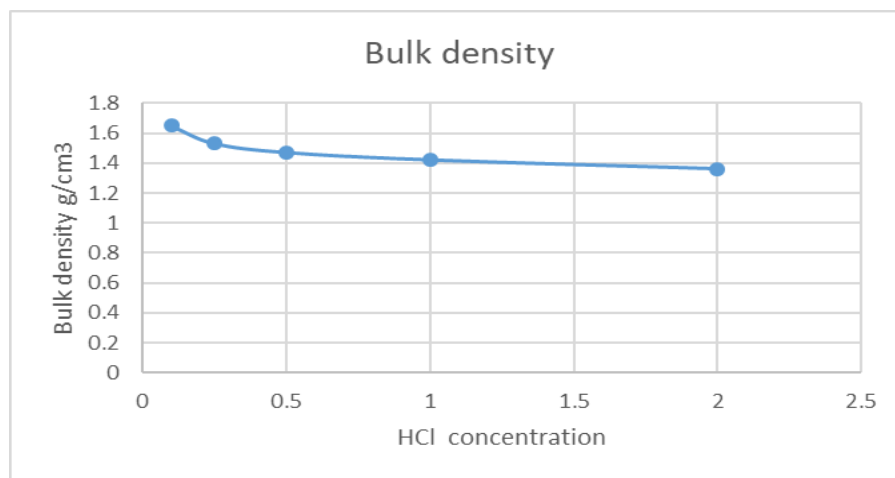


Figure 4. 9: Variation of Bulk density with HCl concentration

From the results in Table 4.5 and 4.6, it is evident that refractory properties of clays from selected sites are significantly affected by acid treatment, this justifies the hypothesis that refractory properties of clays from selected sites in Murang'a and Nyeri Counties are affected by acid-treatment.

4.5 Effects of Calcium Oxide Addition on Refractory Properties of Clays from Selected Sites

Clays samples were blended with different percentages of calcium oxide (CaO) and refractory properties were determined.

Table 4.7 below shows variation in refractory properties of refractory bricks made using raw clays blended with different percentages of calcium oxide (CaO).

Table 4. 7: Variation of refractory properties of clays from selected sites with calcium oxide content

Githima	% CaO	Apparent porosity (%)	Bulk density (g/cm ³)	Linear shrinkage (%)	Refractoriness (°C)
	0	26.31	1.56	1	1609
	1	26.12	1.8	2	1608
	2	25.96	2	1.8	1607
	5	25.52	2.24	1.6	1604
	15	24.02	2.3	1	1594
	30	22.16	2.5	0.8	1579
Kimathi	0	26.72	1.68	3	1655
	1	26.66	2.1	3.3	1654
	2	26.56	2.4	3.1	1653
	5	25.48	2.5	2.92	1650
	15	24.17	2.3	2.85	1640
	30	23.47	2.8	2.71	1625
Ithanje	0	31.33	1.56	3	1686
	1	30.26	1.7	3.1	1685
	2	29.98	2.1	2.97	1684
	5	28.47	2.3	2.84	1681
	15	27.96	2.4	2.72	1671
	30	24.16	2.5	2.6	1656
*Standard		20-30	2.2-2.8	2-10	1500-1700

Githima sample blended with different percentages of calcium oxide (CaO) additive caused a slight decrease in apparent porosity (26.31 to 22.16 %) as the percentage composition of calcium oxide (CaO) increased from 0.0 % to 30 %. However, the values of the apparent porosity fall within the acceptable range of 20-30 % for refractory bricks as reported by (Ugwuoke and Amalu, 2017). As the percentage of calcium oxide (CaO) increases from 0 % to 30 %, bulk density values increases as well (1.56 to 2.5 g/cm³), most of Githima samples blended with calcium oxide (CaO) bulk density values fell within the recommended range of 2.2-2.8 g/cm³ for refractory bricks as reported by (Kipsanai, 2018). Githima samples blended with different percentages of calcium oxide (CaO) linear shrinkage values (1, 2, 1.8, 1.6, 1, and 0.8 %) does not fall within the standard range of 2-10 % for refractory bricks according to (Chester, 1973). Githima samples blended with different percentages of calcium oxide (CaO) have their refractoriness values (1609, 1608, 1607, 1604, 1594, and 1579 °C) within the recommended range of 1500-1700 °C for refractory bricks according to Chester (1973).

Kimathi samples blended with different percentages of calcium oxide (CaO) additive have their apparent porosity values decreasing (26.72 to 23.47 %) with an increase in the percentage of calcium oxide additive (0 to 30 %). However, the values of all apparent porosity fell within the acceptable range of 20-30 % for refractory bricks as reported by Ugwuoke and Amalu (2017). Most of the bulk density values (1.68, 2.1, 2.4, 2.5, 2.3, and 2.8 g/cm³) of Kimathi samples are within the recommended value of 2.2-2.8 g/cm³ for refractory brick as reported by Chester (1973). Kimathi samples blended with calcium oxide (CaO) linear shrinkage values (3, 3.3,

3.1, 2.92, 2.85, and 2.71 %) fell within the recommended range of 2-10 % for refractory bricks according to Chester (1973). All refractoriness values (1655, 1654, 1653, 1650, 1640 and 1625°C) fell within the acceptable range of 1500-1700 °C for refractory bricks (Chester, 1973).

Ithanje samples blended with different percentages of calcium oxide (CaO) have their apparent porosity values decrease (from 31.33 to 24.16 %) as calcium oxide (CaO) percentage increase from 0 % to 30 %. However, the values of apparent porosity for all samples from Ithanje fell within the recommended value of 20-30 % for refractory bricks according to Chester (1973).

Ithanje samples blended with different percentages of calcium oxide (CaO) have most of their bulk density values (1.56, 1.7, 2.1, 2.3, 2.4, and 2.5 g/cm³) within the acceptable range of 2.2-2.8 g/cm³ according to Yami and Umaru (2007). Ithanje samples linear shrinkage values (3, 3.1, 2.97, 2.84, 2.72 and 2.6 %) are within the recommended value for refractory bricks. All refractoriness values (1686, 1685, 1684, 1681, 1671 and 1656 °C) for Ithanje samples are within the standard range of 1500-1700 °C for refractory bricks according to Chester (1973).

The variation of the refractoriness of the clay samples with calcium oxide (CaO) content is shown in Table 4.7, clay sample with 100 % clay possesses the highest refractoriness values (1609, 1655, 1686 °C) while clay sample with 70 % clay possesses the lowest refractoriness values (1579, 1594 °C) (Figure 4.10). This is because the higher proportion of alumina, the higher the refractoriness necessary to form the ceramic bonding material, which characterizes ceramic products as stated by Omotoyinbo and Oluwole (2008). The alumina content therefore is an indicator of clay refractoriness (Owoeye and Olufunke, 2016). However, the

refractoriness values of all clay samples blended with calcium oxide (CaO) additive fell within the acceptable range of 1500-1700 °C for refractory bricks according to Chester (1973).

Figure 4.10 shows variation of refractoriness with CaO addition. An increase in CaO percentage causes a decrease in refractoriness.

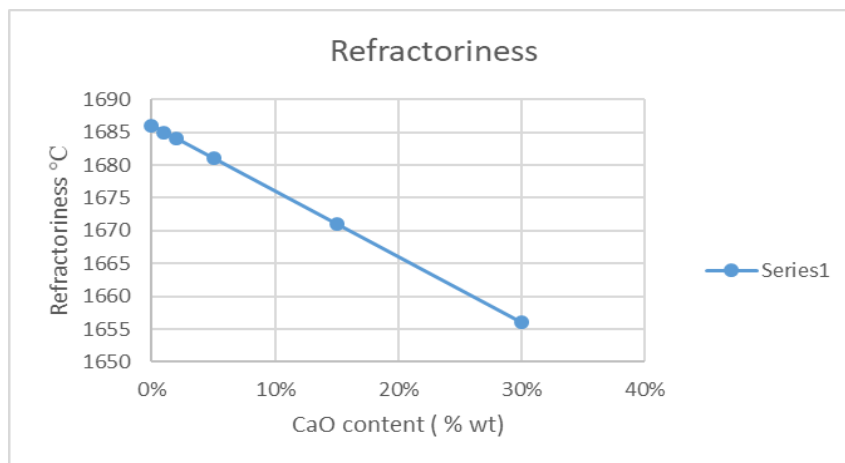


Figure 4. 10: Variation of refractoriness with CaO content

Figure 4.11 shows variation of apparent porosity with CaO addition. Apparent porosity decreases with increase in CaO content.

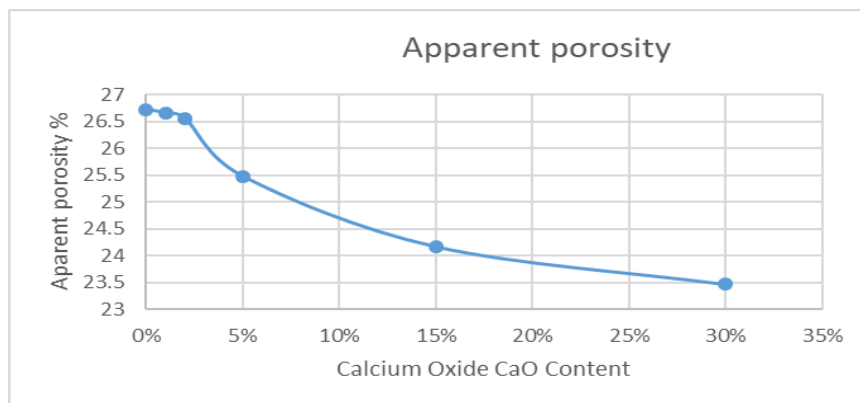


Figure 4. 11: Variation of apparent porosity with CaO content

Figure 4.12 shows variation of bulk density with CaO content. Bulk density increases with CaO addition.

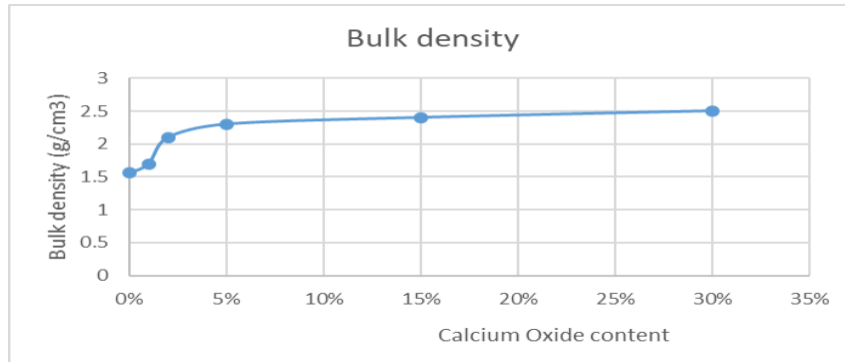


Figure 4. 12: Variation of bulk density with CaO content

Figure 4.13 shows variation of linear shrinkage with CaO content. Linear shrinkage decreases with increase in CaO addition.

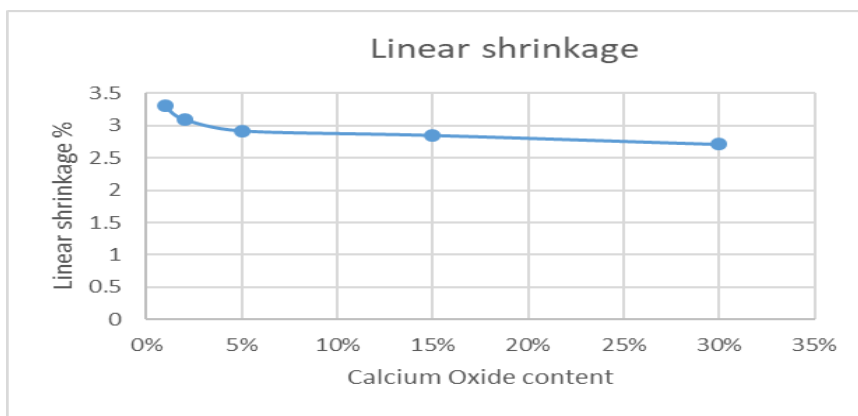


Figure 4. 13: Variation of linear shrinkage with CaO

It is clear that refractory properties of clays from selected sites are affected by use of additive (CaO) as seen in the results in Table 4.7 and, this justifies the hypothesis that refractory properties of clays from selected sites in Murang’a and Nyeri Counties are affected by calcium oxide (CaO) addition.

4.6 Effects of Acid Treatment and Calcium Oxide Addition on Refractory Properties of Clays from Selected Sites

Table 4.8 below shows variation in refractory properties of refractory bricks made using acid treated clays blended with different percentages of calcium oxide (CaO).

Table 4. 8: Effects of acid treatment and Calcium Oxide addition on refractory properties of clays from selected sites

Githima	Acid		1 % CaO		2 % CaO	
			0.1 M	0.25 M	0.1 M	0.25 M
	HCl					
	Conc.		0.1 M	0.25 M	0.1 M	0.25 M
		Apparent porosity	21.00	20.00	26.00	21.00
		Bulk density	2.00	2.20	2.10	2.40
		Linear shrinkage	2.00	2.50	3.00	5.00
		Refractoriness	1607	1602	1606	1601
Kimathi		Apparent porosity	27.00	23.00	24.00	21.00
		Bulk density	2.40	2.60	2.30	2.80
		Linear shrinkage	2.00	3.00	3.00	5.00
		Refractoriness	1649	1647	1648	1646
Ithanje		Apparent porosity	25.00	22.00	28.00	23.00
		Bulk density	2.20	2.50	2.30	2.80
		Linear shrinkage	3.00	3.40	3.00	4.00
		Refractoriness	1679	1676	1678	1675
Githima	Oxalic acid					
		Apparent porosity	21.00	24.00	22.00	25.00
		Bulk density	2.00	2.10	1.90	2.10
		Linear shrinkage	3.00	3.50	2.50	2.80
		Refractoriness	1602	1599	1601	1597
Kimathi		Apparent porosity	24.00	21.00	28.00	23.00
		Bulk density	2.20	2.30	2.40	2.70
		Linear shrinkage	3.00	2.80	4.00	3.50
		Refractoriness	1642	1636	1641	1635
Ithanje		Apparent porosity	25.00	21.00	26.00	22.00
		Bulk density	2.40	2.70	2.10	2.30
		Linear shrinkage	1.90	2.30	3.00	3.70
		Refractoriness	1658	1649	1657	1648

Githima sample treated with HCl and blended with calcium oxide (CaO) have its apparent porosity values decrease (21 to 20 and 26 to 21 for 1% and 2 % blended clays respectively) as hydrochloric (HCl) acid concentration increases from 0.0 M to 0.25 M. However, the values of apparent porosity of the samples are within the recommended range of 20-30 % for refractory bricks as reported by Ugwuoke and Amalu (2017). Bulk density values of Githima

clays treated with hydrochloric acid (HCl) and blended with calcium oxide (CaO) have been improved by the effect of acid treatment and use of additive (improved from 2.0 to 2.2 and 2.1 to 2.4 g/cm³). However, most of bulk density values fell within the recommended values of 2.2-2.8 g/cm³ for refractory bricks as reported by Kipsanai (2018). Linear shrinkage values of Githima clays treated with hydrochloric (HCl) acid and blended with calcium oxide (CaO) all fell within the acceptable range of 2-10 % according to Chester (1973). Refractoriness values of all Githima clay samples treated with hydrochloric (HCl) acid and blended with calcium oxide (CaO) all fell within the recommended value of 1500-1700 °C for refractory bricks according to Chester (1973).

Kimathi sample treated with hydrochloric (HCl) acid and blended with different percentages calcium oxide (CaO) have its apparent porosity values decreasing (from 27 to 23 % and 24 to 21 %) as hydrochloric (HCl) acid concentration increases from 0.0 M to 0.25 M. However, the values of the apparent porosity are within the recommended range of 20- 30 % for refractory bricks as reported by Ugwuoke and Amalu (2017). Bulk density values of all samples of Kimathi clay treated with hydrochloric acid (HCl) and blended with calcium oxide (CaO) are within the standard range of 2.2-2.8 g/cm³ for refractory bricks. Linear shrinkage values of all the samples fall within the acceptable range. Refractoriness values of all the samples are also within the acceptable range of 1500-1700 °C for refractory bricks according to Chester (1973).

Kimathi sample treated with oxalic acid and blended with calcium oxide (CaO) apparent porosity values decreases (24 to 21 and 28 to 23 % for 1% and 2 % blended clays respectively)

as oxalic acid concentration increases from 0.0 M to 0.25 M. However, the values of apparent porosity of all samples are within the recommended range of 20-30 % according to Ugwuoke and Amalu (2017). Bulk density values of Kimathi clays treated with oxalic acid and blended with calcium oxide (CaO) have been improved by the effect of acid treatment and use of additive (improved from 2.2 to 2.3 and 2.4 to 2.7 g/cm³). However, most of bulk density values are good, which are well within the recommended values of 2.2-2.8 g/cm³ for refractory bricks as reported by Yami and Umaru (2007). Linear shrinkage values of Kimathi samples treated with oxalic acid and blended with calcium oxide (CaO) all fall within the acceptable range of 2-10 % according to Chester (1973). Refractoriness values of all Kimathi clay samples treated with oxalic acid and blended with calcium oxide (CaO) (1642, 1636, 1641, and 1635 °C) all fell within the recommended value of 1500-1700 °C for refractory bricks as reported by Chester (1973).

Ithanje sample treated with hydrochloric (HCl) acid and blended with calcium oxide (CaO) apparent porosity values are all within (that is 25, 22, 28, and 23 %) the recommended values of 20-30 % for refractory bricks according to Ugwuoke and Amalu (2017). Bulk density values of Ithanje samples treated with hydrochloric acid (HCl) and blended with calcium oxide (CaO) are all (2.2, 2.5, 2.3 and 2.8 g/cm³) within the recommended range of 2.2-2.8 g/cm³ for refractory bricks as reported by Chester (1973). Linear shrinkage values of all the samples (3, 3.4, 3, and 4 %) are within the acceptable range of 2-10 % for refractory bricks according to Chester (1973). Refractoriness values of all the samples decreases with increase in hydrochloric

acid (HCl) concentration and increase in calcium oxide (CaO) additive. However, the values of refractoriness of all samples fell within the standard range of 1500-1700 °C for refractory bricks as reported by Chester (1973).

Apparent porosity values of Ithanje samples treated with oxalic acid and blended with calcium oxide (CaO) are all within (that is 25, 21, 26, and 22 %) the recommended values of 20-30 % for refractory bricks as reported by Ugwuoke and Amalu (2017). Most of bulk density values of Ithanje samples treated with oxalic acid and blended with CaO are (2.4, 2.7, 2.1 and 2.3 g/cm³) within the recommended range of 2.2-2.8 g/cm³ for refractory bricks as reported by Kipsanai (2018). Linear shrinkage values of most of the samples (1.9, 2.3, 3, and 3.7 %) are within the acceptable range of 2-10 % for refractory bricks as reported by Yami and Umaru (2007). Refractoriness values of all the samples decreases with increase in oxalic acid concentration and increase in calcium oxide (CaO) additive. However, the values of refractoriness of all samples fell within the standard range of 1500-1700 °C for refractory bricks as reported by Chester (1973).

From the results in Table 4.8, it is evident that refractory properties of clays from selected sites are significantly affected by acid treatment and calcium oxide (CaO) addition, this justifies the hypothesis that refractory properties of clays from selected sites in Murang'a and Nyeri Counties are affected by acid treatment and calcium oxide (CaO) addition.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The elemental composition of clays from the three selected sites, in oxide form, are in the following ranges 40.80-55.40 % SiO₂, 16.27-30.33 % Al₂O₃, 3.90-20.53 % Fe₂O₃, 10.84-12.20 % LOI, 0.62-7.62 % TiO₂, 0.84-2.65 % K₂O, 0.02-1.82 % MgO, 0.53-0.67 % CaO and 0.06-0.23 % MnO. Githima, Kimathi and Ithanje clays are composed of Silica (SiO₂) and Alumina (Al₂O₃) as major constituents hence are fit for use as a source of alumino-silicate refractories. However, they require some little enhancement by blending clays from one site with the other site.

The minerals present in raw clays from the selected sites includes kaolinite Al₂Si₂O₅(OH)₄, quartz (SiO₂), dickite Al₂(Si₂O₅(OH)₄, montmorillonite (Ca,Na)_{0.3}Al₂(Si,Al)₄O₁₀(OH)₂.xH₂O. illite (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)], nacrite Al₂Si₂O₅(OH)₄, albite Na(AlSi₃O₈), feldspar KAlSi₃O₈, rutile TiO₂, and ilmenite FeTiO₃. However, some of the minerals present in clays from the selected sites are non-clay minerals including ilmenite, rutile, feldspar, quartz, and albite. Therefore, the major clay minerals present in clays from selected sites were kaolinite and illite. The other clay minerals present in appreciable levels were dickite, nacrite, montmorillonite, halloysite, palygorskite, and sepiolite.

This study showed that there is a variation in elemental composition of clays when treated with different concentration of acid (HCl and oxalic acid). The percentage composition of silica (SiO₂) and Loss On Ignition (LOI) increased progressively with increase in acid concentration. However, the levels of Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂ and K₂O decreased with increase in

acid concentration. This study established that the levels of iron content in clays from selected sites was reduced to satisfactory levels through acid treatment.

This study has shown that refractory properties of clays can be improved through acid treatment. The most suitable acid concentration, according to this study is 0.25 M (for both HCl and oxalic acid) for iron oxides leaching, this is because acid concentration of 0.25 M does not interfere much with the crucial oxides such as Al_2O_3 required to improve refractoriness of clays.

The clay samples exhibited reasonable physico-mechanical (good refractory properties), such as apparent porosity, refractoriness and bulk density that are comparable with standards for fireclay. This makes them to be suitable for thermal insulation applications.

This study has shown that refractory properties of clays can be improved through use of additive (CaO). The most suitable calcium oxide (CaO) additive percentage is 5 % CaO. This percentage gave good refractory properties results which were comparable with the recommended values for refractory bricks.

5.2 Recommendations

The properties of the clay samples are comparable with that of similar clays in literature and international standards. Thus, they are found to be good materials for refractory applications and will suitably compliment imported clays in refractory applications.

If these clays are carefully utilized, it will assist in addressing the nation's economic problem by reducing over dependence on foreign goods.

This study recommends the need to give adequate attention that will enhance proper utilization of available local clay materials for local production of refractory products and ceramic wares instead of relying on imported raw materials and over dependence on agriculture as Kenya's major economic source. This will aid in boosting economy of the country through industrialization and help Kenya to come out permanently from its present economic recession and will further help government achieve one of its Big 4 agenda of Manufacturing and serve as a step towards realization of Vision 2030.

The national and county governments, non-governmental organizations (NGOs) and individuals need to encourage elaborate research studies on clay and other related minerals resources and focus on establishment of small and medium scale refractory firms within the identified clay deposits (environment) to enhance local capacity building, reduce unemployment rate in Kenya and possibly rates of crime among the youths.

This study recommends for further research to be done on other clay deposits in Kenya to determine its potential for refractory application.

This study recommends for further research using other acids and additives..

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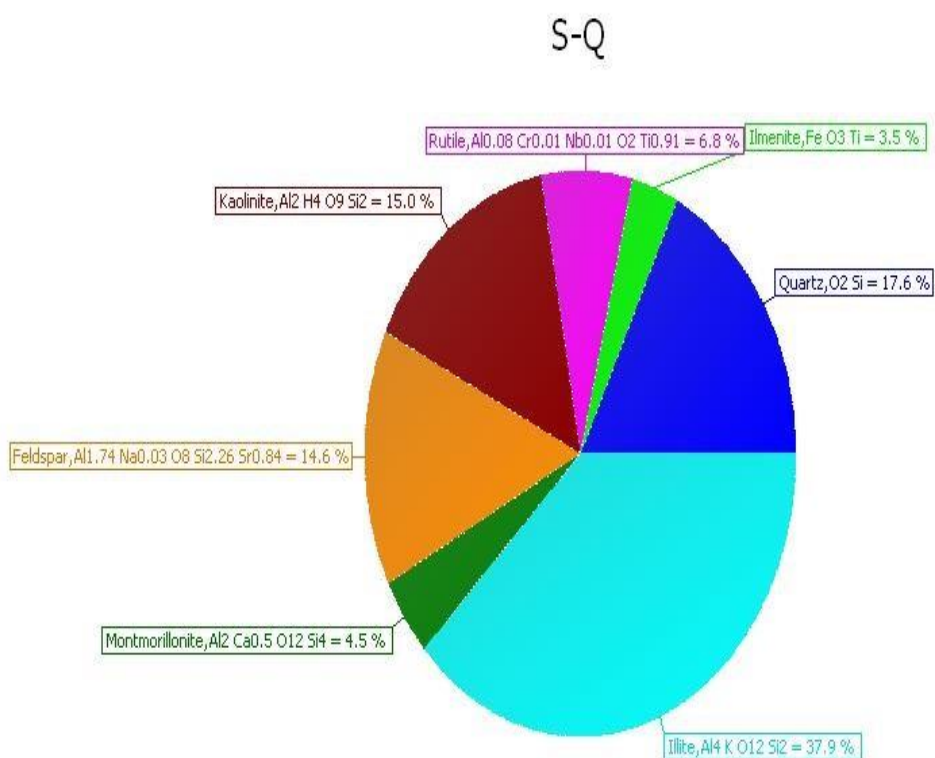
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APPENDICES

APPENDIX I

Githima Raw Sample Mineralogical composition

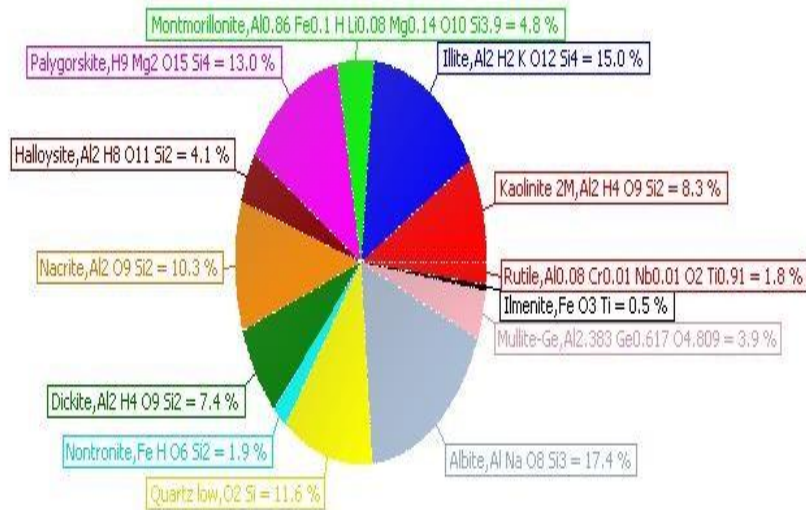
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APPENDIX II

Kimathi Raw clay sample Mineralogical Composition

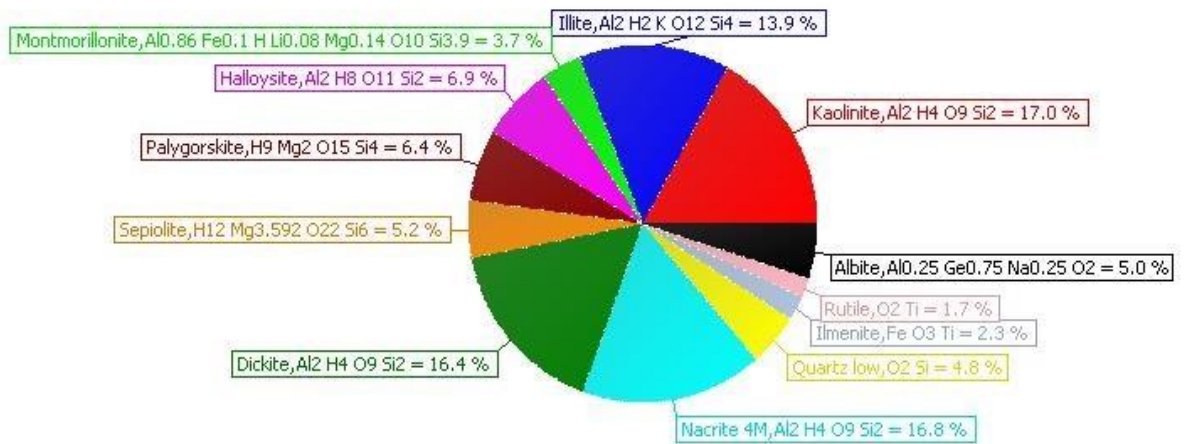
S-Q



APPENDIX III

Ithanje Raw clay Mineralogical Composition

S-Q



APPENDIX IV



XRD Instrument Bruker D2 Phaser model at the department of Geology and Mines, Ministry of Petroleum and Mining.

APPENDIX V



AAS Spectrophotometer at the department of Geology and mines, Ministry of Petroleum and Mining (AAS SPECTRA AA10 Model).

APPENDIX VI



Furnace at the department of Geology and mines, Ministry of Petroleum and Mining firing bricks.

Research Articles

1. Hassan M. Lomertwala*, Peter W. Njoroge, Sylvia A. Opiyo, Brian M. Ptoton (2019) Characterization of Clays from selected sites for Refractory Application DOI: 10.29322/IJSRP.9.11.2019.p9581 <http://dx.doi.org/10.29322/IJSRP.9.11.2019.p9581>
2. Hassan M. Lomertwala*, Peter W. Njoroge, Sylvia A. Opiyo, Brian M. Ptoton (2020). Effect of Acid Treatment on the Chemical Properties of Clays from selected sites in Murang'a and Nyeri counties, Kenya