ANALYSIS AND TREATMENT OF CLAYS FROM MWEA TO ASSESS THEIR VALUE AS A SOURCE OF ALUMINIUM AND CERAMIC PRODUCTS

BY

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DECLARATION

I declare that this thesis is my original work and has not been presented for a degree in any other University or any other award.

Sign..... Date.....6/6/2008

We confirm that the work reported in this thesis was carried out by the candidate under our supervision.

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DEDICATION

To the loving thoughts I hold for my wife Phyllis Wanjira, daughter Christine Wanjiku, son Roy James Karoki and to my parents Mr. and Mrs. James Karoki. Through you, I am who I am.

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ABSTRACT

Clays are alumino-silicate minerals which contain varying amounts of iron, magnesium, calcium and potassium as major contaminants and, trace amounts of many other inorganic elements .This study was undertaken with two main objectives .The first was to carry out elemental analysis of clays from Mwea, Kirinyaga District, in Kenya. The second objective was to find out whether it is possible to reduce the amount of iron in these clays after some chemical treatment with mineral acids without affecting the quality of the clay. Samples for analysis were collected from various sites at different depths. The results of the study have shown that the main materials, expressed as oxides, make up nearly100% of the total mass .These are:- silica, SiO_2(43-51%), alumina, Al_2O_3(17-22%,) Iron(III) oxide, Fe_2O_3(12-16%,) , Rutile, TiO_2(3.5-5.2%,), lime CaO(1.6-2.8%,), magnesium (II) oxide, MgO(1.0-1.3%,), Manganese (ii) oxide, MnO(0.20-0.40%,), Potash ,K_2O(0.15-0.4%,). Mwea clays are, therefore typical clays that could be used as a source of aluminium and aluminium compounds. Titanium was present as the mineral rutile, TiO_2. If further studies could be carried out to confirm the extensiveness and depth of deposits, then this clay could be a reliable source of titanium since is recovered economically from deposits 5 % of titanium oxide. The second important finding of this study was that, the iron in the clay could not be extracted completely with mineral acids even when pre-heated to a temperature of 400°C. The iron was, however, readily extracted with concentrations of 8 M and above of the mineral acids if the clay was pre-heated to a temperature of 500°C. Unfortunately, this pre-treatment also makes the aluminium in the clay readily removable and hence, the heat pre-treatment actually destroys the clay. Elemental analysis was carried out using Atomic Absorption Spectroscopy, X-ray Fluorescence Spectrophotometry, and EDTA titrations. These techniques were used for comparison purposes and, within experimental error; the results were in very good agreement.

ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer.
EDTA	Ethylenediamine-tetra-acetic Acid
ELC	Environmental Literacy Council
IAI	International Aluminium Institute
MRG	Meg gabbro rock standard
Psi	Per square inch
Sy-2	Syenite rock standard
XRFS	X- Ray Fluorescence Spectrophotometer

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1 INTRODUCTION

1.1 Background

Clay can be defined as a mineral or an amorphous solid with high alumino-silicate content (Hammond, 1990). However, there are other definitions of clay depending on one's area of specialization. Geologists define clays as sediments or sedimentary rock particles with diameters of 3900nm or less while Potters define clays as substances which are plastic or which can be made plastic by suitable treatment or by addition of water. On the other hand, Ceramicists, who probably process more clay than any other professionals, define clay as fine-grained rock which, when suitably crushed and pulverized, becomes plastic when wet, leather-hard when dried and on firing, is converted to a permanent rock-like mass (Hanth, 1981).

Clay minerals are hydrous alumino-silicates with varying amounts of iron, magnesium, calcium and potassium as the major impurities and other minor impurities such as lithium and beryllium as indicated in table 1. The presence of magnesium, iron and other elements constitute the impurities in clay (Isaac, 1986). However, these impurities may be essential in determining the unique and specially desired properties of the clay. For example lithium is an essential trace element in life. It has been shown that small amounts of lithium carbonate serve as a cure for mental depression (Greenwood *et al.*, 1984)

Table 1. Percentage chemical composition of some clays in form of their oxides (Gathua, 2004, Grimshaw, 1971).

Sample source	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
Mukurwe-ini (Kenya)	45.55	30.23	3.22	1.36	1.53	0.243	0.904	0.998
Kaolin (Caminau-Germany)	58.2	24.8	3.1	0.4	0.7	0.8	0.3	0.5
Karuri (Kenya)	58.81	17.00	8.15	1.52	0.29	0.189	2.74	2.92
Roseland (USA)	45.44	38.52	0.80	0.16	0.14	0.66	0.80	0.90
Montmorillon (France)	51.14	19.76	0.83	0.0	1.62	3.22	0.04	0.11
Friedensville (Paraguay)	34.46	16.95	6.21	0.24	0.0	1.11	0.0	0.49
Missouri (USA)	48.66	10.24	17.8	0.0	3.56	3.98	0.0	8.31

As noted from table 1, aluminium oxide and silicon dioxide constitute over 70 % of the mineral content in the clays except for the samples from Paraguay and Missouri from USA It is for this reason that clays are an important source of aluminium and its compounds.

1.2 Clay as a source of aluminium and its compounds

Although aluminum is so abundant in the earth's crust, it is rarely found in sufficiently high concentration for direct extraction, hence ore beneficiation is necessary since the various types of clays contain between 10-40 % alumina (Grimshaw, 1971). However, it would be economical to deal with clays containing a higher value of alumina. The use of clay as an alternative source of aluminium dates back to the year 1969, when Larpote Industries in France

contracted Jaffe′ (by then a Ph.D student at the University of Leeds) to undertake research on whether clay could be a source of aluminium. In his study, he observed that when clay is heated to between 500-600^{0}C, nearly fifty percent of the aluminium in it could be extracted readily with sulphuric acid of medium concentration. The reason is that, in this temperature range, the alumino-silicate structure is virtually destroyed to form the respective oxides (Jaffe, 1969).

Clay has also been used as a source of aluminium in Korea and U.S.A, where non-bauxite aluminium bearing minerals like kaolinites have been used. The ore is calcined to 600^{0}C for 2 hours and then leached with concentrated hydrochloric acid at 105^{0}C for 1 hour. The resulting solution which contains both iron and aluminium is then subjected to a purification process where iron is removed by solvent extraction. Aluminium value in the liquor is recovered as aluminium chloride hexahydrate ($AlCl_3.6H_2O$) by crystallization. The chloride is then thermally decomposed and calcined at 1100^{0}C to produce alumina. (Kyun *et al.,* 1997).

1.3 Statement of the problem

The factors influencing the properties and, therefore, the use of clay are, the identity and the abundance of the clay mineral component, the amount and type of non-clay materials, the particle size distribution and particle shape of the clay mineral, and, the kind and amount of exchangeable ions (Bush *et al.,* 1966).

The principal chemical components in clay are alumino-silicates, alkali-bearing minerals, compounds of iron, calcium, barium, magnesium, manganese and other elements which occur in small proportions in some clays (Brinker *et al.,* 1990). Iron is one of the major impurities that determine the use of clay for a particular purpose. The principal effects of iron compounds in clays include: alteration of the colour on firing, reduction on refractoriness of the clay, formation of scum on the ware due to presence of soluble iron compounds and formation of iron spots on the burned clay (Acevedo *et al.,* 2002).

The purpose for which the clay is intended to be used is based on its quality. For example, to a brick manufacturer, presence of iron impurities does not matter much. It is well known that when bricks are calcined, they turn brown due to the high concentration of iron in the raw clay. On the other hand, for high quality ceramic products, the amount of iron oxide should be negligible. In Kenya, there are very few deposits of quality kaolin clay mainly in some parts of Rift valley, Nyanza and Central. Yet even some of these clays contain fairly high iron content of 2-4 % (Kamoni, 1992). Due to this problem, ceramists have gone as far as Egypt to import clay for high quality ceramic products. (Personal confirmation from staff of one of the local Ceramic Industries in Nairobi).

Iron is found in clays mainly in form of hematite (Fe_2O_3) which occurs as steel-grey, iron-black, or reddish hexagonal crystals. However, it may also exist as illuminate ($FeTiO_3$), goethite (FeO.OH), or magnetite (Fe_3O_4), depending on the mode of formation and the subsequent natural treatment but in small proportions (Herren *et al.*, 1980). Hematite is not often present in clays which have been much exposed to the weather as it is readily converted into hydrated limonite ($Fe_2O_3.xH_2O$) (Duncan *et al.*, 1999). Previous studies on laterites have

shown that the iron is present in laterites as the minerals hematite and goethite (Muriithi, 1985). Furthermore, the iron could be extracted almost quantitatively by boiling the laterites with concentrated hydrochloric acid. Kenya is endowed with a lot of clay which cannot be used for quality ceramic work due to their high level iron content. It was of interest to find out whether this iron could be removed from these clays through mineral acid treatment, thus improving their quality. It was also be important to check whether it can be a source of aluminium.

1.4 Hypothesis

Clay being a mineral with high alumino-silicate content and being very plentiful in Kenya is a potential source of aluminium and can also serve as a raw material for high quality ceramic products.

1.5 Objectives of the study

1.5.1 General objective

To determine the chemical and mineral analysis of clays from low-lying areas with particular reference to Mwea to confirm whether they can serve as raw material for high quality ceramic products as well as be a source of aluminium.

1.5.2 Specific objectives

(i) To determine the chemical composition of Mwea clays and where possible, the minerals they are present in.

(ii) To find out whether the iron in these clays can be removed completely by acid treatment or be reduced to levels that would not affect the quality of ceramic products adversely.

iii) To determine the suitable acid concentration that could extract iron from clay.

(vi) To use the data obtained to asses the usefulness of the residue.

1.6 Research justification

This research is necessary because the practical applications to which any clay can be put depends on both the chemical composition and also the minerals these elements are in. secondly, whereas clays are an important source of aluminium and its compounds, clays with high levels of aluminium must be used. A decision as to whether clay from a given site can be used for a particular application can only be based on analytical data. For example, whereas lithium is a biologically essential element which has even medical applications, only clays with 3 % lithium and above can be exploited economically.

In Kenya, the demand for high quality ceramic products and aluminium is increasing day by day. (www.tradeandindustry.go.ke). This has led to the local industries importing these products to meet their daily demand. Mwea lies on the southern slopes of Mount Kenya and its clay soil occupies an estimated area of 400 Km^2 and over 20 m deep (Kamoni, 1992). Though most of the area is under irrigation, there remains a big portion of land still underutilized mainly due to the geomorphology of the land or shortage of water for irrigation bearing in mind the fact that Mwea receives a mean annual rainfall of 893 mm annually (Kenya Metrological Department, 1994). Thus, setting up a ceramics industry or an aluminium manufacturing plant in the area would uplift the economic wellbeing of Mwea people.

2 LITERATURE REVIEW

2.1 Geology and occurrence of clay

Clays may originate from several processes which include, hydrolysis and hydration of silicates, dissolution of limestone or other soluble rock containing relatively insoluble clay impurities that are left behind, slaking and weathering of clay-rich sedimentary rocks (shales), replacement of a pre-existing host rock by invading guest clay whose constituents are carried in part or wholly by solution, deposition of clay in cavities or veins from solution, bacteria and other organic activity including the extraction of metal cations as nutrients by plants, alteration of parent material or diagenetic processes following sedimentation in marine and fresh-water environments, resilication of high alumina minerals and action of acid clays, humus and inorganic acids on primary silicates (Raleigh, 1986).

The geological aspect of Mwea region indicates that the area is covered by basaltic agglomerates series which overlies grantiod gneisses of the basement system (Baker, 1960). The series include a succession of basaltic agglomerates containing porphyritic feldspar basalts, melanocratic basalts and also a series of brecciated balsalts with rare porphytrite feldspar. These basalts are as a result of volcanic eruptions on the flanks of Mount Kenya (Kamoni, 1992).

Feldspar has been known as one mineral that undergoes alteration through slaking and weathering of the clay-rich sedimentary rock (Grimshaw, 1971). It looses its alkalinity, some of its silica and gains water of constitution to form clay. Its presence as porpyritic feldspar

basalt in the basement system of the parent rock must have therefore contributed highly to the presence of clay in this region (Baker, 1960).

Volcanic eruptions may have led to iron (III) oxide deposition on the lower beds of the area. However, bacteria and other organic activities may lead to lowering of the pH of the soil causing leaching of some iron (III) oxide as respective soluble salts. This reduces the percentage composition of the iron oxide in the respective soils (Baker, 1967), and explains why though Mwea lies on the foot of Mount Kenya, the iron content in this clay is relatively low.

2.2 EXAMPLES OF CLAY MINERALS

Clays occur in many minerals (Kirk and Othmer, 1978). Table 2 shows a few examples of such minerals. A common feature of these minerals is that each contains aluminium and silicon, usually as alumino-silicates.

Table 2: Examples of clay minerals (Kirk and Othmer, 1978).

Name	Formulae
Alunite	$Be_3Al_3Si_6O_{18}Cr_2O_3$
Beryl	$Be_5Al_2Si_6O_{18}$
Dumortierite	$Al_8B(OH)Si_3O_{19}$
Anorthite	$CaAl_2Si_2O_8$
Spodumene	$LiAlSi_2O_6$
Lepidolite	$K_2Li_3Al_3(F,OH)AlSi_3O_{10})_2$

As noted in these examples, many of clays contain other metal ions in addition to aluminium. It is the presence of such metals, and the conditions of formation like pressure and erosion which give the various types of clays (Grimshaw, 1971).

Clay deposits usually contain both crystalline and amorphous mineral compounds (Bailey, 1978). In crystalline solids, the particles making up the solid are cations and anions that are arranged in a regular repeating pattern in a three-dimension network (Edward, 1976). In clays, the cations are usually simple and the anions are complex as in the mineral anorthite ($CaAl_2Si_2O_8$). In the amorphous clay, the molecular particles are mixed in any proportion. In such a solid, the constituent particles can be in any ratio (Levy, 1967).

2.3 Types of clays

2.3.1 Kaolins

Kaolin is a soft white-grey plastic clay which is a hydrated aluminium silicate ($Al_2Si_2O_5(OH)_4$). It is mainly formed by the alteration of feldspar and muscovite. Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration while secondary kolins are sedimentary in origin (Bohn, 1982).

Kaolins include Kaolinite, Dickite, Nacrite and Halloysite. The different minerals are polymorphs, meaning that they have the same chemical composition but different structures which are distinguishable through X–ray analysis (Edward *et al.,* 1976). For example, kaolinite is composed of one aluminium hydroxide sheet and one SiO_4 tetrahedral sheet, in which each

apical oxygen ion of the SiO_4 tetrahedral sheet replaces one hydroxyl group of the aluminium hydroxide sheet and forms what, is known as 1:1 type of structure (Fitzpatrick, 1994). Figure 1 shows the structure of kaolinite.

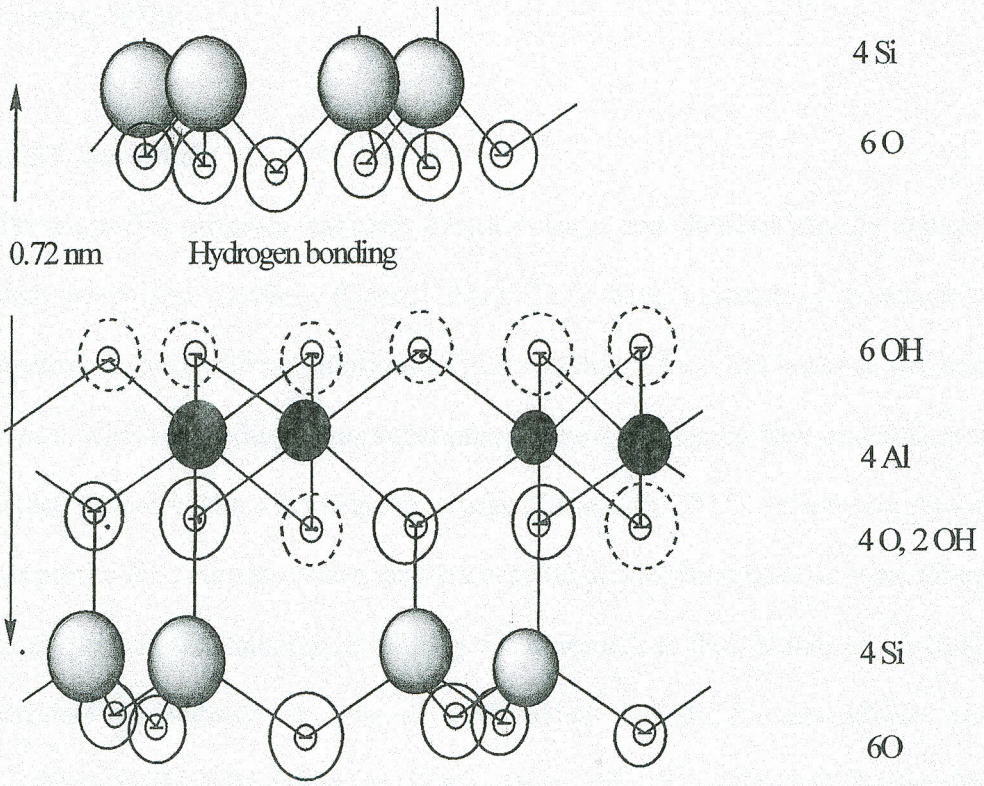


Figure 1: Structure of kaolinite (Fitzpatrick, 1994).

Kaolins are high quality clays in that they have high brightness and relatively low viscosity at high solids concentration (70%). Due to this and their low impurity levels, kaolins are the most widely used clays (Sposito, 1989).

2.3.2 Serpentines

These results from partial substitution of aluminium in the kaolin structure by magnesium, iron or both. Examples of serpentines include Amesite $(Mg_2Al)(SiAl)O_5(OH)_4$, Cronstedite $(Fe^{2+}Fe^{3+})(SiFe^{3+})O_5(OH)_4$ and Chemosite $(Fe^{2+}Mg)_{2.3}$ $(Fe^{2+}Al)_{0.7}(Si_{1.14}Al_{0.86})O_5(OH)_4$ (Taylor, 1978).

2.3.3 Smectites

These are clay minerals that carry a lattice charge and characteristically expand when solvated with water and alcohols (Grim, 1981). They have a structure in which one aluminium hydroxide sheet with substitutions of iron and magnesium lies between two silicon tetrahedral sheets with some aluminium substitution. The presence of iron and magnesium leaves the lattice structure with a net negative charge (Gieseking, 1975). As a result, they are mainly used for purification purposes since they are capable of adsorbing positive ions. Smectites have very small particle size and a great affinity for water due to their ability to expand and contract in response to addition or loss of water. They include Montmorillonite ($[Al_{1.67}Mg_{0.23}(Na_{0.33})]S_4O_{10}(OH)_{2,}$), Beidellite $(Al_{2.17}[Al_{0.33}(Na_{0.33})Si_{3.17}]O_{10}(OH)_2$ and Nontronite $(Fe_3[Al_{0.33}(Na_{0..33})Si_{3.67}]O_{10}(OH)_2)$ (Nelson, 1960). Figure 2 shows the structure of montmorillonite (Fitzpatrick, 1994).

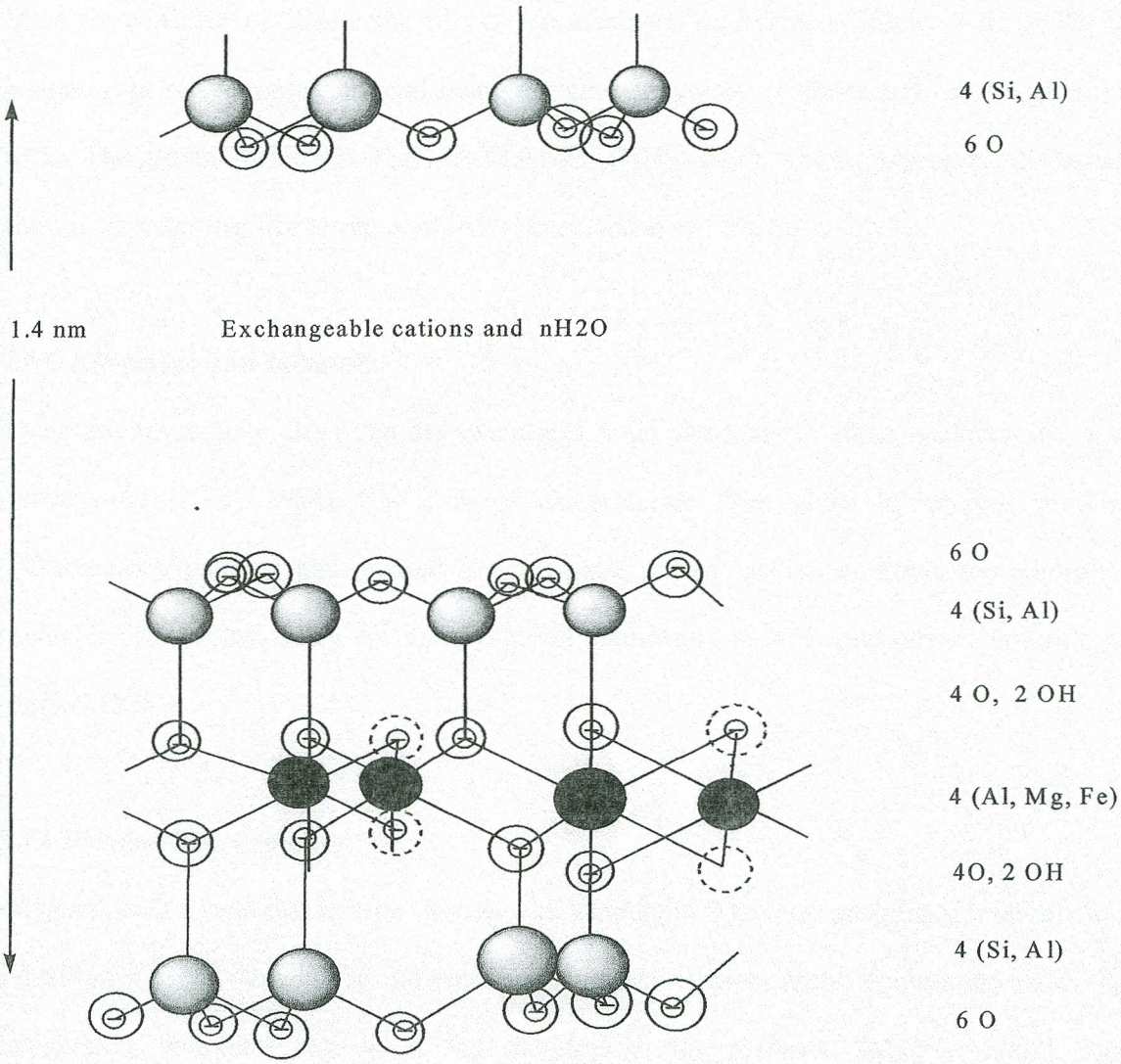


Figure 2: Structure of montmorillonite (Fitzpatrick, 1994).

2.3.4 Illites

This is a general term for the clay constituents or argillaceous sediments that belong to the Mica group. However, Illite is the only common mineral represented (Shreve *et al.,* 1977). It is a significant rock-forming mineral being a main component of shales and other argillaceous rocks. The general formula is $(K,H)Al_2(Si,Al)_4O_{10}(OH)_2\text{-}xH_2O$, where x represents the variable amount of water that this group contains (Greenland *et al.,* 1991).

2.3.5 Allophane and Imogolite

These are amorphous clays that are essentially solid solutions of silica, alumina and water (Greenwood *et al.,* 1984). The lack of characteristic lines given by crystals in X-ray diffractometry patterns and gradual loss of water during heating confirms the amorphous character of the clay. They are mainly found abundantly in soils and altered volcanic ash (Keller, 1978)

2.3.6 Palygorskite-Sepiolite

Palygorskite is a term that is synonymous with attapulgite. The term attapulgite is largely used industrially even though the international mineral nomenclature committee ruled that palygorskite was first term used and therefore is the preferred (Murray, 2002). Both palygorskite and sepiolite are hydrated magnesium aluminium silicates with elongated chain type structures though sepiolite has higher magnesium content than palygoskite and have a slightly larger unit cell. When dispersed in water, these elongated crystals are inert and non-swelling and form a random lattice capable of trapping liquid and providing excellent thickening, suspending, and gelling properties (Amethyst, 1996). Figure 3 shows the structure

of palygorskite. These clays do not flocculate with electrolytes and are stable at higher temperatures, which make them uniquely applicable for many uses (Murray, 2002).

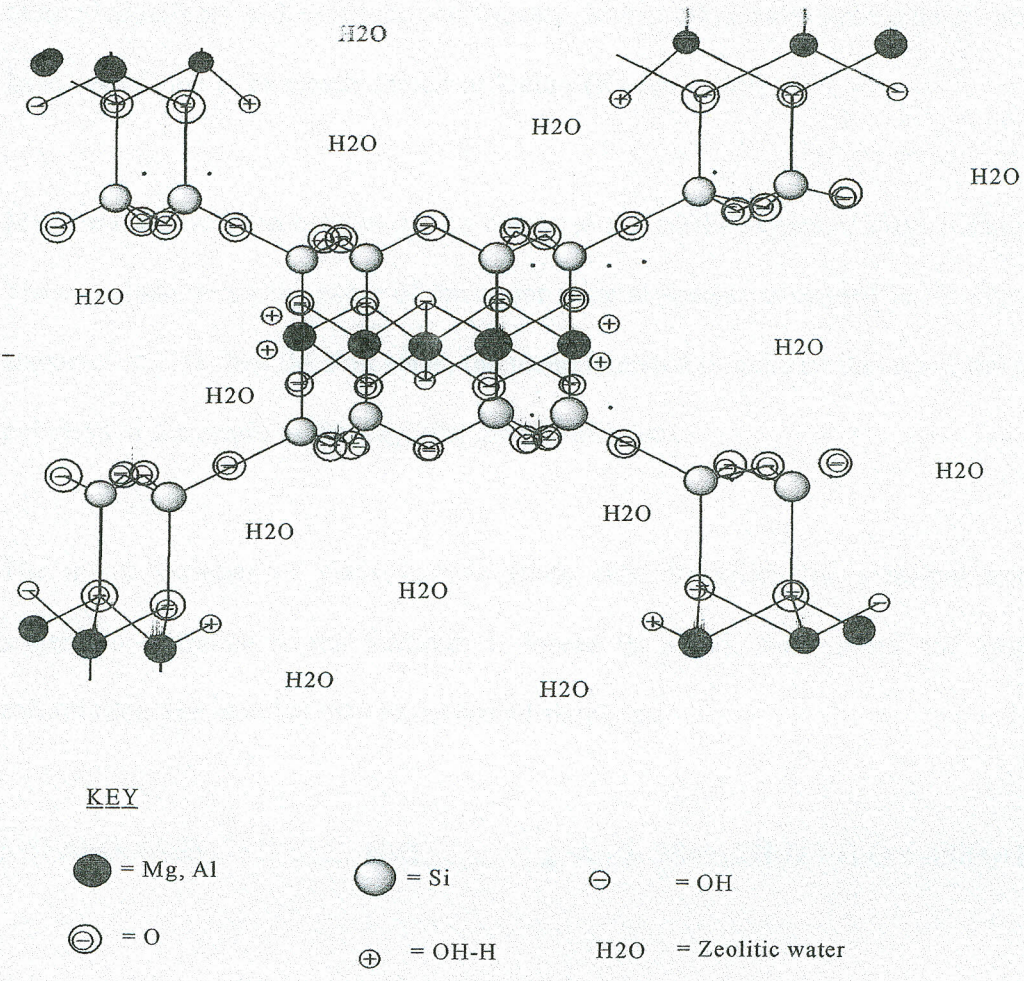


Figure 3: Structure of palygorskite (Fitzpatrick, 1994).

2.4 Composition and naming of clays

Clays in their natural form consist of many different minerals of either primary or secondary origin (Levy, 1967). The proportion of each mineral varies according to the origin and subsequent natural treatment. In most materials described as clays, the clay minerals are the most predominant and essential constituents. Mwea clays have been studied previously and have been found to be mostly montmorilonites (Kamoni, 1992).

Many ways have been used in giving names to the various types of clays (Grimshaw, 1971). These include, using the name of the major mineral species contained in the clay, the type or character of clay, like the flint clays, the name intended to indicate the use of the clay, like the pot clays or the origin of the clay, like montmorillonite.

The major varieties of clays include china clay, in which the principal mineral which undergoes alteration is the feldspar. It looses its alkali, some silica and gains water of constitution. The reaction may be presented simply as;

$$K_2O.Al_2O_3.6SiO_2 \xrightarrow{H_2O} Al_2O_3.2SiO_2.2H_2O + H_2O + 4SiO_2 + K_2O$$

.

The composition of this material varies greatly and may contain about 25-30 % of kaolinite (Wells, 1984). The remainder consists of unchanged quartz, mica and other primary minerals. Halloysite-bearing clays contain the mineral halloysite. These are more plastic and produce a

dense fired body. Ball clays are plastic or sticky and they burn white. One essential feature of ball clays is their fine grain size, which is the main reason for their high plasticity. Ball clays are usually sedimentary in character. They are of value because they can be added to the molded shape and yet maintain the white colour after firing. They contain mainly lignite (Hesse, 1972). Refractory clays are highly resistant to heat without loss of shape while flint clays are hard, virtually non-plastic but have high alumina content. They are mainly composed of kaolin minerals, mostly kaolinite and diaspore. They are extremely dense, hard and highly refractory. They are mainly used as calcined grog in bricks, castable and ramming composition where greater volume and heat stability coupled with high resistance to abrasion are essential (Environmental Literacy Council, 2005). Basically, ball clays, fire clays, flint clays and under clays are associated with kaolinites. Others include bonding clays, building brick clays and clays for ceramic ware (Kirk Othmer, 1978).

2.5 Characteristic of clays

For any substance to qualify to be called clay, it must possess the following properties.

2.5.1 Plasticity

Plasticity may be defined as the behavior of clays when they are mixed with water but in insufficient amounts to permit flow without externally applied stress (Grimshaw, 1971). It is generally accepted that plasticity is associated mainly with particles which are of colloidal size. Therefore, it is related to the fundamental concepts of the colloidal micelle (Astbury *et al.*, 1966).

Plasticity of clays is of primary importance since the success of any pottery depends upon the capacity of the wet clay to maintain its shape under pressure of the hand during the forming process (Roskill Information Service, 2004). The fineness of the individual clay particle has much to do with plasticity. For example, montmorillonite type clays such as bentonite particles average 0.05 microns in diameter and are known to be the most plastic (Moore, 1983). Hence the finer the clay the more plastic it is.

The presence of small amounts of organic matter encourages the formation of acids which in turn breaks down the compounds composing the clay thus increasing its plasticity (Nelson, 1960). The first test for plasticity usually applied to new clay is to roll out a soft wad of the clay into a shape the size of a lead pencil and then coil it around one's finger. If no cracks appear, then it is good (Witt, 1966).

2.5.2 Porosity

This is another important quality which any clay should possess. Strange as it may seem, it is possible for clay to be so plastic that it is too tightly compacted to allow the water to dry out without cracking. In such a case the clay may not be useful; hence the clay should be able to let water dry out with time to allow formation of the dry mold (Wilson, 1990).

2.5.3 Vitrification

It is necessary for the clay body to develop to the proper point of hardness at a temperature at which the glaze used will penetrate the product and form a glassy coating over the ware (Sudo, 1969).

2.5.4 Shrinkage

It is essential that all clay slips used in decorative processes shrink at the same rate as the body or flaking and peeling is likely to result. Because of the shrinkage variations, alterations are occasionally made in the glaze formulation depending upon its use as either raw, wave or bisque (Kirk and Othmer, 1979).

2.6 Some uses of clays

Clays are composed of extremely small particles of alumino-silicate minerals as noted earlier. These are generally crystalline, but some like allophanes have very poor organization, thus diffraction patterns show them as amorphous (Cornelius, 1973). The major use of clay is in the ceramic industries, which includes manufacture of bricks, tiles, heat-resistant refractory materials, porcelain, pottery and chinaware. This is done by plasticizing the clay by addition of water so that it may be shaped into the desired object. The object is then dried to increase its strength so that it may be handled safely. It is then fired at elevated temperatures until fusion of the various components occurs thus making the shape permanent and strong so that the object does not disintegrate in water (Kriegel, 1978).

Clay is also used in making of catalysts used in cracking of petroleum (Bush *et al.,* 1966). These catalysts are produced from halloysites, kaolinite and montmorillonite by leaching the natural clays with dilute sulphuric acid to free them from high levels of iron and various elements such as heavy metals which would favour either catalyst poisoning or unfavorable product distribution.

Clays have also been used to decolourize, deodorize, dehydrate and neutralize vegetable and animal oils (Mickelson *et al.,* 1974). Attapulgite and montmorillonite clays have been used for this since they have good filtration characteristics. That is, the oil is able to pass through fairly rapidly without undue binding of the filters by the clay. Pure white clay (Kaolin) is used as a filler in paper making. This is due to its fine particle size, platy particles, good viscosity, low abrasion, good opacity, high brightness, and good print quality (Murray, 2002). This is done because the cellulose fibers of the paper are not well suited for high-fidelity printing because of transparency and irregularities of the paper surface (Brinker *et al.,* 1990).

Clays have been used for centuries in therapeutic intestinal adsorbent preparations against intestinal irritations (Goodman *et al.,* 1977). This is due to their very fine particles which yield very large surface areas that are physically sorptive and chemically reactive because of the overall negative electron charge owing to internal substitution by low valent cations. This leads to increased reactivity in chemical combination and ion exchange. It is believed that they function by adsorbing toxins and bacteria responsible for intestinal disorder and by coating the inflamed mucus membrane of the digestive tract (Clifford *et al.*, 1973).

For a long time, clays have been used in the preparation of pastes, ointments and lotions for external use (Raleigh, 1986). Many of these cosmetic formulations take advantage of the clay's softness, dispersion, gelling, emulsifying, adsorption or other properties. In paints and plastics, clay is used as inert filler due to its good oil-absorption and suspension properties (Terpstra, 1976).

Clays have been used for a long time in the manufacture of Portland cement. The term cement is used to designate many different kinds of substances that are used as binders or adhesives (Bogue, 1969). The cement produced in the greatest volume and mostly used in concrete for construction is Portland cement. Other types of cement include masonry oil, and calcium aluminate cements which are extensively used for refractory concretes. Portland cement is hydraulic cement meaning that it sets, hardens and does not disintegrate in water. Hence it is suitable for construction of underground, marine, and hydraulic structures (Kirk Othmer, 1981). Hydraulic cements are manufactured by processing and proportioning suitable raw materials, burning (or clinkering) at suitable temperatures, and grinding the resulting hard nodules called clinker to the fineness required for an adequate rate of hardening by reaction with water.(Lea, 1971)

Clay has also found use as an alternative source of aluminium. This has resulted from the dwindling of the world deposits of the minerals cryolite (Na_3AlF_6) and bauxite [AlO(OH)] which have been used as source of aluminium (Greenland *et al.,* 1978). According to the International Aluminium Institute (IAI) Statistical Report, the primary aluminium production was expected to be 26,129,000 of metric tones by June 2006 (IAI, 2005). This has led clay being used as an alternative source of aluminium in countries like Korea and U.S.A (Kyun *et al.,* 1997). Figure 4 shows a summary of the various percentage uses of clay.

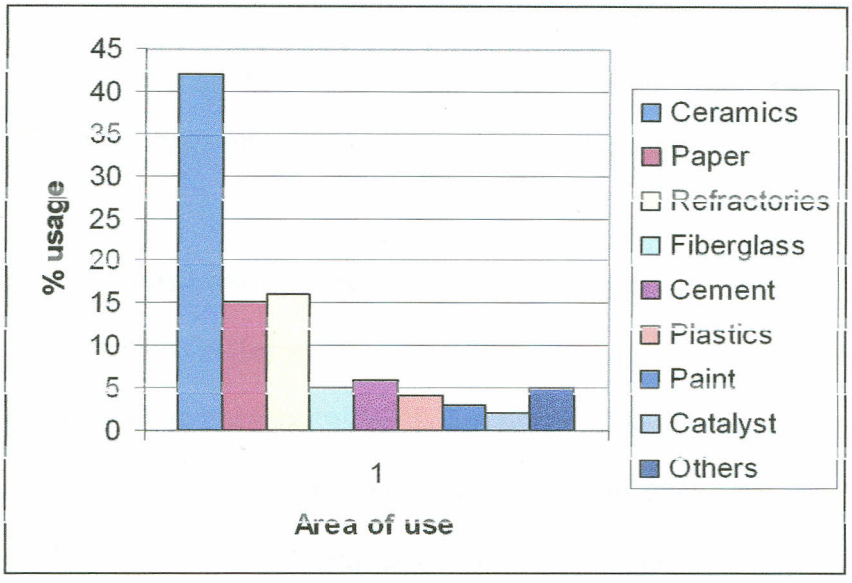


Figure 4. World distribution of clay usage in percentage (Roskil, 2005)

Kaolins are the most widely used clays with an estimated world production of 42 million tons per year. Bentonite is the second with an estimated annual production of 12 million tonnes, while Palygorskite- Sepiolite is third with a production of 1.4 million tons annually. The area of use depends mainly on the quality and character of clay (Roskill, 2004).

2.7 Analytical techniques

Although a number of sensitive and reliable analytical techniques for analysis of clay are known, three techniques, namely X–ray Fluorescence Spectroscopy (XRFS), Atomic Absorption Spectroscopy (AAS) and EDTA titrations were used in this study.

2.7.1 X–Ray Fluorescence Spectroscopy analysis

XRFS involves characteristic X–rays being emitted from transitions involving K and L electrons when chemical elements are subjected to a beam of X-rays. The wavelengths and intensity of emission measurements are used for qualitative and quantitative analysis (Fified *et al.,* 1995). Atoms in the samples are excited by bombardment with X-rays. Primary X-rays are produced by bombardment of a target, e.g. tungsten with a stream of high energy electrons or nuclear particles at 20 or 50 KeV from a radioactive source such as Americium (^{241} Am). The primary X-rays are then directed onto a secondary target (the sample) where a proportion of the incident rays is absorbed. This absorption process leads to ejection of inner K or L electrons from the atoms of the sample. Subsequently the excited atoms relax to the ground state. During relaxation, many excited atoms will lose their excess energy in the form of secondary X-ray photons as electrons from higher orbital drop into the "holes" in the K and L shells (Skoog *et al.*, 1992).

For reasons of sensitivity and versatility, the combination of high power sealed X-ray tube and wavelength dispersion by selected crystals remains the most practical and preferred technique for quantitative X-ray fluorescence analysis (Schenk *et al.*, 1981).

2.7.2 Atomic Absorption Spectroscopy (AAS)

2.7.2.1 Theory of atomic absorption spectroscopy

Atomic absorption is a physical process involving the absorption (by free ions of an element) of light at a wavelength specific to that element. Absorption of light is associated with the process of transition of atoms from one steady state to another (Vanloon, 1980).

For the case of steady states 0 and P (where 0 is the ground state and P the excited state), with energies E_0 and E_P, where $E_P > E_0$, the O→P transition results in the emission of light with frequency

$$V_{OP} = \frac{E_P - E_0}{h} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.1$$

Where h is Planck's constant.

The 0→P absorption transition is always stimulated by external radiation. This phenomenon forms the integral part of Atomic Absorption Spectrometry (Mclerman *et al.,* 1995).

For an unexcited atom, each electron is in the ground state, otherwise it is excited. The proportion of excited to ground state atoms in a population at a given temperature is given by the general statement of the Maxwell-Boltzmann law

$$\frac{N_P}{N_0} = \frac{g_p}{g_o} \exp\left[\frac{Eo-Ep}{KT}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.2$$

Where N – is the number of atoms in state O or P

g – is the statistical weights for states O or P

T – is the temperature

k – is the Boltzmann constant

The wavelength at which an atom with its valency electrons in the ground state can absorb radiation are called resonance wavelength (Skoog *et al.,* 1992)

To calculate how much light is absorbed by a cloud of atoms, parallel beams of light at the resonance wavelength for the atoms concerned are considered when striking a cell containing N atoms. If light of intensity I_0 enters the cell, the intensity remaining after absorption is given by

$$I_1 = I_0 \exp[-kL] \quad \ldots\ldots 2.3$$

Where L is the cell length and k is the absorption coefficient (i.e. the fraction of energy absorbed per unit length).

Taking logarithms of both sides,

$$kL = \log \frac{I_0}{I_1} \quad \ldots\ldots 2.4$$

The expression $\log I_0/I_1$ is defined as absorbance.

Since the product KL is proportional to the number of atoms in the cell, so is absorbance. For this reason, absorption is the preferred readout mode of modern atomic absorption spectrophotometer, giving a linear relationship between absorbance and concentration.

2.7.2.2 Instrumental principles

Any atomic absorption spectrophotometer consists basically of:-

(a) A light source which emits the sharp line spectrum of the element to be determined

(b) A method to produce atomic vapour of the sample to be analyzed

(c) A wavelength selector to isolate the resonance lines

(d) A detector, amplifier, and a readout system

2.7.3 Ethylenediamine-tetra-acetic acid titrations (EDTA)

The EDTA anion (Y^{4-}) has the widest general application in analysis because of the spatial structure of its anion which has six ligand atoms, thus corresponding with the co-ordination number most frequently encountered among the metals. In addition, it forms strain- free five-membered rings on chelation (Vogel, 1978).

The efficiency of metal-EDTA complex formation is determined by the concentration of the Y^{4-} ion, the pH of the solution, the solubility of the metal hydroxide and its solubility constant.

Thus the titration of each metal with EDTA is governed by the pH in which its complex is most stable. Hence, due to its great versatility arising from its inherent potency as a complexing agent and from the availability of the numerous metal-ion indicators, each effective over a range of pH values for different elements, EDTA is the most useful titrant in analysis of metals (Hesse, 1972).

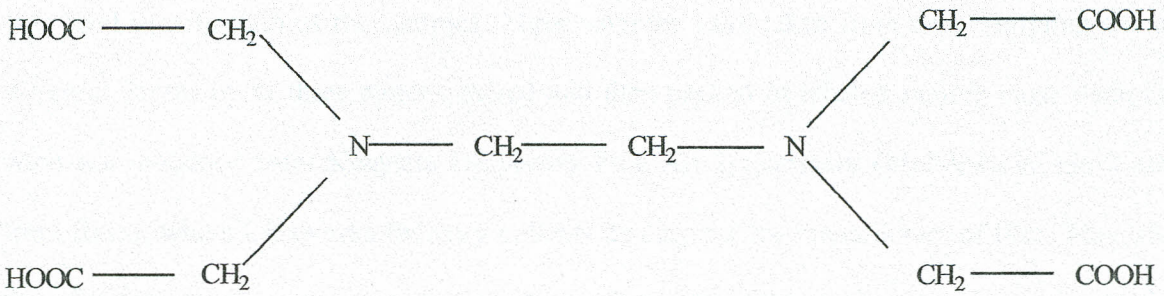


Figure 5. Structure of EDTA

CHAPTER THREE

METHODOLOGY

3.1 Collection of samples

Sampling was done from various parts of Mwea (as indicated on appendix 7). Transient method was used in the collection of samples from the various identified sites. The vegetation cover was first cleared by use of a panga, followed by removal of the topsoil layer. An auger was used in collection of the samples. Three samples were taken from each sampling site at different depths up to three meters, mixed and then packed in labeled sample bags. Samples were also obtained from Kenyatta University Fine Art Department (Mukurwe-ini clay) and from Ruiru, where Clayworks Industry collects its clay for the manufacture of tiles. This was done for comparative purposes with clays from other parts of the region

3.2 Apparatus

All glassware used was scrupulously cleaned. This was done by soaking it overnight in chromic acid followed by further soaking overnight in a detergent and subsequent rinsing with distilled-deionized water. After each analysis, the glassware was rinsed with 50%v/v nitric acid, followed by distilled-deionized water. The glassware was then stored in a closed container. Nickel crucibles were washed in 10%v/v nitric acid followed by a detergent. They were then rinsed with distilled-deionized water. Sample bottles and other plastic containers were washed with 50%v/v nitric acid, followed by a detergent and subsequent rinsing with distilled-deionized water.

3.3 Chemical reagents

Analytical grade reagents were used. The water used throughout the experiment was distilled in a Pyrex distiller and then deionized in an Elgastal micromeg deionizer cartridge.

3.4 Instruments and their settings

3.4.1 pH Meter and Measurements

All pH measurements were done using a Microprocessor pH Meter model 211 from Hannah Instruments. Buffer solutions were prepared for calibration of the instrument. These were prepared by dissolving standard pH buffer tablets; pH 7.0, pH 4.0, and pH 9.0 in 100ml of distilled water.

3.4.2 Weighing balance

All weighing was done using an analytical balance model AAA from the Adam Equipment Co-Ltd.

3.4.3 Atomic Absorption Spectroscopy (AAS) and X-Ray fluorescence Spectroscopy (XRFS)

Both AAS and XRFS were calibrated using SY-2 rock standard for all the analysis except titanium where MRG rock standard was used. This is because the level of titanium in the SY-2 rock standard was low compared with the amount in the MRG rock standard. The SY-2 and MRG rock standards were obtained from Canadian Centre for Mineral and Energy Technology (CCMET) through the Department of Mines and Geology, Ministry of Environment and Natural Resources of Kenya.

Table 3. Percentage chemical composition of the rock standards in oxide form (CCMET, 1991)

Rock	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
SY-2	60.07	12.15	5.92	2.66	8.03	4.37	4.52	0.15	0.33	0.07
MRG	39.09	8.46	17.94	13.55	14.71	0.74	0.18	3.69	0.03	0.09

However, these standards may not give reliable results where the element of interest is less than 0.01 %.

For AAS, the given instrumental condition for each parameter was set as indicated in table 3 while for XRFS, minipal/minimate software was used.

Table 4.Instrumental conditions for AAS analysis

Element	Lamp current (amps)	Slit width (nm)	Wave length(nm)	Acetylene flow(Psi)	Photomultiplier voltage(V)	Flame
Mn	5	0.2	279.5	1.5	349.9	Air-Acetylene
Al	6	0.5	309.3	4.5	287.4	N_2O-Acetylene
Fe	8	0.2	248.3	1.5	340.5	Air-Acetylene
Si	7	0.2	251.6	4.5	359.3	N_2O-Acetylene
Mg	3	0.5	285.2	1.5	318.6	Air-Acetylene
Ti	10	0.5	364.3	4.5	303.0	N_2O-Acetylene
Na	None	0.5	589.0	1.5	365.5	Air-Acetylene
K	None	1.0	766.5	1.5	353.5	Air-Acetylene
Ca	None	0.5	422.7	4.5	231.1	N_2O-Acetylene

3.5 Sample pre-treatment and analysis procedures

Samples of the clays were dried in an oven at 110^0C for 8 hours and then allowed to cool to room temperature in a desiccator. They were then crushed using Elmol-Schafer crusher type WDR 80g to obtain fine particles which were then ground into a finer powder for 6 hours in a ball mill. EDTA titrations, XRFS, and AAS methods were used for the analysis of the various oxide composition of the raw clay.

3.5.1 X-Ray Fluorescence Spectrophotometer Analysis

Ten (10.0) grams sample of the dried clay powder was weighed and ground to pass through a 45μm sieve. 2.0g of flux starch, which acts as a binder were added and a uniform mixture of the two obtained by swirling and shaking in a plastic container. The resulting mixture was made into pellets using a Herzog pellet maker. The pellets were then put into sample cups for sequential X-Ray Spectrophotometer (serial model PW4025) for full assay analysis. The results were recorded in terms of the oxides of the elements.

3.5.2 Atomic Absorption Spectrometer Analysis

A sample of the finely ground clay weighing 0.1g was put in a plastic bottle. 2ml of 1:1 concentrated HCl and HNO_3 were added, the bottle stoppered loosely and left to stand overnight. 3ml of HF was then added and the bottle immediately stoppered to avoid loss of silicon and the sample left to stand for 6 hours. Heating was then done in a water bath to ensure that all the sample had dissolved. 50ml of boric acid was then added and the solution left to stand for 1 hour. 46ml of de-ionized water were then added. SY-2 and MRG rock standards were also digested as the sample and used as the standard during the analysis. For the

standards, dilutions of two, four and eight were made. The samples were then analyzed and the results compared together with those of the standards to determine the percentage composition of the samples with particular reference to aluminium and iron using AAS instrument (Varian AA.10 model).

3.5.3 EDTA Titrations

One gram of the ground clay was fused with 5g of NaOH in a Nickel crucible at 600^0C in a furnace. After allowing the crucible to cool, enough water was added to just cover the fused solid. The crucible was then placed in a water bath and water warmed until the solid residue contents of the crucibles disintegrated. The mixture was filtered through whatman paper No. 42 filter paper and both the residue and the filtrate kept for further analysis. The filtrate was transferred into a 250-ml volumetric flask and diluted to the mark using distilled water. 25ml of the aliquot was transferred using a 25-ml bulb pipette into a 250-ml conical flask. 26ml of 0.01M EDTA was added from a burette and the resulting mixture heated to boiling. After cooling, the pH of the solution was adjusted to 7.5. 50mg of solochrome black -KNO_3 mixture were added and the resulting solution titrated with 0.01M $ZnSO_4$ until a wine red colour was obtained. The titration was done in triplicate and the titre was used to calculate the amount of aluminium (Vogel, 1978).

The residue was washed with 50ml of 12M HCl and refluxed for 10 minutes in a fume hood. The mixture was filtered using whatman paper No. 42, the filtrate put in 250-ml volumetric flask and made to the mark using distilled water. 25ml of this solution was transferred into a 250-ml volumetric flask and made to the mark using distilled water. The pH of the aliquot was

adjusted to 3 and variamine blue indicator added. The aliquot was then warmed to 40^0C and titrated with 0.01M EDTA for the analysis of iron (Vogel, 1978).

3.6 Treatment of clay with acids

The ground clay from each site was divided into six samples each weighing 50g. 100ml of 12M HCl was added to the first sample, 100ml of 10M HCl added to the second sample, 100ml of 8M HCl added to the third sample, 100ml of 6M HCl added to the fourth sample, 100ml of 4M HCl added to the fifth sample and 100ml 2M of HCl added to the sixth sample respectively. The samples were then left to stand for six hours. Another set of six triplicate samples were taken, treated the same way but the resulting mixture heated to boiling. A third set of the samples was also taken and treated the same way with H_2SO_4 of 18M, 10M, 8M, 6M, 4M, and 2M, respectively. A fourth set was also taken, treated as the third set but further heated to boiling.

Filtering was then done using whatman No.42 sintered glass crucible and the residues washed with distilled water. The residues were then analyzed for their full assay using EDTA titrations, AAS, and XRFS with particular reference to aluminium and iron.

3.7. Analysis of clays heated to various temperatures

The ground clay was divided into 5 samples and heated to temperatures of 200^0C, 300^0C 400^0C, 500^0C and 550^0C respectively for 2 hours. Each sample was then refluxed with a known concentration of hydrochloric acid for one hour. The residue was then filtered through whatman No.42 paper and the residue washed with distilled water. The residue was then

analyzed using EDTA titrations, AAS, and XRFS with particular reference to aluminium and iron.

3.8 Analysis of clays treated with concentrated H_2SO_4

A sample of 100.0g of the ground clay was put in a 2-way flask and refluxed with 200ml of concentrated H_2SO_4 for 2 hours at 200^0C. The mixture was then cooled, filtered, and the residue washed with distilled water. The residue was then dried at 130^0 C for 6 hours in an oven, cooled, and analyzed for the various elemental composition using XRFS, AAS, and EDTA titrations as described earlier.

3.9 Loss on ignition (LOI)

A 0.5g of the sample was weighed and heated to 300^0 C in an oven. On cooling to room temperature, the sample was then re-weighed again to determine the amount of water and organic matter content.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Elemental analysis of raw clay

The raw clays from the various sampling sites from Mwea region namely Kiarukungu, Nguka, Kandongu, Cumbiri, Mutithi, Kiandegwa, Kiamanyeki and Mathangauta (as indicated in appendix 7) were analyzed for their full assay in oxide form using AAS and XRF. Table 5 contains results obtained using XRFS while table 6 contains results obtained using AAS. XRFS and EDTA methods were used to confirm the results obtained using AAS.

From the data obtained, silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) in Kenya clays constitute over 60% of the oxides composition of clays from this region. This conforms to the percentage composition of the two as found in other typical clays from various parts of the world (Gathua, 2004). The level of each elemental oxide is given in the tables in percentage of the oxide form. Kiamanyeki clays showed the highest amount of aluminium oxide while Nguka gave the least value of the same.

The levels of titanium oxide were found to be relatively high (3.35-5.17%) when compared to clays from Mukurwe-ini and Ruiru that 1 and 1.1% respectively and are mainly used for ceramics and brick manufacture respectively. These levels are significantly high considering that titanium ore deposit with 5-6 % content is viable for the mineral exploitation (Ong'alo,

2001). The percentage composition of aluminium oxide in Mwea, Mukurweini and Ruiru clays range from 15.7 – 34.3 %. These are levels viable for extraction of the element and compares well with clays from Korea and Japan which contain 16 -27 % aluminium oxide and have been used for aluminium extraction (Downa, 1993). Other elemental oxides occurred in small amounts and hence, their extraction is uneconomical.

The high level of iron (ranging between 12.6 – 15.9 % iron (III) oxide) in these clays implies that whereas they may be suitable for the manufacture of products like bricks, they are unsuitable for high quality ceramic products. Normally clays used for high quality ceramic products such as bathroom tiles should have less than 1% iron oxide (Olale, 1985).

Table 5. Percentage chemical composition of raw clay from the various sites in Mwea analyzed using XRFS.

Sample source	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	K_2O	MnO	LOI	Total
Mathangauta	43.9± 1.5	22.1± 1.1	14.1± 0.24	4.52± 0.11	1.74± 0.09	0.20± 0.06	0.14± 0.01	12.6± 0.59	99.3
Mutithi	44.9± 2.2	19.4± 0.92	13.6± 0.62	4.11± 0.09	1.57± 0.02	0.36± 0.03	0.21± 0.01	13.2± 0.47	97.35
Kiandegwa	47.5.± 1.4	17.9± 1.2	15.1± 0.75	4.81± 0.10	1.76± 0.03	0.21± 0.04	0.42± 0.02	9.80± 0.63	97.49
Kiamanyeki	44.6± 1.7	22.4± 0.83	12.4± 0.87	3.61± 0.07	2.21± 0.04	0.23± 0.06	0.18± 0.03	14.6± 0.67	99.93
Nguka	49.5± 1.0	15.7± 0.64	14.4± 1.2	3.35± 0..09	0.89± 0.03	0.34± 0.04	0.21± 0.03	13.4± 0.76	97.79
Cumbiri	48.6± 1.9	17.5± 0.96	12.6± 0.7	3.72± 0.05	2.05± 0.01	0.27± 0.05	0.19± 0.05	15.6± 0.81	100.42
Kandongu	51.6± 0.97	16.5± 1.1	13.1± 0.68	3.86± 0.06	2.81± 0.02	0.23± 0.04	0.42± 0.02	13.2± 0.64	100.05
Kiarukungu	43.3± 1.2	19.1.± 0.09	15.9± 0.54	5.17± 0.08	2.69± 0.04	0.16± 0.04	0.29± 0.01	12.6± 0.52	99.21

Mean ± S.d (n=3)

Table 6. Percentage chemical composition of raw clay from the various sampling sites in Mwea analyzed using AAS.

Sample source	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2	CaO	MgO	K_2O	MnO	LOI	Total
Mathangauta	42.8 ± 1.7	21.0 ± 0.83	14.6± 0.3	0.39 ± 0.04	4.43± 0.07	1.66 ± 0.02	1.07± 0.02	0.21 ± 0.01	0.14 ± 0.01	12.6 ± 0.59	98.88
Mutithi	45.1 ± 1.6	18.7 ± 0.61	14.9 ± 0.50	0.46 ± 0.02	4.01 ± 0.03	1.62 ± 0.05	0.99± 0.03	0.31 ± 0.02	0.26 ± 0.02	13.2 ± 0.47	101.56
Kiandegwa	46.9 ± 1.2	17.1 ± 0.76	16.6 ± 0.97	0.47 ± 0.03	4.67 ± 0.01	1.93 ± 0.01	1.26± 0.05	0.24 ± 0.01	0.37 ± 0.01	9.80 ± 0.63	99.34
Kiamanyeki	43.6 ± 1.4	22.7 ± 1.6	11.6 ± 0.53	0.40 ± 0.01	3.29 ± 0.06	2.35 ± 0.03	0.5 ± 0.04	0.18± 0.01	0.14± 0.03	14.6 ± 0.67	99.36
Nguka	50.1 ± 2.0	14.8 ± 0.90	15.2 ± 0.66	0.36 ± 0.02	4.00 ± 0.12	1.10 ± 0.02	0.90 ± 0.02	0.26 ± 0.03	0.15 ± 0.02	13.4 ± 0.76	101.27
Cumbiri	47.3 ± 1.7	16.9 ± 0.62	11.7 ± 0.18	0.34 ± 0.02	3.46 ± 0.08	2.54 ± 0.01	1.16 ± 0.02	0.20 ± 0.01	0.22 ± 0.01	15.6 ± 0.81	99.42
Kandongu	50.6 ± 2.1	16.2 ± 1.5	11.9 ± 0.37	0.41 ± 0.02	3.21 ± 0.04	3.09 ± 0.07	1.15 ± 0.03	0.23 ± 0.02	0.46 ± 0.02	13.2 ± 0.64	98.05
Kiarukungu	42.0 ± 1.6	20.2 ± 0.83	16.4 ± 0.71	0.37 ± 0.03	4.89 ± 0.02	2.52 ± 0.06	0.87 ± 0.04	0.19 ± 0.03	0.25 ± 0.03	12.6 ± 0.52	100.29

Mean ± S.d (n=3)

Table 7. Percentage chemical composition of Ruiru and Mukurweini clays in oxide form analyzed using AAS.

Sample source	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2	MnO	Fe_2O_3	MgO	LOI	Total
Mukurweini	57.3± 1.9	34.3± 1.1	0.83± 0.02	0.54± 0.01	0.12± 0.01	1.0± 0.02	0.03± 0.0	2.10± 0.63	0.17± 0.00	5.01± 0.09	101.02
Ruiru	54.6± 1.4	23.0± 0.79	0.71± 0.03	0.41± 0.02	0.45± 0.01	1.1± 0.02	0.19± 0.03	9.5± 0.21	0.09± 0.0	9.8± 0.47	99.67

Mean ± S.d (n=3)

Table 8. EDTA titration results for the determination of aluminium and iron oxides in the raw clay in percentage.

Sample source	Al_2O_3	Fe_2O_3
Mathangauta	19.6± 0.13	12.9± 0.03
Mutithi	18.2± 0.11	13.1± 0.04
Kiandegwa	16.5± 0.05	14.7± 0.02
Kiamanyeki	19.9± 0.06	10.6± 0.03
Nguka	13.4± 0.02	13.9± 0.03
Cumbiri	15.9± 0.04	13.8± 0.01
Kandongu	16.7± 0.02	12.4± 0.05
Kiarukungu	18.8± 0.06	14.7± 0.02

Mean ± S.d (n=3)

EDTA titration results gave results close to those obtained from the other two methods though statistical analysis indicated a significant difference for aluminium. The levels of aluminium obtained using this method were relatively low as compared to those obtained using the other two methods.

Table 7 shows the percentage oxide composition of clays from Ruiru and Mukurwe-ini. Mukurwe-ini clays had the least percentage of iron oxide. This explains why this clay is mainly used in ceramics industry. From the data obtained, the percentage elemental oxide composition of Ruiru clays is almost the same as those of Mwea with exception of titanium which is much higher for Mwea clays.

Table 9 shows the statistical analysis for the comparison of AAS and XRFS methods. Using significance **t**-test at $\mathbb{P} = 0.05$ and 16 degrees of freedom, the calculated absolute value of **t** was found to be less than the critical value at $\mathbb{P} = 0.05$ and $\mathbf{t} = 2.12$. This was for all the elements except sodium and magnesium which could not be analyzed using XRFS due to their low atomic number. However from atomic number 13, reliable results could be obtained using XRFS. Since the calculated value was less than the critical value, then the null hypothesis that there is no significant difference between the two methods holds. However, there was a significant difference for analysis of aluminium analysis using EDTA titration. The calculated **t** value was found to be 3.164 which was higher than the critical value of 2.12. This can be attributed to random errors during the experiment. There was no significant difference for iron since **t** calculated was found to be 0.8186.

Table 9. Statistical **t** - test analysis for AAS and XRFS methods at $\mathbb{P} = 0.05$ and $\mathbf{t} = 2.12$

Oxide	**t** calculated
SiO_2	1.5382
Al_2O_3	0.1483
Fe_2O_3	0.1663
TiO_2	0.8416
CaO	0.7818
K_2O	1.753
MnO	1.553

4.2 Analysis of the acid-washed raw clay

On washing the clays with various concentrations of mineral acids, it was noted that for the same molarity, hydrochloric acid was more effective than sulphuric acid in iron removal. Table 10 gives the results of acid-washed clays from Kiamanyeki. The clay had relatively low iron content as compared to other clays from Mwea. The presence of calcium in the clay might have led to the formation of insoluble calcium sulphate when sulphuric acid was used. The insoluble calcium sulphate formed led to reduced effectiveness of sulphuric acid in removing iron from the clays. The fact that sulphuric acid reacts with organic matter in clays while HCl do not could also have led to its ineffectiveness as compared to HCl. This explains why the levels of iron in the clays washed with sulphuric acid were much higher than in clays washed with hydrochloric acid.

There were also considerable reduction in levels of MgO and MnO in both HCl washed and H_2SO_4 washed clays. This is an indication that they exist as simple oxides in these clays. However, there was no much difference in levels of Na_2O, K_2O and TiO_2 for each of the acid-washed clays. HCl-washed clays showed a slightly higher percentage of aluminium oxide and SiO_2 in the residue while the percentage levels of Fe_2O_3 were much lower as compared to H_2SO_4 washed clays. It is for this reason that HCl was adopted for washing the clays because it was found to be effective in removing iron than H_2SO_4.

Table 10. Percentage composition of various elements (expressed as oxides) of Kiamanyeki clay washed with HCl and H_2SO_4. **Mean ±S.d (n=3)**

Clay	SiO_2	Al_2O_3	MgO	Na_2O	CaO	K_2O	TiO_2	MnO	Fe_2O_3	LOI	Total
Unwashed clay	43.6±1.4	22.7±1.6	0.50±0.04	0.40±0.01	2.35±0.03	0.18±0.01	3.29±0.06	0.14±0.03	11.6±0.53	14.6±0.67	99.36
2 M HCl	50.6±0.7	20.7±0.41	0.11±0.02	0.42±0.03	1.1±0.02	0.21±0.01	4.93±0.08	0.08±0.01	10.6±0.30	9.72±0.21	98.47
2 M H_2SO_4	51.4±0.4	18.7±0.32	0.37±0.06	0.40±0.23	1.47±0.04	0.18±0.01	4.77±0.07	0.05±0.01	11.7±0.46	8.96±0.73	98.00
4 M HCl	52.4±1.2	20.5±0.22	0.08±0.0	0.44±0.02	0.23±0.02	0.20±0.00	4.94±0.07	0.05±0.01	9.65±0.18	9.85±0.13	98.22
4 M H_2SO_4	53.6±0.6	19.5±0.31	0.26±0.03	0.37±0.02	1.40±0.06	0.17±0.01	4.68±0.05	0.03± 0.0	10.9±0.08	7.64±0.59	98.55
6 M HCl	53.5±1.1	21.3±0.31	0.05±0.00	0.44±0.01	0.22±0.0	0.19±0.03	4.93±0.0	0.03±0.01	7.79±0.13	10.4±0.17	98.85
6 M H_2SO_4	55.4±0.3	18.4±0.14	0.25±0.02	0.41±0.04	1.32±0.03	0.23±0.01	4.61±0.04	0.02±0.0	9.42±0.16	8.56±0.21	98.62
8 M HCl	56.7±2.2	21.3±1.2	0.09±0.01	0.44±0.03	0.03±0.00	0.21±0.02	5.10±0.09	0.01±0.0	5.61±0.18	11.32±0.4	101.01
8 M H_2SO_4	58.6±1.3	18.1±0.43	0.27±0.03	0.42±0.03	1.21±0.02	0.22±0.01	4.67±0.06	0.03±0.01	6.65±0.05	10.17±0.2	100.34
10 M HCl	54.0±1.7	23.4±0.97	0.03±0.00	0.45±0.01	0.03±0.00	0.24±0.01	4.99±0.02	0.00±0.0	5.42±0.24	12.9±0.37	101.46
10 M H_2SO_4	58.6±1.3	18.1±0.43	0.27±0.03	0.42±0.03	1.21±0.02	0.22±0.01	4.67±0.06	0.03±0.00	6.65±0.05	10.17±0.2	100.34
12 M HCl	55.2±2.3	22.0±0.94	0.02±0.00	0.47±0.03	0.04±0.00	0.23±0.02	5.01±0.11	0.0	5.53±0.21	11.9±0.33	100.4
18 M H_2SO_4	56.2±1.4	19.3±0.62	0.21±0.03	0.48±0.04	1.09±0.03	0.21±0.01	4.93±0.04	0.01±0.00	7.25±0.12	9.16±0.24	98.87

Tables 11 to 17 shows the results obtained when clays from the various sampling sites in Mwea were treated with various concentrations of HCl. It was evident that dilute HCl was not as effective in removing iron and other metal oxides from clays as concentrated acids.

Table 11. Percentage chemical composition of Kiarukungu raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	42.0± 1.6	20.2± 0.83	2.52± 0.06	0.37± 0.03	0.19± 0.03	4.89± 0.02	0.25± 0.03	0.87± 0.04	16.4± 0.71	12.7± 0.52	100.29
2 M	50.6± 0.73	20.7± 0.41	1.1± 0.02	0.42± 0.03	0.21± 0.01	4.93± 0.08	0.08± 0.01	0.11± 0.02	10.6± 0.3	9.72± 0.21	98.47
4 M	52.4± 0.14	20.5± 0.22	0.08± 0.0	0.44± 0.02	0.23± 0.02	4.94± 0.07	0.05± 0.0	0.08± 0.01	9.65± 0.18	9.85± 0.13	98.22
6 M	53.5± 1.1	21.3± 0.31	0.05± 0.01	0.44± 0.01	0.22± 0.0	4.93± 0.03	0.03± 0.0	0.06± 0.01	7.79± 0.13	10.4± 0.17	98.72
8 M	56.7± 2.2	21.3± 1.2	0.03± 0.00	0.44± 0.03	0.21± 0.02	5.10± 0.09	0.01± 0.0	0.04± 0.0	5.62± 0.15	7.94± 0.06	97.39
10 M	55.9± 0.35	22.5± 0.42	0.03± 0.0	0.45± 0.02	0.24± 0.01	5.09± 0.02	0.0	0.03± 0.0	5.49± 0.06	9.25± 0.13	97.98
12 M	56.5± 0.71	22.6± 0.26	0.02± 0.0	0.46± 0.01	0.23± 0.02	5.13± 0.04	0.0	0.02± 0.0	5.41± 0.03	8.64± 0.09	99.01

Mean ± S.d (n=3)

Table 12. Percentage chemical composition of Mathangauta raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	42.8± 1.7	21.0± 0.83	1.66± 0.02	0.39± 0.04	0.21± 0.01	4.43± 0.07	0.14± 0.01	1.07± 0.02	14.6± 0.71	12.7± 0.52	98.88
2 M HCl	49.4± 0.73	19.7± 0.25	1.3± 0.02	0.45± 0.01	0.23± 0.01	4.98± 0.03	0.08± 0.01	0.09± 0.02	10.2± 0.3	10.9± 0.51	97.42
4 M HCl	52.9± 0.09	20.7± 0.14	0.09± 0.0	0.49± 0.02	0.23± 0.02	4.96± 0.03	0.06± 0.0	0.06± 0.01	9.50± 0.11	9.62± 0.13	98.61
6 M HCl	53.2± 0.1	21.6± 0.24	0.05± 0.01	0.46± 0.01	0.23± 0.0	4.95± 0.02	0.03± 0.0	0.06± 0.01	7.64± 0.13	10.4± 0.17	98.62
8 M HCl	56.4± 1.8	21.0± 1.4	0.03± 0.00	0.44± 0.00	0.21± 0.02	5.13± 0.05	0.01± 0.0	0.04± 0.0	6.69± 0.15	8.19± 0.05	98.14
10 M HCl	56.2± 0.13	22.2± 0.25	0.03± 0.0	0.45± 0.02	0.24± 0.01	5.19± 0.02	0.0	0.03± 0.0	5.84± 0.04	8.95± 0.08	99.13
12 M HCl	56.4± 0.54	22.6± 0.12	0.02± 0.0	0.45± 0.01	0.24± 0.01	5.14± 0.03	0.0	0.02± 0.0	5.64± 0.02	8.76± 0.05	99.27

Mean ± S.d (n=3)

Table 13 Percentage chemical composition of Mutithi raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	45.1± 1.6	18.7± 0.61	1.62± 0.05	0.46± 0.02	0.31± 0.02	4.01± 0.03	0.26± 0.02	1.07± 0.02	14.9± 0.50	13.2± 0.47	101.56
2 M HCl	51.4± 0.25	19.1± 0.17	1.1± 0.02	0.45± 0.01	0.32± 0.01	4.95± 0.02	0.08± 0.01	0.09± 0.02	10.6± 0.21	11.1± 0.32	99.19
4 M HCl	53.2± 0.04	20.5± 0.10	0.09± 0.0	0.49± 0.02	0.33± 0.02	4.97± 0.02	0.05± 0.0	0.06± 0.00	9.32± 0.11	9.89± 0.06	98.80
6 M HCl	53.5± 0.23	20.9± 0.12	0.06± 0.01	0.47± 0.01	0.34± 0.0	4.95± 0.02	0.03± 0.0	0.06± 0.00	8.73± 0.11	9.53± 0.17	98.60
8 M HCl	57.0± 1.4	21.8± 0.6	0.03± 0.01	0.45± 0.01	0.33± 0.02	5.18± 0.06	0.01± 0.0	0.04± 0.0	7.32± 0.07	8.26± 0.05	100.42
10 M HCl	56.9± 0.13	22.6± 0.17	0.03± 0.0	0.45± 0.02	0.34± 0.01	5.17± 0.02	0.0	0.03± 0.0	6.89± 0.02	8.45± 0.04	100.86
12 M HCl	57.4± 0.43	22.9± 0.02	0.02± 0.0	0.45± 0.01	0.35± 0.01	5.23± 0.03	0.0	0.02± 0.0	6.61± 0.02	8.56± 0.05	101.54

Mean ± S.d (n=3)

Table 14. Percentage chemical composition of Kiandegwa raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	46.9± 1.2	17.1± 0.76	1.93± 0.01	0.47± 0.03	0.24± 0.01	4.67± 0.01	0.37± 0.01	1.26± 0.05	16.6± 0.97	9.80± 0.63	99.34
2 M HCl	51.9± 0.06	18.9± 0.11	1.0± 0.02	0.49± 0.01	0.26± 0.01	4.95± 0.02	0.08± 0.01	0.09± 0.02	9.16± 0.14	10.2± 0.42	97.03
4 M HCl	53.6± 0.11	19.8± 0.13	0.07± 0.0	0.51± 0.02	0.29± 0.02	5.06± 0.02	0.04± 0.0	0.07± 0.01	9.05± 0.14	9.76± 0.12	98.16
6 M HCl	54.1± 0.18	21.1± 0.06	0.06± 0.01	0.51± 0.01	0.28± 0.0	5.45± 0.02	0.03± 0.0	0.06± 0.00	8.65± 0.14	9.49± 0.11	99.73
8 M HCl	57.8± 1.5	20.3± 0.8	0.03± 0.01	0.51± 0.01	0.30± 0.02	5.43± 0.02	0.01± 0.0	0.04± 0.0	7.79± 0.04	8.89± 0.03	101.1
10 M HCl	58.1± 0.11	20.1± 0.07	0.03± 0.0	0.52± 0.02	0.30± 0.01	5.47± 0.02	0.0	0.03± 0.0	7.29± 0.02	8.16± 0.06	100.00
12 M HCl	57.9± 0.35	21.4± 0.02	0.02± 0.0	0.54± 0.01	0.30± 0.01	5.53± 0.03	0.0	0.02± 0.0	6.89± 0.02	8.56± 0.05	101.16

Mean ± S.d (n=3)

Table 15. Percentage chemical composition of Nguka raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	50.1± 2.0	14.8± 0.90	1.10± 0.02	0.36± 0.02	0.26± 0.03	4.00± 0.12	0.15± 0.02	0.90± 0.05	15.2± 0.66	13.4± 0.76	101.27
2 M HCl	55.8± 1.6	15.7± 0.01	0.07± 0.01	0.41± 0.01	0.27± 0.01	4.45± 0.02	0.06± 0.00	0.08± 0.02	10.5± 0.54	9.34± 0.13	97.56
4 M HCl	57.8± 0.15	16.2± 0.05	0.06± 0.0	0.42± 0.02	0.29± 0.02	4.44± 0.02	0.04± 0.0	0.05± 0.00	9.65± 0.10	9.28± 0.07	98.23
6 M HCl	58.3± 0.23	16.6± 0.08	0.06± 0.01	0.44± 0.01	0.28± 0.0	4.65± 0.02	0.03± 0.0	0.06± 0.00	8.47± 0.09	9.08± 0.16	97.97
8 M HCl	59.1± 1.1	16.8± 0.4	0.04± 0.00	0.45± 0.01	0.30± 0.01	4.63± 0.02	0.01± 0.0	0.04± 0.0	7.79± 0.04	8.89± 0.03	98.05
10 M HCl	59.0± 0.96	17.4± 0.07	0.03± 0.0	0.48± 0.02	0.30± 0.01	4.67± 0.02	0.0	0.03± 0.0	7.46± 0.02	8.93± 0.12	98.3
12 M HCl	59.4± 0.65	17.3± 0.43	0.02± 0.0	0.48± 0.01	0.30± 0.01	4.65± 0.03	0.0	0.02± 0.0	7.02± 0.02	8.87± 0.16	98.06

Mean ± S.d (n=3)

Table 16. Percentage chemical composition of Cumbiri raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	47.3± 1.7	16.9± 0.62	2.54± 0.01	0.34± 0.02	0.20± 0.01	3.46± 0.08	0.22± 0.01	1.16± 0.02	11.7± 0.18	15.6± 0.81	99.42
2 M HCl	54.1± 2.1	18.9± 0.24	0.13± 0.01	0.38± 0.01	0.27± 0.01	4.03± 0.02	0.06± 0.01	0.08± 0.02	8.05± 0.54	11.3± 0.13	97.30
4 M HCl	54.9± 0.10	19.1± 0.12	0.16± 0.0	0.40± 0.02	0.26± 0.02	4.41± 0.02	0.04± 0.0	0.05± 0.01	7.65± 0.11	10.9± 0.09	97.87
6 M HCl	55.1± 0.19	19.6± 0.08	0.09± 0.01	0.42± 0.01	0.28± 0.0	4.52± 0.02	0.03± 0.0	0.06± 0.01	7.40± 0.06	9.41± 0.11	97.01
8 M HCl	56.1± 1.7	19.8± 0.3	0.05± 0.01	0.42± 0.01	0.30± 0.02	4.67± 0.02	0.01± 0.0	0.04± 0.0	6.79± 0.04	8.99± 0.03	97.17
10 M HCl	57.3± 1.6	19.7± 1.2	0.03± 0.0	0.48± 0.0	0.32± 0.01	4.66± 0.02	0.0	0.03± 0.0	6.56± 0.04	8.58± 0.22	98.66
12 M HCl	58.4± 1.2	19.8± 0.14	0.02± 0.0	0.47± 0.01	0.30± 0.01	4.71± 0.03	0.0	0.02± 0.0	6.67± 0.06	8.87± 0.16	99.26

Mean ± S.d (n=3)

Table 17. Percentage chemical composition of Kandongu raw clay after washing with HCl of various concentrations.

	SiO_2	Al_2O_3	CaO	NaO_2	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	50.6± 2.1	16.2± 1.5	3.09± 0.07	0.41± 0.02	0.23± 0.02	3.21± 0.04	0.46± 0.02	1.15± 0.03	11.9± 0.37	13.2± 0.64	98.05
2 M HCl	56.9± 1.1	18.7± 0.15	0.23± 0.01	0.46± 0.01	0.29± 0.01	3.89± 0.02	0.06± 0.01	0.06± 0.00	8.45± 0.17	10.5± 0.09	99.54
4 M HCl	57.1± 0.10	18.6± 0.07	0.18± 0.02	0.44± 0.02	0.27± 0.02	3.91± 0.02	0.04± 0.0	0.07± 0.01	8.85± 0.05	9.9± 0.12	99.79
6 M HCl	57.4± 0.14	19.1± 0.08	0.07± 0.01	0.47± 0.01	0.28± 0.0	4.05± 0.02	0.03± 0.0	0.06± 0.01	7.49± 0.04	9.41± 0.11	98.36
8 M HCl	58.8± 1.7	19.8± 0.3	0.05± 0.00	0.42± 0.01	0.30± 0.02	4.09± 0.02	0.01± 0.0	0.04± 0.0	6.97± 0.04	8.75± 0.03	99.23
10 M HCl	58.3± 0.8	19.7± 0.5	0.03± 0.0	0.44± 0.01	0.32± 0.01	4.16± 0.02	0.0	0.03± 0.0	6.65± 0.03	8.72± 0.15	98.35
12 M HCl	58.9± 2.7	19.6± 0.08	0.02± 0.0	0.46± 0.01	0.33± 0.01	4.15± 0.03	0.0	0.02± 0.0	6.76± 0.06	8.87± 0.16	99.11

Mean ± S.d (n=3)

As noted from tables 11 to 17, whereas it is possible to reduce the amount of iron, calcium, magnesium and manganese substantially from raw clays using mineral acids, over 40 % of the iron oxide is not removed even after using higher concentrations of the mineral acids. It is also notable that the levels of Na_2O and K_2O are actually higher in acid washed clays than they were in unwashed (raw) clays. This could be due the existence of these oxides in complex form. However, they do not affect the colour of clays. The levels of TiO_2 also went up upon acid treatment indicating that it never reacted with the HCl. X-ray diffraction analysis showed that the titanium existed as the mineral rutile

There was a slight enrichment of the aluminium oxide after washing the clay with mineral acids. However, analysis of the filtrate showed that it contained aluminium. This indicates that Mwea clays, unlike kaolinites, contain acid-soluble aluminium compounds which according to X-ray diffraction analysis is the mineral AlO(OH). The AlO(OH) is not as much as the alumino-silicate aluminium and therefore, a substantial amount of aluminium is left on clay after acid washing. The nature of the iron containing mineral has however not been established.

It was observed that acid concentrations of 8M, 10M and 12M, of the mineral acid were more effective in removal of iron than lower concentrations. This could lead to the process of clay purification being a bit more expensive due to the high concentrations of the acid to be used. However, since the mineral acids are locally available, the process is still viable.

When the clays were treated with various concentrations of HCl and the resulting mixture heated to boiling, it was evident that heating the clay led to increased reduction of iron oxide in the clay as shown in table 18. Metal oxides that are reactive with hydrochloric acid were also washed substantially .It can, however, be observed that potassium oxide, sodium oxide and titanium oxide were not affected by the acid. This can be explained by the fact that these oxides may be existing in complex forms that are not readily soluble in mineral acids (Baker, 1967).

Table 18. Percentage chemical composition of Kiarukungu clays after refluxing the clay with HCl of various concentrations at 100^0 C.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Unwashed clay	42.0± 1.6	20.2± 0.83	2.52± 0.06	0.37± 0.03	0.19± 0.03	4.89± 0.02	0.25± 0.03	0.87± 0.02	16.4± 0.71	12.6± 0.52	100.29
2 M	52.4± 1.1	20.0± 0.4	0.08± 0.0	0.42± 0.02	0.22± 0.,01	5.07± 0.06	0.04± 0.01	0.09± 0.01	9.24± 0.09	12.9± 0.19	99.46
4 M	53.1± 0.4	19.6± 0.73	0.07± 0.01	0.41± 0.02	0.22± 0.03	5.21± 0.03	0.04± 0.01	0.07± 0.02	7.74± 0.04	12.5± 0.31	98.96
6 M	52.6± 1.9	20.1± 1.1	0.04± 0.02	0.43± 0.01	0.26± 0.02	5.63± 0.05	0.01± 0.0	0.05± 0.01	5.90± 0.07	12.8± 0.06	97.82
8 M	55.9± 0.2	21.1± 1.5	0.03± 0.01	0.47± 0.01	0.25± 0.01	5.61± 0.02	0.0± 0.0	0.01± 0.0	4.22± 0.14	12.7± 0.14	100.3
10 M	53.2± 1.3	22.5± 1.2	0.02± 0.01	0.45± 0.02	0.25± 0.01	5.76± 0.09	0.0± 0.0	0.0± 0.0	3.60± 0.04	13.1± 0.07	98.88
Conc HCl (12 M)	54.4± 0.6	22.4± 0.94	0.02± 0.0	0.48± 0.02	0.26± 0.01	5.79± 0.04	0.0± 0.0	0.0± 0.0	3.21± 0.02	11.7± 0.25	98.24

Mean ± S.d (n=3)

The levels of aluminium oxide were not much affected by the boiling the clay in various acid concentrations since the mean levels rose from 20.95 to 21.45 percent, an indication that the alumino-silicate structure was not affected by the rise in temperature. Boiling the clays with mineral acids is thus a more efficient way of clay purification.

Where iron is not an element of interest, ore beneficiation can be improved by refluxing the ore in acids. Figure 6 shows the percentage removal of iron in the refluxed clay from table 18. A marked improvement on the average levels is observed when compared with the percentage removal of iron in clays treated with HCl at room temperature described earlier.

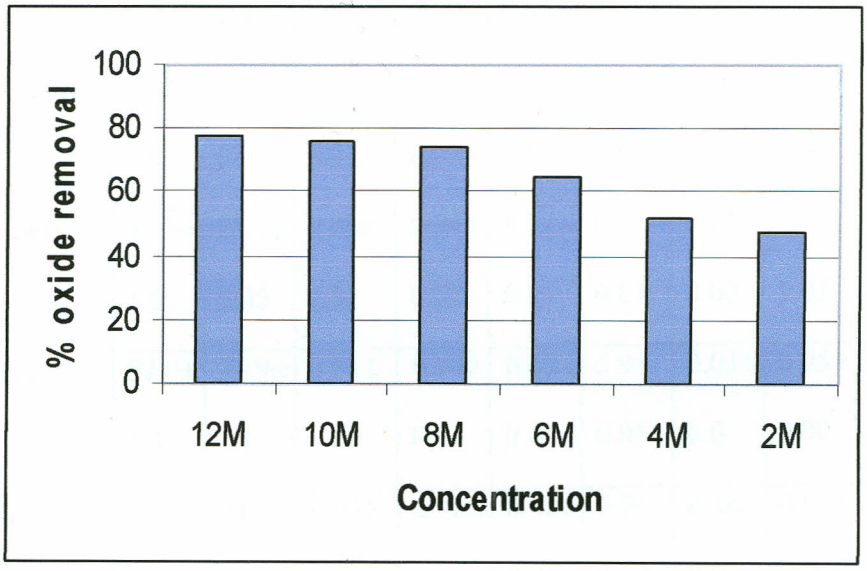


Figure 6. Percentage iron oxide removed from clays when refluxed with HCl of various concentrations.

Results obtained after refluxing the clays at 100^6 C for more than two hours with 12 M HCl showed that the levels of iron (III) oxide remaining in the residue was almost the same as those in the clays refluxed for two hours. Thus, two hours is the optimum time that these clays should be refluxed to for maximum removal of the (III) oxide. Tables 19 to 26 shows results obtained when clay samples from various sites were refluxed to various time durations with 12 M HCl.

Table 19. Percentage chemical composition of Kiamanyeki clays after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	43.6± 1.4	22.7± 1.6	2.35±. 0.03	0.40± 0.00	0.18± 0.03	3.29± 0.01	0.14± 0.06	0.5± 0.03	11.6± 0.53	14.6± 0.67	99.36
1 hour	50.1± 1.4	24.6± 0.9	0.12± 0.0	0.94± 0.02	0.38± 0.01	5. 7± 0.08	0.06± 0.01	0.07± 0.01	8.24± 0.09	8.6± 0.19	98.73
2 hours	52.5± 1.6	25.1± 0.45	0.08± 0.01	0.94± 0.02	0.42± 0.03	6.1± 0.03	0.04± 0.00	0.07± 0.02	4.2± 0.04	8.9± 0.15	98.35
5 hours	52.8± 1.4	24.9± 1.1	0.04± 0.00	0.94± 0.01	0.43± 0.02	5.9± 0.05	0.03± 0.0	0.05± 0.00	4.1± 0.07	8.3± 0.06	97.49
8 hours	53.2± 1.2	24.7± 1.5	0.03± 0.00	0.90± 0.01	0.42± 0.01	5.7± 0.02	0.4± 0.0	0.02± 0.0	4.0± 0.14	8.8± 0.14	98.17
10 hours	53.1± 0.92	25.1± 1.3	0.04± 0.0	0.87± 0.01	0.39± 0.02	5.8± 0.2	0.03± 0.0	0.02± 0.0	3.8± 0.02	8.6± 0.4	97.75

Mean ± S.d (n=3)

Table 20. Percentage chemical composition of Kindegwa clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	46.9± 1.2	17.1± 0.76	1.93± 0.01	0.47± 0.03	0.24± 0.01	4.67± 0.01	0.37± 0.01	1.26± 0.05	16.6± 0.97	9.80± 0.63	99.34
1 hour	56.4± 1.0	17.6± 0.4	0.06± 0.0	0.64± 0.02	0.29± 0.01	5. 7± 0.08	0.06± 0.01	0.08± 0.00	8.24± 0.09	8.9± 0.19	97.96
2 hours	58.5± 0.76	19.1± 0.13	0.06± 0.00	0.69± 0.02	0.32± 0.01	5.9± 0.03	0.04± 0.01	0.04± 0.00	4.0± 0.04	8.8± 0.10	97.45
5 hours	59.1± 0.4	19.9± 0.2	0.05± 0.00	0.64± 0.01	0.33± 0.02	6.1± 0.02	0.03± 0.0	0.05± 0.01	3.9± 0.03	8.0± 0.06	98.1
8 hours	59.2± 1.1	19.7± 0.3	0.04± 0.00	0.70± 0.01	0.35± 0.01	5.9± 0.02	0.04± 0.0	0.02± 0.0	4.0± 0.06	7.8± 0.14	97.77
10 hours	60.1± 0.14	20.1± 1.1	0.04± 0.0	0.67± 0.01	0.39± 0.02	6.2± 0.12	0.03± 0.0	0.02± 0.0	3.9± 0.02	7.7± 0.15	99.54

Mean ± S.d (n=3)

Table 21. Percentage chemical composition of Mathangauta clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	42.8± 1.7	21.0± 0.83	1.93± 0.01	0.39± 0.04	0.24± 0.01	4.43± 0.07	0.14± 0.01	1.07± 0.03	14.6± 0.3	12.6± 0.59	98.88
1 hour	54.4± 1.4	22.4± 0.5	0.12± 0.02	0.56± 0.02	0.29± 0.01	5. 7± 0.08	0.06± 0.01	0.04± 0.00	7.26± 0.04	6.9± 0.07	97.73
2 hours	56.1± 0.23	23.2± 0.07	0.06± 0.0	0.61± 0.02	0.31± 0.01	5.9± 0.01	0.04± 0.00	0.04± 0.00	4.42± 0.04	6.4± 0.10	97.08
5 hours	56.7± 0.14	22.9± 0.12	0.05± 0.00	0.54± 0.01	0.33± 0.02	6.1± 0.03	0.03± 0.0	0.03± 0.0	4.51± 0.06	6.0± 0.06	97.19
8 hours	57.0± 1.1	22.4± 0.5	0.03± 0.00	0.62± 0.01	0.37± 0.01	5.9± 0.05	0.02± 0.0	0.02± 0.0	4.44± 0.06	6.3± 0.14	97.10
10 hours	57.3± 0.14	22.8± 0.45	0.04± 0.0	0.58± 0.01	0.36± 0.02	6.1± 0.10	0.03± 0.0	0.02± 0.0	4.21± 0.02	6.6± 0.15	97.54

Mean ± S.d (n=3)

Table 22. Percentage chemical composition of Cumbiri clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	47.3± 1.7	16.9± 0.62	2.54± 0.01	0.34± 0.02	0.20± 0.01	3.46± 0.08	0.22± 0.01	1.16± 0.02	15.6± 0.81	15.6± 0.81	99.43
1 hour	56.4± 1.1	18.4± 0.7	0.17± 0.02	0.46± 0.02	0.34± 0.01	5.52± 0.08	0.08± 0.01	0.08± 0.00	9.54± 0.5	9.76± 0.11	100.4
2 hours	58.9± 0.23	18.9± 0.07	0.09± 0.01	0.49± 0.03	0.35± 0.01	5.51± 0.04	0.05± 0.01	0.02± 0.00	4.76± 0.06	7.43± 0.24	97.58
5 hours	59.6± 0.12	19.5± 0.09	0.04± 0.00	0.47± 0.01	0.37± 0.02	5.60± 0.03	0.03± 0.0	0.03± 0.00	4.21± 0.06	7.9± 0.09	97.84
8 hours	59.0± 0.9	19.8± 0.3	0.03± 0.0	0.51± 0.01	0.37± 0.01	5.9± 0.02	0.02± 0.0	0.02± 0.0	4.23± 0.06	7.30± 0.11	97.18
10 hours	58.9± 1.2	20.3± 0.14	0.04± 0.0	0.54± 0.01	0.36± 0.02	6.2± 0.10	0.03± 0.0	0.02± 0.0	4.37± 0.02	7.60± 0.08	98.36

Mean ± S.d (n=3)

Table 23. Percentage chemical composition of Kandongu clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	50.6± 2.1	16.2± 1.5	2.54± 0.01	0.41± 0.02	0.23± 0.02	3.21± 0.08	0.46± 0.02	1.15± 0.03	11.9± 0.37	13.2± 0.64	99.90
1 hour	58.4± 1.1	18.1± 0.4	0.11± 0.02	0.54± 0.02	0.35± 0.01	4.98± 0.02	0.05± 0.00	0.04± 0.01	6.79± 0.15	7.77± 0.07	97.13
2 hours	60.1± 0.21	18.9± 0.05	0.06± 0.0	0.56± 0.03	0.35± 0.01	5.52± 0.02	0.03± 0.0	0.02± 0.02	4.56± 0.02	7.43± 0.04	97.53
5 hours	60.7± 0.08	19.1± 0.09	0.04± 0.00	0.52± 0.01	0.37± 0.02	5.67± 0.03	0.03± 0.0	0.03± 0.00	4.21± 0.06	6.93± 0.04	97.6
8 hours	59.8± 0.5	19.8± 0.3	0.03± 0.00	0.51± 0.01	0.37± 0.01	5.9± 0.02	0.02± 0.0	0.02± 0.0	4.23± 0.06	7.21± 0.10	97.89
10 hours	60.9± 0.78	19.3± 0.11	0.02± 0.0	0.52± 0.01	0.36± 0.02	5.6± 0.20	0.03± 0.0	0.02± 0.0	4.37± 0.02	7.34± 0.04	98.46

Mean ± S.d (n=3)

Table 24. Percentage chemical composition of Mutithi clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	45.1± 1.6	18.7± 0.61	1.62± 0.05	0.46± 0.02	0.31± 0.02	4.01± 0.08	0.26± 0.02	0.99± 0.03	14.9± 0.50	13.2± 0.64	101.56
1 hour	54.4± 0.5	20.1± 0.3	0.14± 0.02	0.68± 0.02	0.35± 0.01	5.34± 0.02	0.04± 0.0	0.04± 0.0	8.89± 0.11	7.25± 0.07	97.23
2 hours	57.3± 0.14	21.9± 0.05	0.05± 0.00	0.66± 0.03	0.37± 0.01	5.63± 0.02	0.03± 0.0	0.02± 0.0	4.16± 0.02	7.43± 0.04	97.55
5 hours	58.3± 0.43	22.1± 0.09	0.02± 0.00	0.69± 0.01	0.37± 0.02	5.67± 0.03	0.03± 0.0	0.03± 0.00	4.21± 0.06	6.43± 0.03	97.85
8 hours	58.9± 0.53	20.8± 0.7	0.03± 0.00	0.61± 0.01	0.35± 0.01	5.93± 0.02	0.02± 0.0	0.02± 0.0	4.23± 0.06	6.42± 0.10	97.31
10 hours	58.4± 0.15	21.3± 0.09	0.02± 0.0	0.62± 0.02	0.37± 0.01	5.67± 0.20	0.03± 0.0	0.02± 0.0	4.07± 0.02	7.34± 0.04	96.84

Mean ± S.d (n=3)

Table 25. Percentage chemical composition of Nguka clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	50.1± 2.0	14.8± 0.9	1.10± 0.02	0.36± 0.02	0.23± 0.02	4.00± 0.12	0.15± 0.02	0.90± 0.02	15.2± 0.66	13.4± 0.76	101.27
1 hour	59.4± 0.1	18.1± 0.4	0.14± 0.02	0.51± 0.02	0.37± 0.01	4.98± 0.02	0.05± 0.00	0.04± 0.00	6.79± 0.15	7.23± 0.03	97.61
2 hours	61.7± 0.11	18.7± 0.05	0.06± 0.01	0.54± 0.02	0.35± 0.01	5.22± 0.02	0.03± 0.00	0.02± 0.00	4.56± 0.02	6.43± 0.03	97.61
5 hours	60.9± 0.08	19.1± 0.09	0.04± 0.00	0.52± 0.01	0.37± 0.02	5.67± 0.03	0.03± 0.0	0.03± 0.00	4.21± 0.06	6.93± 0.04	97.6
8 hours	59.8± 0.5	19.8± 0.3	0.03± 0.00	0.51± 0.01	0.37± 0.01	5.91± 0.02	0.02± 0.0	0.02± 0.0	4.23± 0.06	7.21± 0.10	97.89
10 hours	60.3± 0.54	19.8± 0.09	0.02± 0.0	0.57± 0.01	0.39± 0.02	5.87± 0.20	0.03± 0.0	0.02± 0.0	4.35± 0.02	6.39± 0.03	97.74

Mean ± S.d (n=3)

Table 26. Percentage chemical composition of Kiarukungu clay after heating to various duration of time with 12 M HCl.

Clay	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	TiO_2	MnO	MgO	Fe_2O_3	LOI	Total
Untreated clay	42.0± 1.6	20.2± 0.83	2.52± 0.06	0.37± 0.03	0.19± 0.03	4.89± 0.02	0.25± 0.03	0.87± 0.04	16.4± 0.71	12.6± 0.52	100.29
1 hour	55.6± 0.46	22.4± 0.21	0.12± 0.02	0.56± 0.02	0.29± 0.01	5.73± 0.08	0.06± 0.01	0.04± 0.00	7.26± 0.04	6.90± 0.07	98.96
2 hours	56.7± 0.12	22.2± 0.07	0.06± 0.00	0.64± 0.02	0.31± 0.01	5.97± 0.01	0.04± 0.00	0.04± 0.00	4.76± 0.02	6.37± 0.10	97.09
5 hours	56.9± 0.12	22.7± 0.12	0.05± 0.00	0.59± 0.01	0.33± 0.02	6.14± 0.03	0.03± 0.00	0.03± 0.00	4.51± 0.06	6.04± 0.06	97.32
8 hours	57.8± 0.13	22.4± 0.15	0.03± 0.00	0.52± 0.01	0.37± 0.01	5.95± 0.05	0.02± 0.00	0.02± 0.00	4.44± 0.06	6.37± 0.14	97.92
10 hours	57.9± 0.08	22.5± 0.04	0.04± 0.0	0.59± 0.01	0.39± 0.02	6.13± 0.10	0.03± 0.0	0.02± 0.0	4.21± 0.02	6.66± 0.11	98.44

Mean ± S.d (n=3)

It was also noted that, there was enrichment of aluminium, silicon, sodium, potassium and titanium oxides in the residues, while the other oxides were reduced substantially in the process.

4.3 Analysis of clays heated to various temperatures and then leached with HCl of various concentrations.

It was observed that, when the clays were heated to temperatures above 500^0C, over 93 % of iron (III) oxide could be extracted with 12M. 10M and 8M gave similar results for clays heated to over 500^0C However, temperatures below 500^0C gave similar results of iron oxide as when the clays were just boiled with the acid. Lower concentrations of the acids were found not to be effective as they gave higher concentrations of iron (iii) oxide in the residue as shown in figure 7 even when the clays were heated to over 500^0C. Figure 7 to 10 shows the percentage of aluminium oxide and iron oxide remaining after the clays were heated to various temperatures and then leached with various concentrations of HCl.

It was also noted that for clays heated above 500^0C, most of the aluminium oxide was extracted by concentrated mineral acids, an observation which indicates the breaking of the alumino-silicate structure. It has been observed that when clays are heated between 500 – 600^0C and cooled, most of the aluminium in the clay could be extracted with mineral acids (Grimshaw, 1971). This is because; the amorphous Al_2O_3 turns to the γ-Al_2O_3 as a result of heating. The γ-Al_2O_3 is more soluble in mineral acids than the amorphous form. (Jaffe′, 1969). However, when the clays were heated to temperatures below 500^0C, the aluminium content was still high as compared to clays heated above 500^0C. This indicates that the alumino-silicate structure had not been destroyed. The levels of titanium oxide were found to be almost the same in all the samples, an indication that it does not react with HCl.

Over 80 % of the remaining material after acid leaching was found to be SiO_2. Other oxides were found to be in very low percentage indicating that the material was no longer clay but mainly sand. Tables 27 to 34 shows the residue composition of clays from various sampling sites after heating the raw clay to various temperatures for two hours and then leaching them with 12 M HCl.

Table 27 Percentage chemical compositions of Mathangauta clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	42.8 ±1.7	21.0 ±0.83	1.66 ±0.02	1.07 ±0.02	0.21 ±0.01	4.43 ±0.07	0.14 ±0.01	14.6 ±0.3	0.39 ±0.04	12.6 ±0.96	98.88
200^{0}C	55.4 ±0.94	25.2 ±0.51	0.53 ±0.02	0.74 ±0.01	0.19 ±0.03	5.53 ±0.06	0.03 ±0.00	5.30 ±0.08	0.29 ±0.02	8.10 ±0.39	101.3
300^{0}C	55.5 ±1.32	24.6 ±0.93	0.60 ±0.03	0.78 ±0.02	0.18 ±0.02	5.61 ±0.05	0.01 ±0.00	5.00 ±0.04	0.29 ±0.01	5.46 ±0.53	98.03
400^{0}C	55.3 ±0.26	25.3 ±0.47	0.72 ±0.01	0.98 ±0.03	0.17 ±0.00	5.49 ±0.14	0.01 ±0.00	4.80 ±0.07	0.30 ±0.03	7.04 ±0.38	99.8
500^{0}C	66.8 ±1.1	13.41 ±0.03	0.00 ±0.00	0.05 ±0.01	0.11 ±0.01	4.34 ±0.08	0.00 ±0.00	3.19 ±0.03	0.27 ±0.02	10.7 ±0.42	99.02
550^{0}C	82.4 ±0.87	2.89 ±0.07	0.00 ±0.00	0.00 ±0.00	0.07 ±0.00	3.42 ±0.06	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	8.48 ±0.26	97.32

Mean ± S.d (n=3)

Table 28 Percentage chemical compositions of Mutithi clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	45.1 ±1.6	18.7 ±0.61	1.62 ±0.05	0.99 ±0.02	0.31 ±0.01	4.01 ±0.03	0.26 ±0.02	14.9 ±0.5	0.46 ±0.04	13.2 ±0.59	101.56
200^0C	57.4 ±0.23	22.2 ±0.21	0.42 ±0.02	0.07 ±0.01	0.67 ±0.03	5.87 ±0.06	0.03 ±0.00	4.30 ±0.08	0.87 ±0.02	6.10 ±0.11	98.53
300^0C	58.5 ±1.00	23.6 ±0.21	0.50 ±0.03	0.72 ±0.02	0.59 ±0.02	5.96 ±0.02	0.01 ±0.00	4.00 ±0.04	0.79 ±0.01	5.66 ±0.13	100.33
400^0C	60.2 ±0.06	24.7 ±0.12	0.56 ±0.01	0.89 ±0.03	0.57 ±0.00	5.99 ±0.11	0.01 ±0.00	3.80 ±0.07	0.83 ±0.03	5.04 ±0.07	101.59
500^0C	68.8 ±1.1	15.2 ±0.03	0.00 ±0.00	0.03 ±0.00	0.11 ±0.01	4.55 ±0.02	0.00 ±0.00	3.32 ±0.03	0.37 ±0.02	5.07 ±0.42	97.02
550^0C	85.4 ±0.12	3.43 ±0.01	0.00 ±0.00	0.00 ±0.00	0.07 ±0.00	3.56 ±0.01	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	4.48 ±0.26	97.32

Mean ± S.d (n=3)

Table 29 Percentage chemical compositions of Kiandegwa clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	46.9 ±1.2	17.1 ±0.76	1.93 ±0.01	1.26 ±0.05	0.24 ±0.01	4.67 ±0.01	0.37 ±0.01	16.6 ±0.97	0.47 ±0.03	9.8 ±0.63	99.34
200^{0}C	55.4 ±0.94	25.2 ±0.51	0.53 ±0.02	0.74 ±0.01	0.19 ±0.03	5.53 ±0.06	0.03 ±0.00	5.30 ±0.08	0.29 ±0.02	8.10 ±0.39	101.3
300^{0}C	55.5 ±1.32	24.6 ±0.93	0.60 ±0.03	0.78 ±0.02	0.18 ±0.02	5.61 ±0.05	0.01 ±0.00	5.00 ±0.04	0.29 ±0.01	5.46 ±0.53	98.03
400^{0}C	55.3 ±0.26	25.3 ±0.47	0.72 ±0.01	0.98 ±0.03	0.17 ±0.00	5.49 ±0.14	0.01 ±0.00	4.80 ±0.07	0.30 ±0.03	7.04 ±0.38	99.8
500^{0}C	66.8 ±1.1	13.41 ±0.03	0.00 ±0.00	0.05 ±0.01	0.11 ±0.01	4.34 ±0.08	0.00 ±0.00	3.19 ±0.03	0.27 ±0.02	10.7 ±0.42	99.02
550^{0}C	83.8 ±0.12	2.56 ±0.03	0.00 ±0.00	0.00 ±0.00	0.07 ±0.00	3.42 ±0.06	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	6.48 ±0.26	97.32

Mean ± S.d (n=3)

Table 30. Percentage chemical compositions of Kiamanyeki clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	43.6 ±1.4	22.7 ±1.6	2.35 ±0.03	0.5 ±0.01	0.18 ±0.01	3.29 ±0.06	0.14 ±0.03	11.6 ±0.53	0.40 ±0.01	14.6 ±0.67	99.36
200^{0}C	55.4 ±0.94	25.2 ±0.51	0.53 ±0.02	0.67 ±0.01	0.19 ±0.03	5.53 ±0.06	0.03 ±0.00	4.30 ±0.08	0.49 ±0.02	8.10 ±0.39	100.24
300^{0}C	56.5 ±1.1	25.6 ±0.34	0.60 ±0.03	0.72 ±0.02	0.18 ±0.02	6.65 ±0.05	0.01 ±0.00	4.20 ±0.04	0.51 ±0.01	5.46 ±0.53	100.72
400^{0}C	57.3 ±0.21	25.4 ±0.04	0.65 ±0.01	0.77 ±0.03	0.17 ±0.00	6.45 ±0.10	0.01 ±0.00	4.02 ±0.07	0.60 ±0.03	6.04 ±0.03	101.41
500^{0}C	68.2 ±0.2	14.4 ±0.03	0.00 ±0.00	0.05 ±0.00	0.11 ±0.01	6.34 ±0.08	0.00 ±0.00	3.67 ±0.02	0.27 ±0.02	4.7 ±0.02	97.74
550^{0}C	85.3 ±0.02	2.86 ±0.01	0.00 ±0.00	0.00 ±0.00	0.07 ±0.00	4.42 ±0.01	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	5.48 ±0.02	98.44

Mean ± S.d (n=3)

Table 31. Percentage chemical compositions of Nguka clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	50.1 ±2.0	14.8 ±0.9	1.10 ±0.02	0.90 ±0.01	0.26 ±0.01	4.00 ±0.12	0.15 ±0.01	15.2 ±0.53	0.36 ±0.01	13.4 ±0.67	101.27
200^{0}C	58.4 ±0.56	26.2 ±0.01	0.34 ±0.02	0.04 ±0.01	0.29 ±0.01	5.70 ±0.02	0.03 ±0.00	3.30 ±0.08	0.67 ±0.01	5.10 ±0.03	100.07
300^{0}C	58.4 ±1.3	25.6 ±0.04	0.30 ±0.00	0.02 ±0.00	0.31 ±0.02	5.65 ±0.03	0.01 ±0.00	3.80 ±0.02	0.61 ±0.01	4.46 ±0.03	99.16
400^{0}C	57.9 ±0.11	25.4 ±0.05	0.25 ±0.01	0.04 ±0.00	0.32 ±0.00	6.0 ±0.10	0.01 ±0.00	3.02 ±0.03	0.60 ±0.03	4.04 ±0.03	97.58
500^{0}C	70.1 ±0.2	14.3 ±0.02	0.00 ±0.00	0.05 ±0.00	0.14 ±0.01	4.34 ±0.03	0.00 ±0.00	3.63 ±0.02	0.26 ±0.02	4.7 ±0.02	97.92
550^{0}C	85.1 ±0.05	2.98 ±0.01	0.00 ±0.00	0.00 ±0.00	0.06 ±0.00	3.67 ±0.01	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	5.20 ±0.02	97.12

Mean ± S.d (n=3)

Table 32. Percentage chemical compositions of Cumbiri clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	47.3 ±1.7	16.9 ±1.5	2.54 ±0.01	1.16 ±0.02	0.20 ±0.01	3.46 ±0.08	0.22 ±0.01	11.7 ±0.18	0.34 ±0.01	15.6 ±0.81	99.42
200^{0}C	60.8 ±1.3	19.2 ±0.01	0.53 ±0.02	0.05 ±0.01	0.29 ±0.01	5.70 ±0.02	0.03 ±0.00	3.90 ±0.03	0.51 ±0.01	6.78 ±0.03	97.79
300^{0}C	59.3 ±1.1	20.5 ±0.03	0.30 ±0.03	0.02 ±0.02	0.31 ±0.02	5.97 ±0.01	0.01 ±0.00	3.54 ±0.02	0.54 ±0.01	6.76 ±0.03	97.25
400^{0}C	60.5 ±0.15	20.7 ±0.04	0.21 ±0.01	0.03 ±0.00	0.35 ±0.00	6.30 ±0.10	0.01 ±0.00	3.72 ±0.01	0.47 ±0.03	4.96 ±0.03	97.26
500^{0}C	68.9 ±0.3	13.8 ±0.02	0.00 ±0.00	0.05 ±0.01	0.14 ±0.01	5.37 ±0.03	0.00 ±0.00	3.89 ±0.02	0.35 ±0.02	4.78 ±0.02	97.28
550^{0}C	83.7 ±0.23	3.98 ±0.01	0.00 ±0.00	0.00 ±0.00	0.06 ±0.00	4.06 ±0.01	0.00 ±0.00	0.12 ±0.00	0.03 ±0.00	5.30 ±0.02	97.25

Mean ± S.d (n=3)

Table 33. Percentage chemical compositions of Kandongu clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

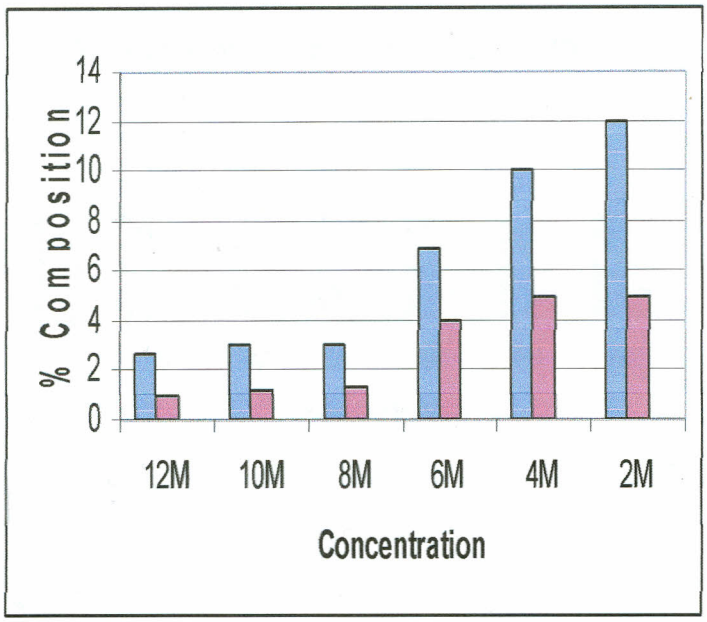
	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	50.6 ±2.1	16.2 ±0.9	3.09 ±0.07	1.15 ±0.03	0.23 ±0.02	3.21 ±0.04	0.46 ±0.02	11.9 ±0.37	0.41 ±0.02	13.2 ±0.64	98.05
200^{0}C	60.6 ±0.43	20.2 ±0.01	0.23 ±0.02	0.04 ±0.01	0.35 ±0.01	5.70 ±0.02	0.03 ±0.00	4.70 ±0.08	0.65 ±0.01	5.10 ±0.05	97.60
300^{0}C	60.4 ±1.5	20.6 ±0.05	0.20 ±0.03	0.02 ±0.00	0.40 ±0.00	5.65 ±0.03	0.01 ±0.00	3.80 ±0.02	0.61 ±0.01	5.76 ±0.02	97.45
400^{0}C	59.9 ±0.11	22.4 ±0.05	0.20 ±0.00	0.04 ±0.00	0.32 ±0.00	6.0 ±0.10	0.01 ±0.00	3.02 ±0.03	0.60 ±0.03	4.04 ±0.03	97.58
500^{0}C	70.7 ±0.2	14.3 ±0.02	0.00 ±0.00	0.05 ±0.01	0.14 ±0.01	4.34 ±0.03	0.00 ±0.00	3.63 ±0.02	0.26 ±0.02	4.76 ±0.02	97.92
550^{0}C	85.7 ±0.05	3.45 ±0.01	0.00 ±0.00	0.00 ±0.00	0.07 ±0.00	3.89 ±0.01	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	4.20 ±0.02	97.42

Mean ± S.d (n=3)

Table 34. Percentage chemical compositions of Kiarukungu clays after heating to various temperatures for two hours and then leaching with concentrated HCl.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	MnO	Fe_2O_3	Na_2O	LOI	Total
Untreated clay	42.0 ±1.6	20.2 ±0.83	2.52 ±0.06	0.87 ±0.02	0.19 ±0.03	4.89 ±0.02	0.25 ±0.03	16.4 ±0.71	0.37 ±0.03	12.6 ±0.52	100.29
200^{0}C	56.8 ±0.43	23.8 ±0.21	0.45 ±0.02	0.08 ±0.01	0.46 ±0.03	5.53 ±0.06	0.03 ±0.00	5.01 ±0.08	0.39 ±0.02	6.10 ±0.07	98.54
300^{0}C	55.9 ±1. 2	24.1 ±0.93	0.30 ±0.01	0.05 ±0.00	0.38 ±0.02	5.98 ±0.05	0.01 ±0.00	4.76 ±0.04	0.42 ±0.01	5.46 ±0.53	97.36
400^{0}C	57.3 ±0.6	23.3 ±0.41	0.22 ±0.01	0.08 ±0.01	0.17 ±0.00	5.49 ±0.11	0.01 ±0.00	4.80 ±0.07	0.40 ±0.00	5.04 ±0.13	97.21
500^{0}C	72.8 ±1.3	12.4 ±0.03	0.00 ±0.00	0.02 ±0.00	0.11 ±0.01	3.34 ±0.08	0.00 ±0.00	3.32 ±0.03	0.27 ±0.02	5.7 ±0.12	97.96
550^{0}C	85.7 ±0.41	2.66 ±0.01	0.00 ±0.00	0.00 ±0.00	0.03 ±0.00	3.22 ±0.02	0.00 ±0.00	0.08 ±0.00	0.03 ±0.00	5.48 ±0.12	97. 20

Mean ± S.d (n=3)

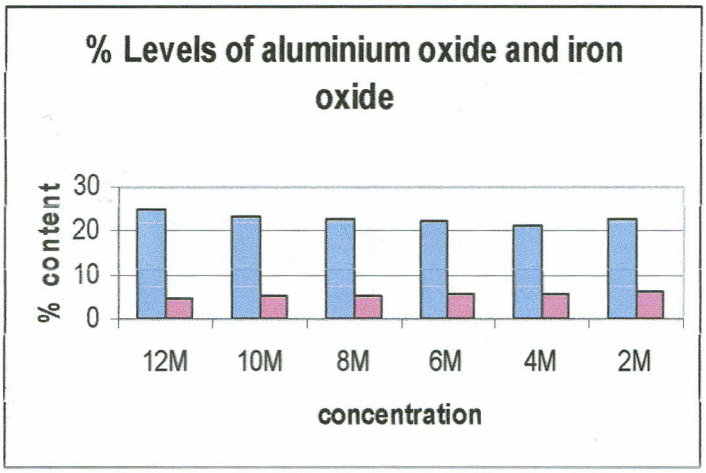


Key: Represents aluminium oxide

Represents Iron (iii) oxide

Figure 7. Percentage levels of aluminium and iron oxides in Mathangauta clays heated to 550^0C and then leached with HCl of various concentrations.

Figure 8 shows the percentage content of aluminium oxide and iron (III) oxide in clays heated to 300^0 C and then leached with HCl of various concentrations. From the graph, it can be noted that, there is no much difference in the levels of the two compounds as compared to when the clays were dried at 110^0C and treated in the same way earlier. Thus, heating the clays to temperatures above 500^0C is necessary if the alumino silicate structure has to be broken.



Key:

Represents Aluminium oxide

Represents Iron (iii) oxide

Figure 8. Percentage levels of aluminium and iron oxides in Mathangauta clays heated to 300^0C and then leached with HCl of various concentrations.

Figure 9 and 10 shows the percentages of Al_2O_3 and Fe_2O_3 remaining after the clays were heated to 200^0C and 400^0C respectively. It is observed that, there is no much difference on the levels of aluminium oxide after heating to the respective temperatures, however, the levels of Fe_2O_3 went slightly down.

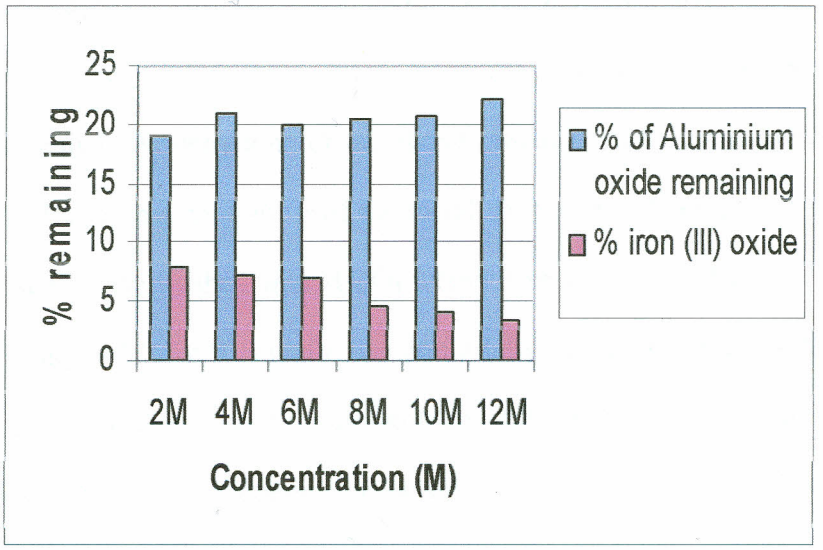


Figure 9. Percentage levels of Al_2O_3 and Fe_2O_3 remaining after heating Mathangauta clays to 200^0C and then leaching it with HCl of various concentrations

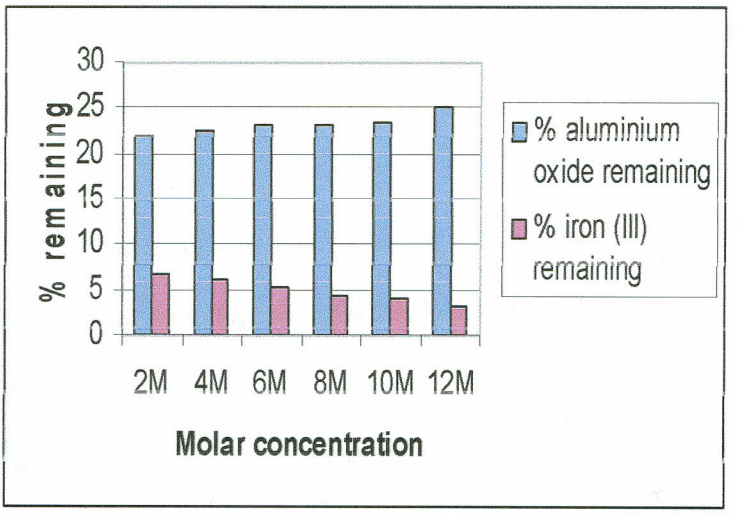


Figure 10. Levels of Al_2O_3 and Fe_2O_3 remaining after heating Mathangauta clays to 400^0C and then leaching it with HCl of various concentrations

4.4 Comparison of HCl and H_2SO_4 in metal oxide removal

Table 35 shows the results obtained when samples were pre-heated to 550^0C and then treated with equal concentrations of the above mineral acids. It was observed that both acids were effective in removing most of the metal oxides except SiO_2. However the levels of titanium oxide in clays washed with H_2SO_4 were lower as compared to the levels in HCl washed clay. Actually, 97 % of titanium oxide could be washed from clays with higher concentrations of H_2SO_4. This was however not possible with the same concentrations of HCl. Sulphuric acid is known to react with titanium oxide to form titanium sulphate (Bureu of Mines, 1990). Thus, when the clay is calcined, concentrated sulphuric acid is able to react with the free titanium oxide hence the low levels of TiO_2 in the acid-washed clays.

$$TiO_2 + 2H_2SO_4 \rightarrow Ti(SO_4)_2 + 2H_2O$$

There were also higher levels of calcium oxide in clays washed with H_2SO_4 as compared to those washed with HCl. This can be attributed to the formation of insoluble calcium sulphate.

From these results, it can be noted that if clay is going to be used for other purpose like aluminium extraction, then HCl is better than H_2SO_4 since the filtrate will not have impurities of titanium and calcium. Also the fact that HCl is not an oxidizing agent like H_2SO_4, implies that it will not react with the organic matter in the clays hence less impurities in the filtrate.

Table 35 Analysis of Kiandegwa clays heated to 550^{0}C and then washed with various concentrations of HCl and H_2SO_4.

	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	MgO	Na_2O	LOI	Total
Untreated clay	46.9± 1.2	17.1± 0.76	0.24± 0.01	1.93± 0.01	4.67± 0.01	0.37± 0.01	16.6± 0.97	1.26± 0.05	0.47± 0.03	9.80± 0.04	99.34
18 M H_2SO_4	82.8± 0.93	4.68± 0.09	0.16± 0.02	0.03± 0.00	0.45± 0.02	0.00± 0.00	0.65± 0.03	0.00± 0.00	0.04± 0.00	8.71± 0.42	97.46
12M HCL	84.4± 0.46	2.67± 0.12	0.07± 0.03	0.00± 0.00	3.10± 0.10	0.00± 0.00	1.02± 0.01	0.00± 0.00	0.02± 0.00	6.05± 0.14	97.31
10M H_2SO_4	86.4± 1.2	4.84± 0.54	0.18± 0.03	0.05± 0.01	0.79± 0.01	0.00± 0.0	0.82± 0.02	0.00± 0.0	0.05± 0.01	5.21± 0.36	98.29
10M HCl	85.3± 0.51	2.98± 0.04	0.05± 0.02	0.00± 0.0	4.23± 0.04	0.00± 0.0	1.21± 0.01	0.00± 0.0	0.04± 0.01	5.73± 0.34	99.54
8M H_2SO_4	83.4± 0.65	4.39± 0.03	0.21± 0.02	0.09± 0.01	0.97± 0.03	0.00± 0.0	1.09± 0.03	0.00± 0.0	0.06± 0.01	7.03± 0.41	97.6
8M HCl	82.9± 1.4	3.04± 0.04	0.06± 0.02	0.00± 0.0	4.25± 0.04	0.00± 0.0	1.34± 0.02	0.00± 0.0	0.05± 0.01	6.47± 0.26	98.11

Mean ± S.d (n=3)

4.5 Extraction of aluminium from clay in form of $AlCl_3$ and $Al_2(SO_4)_3$

From table 35, it is evident that almost all the aluminium oxide was removed by 18M sulphuric acid and 12 M HCl, though HCl gave much higher levels of Al_2O_3 as compared to H_2SO_4. From this analysis, it is evident that calcining the clay to temperatures of 550^0C led to substantial reduction of aluminium oxide from the parent clay. Much of it was thus able to be washed by the acid and obtained as the filtrate. The levels of titanium in the two acid washed samples confirmed that sulphuric acid reacts with titanium oxide more than HCl does. The levels of Na_2O and K_2O also went down, an indication that heating resulted in the breaking of the complexes hence being attacked by the acid. The residue obtained was mainly silica which can find use in the glass and construction industries.

From this analysis, it is notable that over 72.0 % of aluminium oxide could be extracted using concentrated sulphuric acid while over 84.0 % of aluminium oxide could be extracted using concentrated hydrochloric acid. It is also notable that over 90 % of titanium oxide could be extracted using sulphuric acid, thus where titanium is an element of interest then sulphuric acid can be used for its extraction.

Table 36 shows the filtrate analysis from the various sampling sites in Mwea after the clay had been boiled with 12M HCl for two hours, then washed with de-ionized water, dried, heated to 550^0C, and then washed with 12M HCl. Form this analysis, it is evident that the filtrate obtained from clays washed with 12M HCl gave higher yields of aluminium as compared to those filtrates obtained from clays washed 18M H_2SO_4. However, filtrates obtained from 18M H_2SO_4 gave higher yields of titanium as compared to those filtrates from HCl. This is due to

fact that H_2SO_4 reacts more with titanium oxide as compared to HCl. Iron was the other major impurity in the filtrates though the sulphuric acids filtrates gave lower yields as compared to HCl filtrates. This is because; the sulphuric acid filtrate had higher levels of titanium thus the overall effect on the percentages.

Table 36. Concentrations of Aluminium, Iron and Titanium in the filtrates in mg/g

Sample source	Acid used	Aluminium (mg/g)	Iron (mg/g)	Titanium (mg/g)
Mathangauta	18M H_2SO_4	65.1 ± 2.1	10.2 ± 0.42	16.4 ± 0.91
	12M HCl	74.3 ± 1.7	20.7 ± 0.79	0.63 ± 0.03
Kiarukungu	18M H_2SO_4	69.4 ± 4.2	12.5 ± 1.7	14.5 ± 1.3
	12M HCl	77.6 ± 3.4	17.6 ± 2.4	0.99 ± 0.02
Nguka	18M H_2SO_4	63.8 ± 2.9	8.6 ± 1.1	15.4 ± 0.67
	12M HCl	72.7 ± 4.8	22.3 ± 2.4	1.1 ± 0.04
Kiamanyeki	18M H_2SO_4	67.2 ± 3.9	9.5 ± 1.4	12.4 ± 0.89
	12M HCl	78.9 ± 5.2	16.5 ± 0.96	0.74 ± 0.04
Mutithi	18M H_2SO_4	59.7 ± 1.8	15.5± 1.6	16.1 ± 1.1
	12M HCl	68.9 ± 3.7	21.4 ± 2.6	0.92 ± 0.02
Kandongu	18M H_2SO_4	61.8 ± 3.5	7.5 ± 0.78	13.6 ± 1.3
	12M HCl	70.6 ± 2.6	19.5 ± 1.6	1.3 ± 0.07
Cumbiri	18M H_2SO_4	66.9 ± 3.6	11.9 ± 0.67	17.6 ± 2.1
	12M HCl	74.8 ± 4.8	18.7 ± 2.1	0.58 ± 0.02
Kiandegwa	18M H_2SO_4	69.2 ± 1.4	8.4 ± 1.1	14.7 ± 1.2
	12M HCl	76.7 ± 3.0	20.3 ± 1.3	0.89 ± 0.06

From these results, it is evident that hydrochloric acid method is better than sulphuric acid method since it gives higher yields of aluminium in the filtrate. Much purification of the hydrochloric acid washed filtrate can be done by removing iron (iii) chloride through the solvent extraction. This involves passing the solution in an organic phase containing 15 % volume alamine (tertiary amine), 10 % volume decyl alcohol and 75% volume kerosene. This leaves the filtrate with over 90 % $AlCl_3.6H_2O$. The aluminium value in the purified liquor is

recovered as $AlCl_3.6H_2O$ by crystallization. The chloride is then thermally decomposed and calcined at 1100 ^{0}C to produce alumina (Kyun, 2002).

Iron can also be removed from the solution by adjusting the pH of the solution to be just slightly basic. Under these conditions, iron is precipitated as an insoluble hydroxide leaving the soluble aluminium in solution. The solution can then be crystallized and thermally decomposed to alumina.

Conclusions

This research has shown that the major constituents of Mwea clays make up approximately 100 % of the total mass. Thus, using the data in tables 5 and 6, we note that their analyses fall within the ranges indicated below

Al_2O_3.....15 – 23 %
SiO_2 .....40- 51 %
Fe_2O_3.....11.5- 16.7%
CaO .....1.0 – 3%
TiO_2 .....3.5- 5.2 %
Na_2O .....0.34 – 0.48 %
K_2O .....0.15 - 0.36%
MgO .....1.0 - 3.0 %
MnO .....0.15 – 0.5 %

These data are in agreement with analytical data of clays from other parts of the world.
These results indicate that, this clay qualifies to be a raw material for the manufacture of cement and can also serve as a raw material for aluminium extraction.

The clay from Mukurwe-ini which was analyzed for comparison purposes has the higher levels of alumina at 34 %. This clay is therefore, by far the best for extraction of aluminium or the manufacture of aluminium compounds.

It has been noted that refluxing the clay with concentrated acids led to much reductions of the levels of iron. However it was not possible to remove all the iron or reduce it to levels that can make the residue to be a raw material for quality ceramic material.

The clay from Mwea was found to contain higher levels of titanium oxide as compared to others. Studies by other workers have shown that titanium can be recovered economically from minerals with 5 % TiO_2 and above. Whereas Mwea clays has TiO_2 values of between 3.5 % and 5.17 %, clay treatment such as that described below suggests that the process can be economical.

It was observed that when clays were calcined at 550^0C for three hours and then refluxed in either 18 M H_2SO_4 or 12 M HCl, over 70 % of the aluminium and iron were removed from clays. Interestingly, whereas 97 % of TiO_2 in clays was removed by 18 M H_2SO_4, HCl did not appear effective. This heat treatment can, therefore, be used to recover aluminium, iron and titanium from these clays economically

Recommendations for further research

This clay has been found to have high levels of titanium oxide as compared to other clays (Ruiru and Mukurweini). Investigation on the depth and extensiveness of the mineral should be carried out to quantify the ore and determine its beneficiation. It would also be important to determine the nature of the mineral so that best method for extraction can be determined.

With the necessary equipment, it would also be of interest to determine the quality of cement that can be obtained from this clay since clays have been used in the manufacture of cement.

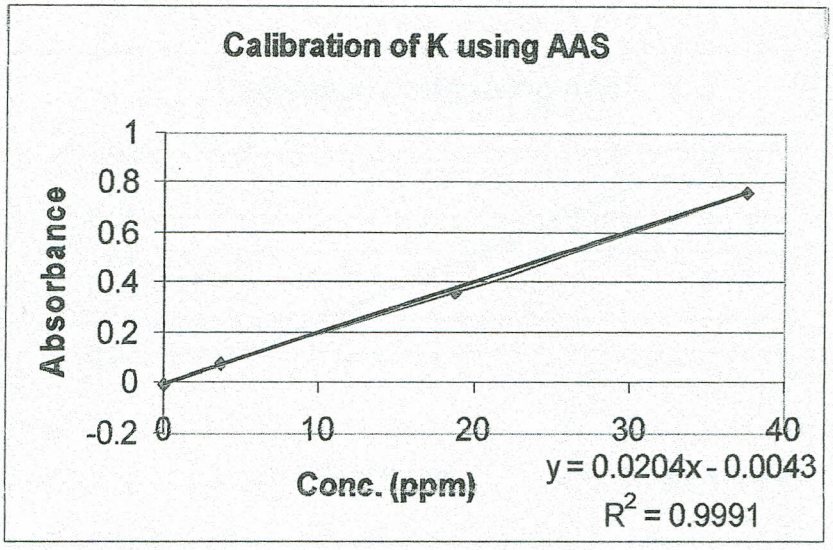
X-ray diffraction analysis needs to be carried out to establish the nature of the iron mineral in Mwea clays as to establish why it cannot be exhaustively leached by the mineral acids.

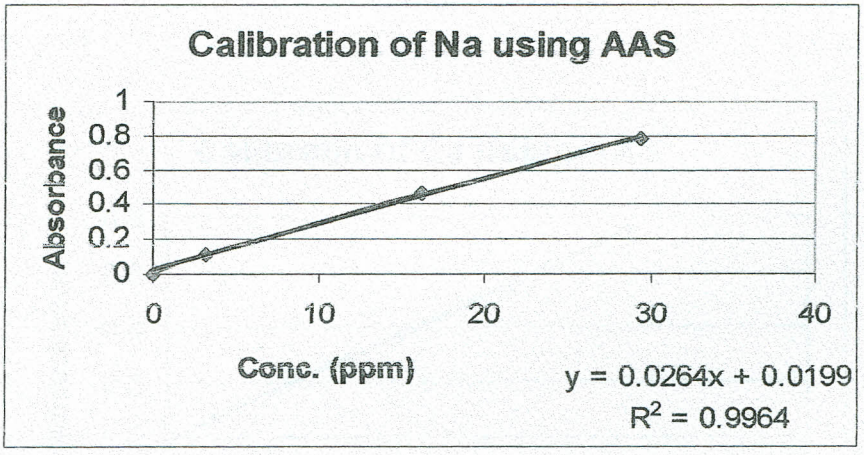
More studies should be carried out to find out the nature of the iron –containing mineral. This is of interest because the iron was not easily extracted with mineral acids unless the clay was heated to 550^{0}C.

After the acid treatment, the clay was found to have lost the ability to stick together or lost plasticity which is one quality of clay. It would be of necessary to find out weather the original state of the clay can be restored back after the acid treatment.

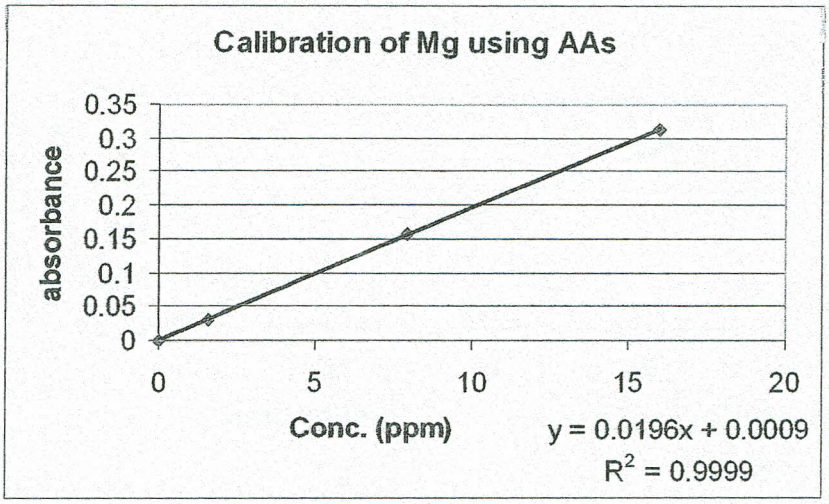
Appendixes

Appendix 1





Appendix 2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0.25
0.2
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0.1
0.05
0
0
5
10
15
20
Conc. (ppm)
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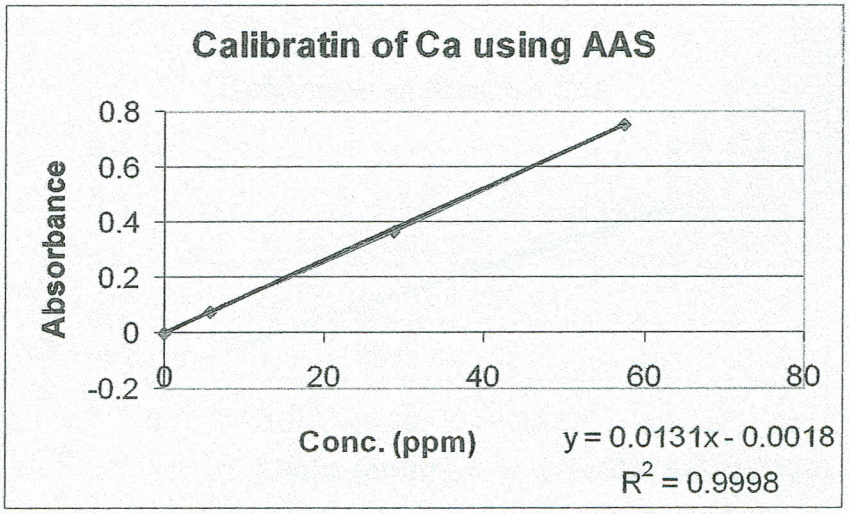
R2 = 0.9999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Absorbance
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0.2
0
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0
20
40
60
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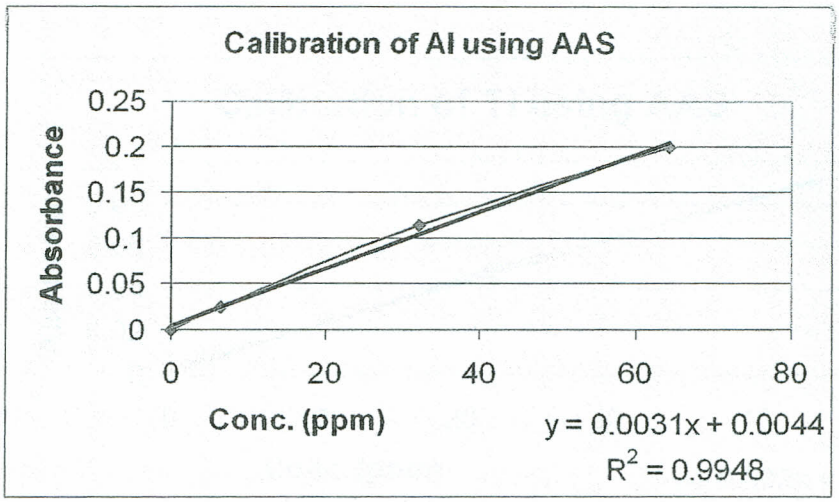
Conc. (ppm)
y = 0.0131x - 0.0018
R2 = 0.9998

Appendix 3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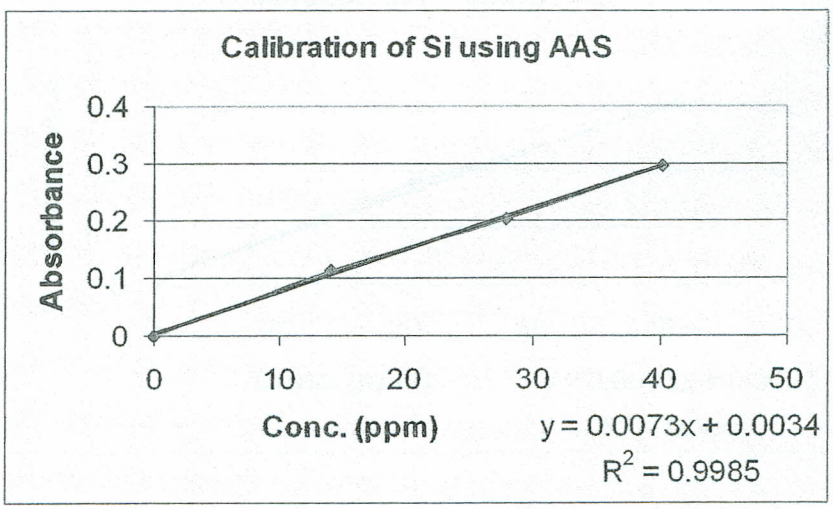
R2 = 0.9948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30
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50
Conc. (ppm)
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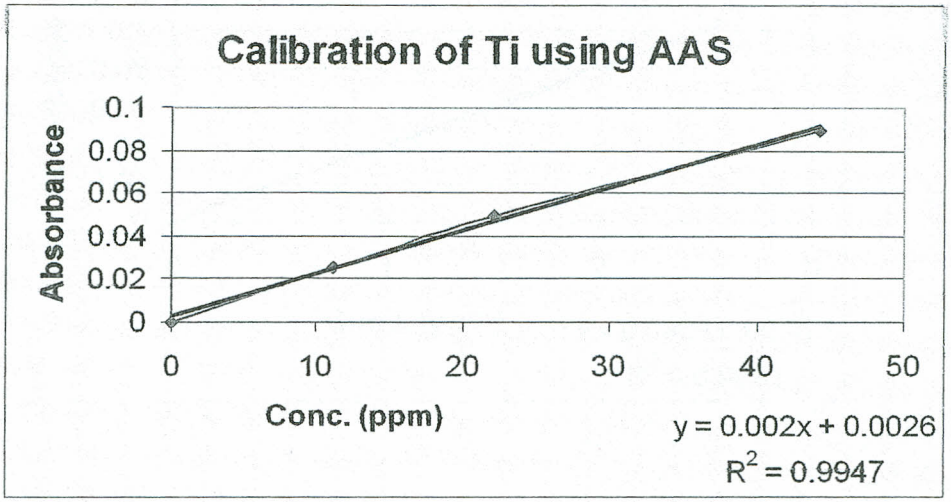
R2 = 0.9985

Appendix 4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0.06
0.04
0.02
0
0
10
20
30
40
50
Conc. (ppm)
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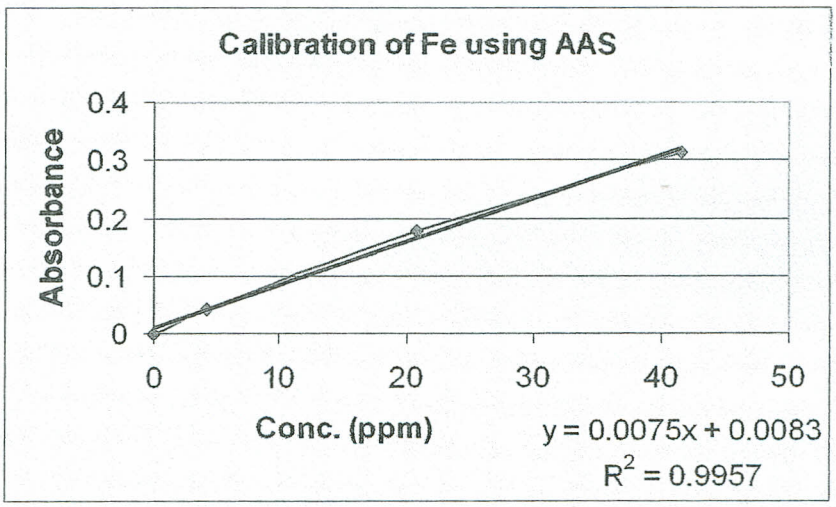
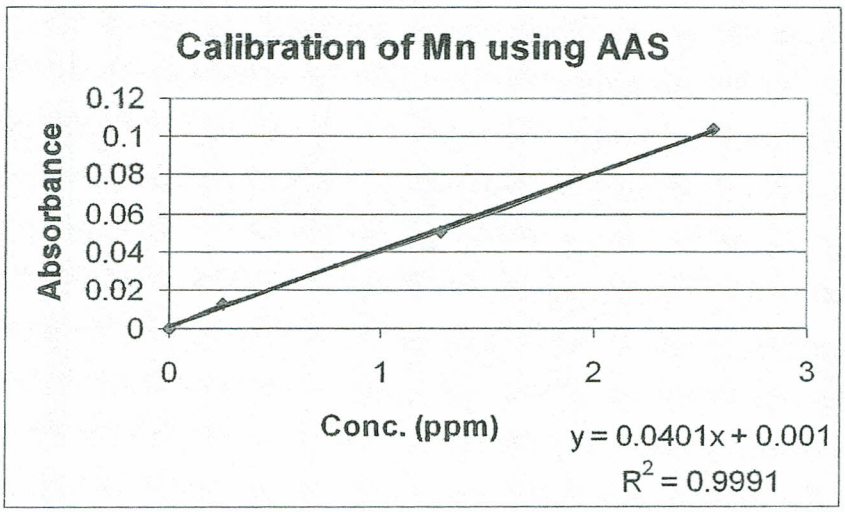
R2 = 0.9947

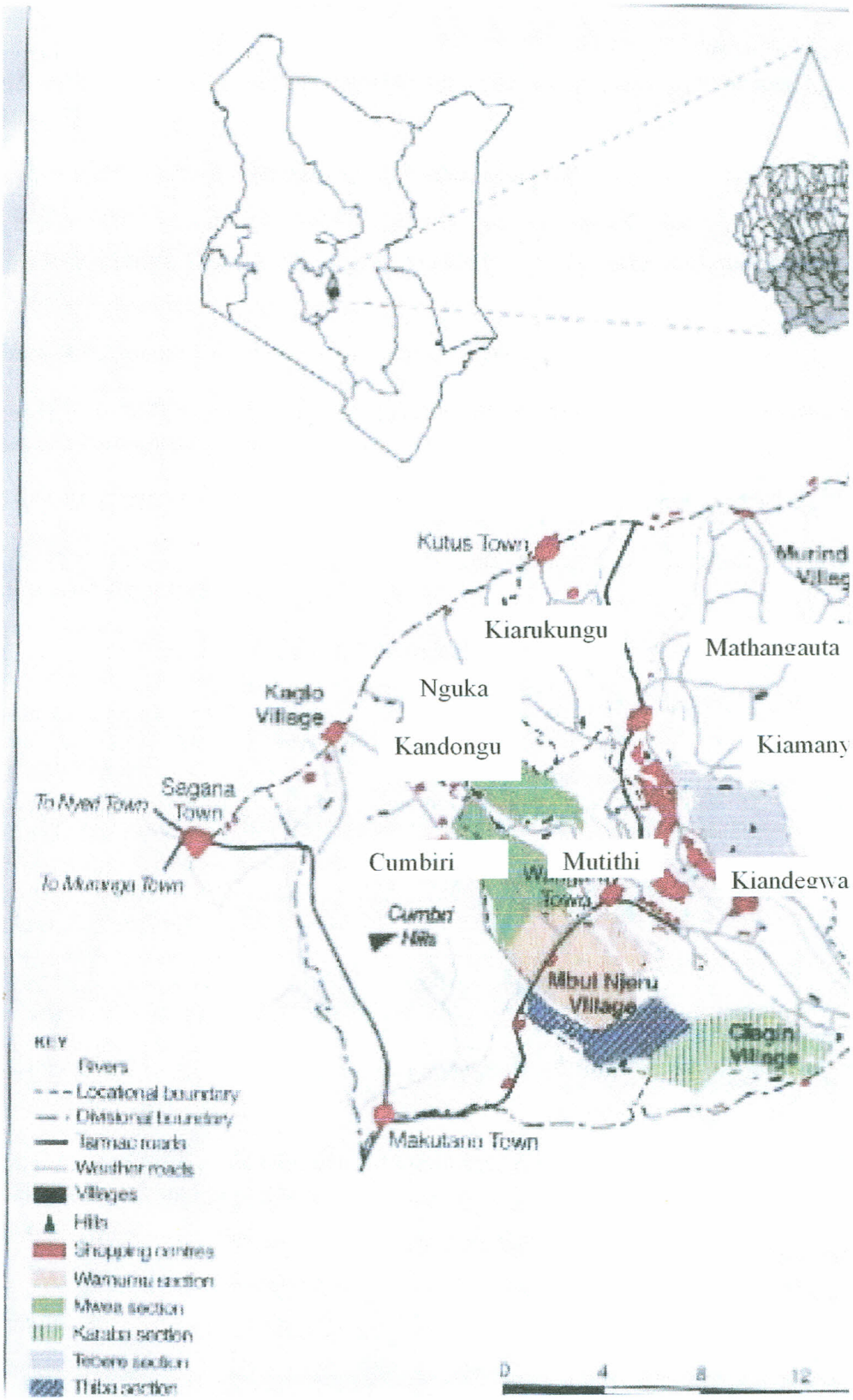

Calibration of Fe using AAS
Absorbance
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Conc. (ppm)
y = 0.0075x + 0.0083
R2 = 0.9957

Appendix 5


Calibration of Mn using AAS
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
0
1
2
3
Conc. (ppm)
y = 0.0401x + 0.001
R2 = 0.9991

Map of Mwea showing the various sampling sites

Appendix 6



REFFERENCES

Acevedo-Saandoval (2002). *Distribution of Iron, Aluminium and Silicon oxides in Hardened horizons of volcanic sources.*Institute de investigaciues en ciencials de la Tierra. Articulo Mexico. p 401-409.

Amethyst G.T. (1996). The mineral Chlorite. *The clay mineral society Journal.* **TOC37**: 5.

Atkins P.W. (1990). Structural Inorganic chemistry, 4th edition Oxford university. p320-328.

Astbury N.F., Moore F.G., Locket J.A. (1966). Clays. *Brit. Ceram. Soc.***65**: 435

Baker H.B. (1967). Geology of Mount Kenya Area. Ministry of Natural Resources: Mines and geology department. Nairobi. p46-49

Bailey S.W. (1978). The status of clay mineral structures. Oxford press. p56-57.

Bogue G.T. (1969). The chemistry of Portland Cement, 3rd Edition. Rheinhold publishing Corp. Toronto. p6-8.

Bohn H.L. (1982). Soil chemistry. John wiley and sons. New York. p123.

Brinker C.J., Scherer G,W. (1990). *Physics and chemistry sol gel processing.* Sol-Gel Science Academic Press Inc.New york. p5-9.

Bureau of Mines. (1982). "Iron Ore" Minerals commodity profile, Mpc-13. US Dept. of interior design. Washington D.C. p6-8.

Bush D.C., Jenkins R.E., McCalb S.B. (1966). Clay ad Clay minerals. 14th Nat Conference. Pergamon press. p0-14.

Clifford A.H., Gessuer G.H. (1973). The Encyclopedia of Chemistry, 3rd Edition. Van. Nostraud Reinhold Company Canada. p56.

Cornelius S.H. (1985). Dana's manual of mineralogy, 6th Edition. John Wiley& sons. New York. p30-31.

Downa A. J. (1993). Chemistry of Aluminium, Gallium, Indium and Thallium. Blackie Academic and professionals. p81-87.

Duncan M.M., Franzmeier D.P. (1999). Role of free Silicon Aluminium and iron in fragipan formation. *Amercan Journal of Soil Science society*.**48**: 63.

Edward H.K., Walter F.H., Lewis S.R. (1976). Mineralogy, an introduction to the study of minerals and crystals. Krypton New Jersey. p41.

Environmental Literacy Council. (2005). Aluminium in the world. Enivironmental Literacy Council.New York. p1-2.

Fified F.W., Kealy D.N. (1995). Principles of Analytical Chemistry, 4th edition. Chapman and Hall. New York. p179.

Fitzpatrick E.A. (1994). An introduction to soil science, 2nd Edition. Longman group. p4-6.

Gathua J.M. (2004). Pozzolanicty of selected kaolinites with special focus on pyroprocessing parameters. PHD thesis, Kenayatta university. Nairobi. p46-60.

Gieseking E.J. (1975). Soil components,vol.2.Springer-Verlag. New York inc. p98-100.

Goodman L.S., Gilman A.T. (1977). The pharmacological basis of therapeutics, 4th Edition. Macmillan Co. New York. p69-70.

Greenland D.J., Hayes M.B. (1991). The chemistry of soil processes. John Wiley & sons. Toronto. p4-5.

Greenwood N.N., Earnshaw A.K. (1984). Chemistry of Elements. Pergamon press. London. p88-93.

Grim R.E., Culhbert F.L. (1981). Technology of clay. *J.Am.ceramic.soc.* **41**:90

Grimswhaw R.W. (1971). The chemistry and physics of clays, 4th edition. Ernest Benn limited. London. p272-290.

Hammond C.R. (1990). Handbook of chemistry and physics. CRC press. p39.

Hanth W.E. (1971). Crystal chemistry in ceramics. *Bull. Am. journal of Ceramics.***12**:5.

Herren P.N., Fischer A.L., Halg W.T. (1980). Inorganic Chemistry. Chemical Publishing Co. New York. p356.

Hesse P.R. (1972). A textbook of soil chemical analysis. Chemical publishing Co.,inc. New York. p4-5.

http//www.tradeandindustry.go.ke

Isaac O.N. (1986). Effects of clay minerals on the stabilization of black cotton and laterite soils .*Kenya Journal of Science and Technology series.*7 (1). 5-10.

IAI (2005).World of Aluminium. IAI. New York. p1-4.

Jaffe D.H. (1969). The effect of heat treatment on the reactivity of minerals. PHD Thesis University of Leeds. p88.

Kamoni P.T. (1992). Detailed soil survey of Mwea irrigation agricultural development project (MIAD). Kenya soil survey. Nairobi. p 3.

Keller W.D. (1978). Clay and clay minerals in natural systems. *Clays clay miner.***26**(1):45.

Kenya metrological department. (1992). Summary of rainfall in Kenya. Kenya metrological department. P12.

Kirk R.E., Othmer D.F. (1979). *Encyclopedia of chemical technology,* 3rd Edition John wiley & sons. New York. **6**:190-222.

Kirk R.E., Othmer D.E. (1978). *Encyclopedia of chemical technology*, 3rd Edition. John wiley & sons. New York.**2**:129-241.

Kirk R.E., Othmer D.E. (1978). *Encyclopedia of chemical technology*, 3rd Edition. John wiley & sons. New York.**13**:635-645.

Kirk R.E., Othmer D.E. (1981). *Encyclopedia of chemical technology*, 3rd Edition. John wiley & sons. New York.**5**:223-234.

Kriegel W.W. (1970). Ceramic clays. North Carolina state college, Carolina. p38-39.

Kyun Y.P., Kim K.J., and Choi Y.J. (1997). Production of poly (Alumnium chloride) and Sodium silicate from clay. Department of materials development, Korea institute of geology. Korea. p1-6.

Lea R.M. (1971). The chemistry of cement and concrete, 3rd Edition. Edward Arnold (publishers) Ltd. London. p26-30.

Levy F.N. (1967). Crystallography and Crystal Chemistry of materials with layered structures. Reidel Publishing Company. Boston. p237.

Mclerman F.T., Kolwalsiki B.R. (1995). Process Analytical Chemistry. Blackie Academic and professional. London. p340.

Mickelson G.A., Secor R.B. (1983). Activated clays. Filtrol Corporation. Canada. p53-54.

Moore F.G., Locket J.A. Trans. *Brit. Ceram. Soc.* **66**:123

Muriithi N.T. (1985). Iron content of some samples of the black murrams and red ochres from different parts of Kenya. *Kenya Journal of Science and Technology series.* **6** (2): 103-108.

Murray H.D. (2002). Industria clays: Case study. International Institute for Envt. And Devt (IIED). England. p1-4.

Olale A.E. (1985). Silicate Technology. Kenya literature Bureau. Nairobi. P3-4.

Ong'alo D.O. (2001). International investment and environment issues : The case of Kenya's Kwale mineral sands project. Cuts-Arc. Lusaka. P2-3.

Nelson G.C. (1960). Ceramics. Hof Renehart and Winston Inc. p5 –12.

Raleigh N.C. (1986). Clay and clay minerals. *Journal of Mineralogical society of America.* **34**: 250-256.

Roskill information services Ltd. (2004). Industrial Minerals and rocks, 6th Edition. US Geology survey. p1-7.

Schenk G.H., Hahn B.R., Hartcopf A.V. (1981). Introduction to analytical chemistry 2nd edition. Allyn and Bacon Inc Sydeny. p349 - 358.

Shreve R.N., Brink J.A. (1977). Chemical process in industries, 4th Edition. Mcgraw - Hill Kagakusha limited press. p112-114.

Skoog D.A., Leavy S.S. (1992). Principles of instrumental analysis, 4th Edition. Sanders college publishers forthworth. p172-178.

Sposito G. N. (1989). The chemistry of soils. Oxford university press.London. p31.