CONCENTRATION OF IRON IN LATERITES FROM DIFFERENT LOCALITIES OF TUNYAI DIVISION IN THARAKA NITHI COUNTY IN KENYA USING MAGNETIC SEPARATION

BY

MUTEMBEI PETERSON KUGERIA (B.Ed. (Sci.))

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DECLARATION

I hereby declare that this is my original work and has not been presented for the award of a degree or any award in any other university

Signed: …………………………………. Date...

MUTEMBEI PETERSON KUGERIA

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

1. PROF. NAFTALI T. MURIITHI

Department of Chemistry

Kenyatta University

Signature……………………………………….Date……………………

2. Dr. JACKSON WACHIRA MUTHENGIA

Department of Chemistry

Kenyatta University

Signature……………………………………….Date……………………………….

DEDICATION

This work is dedicated to my mother Anastasia Mukwanjagi, my wife Faith Kendi and my children Loveyn and Edwin.

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ABSTRACT

Iron is the single element used in industries in larger quantities than all the other metallic elements combined. This is because of the very wide applications of the metal in manufacture of machinery, vehicles, utensils, trains and train rails, ships and bars used in re-enforced concrete. Whereas the element occurs in more than 80 minerals, only a small number is important as a source of iron. However, even these must be concentrated to make them suitable for putting in a blast furnace. In Kenya, laterites commonly called murram, are currently being used mainly for surfacing roads. This study set out to show that laterites can be converted to high quality iron ore which should make Kenya self-reliant in as far as supply of metallic iron is concerned. The area of study was chosen because some of the iron in this area is known to be present as the mineral ilmenite. It was, therefore, of interest to find out whether the heat treatment that converts hematite to magnetite is adequate to decompose ilmenite. The samples of this study were obtained from Tunyai Division, in Tharaka Nithi County, in the Republic of Kenya. During sampling, three sampling sites from each location were selected within a distance of about a km apart. Within a given sampling site, three holes which were at least ten metres apart were dug. The surface materials of up to 30 cm deep were discarded since they contained a lot of organic matter. Three Samples from this depth were obtained, mixed and about one kg of the sample-mixture packed in plastic bags labeled level A awaiting analysis. For each hole, samples were also picked from a depth of one metre, mixed and labeled, B. Laterite samples were concentrated by heating charcoal/laterite mixtures in the ratios of 1:10 by mass in a slow current of air and in the temperature range of 500-700^{o}C. Elemental analysis was carried out on both the raw laterites and the heat treated samples with particular interest on the level of iron using Atomic Absorption Spectroscopy (AAS) and EDTA Titrations for comparison purposes. The minerals present were determined using a Bruker D8 Advance Diffractometer. The results of elemental analysis showed that, raw laterites contain 28-31% iron depending on source. On the other hand, after the heat treatment, the level of iron in the heat-treated sample had increased to 55-64%. Iron ore with this level of concentration is usually what is normally put in a blast furnace. The X-ray diffraction data confirmed that, iron in the raw laterites was present predominantly as the minerals goethite and hematite since these are known to have diffraction peaks at angles $2\theta = 21.51^{\circ}$ and $2\theta = 54.11^{\circ}$, respectively. In this study, whereas these peaks were observed in the raw laterites, they were absent in the heat-treated magnet-separated samples and instead, a strong peak was observed at angle $2\theta = 36^{\circ}$. This peak is attributed to magnetite. This observation confirms that, when the laterite-charcoal mixture is heated in the temperature range 500-700^{o}C in a current of air, both goethite and hematite are converted to the mineral magnetite. The iron present in laterites can, therefore, be readily concentrated using magnetic separation. Furthermore, any ilmenite present in laterites is not affected by this heat treatment.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
B	Magnetic Induction
BIF	Banded Iron Formations
DSC	Delta Steel Company
EDA	Etherdiamineacetate
EDTA	Ethylenediaminetetraacetic
H	Field Intensity in Tesla
kG	kilo Gauss
KNBS	Kenya National Bureau of statistics
LKAB	Luossavaara-Kiirunavaara AB
LOI	Loss on Ignition
M	Intensity of Magnetization
MIBC	Methylisobutylcarbinol
MRG	Mount Royal Gabbro
Mt	Million Tonnes
PO	Propylene Oxide
STC	Swedish Trade Council
NIOMCO	Nigerian National Iron Mining Company Limited
SY-3	Syenite
T	Tesla
UAE	United Arab Emirates
USGS	United States Geological Survey
XRD	X-ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Iron is a metal in the first transition series. Like other group 8 elements, iron exists in a wide range of oxidation states, from −2 to +8, with +2 and +3 being the most common (Alan, 2006). Elemental iron occurs in meteoroids and other low oxygen environments. However, since it is reactive to oxygen and water, it is usually found in oxidized form. Fresh iron surfaces appear lustrous silvery-grey, but oxidize in normal air to give iron oxides, also known as rust. Unlike many other metals which form passivating oxide layers, iron oxides occupy more volume than the metal, and thus the oxides flake off and expose fresh surface to corrosion (Kohl, 1995). Iron is the fourth most abundant element in the earth's crust with 6.3% after oxygen, 45.5 %, silicon, 27.2 %, and aluminium, 8.3 % (Jorgensen, 1993). Iron-made products such as railway lines and its compounds are produced in larger tonnage than that of all the other metallic elements combined (Emsley, 2001).

Iron occurs in more than 80 minerals and only a small number is important as a source of iron. Such minerals includes hematite, Fe_2O_3 (70 % Fe), goethite, FeO.OH (63 % Fe), limonite, $FeO(OH).nH_2O)$ (up to 60 % Fe), and magnetite, Fe_3O_4 (72.4 % Fe). However, even these must be concentrated to make them suitable for putting in a blast furnace. Iron is also obtained during extraction of sulphur from minerals marcasite, FeS_2 and pyrrhotite, FeS (flash process) after sulphur is converted to sulphuric acid. During extraction of titanium from ilmenite, $FeTiO_{3,}$ iron is also obtained separately. Most of the world's important iron ore sources occur in iron-rich sedimentary rocks known as Banded Iron Formations (BIF) which are estimated to be over 600 million years old. In many instances, they are mined as iron ores, but most importantly they are the source rocks for most of the large high-grade concentrations of iron ore currently mined throughout the world (Rostoker *et al.,* 1984). The BIF enrichment deposits sometimes comprise of much lower percentages of iron, 18-60% and hence some ore concentration is necessary (Johnstone and Johnstone, 1961). Some ores such as those from Kiruna Mine in Sweden (Park and MacDiarmid, 1970), contain 62-68% iron. However, even such ores must be refined because they contain apatite to the extent of 1% phosphorous. If the ore is not refined, the phosphorous will combine with iron to form iron sulphide and thus lower the quality of steel.

Iron is of greatest importance when mixed with carbon and certain metals such as Cr, Ni, V, Ti Nb to form steels (Martin, 2007). Powdered iron is mainly used in metallurgy products, magnets, high-frequency cores, auto parts and catalyst. Radioactive iron (Fe 59) is used in medicine, tracer element in biochemical and metallurgical research. Iron blue on the other hand, is used in paints, printing inks, plastics, cosmetics (eye shadow), artist colours, laundry blue, paper dyeing, fertilizer ingredient, baked enamel finishes for autos and appliances and industrial finishes. Black iron oxide is used as pigment in metallurgy, medicine, magnetic inks and in polishing compound (Camp and Francis, 1920).

Iron catalysts are used in the Haber - Bosch Process for the production of ammonia, and the Fischer-Tropsch Process for conversion of carbon monoxide to hydrocarbons for fuels and lubricants (Kolasinski, 2002). Powdered iron in an acidic solvent is used in the Bechamp reduction, the reduction of nitrobenzene to aniline (McKetta, 1989). Iron (III) chloride finds use in water purification and sewage treatment, in the dyeing of cloth, as a colouring agent in paints, as an additive in animal feed, and as an etchant for copper in the manufacture of printed circuit boards (Wildermuth *et al.,* 2000). Iron is dissolved in alcohol to form tincture of iron; iron (II) sulphate is used as a precursor to other iron compounds as well as reducing chromate in cement. According to Durupt *et al.,* (2000), iron is also used to fortify foods and treat iron deficiency anaemia. Iron (III) sulphate is used in settling minute sewage particles in tank water. Iron (II) chloride is used as a reducing flocculating agent, in the formation of iron complexes and magnetic iron oxides, and as a reducing agent in organic synthesis (Holleman *et al.*, 1985).

Iron is mainly used in the manufacture of vehicles, ships, kitchen utensils, metal bars for re-enforced concrete used in building bridges and high rise buildings, manufacture of heavy machinery such as tractors, and lorries (Bramfitt and Benscoter, 2002; Dauphas and Rouxel, 2006). It is for this reason that both developed and developing countries spend a big portion of their national budgets on buying iron–made products. In 2005, approximately 1,544 million metric tons of iron ore were produced worldwide. According to the Benham and Brown (2007), China was the top producer of iron ore with at least one quarter world share, followed by Brazil, Australia and India. Kenya on the contrary is an importer of iron. During the year 2010, for instance it was estimated that Kenya imported iron and iron products in excess of 60 billion Kenya shillings, Kenya National Bureau of statistics (KNBS, 2010).

Reports from Geological Surveys of Kenya show that Kenya has economically viable iron ore deposits, an example being the ore in Ikutha in Kitui District which contain 68 % Fe. Iron ore deposits are also found in Marimante, Meru with 46 % Fe and Macalder in South Nyanza with 45.25 % iron (Du Bois and Waish, 1970). The ore in Marimante also contains titanium (2-5%) while the ore in macalder is from the minerals pyrites. The ore in Kitui has iron concentration which is as high as the best iron ore in the world found at Kiruna mine in Sweden, with 68 %

iron (Kiruna Iron Ore Mine Report, 2010). China Mining Association (2011), reports that intensive prospecting over the past few years has yielded promising data on availability of iron ore in the country. Currently, Wanjala Mining Company, a Kenyan company is mining iron ore at Kishushe Location in Taita Taveta County.

Laterites are types of soil rich in iron formed in hot and wet tropical areas. Nearly all laterites are rusty-red because of iron (III) oxides (Hill *et al.*, 2000). Iron from these soils can be concentrated using methods such as jigging, magnetic separation and froth flotation. Different techniques used depend on the minerals being concentrated. Magnetite for instance, is concentrated using magnetic separation while hematite is concentrated using froth flotation (Sharma, 2004). The current study dwelt on enriching iron from laterite materials containing titanium. A newly technique uses magnetic separation after converting both goethite and hematite to magnetite by heating a laterite-charcoal mixture in a current of air at temperature range of 500-700 ^{o}C, thus generating the carbon (II) oxide (a reducing agent) needed *in situ* which thereafter reduces some iron oxides in laterites to magnetite (Keru, 2011). The level of titanium in the concentrate was observed to increase from about 1% to 5%. Whereas wood charcoal was used for experimental purposes, it has been proven that charcoal is readily obtained by carbonization of municipal biomass (Njoroge, 2013).

1.2 Statement of the Problem

Laterites are known to contain 15-45 % iron. Currently the main application of laterites in Kenya is for surfacing roads, yet as mentioned above, some of them have been shown to contain much higher concentration of iron than some ores used elsewhere in the world. Ironically the country spends billions of shillings to import iron and iron-made products from such ores. The problem to be investigated is: can the iron-containing minerals in Kenyan laterites be concentrated using magnetic separation? If iron in lateritic materials can be concentrated then, This may provide an alternative method of obtaining iron economically from the available laterite deposits in Kenya.

1.3 Null Hypothesis

Iron in laterites from Tunyai Division cannot be concentrated using magnetic separation even after heating laterite-charcoal mixture in a current of air in the temperature range of 500-700 ^{o}C.

1.4 Objectives of the Study

1.4.1 General Objective

The main goal was to investigate the possibility of enrichment of iron from laterite deposits obtained from selected sites of Tunyai Division in Tharaka Nithi County.

1.4.2 Specific Objectives

i) To convert the minerals goethite, FeO.OH and hematite, Fe_2O_3, present in murrams from Tunyai to magnetite, Fe_3O_4, by heating a charcoal-murram mixture in a current of air in the temperature range of 500-700 ^{o}C.

ii) To determine the mineralogical composition in laterites, both before and after heating the laterite-charcoal mixture in a current of air using X-ray Diffraction Spectrometry (XRD).

iii) To determine elemental composition in raw laterites from selected sites within Tunyai Division.

iv) To concentrate iron in laterites containing rutile using magnetic separation and thereafter carrying out elemental analysis using AAS and EDTA titration.

1.5 Justification of the Study

Kenya, like any other country, needs more iron if it has to develop economically and in particular attain the objectives of vision 2030. There are few established iron deposits in the country yet none of iron and steel industries process raw materials from these deposits. Currently there are steel mills situated at Ruiru and Dandora area in Nairobi and in Mombasa which are involved in collecting and smelting of scrub metal to obtain iron and steel products. The country, as noted earlier has large deposits of iron-rich laterites, also known as murram which consist of 15 to 40 % iron and mainly used to spread on roads. Iron ore deposits with this level of iron are currently being used in other countries as a source of iron after ore concentration (Boltz, 1970; Umunakwe, 1985).

A newly-developed technique has shown that iron in laterites can be concentrated using magnetic separation (Keru, 2011). In this study, it was shown that when a laterite-charcoal mixture was heated in the temperature range of 500-700 ^{o}C in a current of air, the level of iron could be raised from 30 % in raw laterites to well over 64 %. The concentrate with this level of iron is suitable to be fed in a blast furnace. From this study, lateritic materials can therefore be treated as suitable iron ores.

1.6 Scope and Limitation of the Study

Iron in laterites from selected sites in Tunyai Division in Tharaka South District in Tharaka Nithi County have been concentrated by heating a mixture of charcoal-laterite in different mass ratios in the temperature range of 500-700 ^{o}C in a controlled current of air. A ratio of charcoal-laterite, 1:10 by mass has been established as most economical. The present study concentrated on work in laboratory scale. A large scale study is, however, needed. This will require more capital investment on the type of the equipment for pilot study scale.

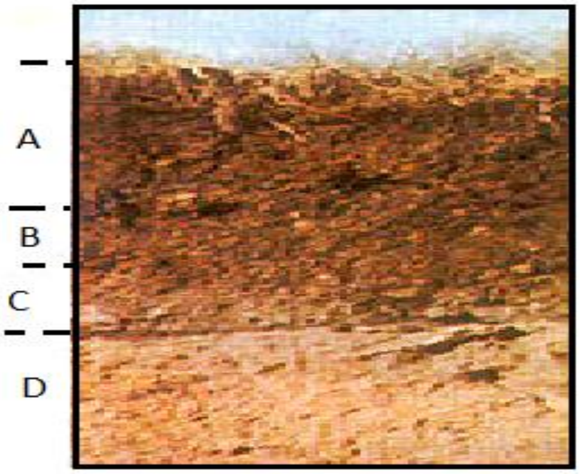
CHAPTER TWO

LITERATURE REVIEW

2.1 Laterites

Laterites are soils which are mainly of iron and aluminum minerals. The term Laterite is a Latin word ‘later’ which means a brick (Thurston, 1913). Laterites are also defined as heavily altered material, rich in secondary iron or alumina oxides or both. They practically contain bases and primary silicates, but may also contain large amounts of quartz (SiO_4^{4-}) and kaolinite ($Al_2Si_2O_5(OH)_4$). They may be hardened *in situ* or indurate only after successive humidification and desiccation (Alexander and Cady, 1962).

The word “Laterite” has been used for variably lamented sesquioxide-rich soils. These are oxides with the general formula M_2O_3, (M= Al, Fe) and mainly located under residual soils (Butzer and Helgren, 1977). An example of soil profile composed of mainly lateritic materials is shown in plate 2.1 (Tardy, 1997).



Where; A - Top soil, B – Lateritic materials known as regolith, C – Saprolites materials which are less-weathered regolith, D - Bedrock.

Plate 2.1: Soil profile made of lateritic materials

Tropical weathering (laterization) is a prolonged process of chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils. According to Schellmann (1994), the initial products of weathering are essentially kaolinized rocks called saprolites. Laterites are formed from the leaching of parent sedimentary rocks (sandstones, clays, limestone) metamorphic rocks (schists, gneisses, magnetites), igneous rocks (granites, basalts, gabbros, peridotites) and mineralized proto-ores which are predominantly iron and aluminium (Tardy, 1997). The mechanism of leaching involves acid dissolving the host mineral lattice, followed by hydrolysis and precipitation of insoluble oxides and sulphates of iron and aluminium. This process occurs under high temperature conditions of humid tropical and sub-tropical monsoon climate and according to Hill *et al.* (2000), an essential feature for the formation of laterite is the repetition of wet and dry seasons which facilitates weathering processes.

All laterites are marked by an enrichment of iron and a decrease of silica together with the highly soluble alkalis and alkaline earths. Two principal groups of laterites have been distinguished (Schellmann, 1994). One group is laterites from mafic rocks (basalt, gabbro) and ultramafic rocks (serpentinite, peridotite, dunite). These rocks show lower silica and higher iron content. The other group is laterites from acidic rocks which includes mainly granites and granitic gneisses and many types of sediment like clays, shales and sandstone. These rocks contain quartz and have higher silica and lower iron content. Table 2.1 shows typical average values of major oxides in numerous laterite samples and their parent rocks which were collected by Schellmann (1994), in many tropical countries.

Table 2.1 : Percentages of major oxides found from mafic and acidic rocks

Minerals	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**$Fe_2O_3 : Al_2O_3$**
Granitic rocks	73.3	16.3	3.1	0.19
Laterite	46.2	24.5	16.3	0.67
Clay rocks	56.5	24.4	5.3	0.22
Laterite	39.2	26.9	19.7	0.73
Basaltic rocks	47.9	13.7	14.9	1.09
Laterite	23.7	24.6	28.3	1.15
Serpentinite rocks	38.8	0.7	9.4	14.1
Laterite	3.0	5.5	67.0	12.2

Source: (Schellmann, 1994)

Laterites and bauxites can be re-deposited into sedimentary sequences, and remain as ores if not transported far and diluted with other materials. The age of re-deposited laterites and bauxites, and their respective paleosols, can be established from the geological age of overlying rocks. The dating is effective in paleosols within sequences of isotopically datable volcanic rocks. Lateritic profiles can also be dated by paleomagnetic inclination found along continental margins such as those in Australia and India which drifted apart during Cenozoic time (Gregory, 2010)**.**

In Kenya, laterites are widely distributed in almost all parts of the country (Bourman, 1993). According to Bourman (1993), laterites are formed in hot and wet tropical areas where intensive and prolonged weathering of the underlying parent rock occurs. Lateritic materials reflect past weathering conditions. For instance, some studies by Tardy (1997) show that mineralogical and chemical compositions of laterites are dependent on their parent rocks (mainly quartz and oxides of titanium, zirconium, iron, tin, aluminum and manganese).

Laterites vary significantly according to their location, climate and depth. Iron oxides are derived from mafic igneous rocks and other iron-rich sedimentary rocks, while bauxite is derived from granitic igneous rocks and other iron-poor rocks. According to Schellmann (1994), high grade iron ores on top of tropical deposits of BIF are also attributed to lateritic weathering which causes dissolution and removal of siliceous constituents in the iron ores. Laterites which are presently found in non-tropical areas are products of former geological epochs, when that region was near the equator (Guerassimov, 1962). Where laterites occur outside the humid tropical regions they are considered to be the indicators of climatic change, continental drift or a continuation of both (Hill *et al.,* 2000).

2.2 Iron- Bearing Minerals

Iron ores are rocks and minerals from which metallic iron can be extracted economically. The ores are usually rich in iron oxides and vary in colour from dark grey, bright yellow, deep purple, to rusty red. The iron itself is usually found in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite (FeO.OH), limonite ($FeO.OH.n(H_2O)$), ilmenite ($FeTiO_3$) or siderite ($FeCO_3$) (Hill *et al.*, 2000). Hematite is also known as "natural ore", a name which refers to the early years of mining, when certain iron ores containing up to 66 % iron could be fed directly into iron-making blast furnaces (Bonifas, 1959). Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel. A 98 % of the mined iron ore is used to make steel. Indeed, it has been argued that iron ore is more integral to the global economy than any other commodity, except perhaps oil (Camp and Francis, 1920).

Iron ores occur in deposits of all geological ages (Snell *et al.*, 1972). According to Luttrell (1975), principal types of deposits yielding iron ores are bedded ores, igneous segregations, contact metamorphic deposits, vein deposits and superficial residues. In Kenya, iron ore deposits are found in the form of magnetite, hematite, goethite, limonite, siderite and anchorites. These deposits occur as bands among the regionally metamorphosed sediments and also within sedimentary rocks. One of the BIF is found on Samia hills in Busia district where it is associated with volcanic rocks (Dubois and Walsh, 1970). The chief iron-bearing minerals are given in table 2.2.

Table 2.2 Iron-bearing minerals

Class	**Mineralogical name**	**Chemical formulae**	**Common designation**	**% Iron**
Oxides	Magnetite	Fe_3O_4	Ferrous-Ferric Oxide	72.4
	Hematite	Fe_2O_3	Ferric Oxide	70.0
	Ilmenite	$FeTiO_3$	Iron-Titanium Oxide	36.8
	Limonite(goethite)	$Fe_2O_3.H_2O$	Hydrous Iron Oxide	62.9
Carbonates	Siderites	$FeCO_3$	Iron Carbonate	43.8
Silicate	Chamosite	All are often complex	Iron Silicate	
	Silomelane			
	Greenalite			
	Mineresataite			
	Gruenerite			
Sulphides	Marcasite	FeS_2	Iron Sulphide	46.7
	Pyrrhotite	FeS		63.6

Source: (Snell *et al.*, 1972)

The amount of iron needed in any mineral deposit to make it profitable to mine must be in millions of tons (Harry *et al.*, 1973). Hematite deposits are mostly sedimentary in origin, such as the BIFs which consist of alternating layers of chert (a variety of the mineral quartz), hematite and magnetite (Harry *et al.,* 1973; Dalstra *et al.,* 2003). They are found throughout the world and are the most important iron ores in the world today. Their formation is not fully understood, though it is speculated that they are formed by the chemical precipitation of iron from shallow seas about 1.8 to 1.6 billion years ago, during the Proterozoic era (Harry *et al.,* 1973). Table 2.3 gives the iron content of some minerals found in various countries. From the table, it is evident that iron ores from countries such as U.K and France have relatively low iron concentrations, actually even lower than some ores found in Kenya (Dubois and Walsh, 1970).

Table 2.3 : Typical iron ores from different countries

Country	**District**	**Ore**	**Iron (Fe) %**
France	Sancy	Calcareous	32.0
France	Mont-St-Martin	Siliceous	37.3
India	Cuddapah	Hematite	50.7 to 61.2
Russia	Krivoi-Rog	Hematite	61.0
Russia	Kerch	Brown	40.2
Sweden	Kiruna	Magnetite with Hematite	65 to 68
U.K	Frodingham	Brown Ores	18 to 24
U.S	Wacootah (Late Superior Mesabi)	Limonite, Martite, (Magnetite)	59.37

Source: (Boltz, 1970)

The world's iron ore resource base has been estimated at 180,000 million tonnes (Mt), while the reserves are 79,000 Mt. China is currently the largest consumer of iron ore, which translates to be the world's largest steel-producing country. It is also the largest importer, of iron ore, buying about 52 % of the seaborne trade in iron ore since 2004. In 2009, China, produced 880 Mt of iron ore, with an annual growth of 38 %. In 2011, China was also the leading producer with 1,200 Mt of iron ore with an annual growth of about 40 % (Upadhyay and Venkatesh, 2006). According to the U.S. Geological Survey (USGS) (2012), the mine production estimates for China was based on crude ore, rather than usable ore.

Iron ore is the mineral produced in largest quantity by Australia. Thus, during the years, 2009, 2010 and 2011, the country produced 394 Mt, 420 Mt and 480 Mt respectively (Javier *et al.*, 2009; USGS, 2012). The country is the world's second largest producer of iron ore after China. The Hamersley Range in the Pilbara region of Northwest Australia is the host to 98 % of Australia's iron ore mines, with minor production from Tasmania, New South Wales, Queensland and South Australia. Brazil is the world's third largest iron ore producer and exporter after China and Australia. Iron ore production in Brazil reached 390 Mt in 2011 compared to 300 Mt in 2009. Crude ore reserves are estimated to be 29,000 Mt. Iron ore has traditionally been one of the country's largest export products (USGS, 2012). Brazilian iron ore deposits are the third major deposits in the world with Minas Gerais State reserves representing about 72.2 % of total national reserves, Pará State with 23.3 %, Mato Grosso do Sul state with 4.3 % and São Paulo State with 1 % (Rabelo and Turrer, 1999).

India ranks the fourth among producers of iron ore, with a 6,200 Mt reserve base. The majority of Indian iron ore deposits occur in the Eastern, Central and Southern parts of India in the regions of Jharkhand, Orissa, Karnataka, Chhattisgarh and Goa. India's iron ore production has just doubled in the last 5 years, achieving a total of 154 Mt in 2005–06 compared with 86 Mt in

2001–2002 (Upadhyay and Venkatesh, 2006). In the year 2009, India production was 245 Mt and 240 Mt in the year 2011. Other major producers of iron ore are given in table 2.4 (USGS, 2012).

Table 2.4 : Estimated iron ore production in million metric tons for 2012

Country	**Production**	**Country**	**Production**
China	1200	Iran	30
Australia	480	Canada	37
Brazil	390	United States	54
India	240	Kazakhstan	24
Russia	100	Sweden	25
Ukraine	80	Venezuela	16
South Africa	55	Other countries	75
Total world			**2800**

Source: (USGS, 2012)

The Kiruna mine in Sweden is the largest and most modern underground iron ore mine in the world. The mine is located in Kiruna in Norrbotten County, Lapland. The original reserve at Kiruna was some 1,800 Mt. By the end of 2008, the Luossavaara-Kiirunavaara AB (LKAB), a Swedish mining company estimated that the current proven reserve at the mine was 602 Mt grading at 48.5 % iron, with probable reserves of 82 Mt at 46.7 % iron (Kiruna Iron Ore Mine report, 2010). Sweden has an annual production capacity of over 25 Mt of iron ore (USGS, 2012). The ore grade was more than 60 % iron and an average of 0.9 % phosphorus. Since mining began at the site over 100 years ago, LKAB has produced over 950 Mt of ore, yet only one third of the original ore body has been extracted. The Swedish Trade Council (STC) has been exporting its iron and steel products mainly to United Arab Emirates (UAE) over the years. In the year 2007, STC exports of iron and steel products grew from 99.76 million kronor in 2006 to 332.74 million kronor, with a 234 % increase. In addition, exports of agricultural machinery to the UAE, increased from 2.38 million kronor in 2006 to 6.62 million kronor in 2007 which was 179 % increase (Kiruna Iron Ore Mine report, 2010).

In the Itakpe iron ore in Nigeria, magnetite and hematite are the main ores. Proven iron ore reserves are at least 200 Mt with a life-span of over 100 years. The commercial ore grades range in ferrous content from rich ores with over 50 % Fe, to poor ores with 25-30 % Fe. The Nigerian National Iron Mining Company Limited (NIOMCO), was established to upgrade Itakpe iron ore to sinter grade of 63-64 % Fe. The upgraded ore was used for the blast furnace based at Ajaokuta Integrated Steel Plant and Ajaokuta in Kogi State. The Itakpe sinter grade concentrate is, however, not suitable for direct reduction operations at the Delta Steel Company (DSC) in Aladja and Delta State. The concentrate needs to be up-graded to a super concentrate grade with 66 % to 66.88 % Fe (Umunakwe, 1985).

2.3 Beneficiation of Iron Ores

Beneficiation is the process of increasing the concentration of a particular element in an ore. The most common mineral beneficiation processes include sample preparation, comminution, size classification, and concentration. During beneficiation, extracted ore from mining is separated into mineral and gangue (Carter *et al.,* 2007). Beneficiation methods of iron vary depending to the type of mineral. Concentration methods used commonly include jiggling, flotation and magnetic separation (Sharma, 2004).

2.3.1 Froth Flotation

Froth flotation is a process for selectively separating hydrophobic materials from hydrophilic ones (Eisele and Kawatra, 1992; Barry, 1997). The flotation process is used for the separation of a large range of sulphides, carbonates and oxides prior to further refinement **(**De Gennes, 2004). Froth flotation commences by crashing and grinding process which is used to increase the surface area of the ore for subsequent processing. The basic principle in froth flotation is that some minerals have a higher affinity for air bubbles than others (Barry, 1997). When the mineral particles are introduced into a water bath which is aerated, the mineral particles attract air bubbles and hold them. This results in the overall density of the mineral particle and the air bubbles becoming lower than that of the liquid medium, and hence float as illustrated in figure 2.1.

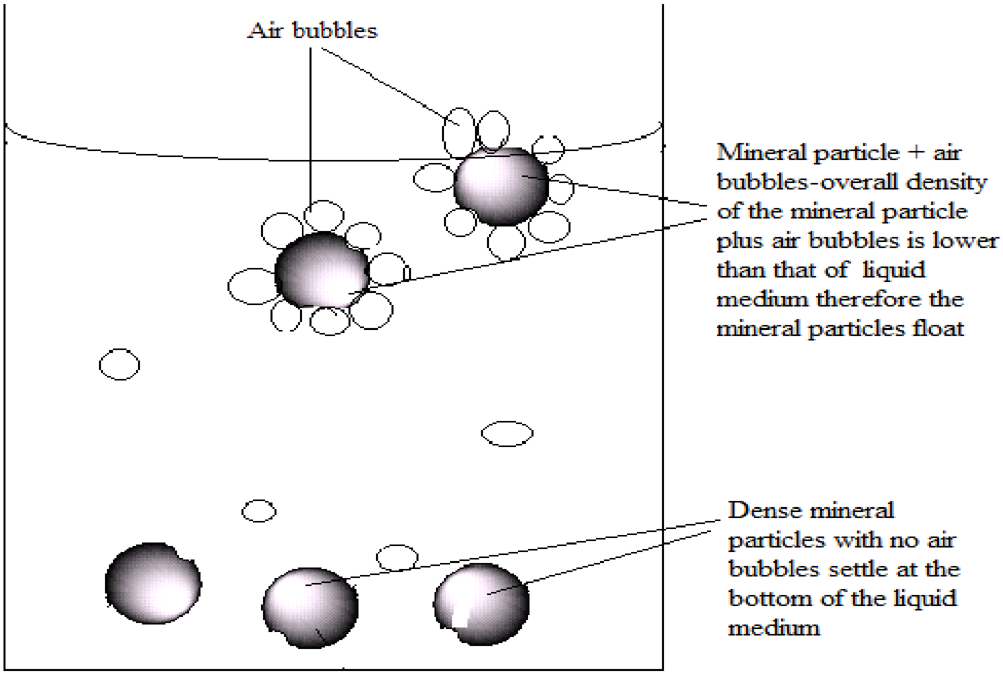


Figure 2.1 : Air bubbles attached to mineral particles

In cases where the mineral particles are not frothable, chemical compounds known as frothing agents are added. Where bubbles are larger than the ore particles and the particles are equal to or less than 1mm radius, then, the particles will rise into the froth layer (De Gennes, 2004). Those particles which are larger than the bubbles also rise into the froth. Since each of these particles is buoyed by a swarm of bubble forming a stable froth, the froth is then skimmed off to another container as illustrated in figure 2.2 (Eisele and Kawatra, 1992).

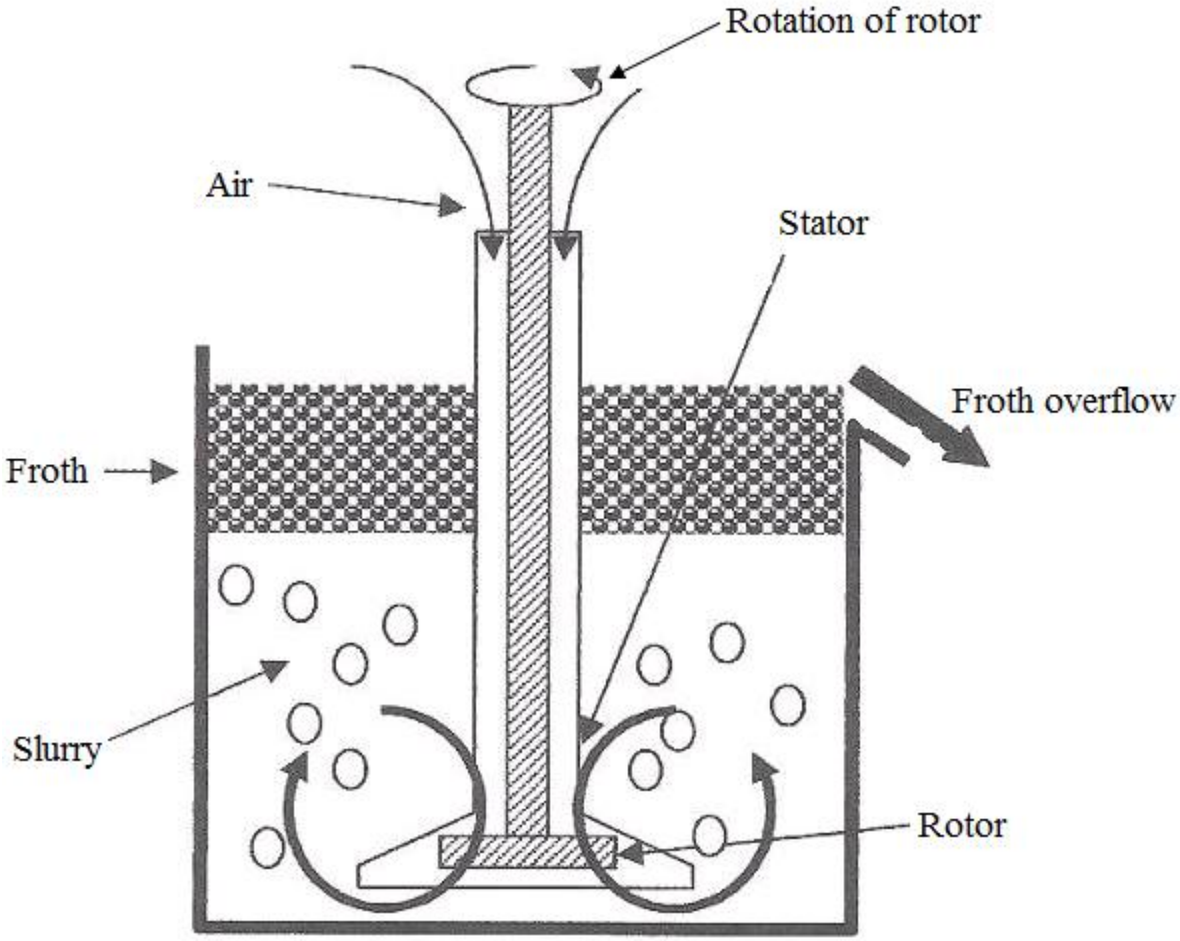


Figure 2.2 : A flotation cell

Froth flotation is a good example of an engineering "system", in that the various important parameters are highly inter-related, as shown in Figure 2.3 (Eisele and Kawatra, 1987).

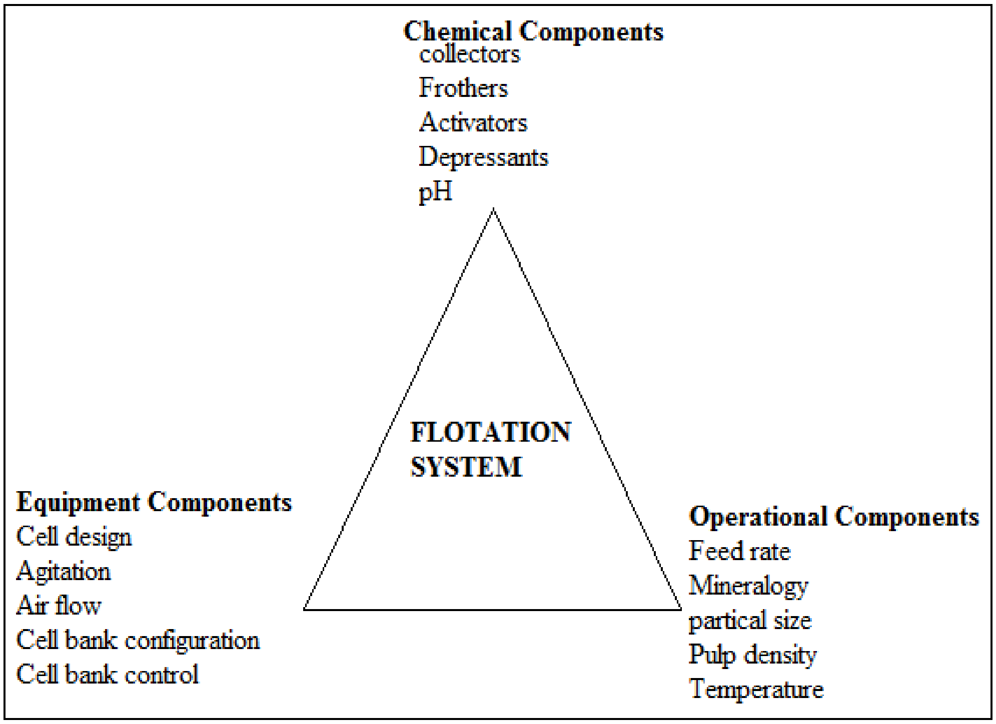


Figure 2.3 : The flotation system including many interrelated components

According to Eisele and Kawatra (1987), it is important to take all of these factors into account in froth flotation operations. Changes in the settings of one factor (such as feed rate) will automatically cause or demand change in other parts of the system (such as flotation rate, particle size recovery, air flow, pulp density, among others.). As a result, it is difficult to study the effects of any single factor in isolation. Compensation effects within the system can keep the process changing from producing the expected effects (Klimpel, 1995).

Graham and Madeley (1966) studied the effect of pH and flotation-collector type upon the flotation rates of natural rutile particles. The study has shown that from pH of 2.5, flotation rate decreases with increasing pH for anionic collectors and increases with increasing pH for a cationic collector. At a fixed pH the rate of flotation is influenced by the length of the carbon chain associated with the collector. Below pH of 2.5, the flotation rate with anionic collectors decreases with fall in pH, whereas with the cationic type a small increase in rate is shown as pH of 1 is approached. Types of common collectors are shown in figure 2.4 (Eisele and Kawatra, 1992).

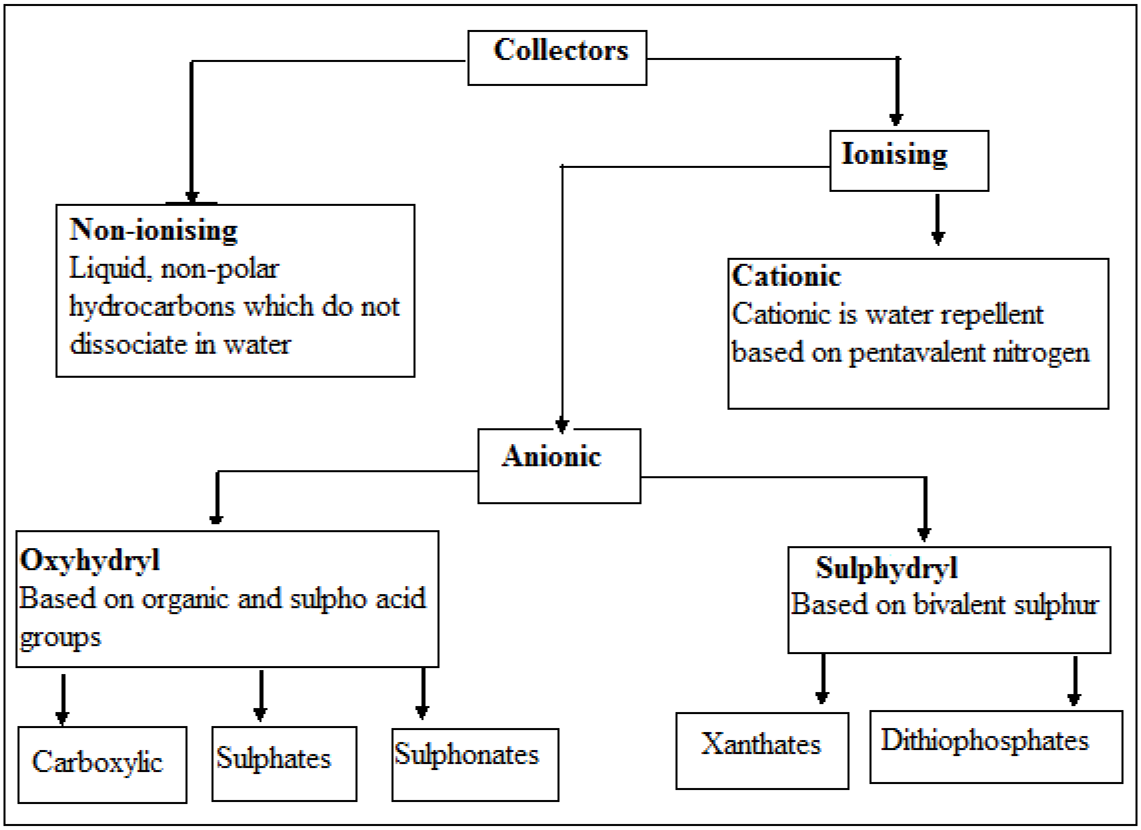


Figure 2.4 : Types of collectors

Anionic collectors are weak acids or acid salts that ionize in water, producing a collector that has a negatively-charged end that will attach to the mineral surfaces. An anionic collector has a hydrocarbon chain that extends out into the liquid, as shown in Figure 2.5 (Eisele and Kawatra, 1992).

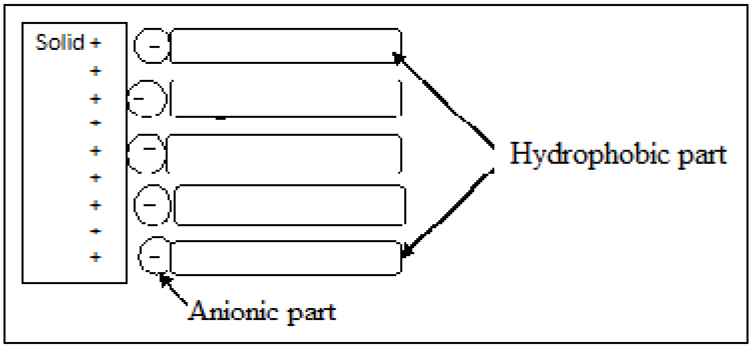


Figure 2.5 : Adsorption of anionic collector onto a solid surface

The anionic portion is responsible for the attachment of the collector molecule to the mineral surface, while the hydrophobic part alters the surface. Examples of anionic collectors are sodium oleate and fatty acids which occur in vegetable oils, and are found with polar groups such as $RCOO^-$, $ROSO_3^-$, RSO_3^-, $ROCS_2^-$ and $R_2O_2PS_2^-$. They are strong collectors with low selectivity for hematite and other metal oxide minerals (Eisele and Kawatra, 1992). Other chemical reagents used as frothers are methylisobutylcarbinol (MIBC), pine oil and cresylic acid (Klimppel, 1995).

Modifiers are substances which influence the way the collectors attach to the mineral surfaces. Modifiers either increase the adsorption of the collector on a given mineral (activators), or prevent collectors from adsorbing onto a mineral (depressants) (Eisele and Kawatra, 1992). An example of an activator is copper sulphate which acts as an activator for sphalerite (ZnS) flotation with xanthate collectors (Fuerstenau *et al.*, 1985). Depressants prevent collectors from being adsorbed onto particular mineral surfaces. Their typical use is to increase selectivity by preventing one mineral from floating while allowing another mineral to float (Eisele and Kawatra, 1992).

Chemical reagents classified into three main groups, may be used in flotation. The groups include collectors, frothers and anti-foams (Weiss, 1985; U.S. EPA, 1985). Collectors/ amines cause adherence between solid particles and air particles in a flotation cell. Frothers on the other hand are compounds that act to stabilize air bubbles so that they will remain well-dispersed in the slurry. Frothers also form a stable froth layer that can be removed before the bubbles burst. The most commonly used frothers are alcohols, particularly MIBC, 2-butoxyethanol or 4-methyl-2-pentanol (a branched-chain aliphatic alcohol) or any of a number of water-soluble polymers based on propylene oxide (PO) such as polypropylene glycols (Eisele and Kawatra, 1992).

Antifoams or depressants react with surfaces of gangue materials in the flotation cell, preventing them from remaining in the froth and instead, fall to the bottom as tailings. Several factors are important when conditioning ore for flotation with chemical agents. These include thorough mixing and dispersal of reagents through the pulp, repeated contact between the reagents and all the relevant ore particles and time for the development of contact with reagent and ore particles to produce desired reactions (Fuerstenau, 1970).

Cationic collectors are water repellent, based on pentavalent nitrogen. These collectors use aminium cation to attach to negatively-charged mineral surfaces. They are mainly used for flotation of silicates, SiO_4^{4-} and aluminates, $Al(OH)_4^-$ ions and certain rare-metal oxides, and for separation of potassium chloride (sylvite) from sodium chloride (halite) (Eisele and Kawatra, 1992). Examples of cationic collectors are RNH_3^+, $R_2NH_2^+$ and R_3NH^+ where R is an alkyl group. The process of using cationic collectors is basically known as reverse froth flotation. This involves obtaining mainly the silicates and aluminate ions in the froth leaving out the mineral concentrate in the sinter.

Reverse cationic flotation was carried out at Joda iron ores in India, to float silica and alumina gangue using amine-based cationic collectors. Potato starch was used as a depressant for iron-bearing minerals. Sodium hydroxide was used as a pH regulator at pH 9.5. Around 50 % of the slimes were present in less than 25 Micron fractions having 58.28 % Fe and 4.76 % SiO_2 and 3.43 % Al_2O_3. The result obtained was 64.5 % Fe, 2.18 % Al_2O_3 and 1.69 % SiO_2 with Fe increase of about 7 % (Thella *et al.,* 2010). The result shows that reverse flotation is a suitable method for removal of aluminosilicates from laterites thus improving iron concentration in iron beneficiation.

Reverse flotation has also been investigated in iron ores from the Samarco, Mariana, Minas and Gerais mines, in Brazil. Studies were carried out on flotation tests with a Wemco agitation cell containing 1150 g of ore, which resulted in 45 % of solids in the pulp. Flotation tests were carried out considering the process conditions used in the Samarco plant. The used amounts of reagents were collector amine known as etherdiamineacetate (EDA) flotigam (different concentrations), depressor starch 300 g/t working at pH of 10.5. Condition time was 3 minutes dispersing of ore, 5 minutes conditioning of starch, 3 minutes conditioning of amines and 5 minutes of floatation. It was observed that the iron content increased from 54 % to 66 % with increasing concentration of collector. The opposite happened with the silica content that decreased from 21 % at 30 g/t to 3.6 % at 80 g/t collector amount. The recovery of iron decreased with the increasing amount of collector (Rabelo and Turrer, 1999).

Some rich iron ores are normally comminuted and classified. For low-grade iron ores such as the Brazilian Itabirite found at the Ponto Verde iron ore, the mineral is concentrated using gravity and magnetic concentration or reverse flotation (Iwasaki, 1983). This improves the grade from 44.5 % to over 60 % Fe. Brazilian Itabirite ore is mainly characterized by layering of iron ore within silica mineralization (Iwasaki, 1983; Iwasaki and Numela, 1986). The final product is sold to either local or export markets for the production of steel. Reverse flotation is the most important concentration method, which is utilized in low concentration iron ores (Iwasaki and Numela, 1986).

2.3.2 Magnetic Separation

Magnetic separation is the method of using a magnet to separate materials with different magnetic intensity (Svoboda, 1987). Magnetic separation is the most popular method used to beneficiate black metal ore. There are two kinds of magnetic separations; normal and high density (Harry *et al.*, 1973). Normal magnetic separation is adopted to separate magnetite. High density magnetic separation is used to separate hematite and other ores which are weakly magnetic. The unit of measurement of magnetic flux density or magnetic induction (B), which is the number of lines of force passing through a unit area of material, in tesla (T). μ_0 is the vacuum permeability which is given in $4\pi\times10^{-7}$ V.S/(A.M). The magnetizing force, which induces the line of force through a material, is called the field intensity (H). The intensity of magnetism or the magnetization (M) of a material relates to the magnetization induced in the material as shown in equation 2.1 (Svoboda, 1987)

$$B = \mu_0 (H + M) \quad (2.1)$$

In vacuum, M = 0 and it is extremely low in air, therefore equation 2.1 reduces to equation 2.2

$$B = \mu_0 H \quad (2.2)$$

The capacity of a magnet to lift a particle is not only dependent on field intensity but also field gradient (Svoboda, 1987). Paramagnetic minerals have higher magnetic permeability than surrounding medium. They concentrate the lines of force of an external magnetic field. The magnetic susceptibility in the particle increases with increase in the magnetic field intensity. Diamagnetic minerals have lower magnetic susceptibility than their surrounding medium and hence expel the lines of force of the external magnetic field (Cohen, 1986).

The typical grade of iron at which a magnetite-bearing loaded iron formation becomes economic is about 25 % Fe, which can generally yield 33-40 % recovery of magnetite by weight. This also produces a concentrate grading in excess of 64 % Fe by weight. The magnetic separation involves passing the sand and dust over a magnetically-charged rotating chamber. The particles with some iron stick to the drum, and are then scraped off on the other side of rotating drum. A 98 % of the loam soil would simply pass through and not interact with the magnet (Harry *et al.*, 1973).

A magnetic separation for processing iron from fly ash is able to remove around 92 % iron using magnetic coating of up to 11.8 kilo Gauss (kG) from low grade iron ore by reduction treatment.

The iron recovery of up to 90 % can also be obtained by using wet low intensity magnetic separator and assaying about 55 % Fe from 45 % in original ore (Morsi and Youssef, 1998). Recently, Purwanto and co-workers have concentrated iron in sand beach laterites magnetic separation (Purwanto *et al.*, 2003). Basically heating the ores to around 500^{o}C converts any goethite to hematite as shown by equations 2.3.

$$Fe_2O_3 \cdot H_2O(s) \xrightarrow{500^oC} Fe_2O_3(s) + H_2O(g) \quad\text{.............}(2.3)$$

On raising the temperatures 600-700^{o}C, in an atmosphere of carbon monoxide, the hematite is converted to magnetite as shown by equations 2.4.

$$3Fe_2O_3(s) + CO(g) \xrightarrow{600-700^oC} 2Fe_3O_4(s) + CO_2(g) \quad\text{.............}(2.4)$$

Within the temperature range 400-500^{o}C, goethite is converted to hematite. On the other hand, within the temperature range 600-700^{o}C, hematite is converted to magnetite. The iron in the sand could therefore be removed by use of a strong magnet. Purwanto and co-workers was first generating CO gas elsewhere which was later used to reduce goethite to magnetite.

The mineral Ilmenite is a naturally occurring iron titanate ($FeTiO_3$) and is abundant in nature. The commercial grades of Ilmenite contain 45 to 65.8 % TiO_2 and are regarded as a huge resource to the production of rutile (TiO_2) which can be used for manufacture of pigment grade TiO_2 or the metal itself. However extraction of the iron from the Ilmenite has been, and still is an expensive undertaking. Therefore the search for an environmentally friendly, cost effective extraction method remains a strong industrial imperative. In a commonly used extraction process

(Becher process), Ilmenite is reacted with coal in iron reduction kiln at 860 to 1,100 ^{o}C. The iron is reduced from Ilmenite to the metallic form and titanium oxide at 860 ^{o}C as shown in the equation 2.5 (Cheng *et al.*, 1997).

$$FeTiO_3(s)+C(s)\longrightarrow Fe(s)+TiO_2(s)+CO(g)\ldots\ldots(2.5)$$

Gaseous reduction then took place at temperatures above 1,000 ^{o}C. Above 1,200 ^{o}C reduction of rutile takes place as shown by equations 2.6 and 2.7.

$$FeTiO_3(s)+CO(g)\longrightarrow TiO_2(s)+Fe(s)+CO_2(g)\ldots\ldots(2.6)$$

$$TiO_2(s)+CO(g)\longrightarrow Ti_3O_5(s)+CO_2(g)\ldots\ldots(2.7)$$

Carbothermal reduction of ilmenite with charcoal powder has also been studied between 975 °C and 1,100 °C. Ilmenite was reduced by CO and products obtained were studied using SEM and XRD. The major products obtained are α-Fe and TiO_2 at temperatures below 1,000 °C; at 1,050 °C, α-Fe and Ti_9O_{17} were observed; at 1,100 °C, α-Fe and Ti_4O_7 were observed (Du, 1960; Wen-bing *et al.*, 2005).

Iron ore from Marimante, found approximately seven kilometres west of Tunyai, contains millions of tons of massive iron containing about 46 % Fe. High titanium content of 5 to 15 % TiO_2 makes it unlikely to be workable unless a cheap method is found to reduce the titanium oxide from the ore to about 2 % (Du Bois and Waish, 1970). In this study, laterite soils from Tunyai were found to contain about 1% rutile in form of Ilmenite mineral (see X-ray diffraction spectrum on page 41). Effort of concentrating iron from laterite containing Ilmenite was meant to investigate if titanium could be reduced in the concentrate at temperatures 500 to 700 ^{o}C.

2.4 Analytical Techniques

The main methods used in the analysis of laterite samples included Atomic Absorption Spectroscopy, Atomic Emission Spectroscopy, X-ray Diffraction Spectroscopy and Complexometric Titration using ethylenediamine tetra-acetic acid (EDTA).

2.4.1 Atomic Absorption Spectroscopy

The technique is used for those elements which are not atomized easily. The light of the right wavelength impinges on a free, ground state atom, where the atom may absorb the light as it enters an excited state through a process known as atomic absorption. Atomic absorption measures the amount of light at the resonant wavelength which is absorbed as it passes through a cloud of atoms (Mendham *et al.,* 2000). As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made (Gary, 2003). The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose (Gary, 2003). Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp (Jerry and Skoog, 1992). The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals. The technique requires standards with known analytical content to establish the relation between the measured absorbance and the analytical concentration and relies therefore on Beer-Lambert's law shown in equation 2.8 (Mendham *et al.*, 2000).

$$A = \log_{10}\left({}^{I_o}\!/_{I} \right) = \in .\ c.\ l \text{..} (2.8)$$

Where; A - Absorbance, I_o - incident radiation at a given wavelength, I - transmitted intensity or attenuated radiation, l- the path length through the sample (cm), c - concentration of the absorbing species ($moldm^{-3}$), $\in$ - molar absorptivity or extinction coefficient ($Lmol^{-1}cm^{-1}$).

Molar absorptivity is a constant which is a fundamental molecular property in a given solvent, at a particular temperature and pressure. The method is largely free from spectral and radiation interferences. This is because every metal has its own characteristic absorption wavelength. For an unexcited atom, each electron is in ground state, otherwise it is excited. An example of an atomic absorption curve is given in appendices 1and 2.

2.4.2 Atomic Emission Spectroscopy

In atomic emission, a sample is subjected to a high energy, thermal environment in order to produce excited state atoms, capable of emitting light. The energy source can be an electrical arc, a flame or plasma (Jerry and Skoog, 1992). The emission spectrum of an element exposed to such an energy source consists of a collection of the allowable emission wavelengths, commonly called emission lines, because of the discrete nature of the emitted wavelengths. This emission spectrum can be used as a unique characteristic for qualitative identification of the element (Gary, 2003). Atomic emission using electrical arcs has been widely used in qualitative analysis. For a quantitative analysis, the intensity of light emitted at the wavelength of the element to be determined is measured. The emission intensity at this wavelength will be greater as the number of atoms of the analyte element increases. The technique is mainly used for the analysis of alkali and alkaline earth metals (Mendham *et al.,* 2000).

2.4.3 X-ray Diffraction (XRD) Spectroscopy

XRD analysis utilizes X-rays of a known wavelength that are passed through a sample for identification of the crystal structure. The wave nature of the X-rays diffracted by the lattice of the crystal, gives a unique pattern of the peaks at different angles and of different intensity. This condition is given by Bragg equation 2.9 and figure 2.6 (Myers, 2002).

$$2dSin\theta = n\lambda \qquad (2.9)$$

Where; d - spacing between diffracting planes in the atomic lattice, λ - wavelength of the incident ray, θ – the angle between the incident ray and scattering plane, n – is an integral which is a multiple of the wavelengths for the phases of n^{th} number of beams that strikes the layers of atoms in a mineral.

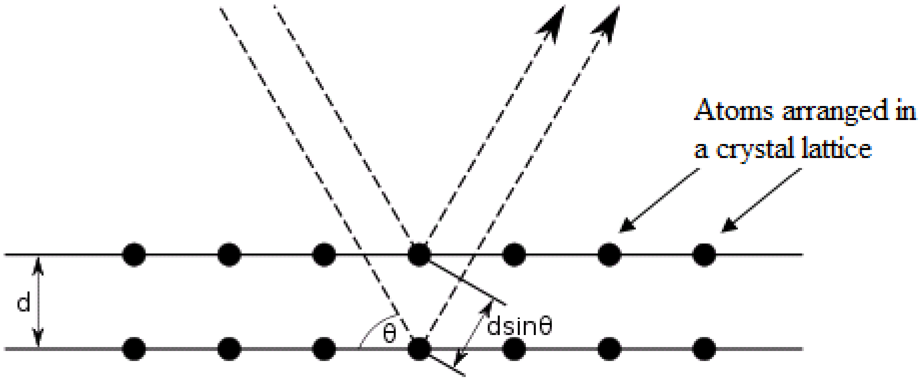


Figure 2.6 : Bragg's law reflection

Bragg diffraction occurs when two beams of X-rays with identical wavelength and phase approach a crystalline solid and are scattered off by two different atoms within it. The lower beam traverses an extra length of 2dsinθ. Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation (Myers, 2002). The most common X-rays used are of the copper metal, with a wavelength of 1.54056 x 10^{-10} m. Copper is used because it is easily kept cool and has high thermal conductivity, and which produces strong K_α and K_β lines. The K_β line is sometimes suppressed with a thin (~10 µm) nickel foil. The simplest and cheapest variety of sealed X-ray tube has a stationary anode (the Crookes tube) and produces ~2 kW of X-ray radiation. The more expensive variety has a rotating-anode type source that produces ~14 kW of X-ray radiation (Jeruzalmi, 2006).

Every mineral has a set of unique d-spacing. Therefore the X-ray detector moves around the sample and measures the intensity of these peaks and the position of these peaks (diffraction angle 2θ). The highest peak is defined as the 100 % peak and the intensity of all the other peaks are measured as a percentage of the 100 % peak. The measurement is achieved by comparison of d-spacing with standard referencing pattern. The intensity of the X-rays is measured on the Y axis, and increasing values of the 2θ are shown on the X axis. The height of the peaks (intensity) depends upon the number of crystallites diffracting the X-Rays, thus a sample more finely ground will give higher but narrower peaks than the same sample coarsely ground. The area under the graph measuring crystallinity will yield the same result in each case whether the sample is finely or coarsely ground. The sample is run on the machine and then the hydroxyl apatite standard is run for comparison (Moore and Reynolds, 1997).

2.4.4 Ethylenediaminetetraacetic Acid Titrations (EDTA)

This technique involves titrating metal ions with a complexing agent or chelating agent (ligand) and is commonly referred to as complexometric titration (Gary, 2003). In this method, a simple ion is transformed into a complex ion and the equivalence point is determined by using metal indicators or electrometrically. Various other names such as chilometric titrations, chilometry, chilatometric titrations and EDTA titrations have been used to describe this method (Mendham *et al.,* 2000). These chilons react with metal ions to form a special type of complex known as chelate.

EDTA, ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a hexadentate ligand. However, in practice, EDTA with molecular formula $C_{10}H_{16}N_2O_8$ is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations. Disodium salt of EDTA is a water-soluble chelating agent and is always preferred. It is non-hygroscopic and a very stable sequestering agent. These are chelating agents that form water-insoluble chelates with metal ions, for example oxine or 8-hydroxy quinoline (Gary, 2003).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sampling Sites and Sampling Design

Sampling was done randomly from ten localities of Tunyai Division in Tharaka Nithi County. The ten localities were Gitong'o, Gitara Kianderi, Kibuuka, Kithino, Kianamuthi, Kamujwa, Kinyuru, Mithigini, Ntendera and Tubui regions, located at latitudes 0° 10' 26" S to 0° 12' 52" S and longitudes 37° 48' 40" E to 37° 49' 12" E. The area covered by Tunyai Division is shown on the map of Tharaka District in the Republic of Kenya as given in appendix 9. Three sampling sites from each location were selected within a distance of about a km apart. Within a given sampling site, three holes which were at least ten metres apart were dug. The surface materials of up to 30 cm deep were removed because it contained a lot of organic matter. Three Samples from this depth was obtained, mixed and about one kg of the sample-mixture packed in plastic bags labeled level A. In the same holes a further one metre depth and 30 cm wide was dug. Samples were collected mixed and about one kg of the sample-mixture obtained and labeled level B. A total of two samples were collected from every site giving a total of six samples from every location.

3.2 Cleaning of pulverizer, glassware and plastic containers

Plastic containers were washed with 1:1 nitric acid, followed by appropriate detergent and rinsed with distilled water. They were then dried in an oven at 50 ^{o}C. All glassware used was cleaned by soaking in 1:1 nitric acid overnight. They were thereafter cleaned using detergent, rinsed with distilled water and then dried in the oven at 105 ^{o}C. Pulverizer was washed using distilled water after each sample was pulverized then dried using gas pump.

3.3 Sample Treatment and Analytical Procedures

About a kilogram of each laterite sample was weighed and put in a paper bag and transferred to the oven for drying at 105 ^{o}C for 9 hours. Samples were then removed from the oven and cooled. A mass of 100 g of the sample were pulverized to 300 microns (150 meshes) using a pulverizer. Minerals present were determined using a Bruker D8 Advance Diffractometer. Chemical analysis was carried out by AAS and EDTA titrations. The remaining amount of pulverized laterite was used in concentration using charcoal for magnetic separation.

3.3.1 Loss of Ignition

About 1.00 gram each of pulverized samples were weighed into crucible boats and transferred into the furnace. The samples were heated to 1,000 ^{o}C for about 6 hours to burn all organic materials. The samples were then cooled in a desiccator, re-weighed and the percentage difference determined (Heiri *et al.*, 2001; Santisteban *et al.*, 2004).

3.3.2 Chemical Analysis using AAS

About 0.100 g of the pulverized sample was weighed using analytical balance Model Mettler AJ150 and put into a labeled 125-ml plastic bottle. About 1 ml of concentrated aqua-regia (mixture of concentrated HCl and HNO_3 in the ratio 3:1) was added followed by 3.0 ml of hydrofluoric acid. The samples were left to digest for 8 hours. A 50.0 ml of concentrated boric acid was added in each container and left to digest for one hour. Distilled water was added to make the total volume of 100.0 ml. Syenite (SY-3) and Mount Royal Gabbro (MRG) rock standards were also digested following the same procedure used to digest the samples. Dilutions of the sample solutions were made by putting 5.0 ml in 100-ml labeled volumetric flask and made up to the mark using distilled water (Abbey and Gladney, 1986). The samples were analyzed using AAS instrument (Spectr AA.10 model from SEANAC Company).

3.3.3 Titrimetric Analysis

About 1.0 g of pulverized laterite sample was weighed into 200-ml beaker. A 25 ml of aqua-regia was then added. The sample was digested on a hot plate to expel fumes. The volume was reduced as much as possible without allowing it to dry up. The beaker was removed from the hot plate and 10 ml of distilled water added and allowed to settle. The content was filtered by decantation with a filter paper number 541 or number 4, followed by washing at least 4 times with hot water portion. The filtrate was then transferred into 250-ml volumetric flask and topped to the mark using distilled water. Aliquot of 25 ml was taken into 250-ml beaker and its pH adjusted to between 2 and 3 using 1:1 HCl acid. Titration was done in triplicate using 0.1M EDTA as a titrant and potassium thiocynate as indicator. The average titre was used to calculate the amount of iron using equation 3.1.

$$V_E \times M_E \times 10 \times A.W\ of\ Fe = mg\ of\ Fe \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Where; V_E is volume of EDTA, M_E is molarity of EDTA and A.W is atomic weight of iron (55.847).

3.3.4 X-ray Diffraction (XRD) Analysis

About 30 g of pulverized laterite samples were put in sample holders. They were then loaded for analysis of minerals using data collector software. Results of analysis of minerals present in each sample were given using Bruker D8 Advance Diffractometer.

3.3.5 Concentration of Iron in Laterites

A 30.0 g of laterite sample and 3.0 g of charcoal powder were mixed and transferred into fire clay crucibles. The mixture was heated at temperature range of 500 - 700 ^{o}C in controlled current of air for 2 hours using a charcoal burner shown in plates 3.1 and 3.2. The fire was monitored by looking at the amount of charcoal consumed. Charcoal was then added into the burner every time there was weight reduction.

Plate 3.1 : Charcoal Jiko with fire clay crucibles containing laterite-charcoal mixture.

Plate 3.2 : Charcoal Jiko with laterite-charcoal mixture heated in a controlled air current.

After 2 hours, the roasted samples were allowed to cool to room temperature, and then transferred into a rotating magnetic separator. Serial separation was done on the samples by returning the concentrate three times into the rotating magnetic separator. The samples were concentrated using magnetic separator shown in plate 3.3.

Plate 3.3 : Laboratory Magnetic Separator.

The mineralogical and elemental compositions for the concentrate were determined using XRD, AAS and EDTA titrations as described previously. The results of the minerals present are given in figures 4.1 and 4.2 and tables 4.2 and 4.3, respectively.

3.4 Data Analysis

The results of the analyses in all measurements were done in triplicate and the arithmetic mean obtained by use of equation 3.2.

$$\bar{x} = \sum_i x_i / n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where; $\bar{x}$ - Arithmetic mean of the samples, x_i - Sample measurements and n - Population.

Comparison of experimental means of methods of analysis, AAS and EDTA titration was done using significance test (t- test) (Miller and Miller, 1988; Harvey, 2000).

Standard deviation of the means was calculated using equation 3.3.

$$s = \sqrt{\sum_i (x_i - \bar{x})^2 / (n-1)} \quad \ldots\ldots (3.3)$$

t- Calculated was given by equation 3.4 (Miller and Miller, 1988).

$$t_{cal} = \left(\bar{x}_1 - \bar{x}_2 \right) \Big/ \sqrt{\left({s_1^2}\big/{n_1} + {s_2^2}\big/{n_2} \right)} \quad \ldots\ldots (3.4)$$

The number of degrees of freedom was calculated from equation 3.5.

$$Degrees\ \ of\ \ freedom = \frac{(s_1^2 / n_1 + s_2^2 / n_2)^2}{(s_1^2 / n_1)^2 /(n_1 + 1) + (s_2^2 / n_2)^2 /(n_2 + 1)} \ \Big\} - 2 \quad \ldots\ldots (3.5)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Determination of Appropriate Ratios of Charcoal to Laterites Needed for Complete Beneficiation

Samples from Gitong'o, Kibuuka, Kianamuthi, Ntendera and Gitara Kianderi were used to determine the appropriate ratios of charcoal to laterite and the results given in table 4.1.

Table 4.1 : Determination of Appropriate Ratios of Charcoal to Laterites Needed for Complete Beneficiation

		Masses of charcoal used per 30.0 g of laterites				
	Sample site	1.0 g	2.0 g	**3.0 g**	4.0 g	5.0 g
Percentage iron in the obtained magnetic concentrate after separation and analyzed using AAS	Gitong'o	48.94± 0.03	53.48± 0.06	**64.19± 0.04**	64.28± 0.03	64.72± 0.01
	Kibuuka	51.44± 0.03	57.30± 0.02	**62.76± 0.04**	63.45± 0.02	63.57± 0.02
	Kianamuthi	49.43± 0.04	53.44± 0.03	**63.79± 0.04**	63.74± 0.04	63.78± 0.06
	Ntendera	49.95± 0.04	55.78± 0.01	**64.18± 0.04**	64.25± 0.03	64.31± 0.05
	Gitara Kianderi	48.05± 0.01	58.60± 0.04	**64.92± 0.04**	64.96± 0.04	64.95± 0.02

Note: Each value is mean±SE of 2 replicates

The mean of the results obtained using 3.0 g of charcoal per 30.0 g of laterites was economical for reduction of laterite samples. All the samples were therefore reduced using a ratio of 1:10 by mass of charcoal to laterites and the concentrate obtained analyzed for mineralogical and chemical composition.

4.2 Mineralogical Composition of the Raw and Beneficiated Laterite Samples Using Magnetic Separation Method

Laterite samples from identified sampling sites in Tunyai Division of Tharaka South District (appendix 9) namely Gitong’o, Kibuuka, Kithino, Mithigini, Tubui, Gitara Kianderi, Kamujwa Ntendera, Kinyuru and Kianamuthi were analyzed for their mineral content using X-ray diffraction technique. The figure 4.1 shows XRD spectra for minerals found in raw laterite samples from a selected site in Kibuuka region. The table 4.2 shows the common minerals found in raw laterite from Tunyai Division.

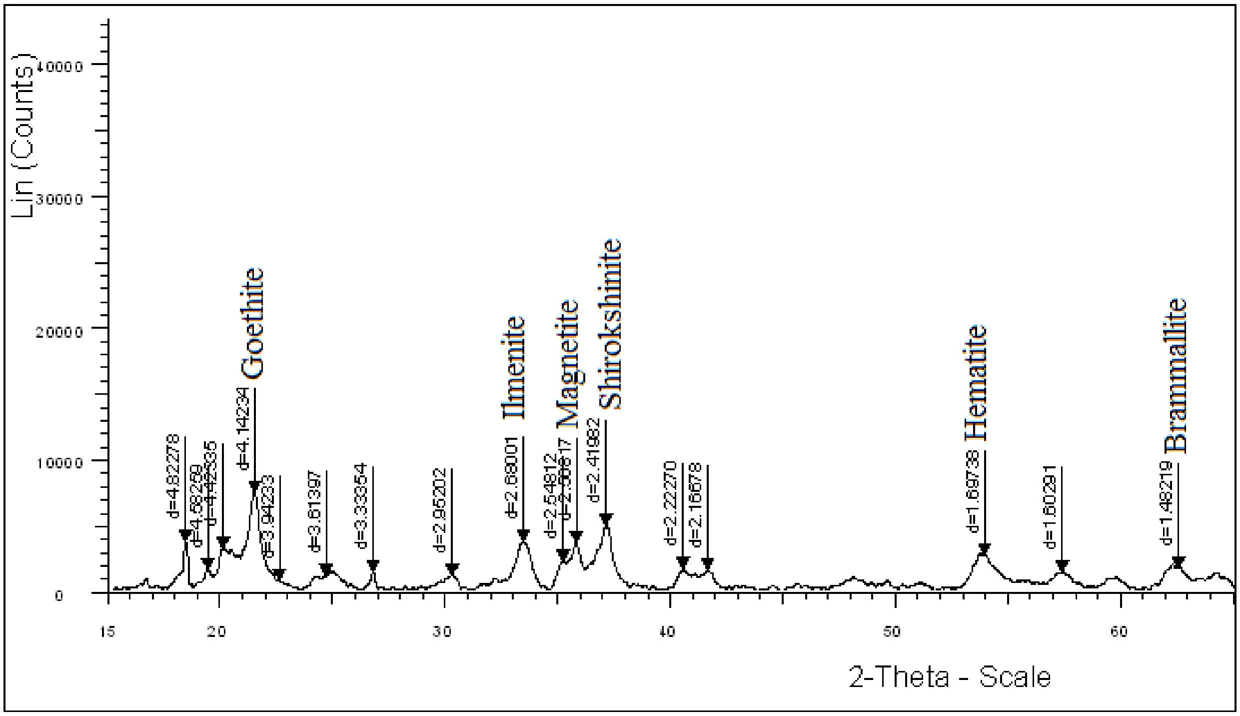


Figure 4.1 : XRD Spectrum for Raw Laterites from Kibuuka Region at Level A with 26.46 % Iron

Table 4.2 : Common Minerals found in Raw Laterite from Tunyai Division

Mineral name	**(2Θ) Å**	**Chemical formula**
Goethite	**21.51° (4.13Å)**	**FeO.OH**
Brammallite	62.49° (1.485Å)	$(Na,H_2O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Magnetite	**36° (2.520Å)**	$\mathbf{Fe_3O_4}$
Preiswerkite	36.54° (2.457Å)	$NaMg_2Al_3Si_2O_5(OH)_4.n(H_2O)$
Siderite	32.5° (2.762Å)	$FeCO_3$
Hematite	**54.11° (1.69Å) & 33.51° (2.69Å)**	$\mathbf{Fe_2O_3}$
Shirokshinite,	37° (2.410Å)	$K(NaMg_2)Si_4O_{10}F_2$
Zincostaurolite	37.60°(2.390Å)& 33.43°(2.678Å)	$4Zn_4Al_{16}(Al,[\ ])_2Si_8O_{40}[O_6,(OH)_2]$
Ilmenite	**33.12° (2.74Å)**	$\mathbf{FeTiO_3}$

After beneficiation, the XRD spectra for the same sample from Kibuuka region is given in figure 4.2. Other XRD spectra are placed as appendices 3-6. Some of the common minerals obtained in the concentrates from the ten sampled regions are given in table 4.3.

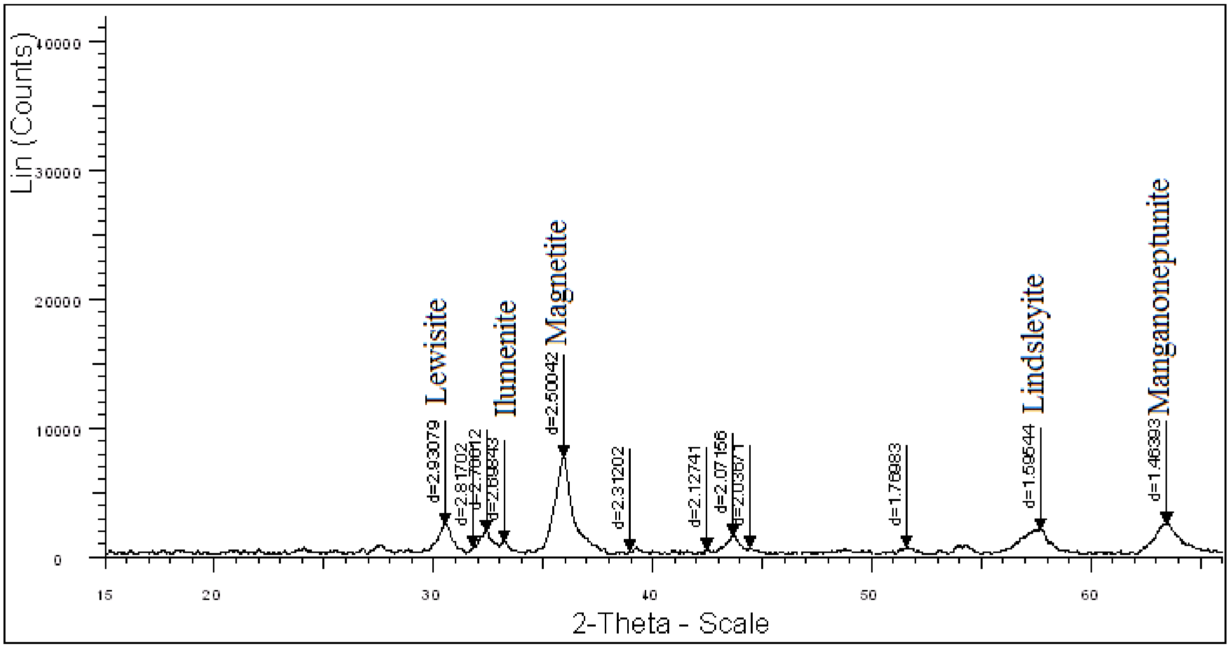


Figure 4.2 : XRD Spectrum for Beneficiated Laterites from Kibuuka Region at Level A with 62.59 % Iron

Table 4.3 : Common Minerals Found in Beneficiated Laterites after Magnetic Separation

Mineral name	**(2Ө) Å**	**Chemical formula**
Magnetite	**36° (2.520Å)**	**Fe_3O_4**
Manganoneptunite	63.5° (1.483Å)	$KNa_2Li(MnFe^{2+})_2Ti_2Si_8O_{24}$
Biotite	25.41°(3.53Å),	$Ba_4(Ti,Nb)_8Si_4O_{28}Cl$
Olkhonskite	32.5°(2.762Å),	$(Cr^{3+},V^{3+})_2Ti_3O_9$
Lindsleyite	58° (1.599Å).	$(Ba,Sr)(Ti,Cr,Fe,Mg)_{21}O_{38}$
Ilmenite	**33.12° (2.74Å)**	**$FeTiO_3$**
Lewisite	30.38° (2.940Å)	$(Ca,Fe{+}{+},Na)_2(Sb,Ti)_2O_7$

The results from the spectra show that all goethite and hematite minerals were converted to magnetite. This is confirmed by the disappearing peaks from goethite (2Ө 21.51°) and hematite (2Ө of 54.11° & 33.51°) spectra of raw samples, and increasing intensity of the magnetite peaks (2Ө of 36°) from beneficiated samples. The peak for Ilmenite mineral found at 2Ө of 33.12° reduced but present in the spectra of the concentrated samples. This shows that not all ilmenite minerals were able to be reduced at temperatures of 500-700 °C. From the results, other minor minerals containing titanium were formed. The minerals include; Manganoneptunite, Lewisite, Lindsleyite, Olkhonskite, and Biotite. The XRD spectra were interpreted using reference data given in appendix 7. The XRD reference data is a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacing (D), relative intensities (I/Io), mineral name and chemical formulae (John, 1989). Charcoal in the mixture was heated in a limited current Air at a temperature range of 500-700 °C to produce CO gas *in situ*, which reduced hematite and goethite to magnetite. Since magnetite is more attracted to the magnet than goethite and hematite, magnetite was able to be separated using a strong magnet. The reactions involved are given by equations 4.1 and 4.2.

$$2C(s)+O_2(g)\longrightarrow 2CO(g)\text{.....}(4.1)$$

$$3Fe_2O_3\cdot H_2O(s)+CO(g)\longrightarrow 2Fe_3O_4(s)+CO_2(g)+3H_2O(g)\text{.....}(4.2)$$

Purwanto *et al.* (2003), while working with sand beaches from India were able to convert goethite to magnetite using CO/CO_2 in the ratio of 1:3. Keru (2011), while working with Ruiru laterites in Kenya, was also able to convert goethite to magnetite using charcoal-laterite in the ratio 3:20 by mass. This new technique of beneficiation provides a convenient method which when used may help to exploit iron from laterite/murram materials than relying on the few iron ore deposits available in the country. In addition the technique investigated the possibility of separating titanium mineral from magnetite found in the concentrates after reduction process.

4.3 Total Elemental Composition of Raw and Beneficiated Laterites Using Magnetic Separation and Analyzed Using AAS and EDTA Titration

Laterite samples from identified sites in Tunyai Division were analyzed for elemental composition before and after beneficiation and the results are given in tables 4.4, 4.5 and 4.6.

Table 4.4 : Percentage Elemental Composition of Raw Laterite from Different Sites in Tunyai Division and Analyzed using AAS.

Sample Source	SiO_2 Mean ±SE	Al_2O_3 Mean ±SE	K_2O Mean ±SE	Na_2O Mean ±SE	CaO Mean ±SE	TiO_2 Mean ±SE	MnO Mean ±SE	Fe_2O_3 Mean ±SE	MgO Mean ±SE	LOI Mean ±SE	Total Mean ±SE
Gitong'o	17.41± 0.72	16.12± 2.47	0.06± 0.03	0.08± 0.08	0.07± 0.04	1.87± 0.38	0.40± 0.13	**42.50± 0.89**	0.27± 0.08	20.17± 3.06	99.06± 4.97
Kibuuka	28.09± 5.82	15.57± 2.57	0.29± 0.08	0.18± 0.06	0.05± 0.03	1.16± 0.21	1.10± 0.35	**42.64± 0.58**	0.13± 0.02	12.83± 6.94	101.78± 2.76
Kithino	22.71± 6.13	16.78± 2.09	0.24± 0.10	0.18± 0.08	0.08± 0.01	1.21± 0.13	1.50± 0.41	**43.84± 0.32**	0.14± 0.04	16.83± 4.62	103.58± 1.50
Tubui	22.34± 6.13	10.32± 1.78	0.30± 0.07	0.20± 0.08	0.10± 0.01	1.13± 0.32	1.63± 0.75	**43.50± 0.69**	0.14± 0.02	16.67± 1.97	96.98± 6.06
Mithigini	24.99± 2.33	10.97± 3.84	0.24± 0.10	0.22± 0.06	0.09± 0.02	0.94± 0.27	1.07± 0.43	**44.50± 0.84**	0.14± 0.03	17.67± 4.13	100.64± 2.09
Kianamuthi	24.64± 5.04	16.45± 3.53	0.30± 0.10	0.25± 0.08	0.11± 0.03	1.16± 0.36	1.20± 0.72	**40.94± 0.19**	0.13± 0.04	14.83± 2.48	99.89± 3.10
Kamujwa	18.43± 3.70	17.20± 4.73	0.28± 0.14	0.19± 0.10	0.08± 0.03	0.76± 0.33	1.27± 0.39	**42.47± 0.58**	0.12± 0.03	19.67± 3.88	100.54± 2.82
Kinyuru	22.49± 4.53	14.72± 3.16	0.25± 0.06	0.19± 0.07	0.07± 0.01	0.89± 0.42	1.33± 0.27	**40.81± 0.65**	0.13± 0.02	17.83± 2.23	98.98± 5.66
Ntendera	21.04± 1.89	11.22± 2.48	0.30± 0.09	0.16± 0.04	0.07± 0.02	0.98± 0.18	1.67± 0.84	**43.81± 0.31**	0.10± 0.03	18.17± 5.00	97.58± 6.71
Gitara Kianderi	21.35± 3.86	14.60± 1.75	0.16± 0.08	0.12± 0.05	0.10± 0.02	1.25± 0.44	0.57± 0.45	**43.35± 0.32**	0.13± 0.02	19.11± 7.13	100.62± 2.33

Note: Each value is mean±SE of 18 replicates

Table 4.5 : Percentage Elemental Composition of Beneficiated Laterites Samples using Magnetic Separation and Analyzed using AAS.

Sample Source	**SiO_2 Mean ±SE**	**Al_2O_3 Mean ±SE**	**Fe_2O_3 Mean ±SE**	**CaO Mean ±SE**	**MgO Mean ±SE**	**Na_2O Mean ±SE**	**K_2O Mean ±SE**	**TiO_2 Mean ±SE**	**MnO Mean ±SE**	**LOI Mean ±SE**	**TOTAL Mean ±SE**
Gitong’o	2.09 ± 1.80	1.12± 0.75	**90.72± 0.91**	0.16± 0.02	0.07± 0.12	0.05 ± 0.03	0.09 ± 0.20	1.02 ± 0.42	0.30 ± 0.12	7.18 ± 1.43	100.54± 1.07
Kibuuka	2.11 ± 1.07	0.13± 0.11	**88.21± 0.16**	0.18± 0.02	0.14± 0.02	0.18 ± 0.02	0.12 ± 0.13	1.03 ± 0.20	0.07 ± 0.44	8.17 ± 0.55	100.15± 2.74
Kithino	8.61 ± 2.10	7.62± 1.71	**72.24± 0.90**	0.35± 0.05	0.18± 0.06	0.21 ± 0.07	0.60 ± 0.24	4.12 ± 0.21	0.82 ± 0.61	8.60 ± 2.29	100.99± 3.07
Tubui	7.75 ± 0.88	6.67± 0.89	**73.70± 0.16**	0.41± 0.06	0.17± 0.04	0.25 ± 0.16	0.65 ± 0.08	5.02 ± 0.67	1.25 ± 0.71	9.00 ± 2.98	98.90± 4.55
Mithigini	11.5 ± 1.29	7.27± 1.11	**78.97± 0.99**	0.37± 0.06	0.23± 0.04	0.28 ± 0.10	0.53 ± 0.15	2.49 ± 0.49	0.47 ± 0.40	8.82 ± 1.67	101.19± 3.38
Kianamuthi	1.30 ± 0.17	0.08± 0.27	**91.40± 0.56**	0.24± 0.05	0.02± 0.03	0.01 ± 0.15	0.31 ± 0.05	1.08 ± 0.38	0.37 ± 0.21	3.87 ± 0.72	101.27± 1.93
Kamujwa	8.81 ± 2.74	6.93± 1.95	**76.92± 0.90**	0.39± 0.14	0.18± 0.92	0.20 ± 0.76	0.52 ± 0.26	3.96 ± 0.28	0.75 ± 0.91	9.44 ± 3.61	99.10± 5.09
Kinyuru	9.85 ± 1.27	6.97± 1.37	**69.26± 0.98**	0.38± 0.07	0.17± 0.12	0.28 ± 0.14	0.68 ± 0.17	5.98 ± 0.46	0.76 ± 0.25	7.82 ± 4.05	98.99± 5.41
Ntendera	1.12 ± 0.28	0.28± 0.54	**91.06± 0.81**	0.13± 0.07	0.08± 0.02	0.09 ± 0.03	0.03 ± 0.01	1.81 ± 0.45	0.16 ± 0.19	6.39 ± 0.46	100.06± 1.05
Gitara Kianderi	2.18 ± 0.34	0.23± 0.02	**89.07± 0.66**	0.13± 0.03	0.09± 0.12	0.03 ± 0.19	0.18 ± 0.25	1.52 ± 0.18	0.48 ± 0.29	4.51 ± 0.42	98.96± 1.53

Note: Each value is mean±SE of 18 replicates

Table 4.6 : Percentage Composition of Iron (III) oxides in Raw and Beneficiated Laterites using EDTA Titration

Sample Source	Raw Laterite % Fe_2O_3 Mean±SE	Beneficiated Laterite % Fe_2O_3 Mean±SE
Gitong'o	41.94±0.89	90.81±0.23
Kibuuka	42.52±0.63	88.85±0.73
Kithino	44.16±0.42	72.31±0.04
Tubui	43.06±0.60	74.00±0.19
Mithigini	44.18±0.04	79.02±0.13
Kianamuthi	40.66±0.22	91.38±0.35
Kamujwa	42.58±0.58	76.34±0.05
Kinyuru	40.76±0.67	69.67±0.09
Ntendera	44.32±0.22	91.14±0.73
Gitara Kianderi	42.64±0.49	89.15±0.61

Note: Each value is mean±SE of 18 replicates

Results of the elemental analysis gave high levels of iron (III) oxide, which ranged between 40 and 44 %. The results show that iron (III) oxide is uniformly distributed in all the ten sampled regions, with a composition which is convenient for extraction. These values are greater than the values of other laterites in different parts of the country. For instance, study conducted by Muriithi, (1985) found out that laterites in Ruiru had 22 to 40 % iron (III) oxide (Keru, 2011), Ruguru location in Nyeri District 26.29 % Fe_2O_3, Kiganjo in Nyeri District 23.71 % Fe_2O_3, Kiria-ini in Murang'a District 34.29 % Fe_2O_3, Tala in Machakos District 35 % Fe_2O_3, and Kairo in Murang'a District 14.29 % Fe_2O_3.

The AAS and EDTA results from the beneficiated samples gave values which ranged between 60 and 92 % iron (III) oxide. This occurred because hematite and goethite minerals in the heated laterite-charcoal mixture were converted to magnetite. The results also gave significant reduction of silica and alumina in raw laterite with about 22 and 14 % to 1.12 and 0.13 %, respectively after magnetic separation. After analysis, the percentage iron in raw and beneficiated laterites were determined and the results given in table 4.7.

Table 4.7 : Percentage Composition of Iron in Raw and Beneficiated Laterites Analyzed using AAS

Sample Source	Raw Laterite % Fe Mean±SE	Beneficiated Laterite % Fe Mean±SE
Gitong'o	29.75±0.62	63.56±0.16
Kibuuka	29.85±0.41	62.19±0.51
Kithino	30.69±0.23	50.57±0.03
Tubui	30.45±0.48	51.59±0.13
Mithigini	31.15±0.59	55.28±0.09
Kianamuthi	28.66±0.13	63.97±0.25
Kamujwa	29.73±0.41	53.84±0.04
Kinyuru	28.57±0.46	48.48±0.06
Ntendera	30.67±0.22	63.80±0.51
Gitara Kianderi	30.35±0.21	62.41±0.43

Note: Each value is mean±SE of 18 replicates

This technique of enriching iron in the heated laterite mixed with charcoal can be used to increase the percentage of iron in laterites from about 30 to 64 %, which represents 35 % increase. This technique was able to raise the percentage of iron to that of available iron ores in other countries. In Kenya, iron ores in Marimanti in Meru contains 46 % iron and Macalder in South Nyanza contains 45.25 % iron (Du Bois and Waish, 1970). In Krivoi-Rog District in Russia, hematite ore contains 61.0 % iron, magnetite ore at Kiruna in Sweden contains 65-68 %

and limonite ore at Mesabi District in U.S. contains 59.37 % iron (Boltz, 1970). Brazilian Itabirite found at the Ponto Verde iron ore contains 44.5 % Fe (Iwasaki, 1983; Iwasaki and Numela, 1986).

Keru, (2011), while working with laterites in Ruiru region in Kenya, was able to increase the level of iron by 17.98 %. This shows that laterite materials can be reduced using charcoal and iron oxides obtained used in blast furnace for iron extraction. Morsi and Youssef (1998) were also able to reduce iron ore in Aswan region (Egypt) using CO or H_2 and increased iron from 45.25 to 59.6 %. Another study by Purwanto *et al.,* (2003), while working with sand beaches from Sebuku Island (Indonesia) were able to reduce goethite using CO/CO_2 (30/70 vol %) and 93.9 % of magnetite was upgraded with 90 % recovery. Iron was increased from 51.85 to 68.24 % using magnetic separation.

The percentage composition of iron in both levels A and B was also determined and the results given in table 4.8.

Table 4.8 : Percentage Composition of Iron in Raw Laterites Using AAS and EDTA Titration Methods in Levels A and B

Sample Source	**Raw laterite Level A**		**Raw laterite Level B**	
	AAS %Fe Mean±SE	**Titration %Fe Mean±SE**	**AAS %Fe Mean±SE**	**Titration %Fe Mean±SE**
Gitong'o	29.44±0.71	29.36±0.76	31.07±0.83	30.85±0.74
Kibuuka	29.85±0.55	29.76±0.63	30.79±0.40	30.84±0.38
Kithino	30.69±0.29	30.14±0.36	30.61±0.33	30.80±0.49
Tubui	30.45±0.67	30.14±0.68	31.21±0.64	31.36±0.50
Mithigini	31.15±0.86	30.93±0.95	31.65±0.82	31.54±0.12
Kianamuthi	28.66±0.22	28.46±0.29	28.70±0.15	28.56±0.11
Kamujwa	29.73±0.26	29.81±0.18	28.90±0.66	28.71±0.61
Kinyuru	28.57±0.61	28.53±0.73	28.25±0.69	28.16±0.62
Ntendera	30.67±0.33	31.02±0.21	31.25±0.28	31.19±0.19
Gitara Kianderi	30.35±0.37	29.85±0.31	30.39±0.29	29.30±0.56

Note: Each value is mean±SE of 9 replicates

The results from the table show that there was no significance difference in elemental composition between level A and that of level B. Samples for analysis were taken from three sites which were about a kilometre apart in every region. In a given site, a sample was obtained from 30 cm deep and labeled level A, and a further one meter deep and labeled level B. This uniform distribution of iron minerals with depth shows that there is abundant deposit which is worthy investigation, whether it can sustain iron and steel industry.

The concentration of iron in raw laterites in Tunyai ranged between 28-31 %, which is an average of 30 %. The iron levels in these laterites also compares favorably with iron ores in other countries. In Itakpe region in Nigeria, some iron ores used contains 25 to 30 % iron (Umunakwe, 1985). In Sancy District (France), iron is mined from calcareous ore with 32 % iron. In U.S. in the Mesebi Range, iron ores contains 34 % iron while in Frodigham District (U.K), Brown ore contains 18 to 24 % iron (Boltz, 1970). The values obtained in Tunyai Division are better than those of some iron ores in some countries.

The results of the analysis from raw and beneficiated laterites using EDTA titration and AAS were compared to determine if the two methods were statistically different and the results given in tables 4.9 and 4.10.

Table 4.9 : Statistical Analysis of AAS and EDTA Titration Methods before Beneficiation

Sample Source	**AAS Mean± SE Fe_2O_3**	**EDTA Mean± SE Fe_2O_3**	**t-cal**
Gitong’o	42.50±0.89	41.94±0.89	0.449
Kibuuka	42.64±0.58	42.52±0.63	0.132
Kithino	43.84±0.31	44.16±0.42	0.614
Tubui	43.50±0.69	43.06±0.60	0.486
Mithigini	44.50±0.84	44.18±0.04	0.238
Kianamuthi	40.93±0.19	40.66±0.22	0.348
Kamujwa	42.47±0.57	42.58±0.58	0.136
Kinyuru	40.81±0.65	40.76±0.67	0.052
Ntendera	43.81±0.31	44.32±0.22	0.431
Gitara Kianderi	43.35±0.32	42.64±0.49	0.506

Note: Each value is mean±SE of 18 replicates

Table 4.10 : Statistical Analysis of AAS and EDTA Titration Methods after Beneficiation

Sample Source	AAS	EDTA	t-cal
	Fe_2O_3 Mean± SE	**Fe_2O_3 Mean± SE**	
Gitong'o	90.72± 0.91	90.81±0.23	0.754
Kibuuka	88.21±0.16	88.85±0.73	0.849
Kithino	72.24±0.90	72.31±0.04	0.217
Tubui	73.70±0.16	74.00±0.19	0.646
Mithigini	78.97±0.99	79.02±0.13	0.233
Kianamuthi	91.40±0.56	91.38±0.35	0.805
Kamujwa	76.92±0.90	76.34±0.05	0.832
Kinyuru	69.26±0.98	69.67±0.09	0.688
Ntendera	91.06±0.81	91.14±0.73	0.521
Gitara Kianderi	89.07±0.66	89.15±0.61	0.599

Note: Each value is mean±SE of 18 replicates

The results of T-test analysis shows no significant difference between the two methods used. Their t_{cal} was less than t_{crit} at 95 % confidence level. The t-crit was 0.960 at 34 degrees of freedom.

The use of EDTA titration method was used to validate the AAS results and within the experimental error, the results of the two methods of analysis were similar. From this study, the newly developed technique is more economical compared to the convectional known methods of direct and indirect froth flotation, which requires use of chemicals like frothing agent, collectors, activators and depressants. In large scale beneficiation of iron ore, froth flotation methods require large financial capital for buying chemicals. Percentage composition of silica, alumina and iron (III) oxide in raw and in the concentrate in both levels A and B were also investigated and results given in appendix 8.

CHAPTER FIVE

CONCLUSION AND RECOMMEDATIONS

5.1 Conclusions

From the results obtained and analysis of this study the following conclusions can be drawn:

1) Iron in the raw laterites from Tunyai Division was present as minerals goethite, hematite and ilmenite. On the other hand, after heat treatment, iron was present as minerals magnetite and ilmenite. Thus, the heat treatment in the temperature range 500-700^{o}C does not affect the mineral ilmenite, which is just like magnetite, attracted strongly by a permanent magnet. Thus, in the analysis of beneficiated laterites, the level of titanium (IV) oxide increased from about 1 % in raw laterites to 5 %.

2) The amount of iron in raw laterite in Tunyai Division was in the range between 28 to 31 %. This composition is of the ore grade since it exceeds 25% content which is considered economical for extraction. After heat treatment, iron concentration increased to well over 64%. This occurs because goethite and hematite minerals in laterite are converted to magnetite. A concentrate with such high level of iron can therefore be fed into a blast furnace.

5.2 Recommendations for further research

The study was limited to laboratory analysis and therefore a feasibility study is necessary to determine the possibility of extracting iron from laterites.

Silica and alumina concentration in the tailing was found to be about 43 % and 23 %, respectively. It is necessary to investigate whether the tailing can be used as raw material in the manufacture of cement and ceramics, making ferro-silicon for the manufacture of silicon steel and glass making.

The analysis of beneficiated laterites with charcoal was found to increase the levels titanium (IV) oxide with about 1-5 %. Further research should be done on possibility of separating titanium mineral from the concentrate.

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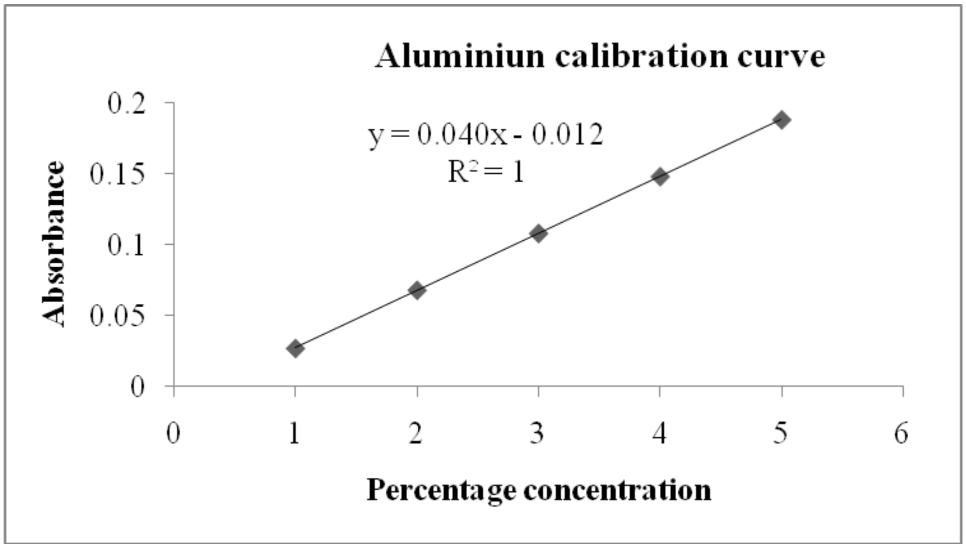
APPENDICES

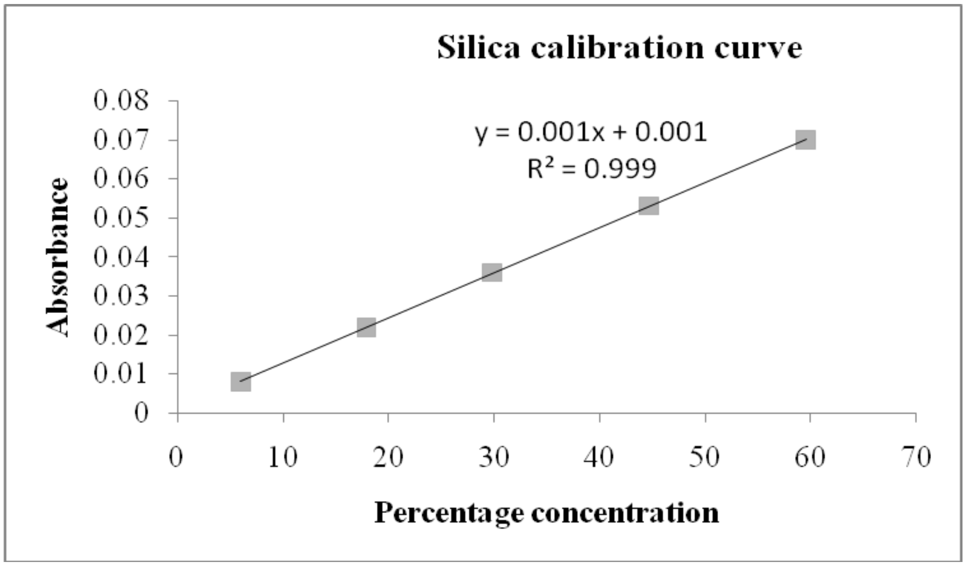
Appendix 1: Aluminium calibration curve

Method: AAS

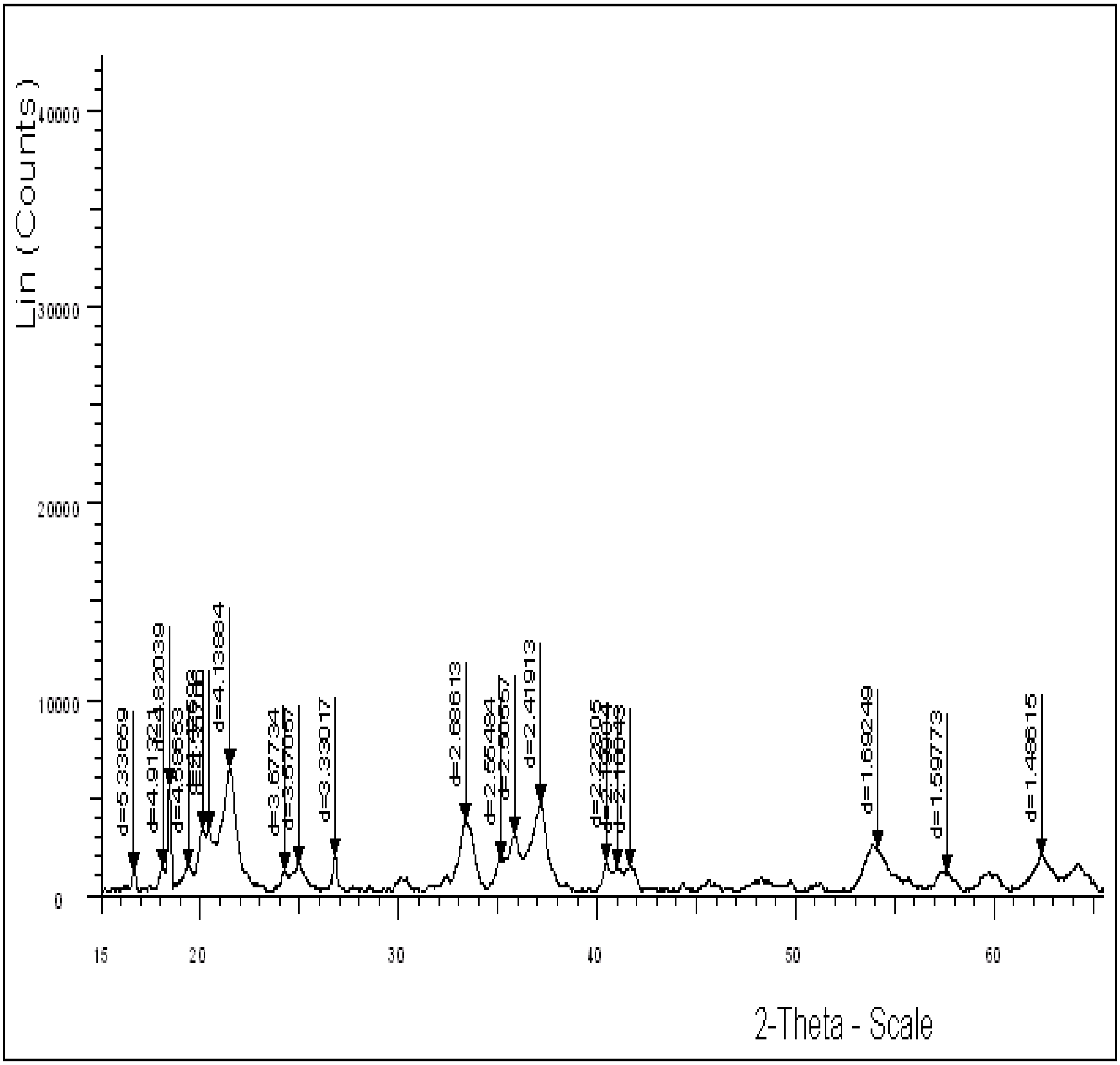


Appendix 2: Silica calibration curve

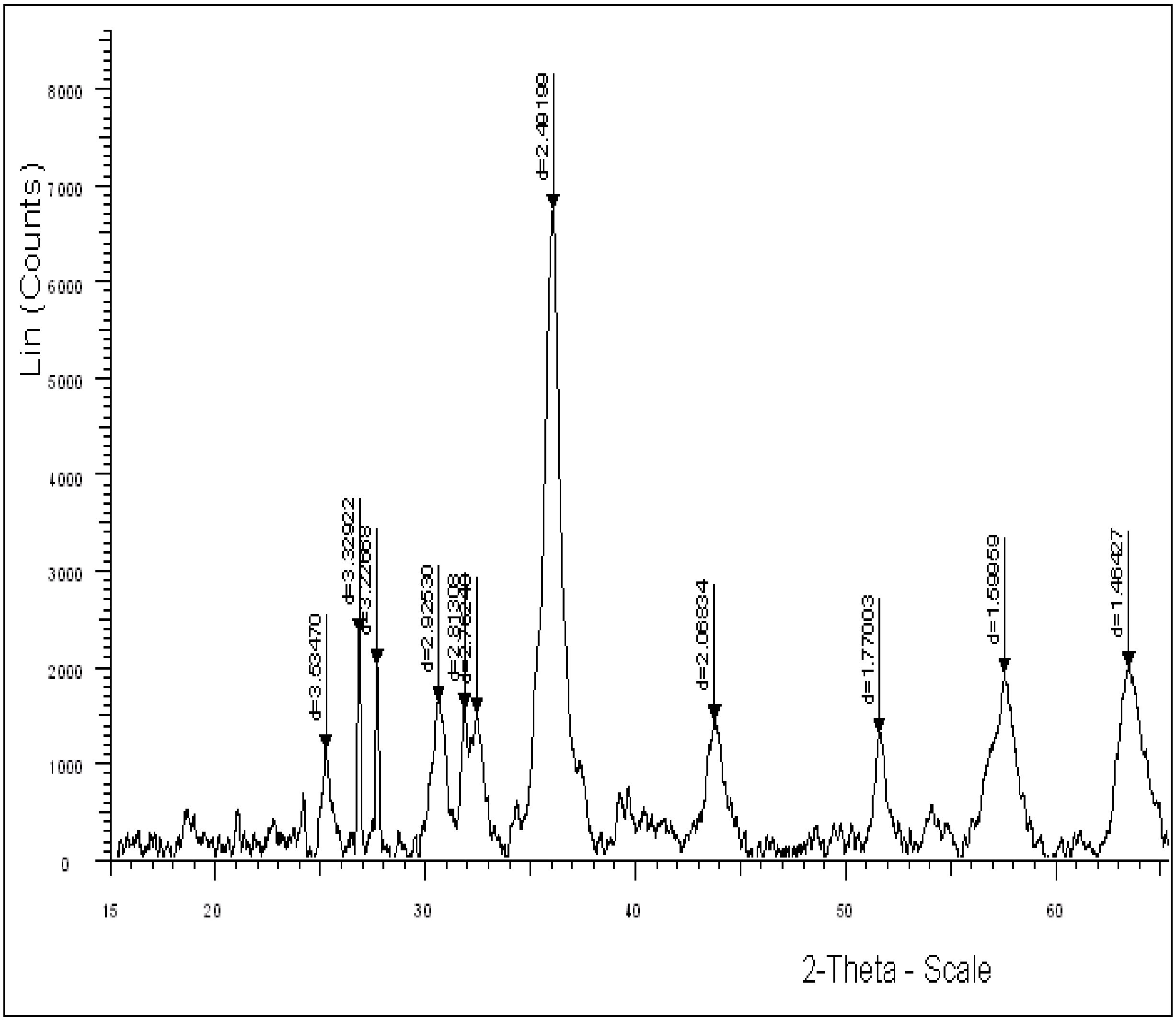
Method: AAS



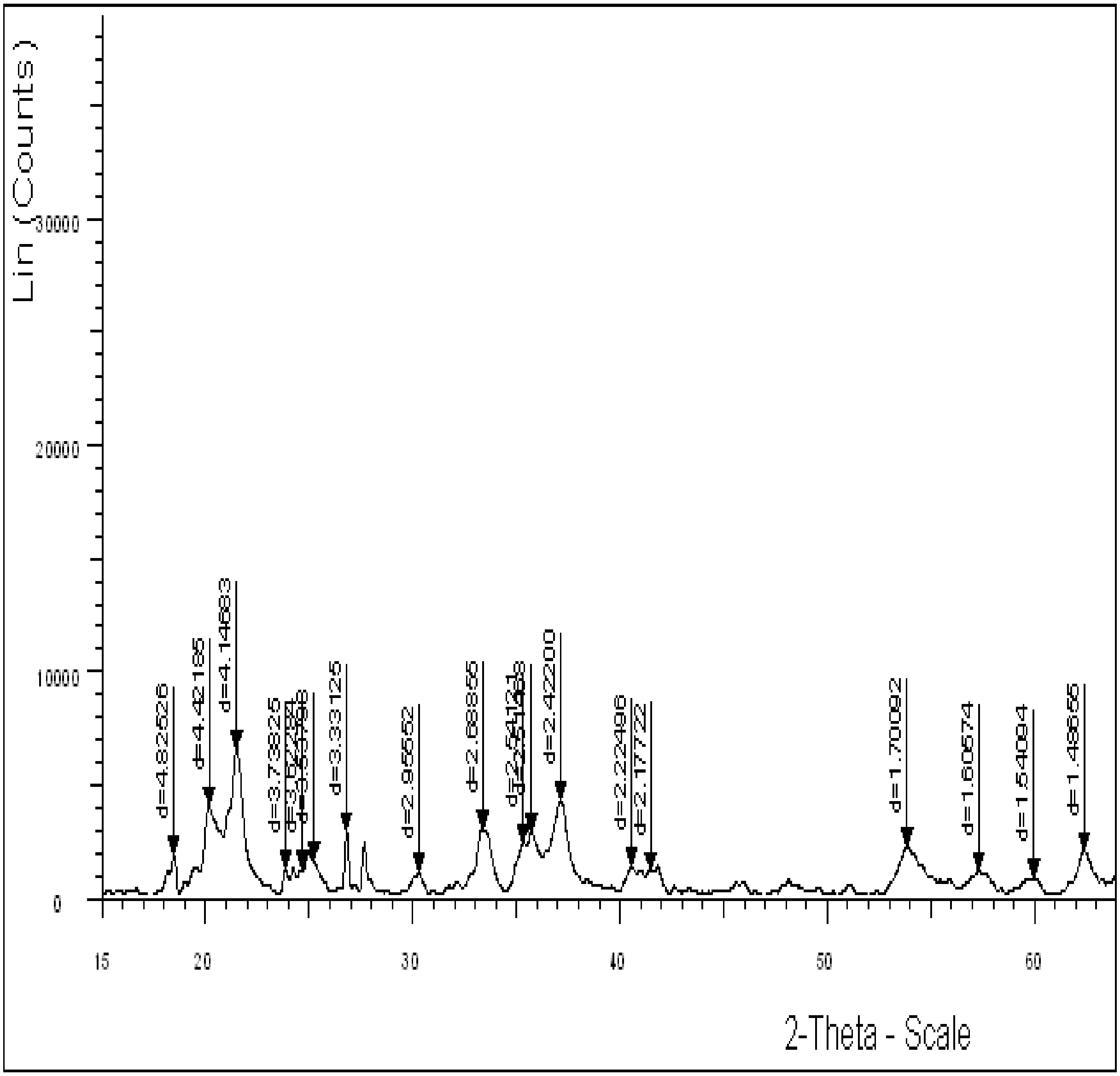
Appendix 3: XRD Spectra for Raw Laterites from Gitong'o Region at Level B with 34.49 % Iron



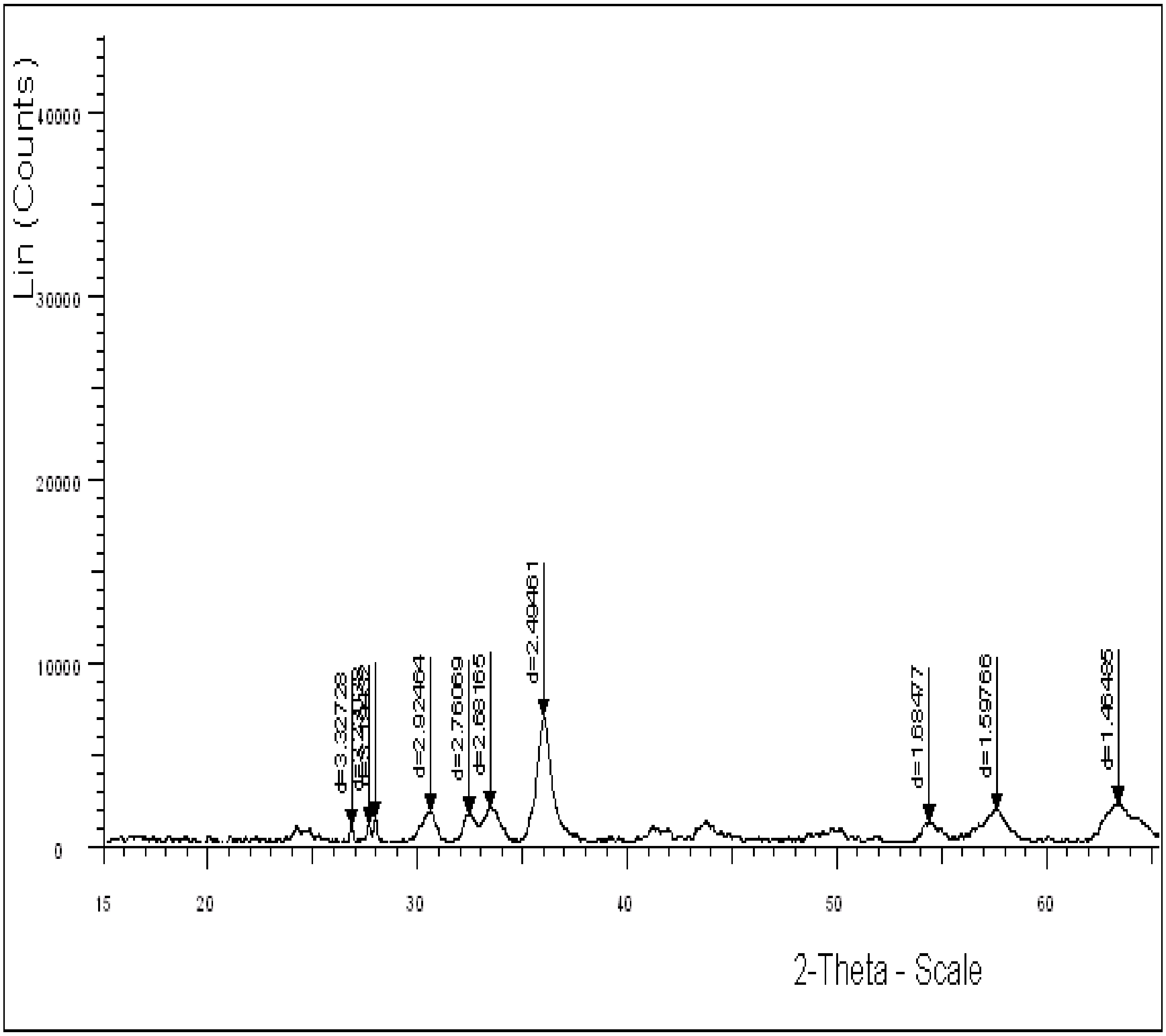
Appendix 4: XRD Spectra for Reduced Laterites from Gitong'o Region at Level B with 63.85 % Iron



Appendix 5: XRD Spectra for Raw Laterites from Ntendera Region at Level A with 32.12 % Iron



Appendix 6: XRD Spectra for Reduced Laterites from Ntendera Region at Level A with 65.32 % Iron



Appendix 7

Appendix 7: X-Ray Diffraction Table of Minerals Arranged by X-Ray Powder Diffraction, by John Weinrich Minerals Auctions

D_1 Å (2Θ)	I_1 %	D_2 **Å (2Θ)**	I_2 %	D_3 **Å (2Θ)**	I_3 %	**Mineral**	**Formula**
0.779(162.84)	100	2.180(41.38)	100	0.824(138.39)	90	Sudburyite	(Pd,Ni)Sb
0.787(156.34)	100	0.862(126.66)	80	0.885(121.00)	70	Rhodium	(Rh,Pt)
0.788(155.65)	100	0.777(164.92)	100	3.000(29.76)	100	Bowieite	$(Rh,Ir,Pt)_{1.77}S_3$
0.867(125.36)	100	2.122(42.57)	100	0.802(147.66)	70	Skaergaardite	CuPd
1.019(98.21)	100	1.081(90.89)	75	1.887(48.18)	63	Nowackiite	$Cu_6Zn_3As_4S_{12}$
1.019(98.21)	100	1.757(52.00)	100	1.910(47.57)	80	Kalininite	$ZnCr_2S_4$
1.066(92.54)	100	9.630(9.18)	100	2.050(44.14)	100	Freboldite	CoSe
1.089(90.04)	100	1.846(49.32)	100	2.371(37.92)	90	Ferdisilicite	$FeSi_2$
1.120(86.90)	100	5.440(16.28)	100	2.720(32.90)	100	Arsenolamprite	As
1.142(84.83)	100	2.180(41.38)	80	1.094(89.51)	80	Chengdeite	Ir_3Fe
1.156(83.57)	100	2.000(45.30)	90	1.003(100.34)	70	Gupeiite	Fe_3Si
1.160(83.22)	100	2.020(44.83)	100	1.430(65.18)	80	Chromferide	Fe_3Cr1-x (x=0,6)
1.163(82.95)	100	2.228(40.45)	90	1.932(46.99)	70	Isoferroplatinum	$(Pt,Pd)_3(Fe,Cu)$
1.195(80.27)	100	2.240(40.23)	100	0.797(150.24)	90	Tetra-auricupride	AuCu
1.196(80.19)	100	1.991(45.52)	100	1.817(50.17)	90	Fersilicite	FeSi
1.202(79.71)	100	2.295(39.22)	100	1.408(66.33)	90	Rustenburgite/ Atokite	$(Pt,Pd)_3Sn$
1.72(51.51)	100	2.54(35.44)	100	2.74(33.12)	90	Illmenite	$FeTiO_3$

Appendix 7: (continuation)

X-Ray Diffraction Table of Minerals Arranged by X-Ray Powder Diffraction, by John Weinrich Minerals Auctions

D_1 Å (2Θ)	I_1 %	D_2 **Å (2Θ)**	I_2 %	D_3 **Å (2Θ)**	I_3 %	**Mineral**	**Formula**
1.433(65.03)	100	2.850(31.36)	100	1.582(58.27)	100	Batisivite	$(Ti,V,Cr)_{14}Ba[Si_2O_7].O_{22}$
1.440(64.68)	100	2.140(42.19)	100	2.250(40.04)	90	Mathiasite	$(K,Ca,Sr)(Ti,Cr,Fe,Mg)_{21}O_{38}$
1.440(64.68)	90	2.840(31.47)	90	1.690(54.23)	85	Romanite	$(Fe++,U,Pb)_2(Ti,Fe+++)O_4$
1.450(64.18)	100	2.480(36.19)	100	2.043(44.30)	90	Bityite	$CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$
1.483(62.58)	100	1.057(93.56)	100	3.527(25.23)	100	Ustarasite	$Pb(Bi,Sb)_6S_{10}$
1.485(62.49)	100	3.170(28.13)	100	9.770(9.04)	100	Brammallite	$(Na,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2(H_2O)]$
1.486(62.44)	100	2.150(41.99)	100	2.050(44.14)	100	Niggliite	PtSn
1.487(62.40)	100	1.593(57.83)	100	2.900(30.81)	90	Shuiskite	$Ca_2(Mg,Al)(Cr,Al)_2(SiO_4)(Si_2O_7)(OH)_2\bullet(H_2O)$
1.494(62.07)	100	2.920(30.59)	80	8.300(10.65)	60	Chrysocolla	$(Cu,Al)_2H_2Si_2O_5(OH)_4.n(H_2O)$
1.495(62.03)	100	1.204(79.55)	90	2.830(31.59)	70	Luanheite	Ag_3Hg
1.503(61.66)	100	2.572(34.85)	100	2.457(36.54)	70	Preiswerkite	$NaMg_2Al_3Si_2O_{10}(OH)_2$
1.506(61.52)	100	2.485(36.12)	100	1.483(63.58)	90	Mangano-neptunite	$KNa_2Li(Mn,Fe++)_2Ti_2Si_8O_{24}$
1.508(61.43)	100	3.020(29.55)	100	1.793(50.88)	70	Calciotantite	$Ca(Ta,Nb)_4O_{11}$
1.511(61.30)	100	2.600(34.47)	90	5.200(17.04)	85	Takeuchiite	$Mg_2Mn+++O_2(BO_3)$

Appendix 7: (continuation)

X-Ray Diffraction Table of Minerals Arranged by X-Ray Powder Diffraction, by John Weinrich Minerals Auctions

D_1 Å (2Θ)	I_1 %	D_2 **Å (2Θ)**	I_2 %	D_3 **Å (2Θ)**	I_3 %	**Mineral**	**Formula**
1.220(78.30)	100	2.130(42.40)	100	1.350(69.58)	60	Osmium	(Os,Ir)
1.299(72.74)	100	2.163(41.72)	100	1.529(60.50)	80	Khamrabaevite	(Ti,V,Fe)C
1.306(72.29)	100	16.000(5.52)	100	4.620(19.20)	100	Perlialite	$K_8T_{l4}Al_{12}Si_{24}O_{72}$ •20(H_2O)
1.331(70.72)	100	3.070(29.06)	100	1.884(48.27)	80	Maikainite	$Cu_{20}(Fe,Cu)_6Mo_2 Ge_6S_{32}$
1.335(70.48)	100	3.516(25.31)	90	2.243(40.17)	90	Baotite	$Ba_4(Ti,Nb)_8Si_4O_{28}Cl$
1.375(68.14)	100	3.550(25.06)	100	3.230(27.59)	100	Julienite	$Na_2Co{+}{+}(SCN)_4$ •8(H_2O)
1.379(67.92)	50	1.717(53.31)	50	2.440(36.80)	50	Oxyvanite	V_3O_5
1.386(67.53)	100	2.750(32.53)	100	2.880(31.03)	70	Olkhonskite	$(Cr{+}{+}{+},V{+}{+}{+})_2Ti_3O_9$
1.388(67.42)	100	4.270(20.79)	100	2.190(41.19)	90	Jeremejevite	$Al_6B_5O_{15}(F,OH)_3$
1.390(67.31)	100	10.800(8.18)	100	2.410(37.28)	100	Glucine	$CaBe_4(PO_4)_2(OH)_4$ •0.5(H_2O)
1.391(67.25)	100	2.390(37.60)	87	2.678(33.43)	71	Zincostaurolite	$4Zn_4Al_{16}(Al,[\ ])_2 Si_8O_{40}[O_6,(OH)_2]$
1.400(66.76)	100	1.490(62.26)	100	2.490(36.04)	50	Leadamalgam	$HgPb_2$
1.430(65.18)	100	2.990(29.86)	100	1.620(56.78)	100	Augite	(Ca,Na)(Mg,Fe,Al,Ti) $(Si,Al)2O_6$

Appendix 7: (continuation)

X-Ray Diffraction Table of Minerals Arranged by X-Ray Powder Diffraction, by John Weinrich Minerals Auctions

D_1 Å (2Θ)	I_1 %	D_2 Å (2Θ)	I_2 %	D_3 Å (2Θ)	I_3 %	Mineral	Formula
1.516(61.07)	100	3.190(27.95)	100	2.163(41.72)	100	Babefphite	$BaBe(PO_4)(F,O)$
1.519(60.94)	100	2.600(34.47)	100	4.520(19.62)	80	Chromphyllite	$(K,Ba)(Cr,Al)_2[AlSi_3O_{10}](OH,F)_2$
1.520(60.90)	100	15.400(5.73)	100	4.560(19.45)	100	Nontronite	$NaO.3Fe{+}{+}{+}_2(Si,Al)_4O_{10}(OH)_2 \bullet n(H_2O)$
1.522(60.81)	100	2.410(37.28)	100	3.360(26.51)	90	Shirokshinite	$K(NaMg_2)Si_4O_{10}F_2$
1.530(60.46)	-	2.610(34.33)	-	3.910(22.72)	-	Kurumsakite	$(Zn,Ni,Cu)_8Al_8V_2Si_5O_{35} \bullet 27(H_2O)$ (?)
1.530(60.46)	100	4.580(19.36)	100	15.800(5.59)	80	Hectorite	$NaO,3(Mg,Li)_3Si_4O_{10}(OH)_2$
1.539(60.07)	100	2.940(30.38)	100	1.804(50.55)	100	Tazheranite	$CaTiZr_2O_8$
1.540(60.02)	100	2.580(34.74)	100	2.880(31.03)	60	Majorite	$Mg_3(Fe,Al,Si)_2(SiO_4)_3$
1.540(60.02)	100	2.580(34.74)	100	2.880(31.03)	60	Pyrope	$Mg_3Al_2(SiO_4)_3$
1.540(60.02)	100	3.590(24.78)	100	4.360(20.35)	100	Neotocite	$(Mn,Fe{+}{+})SiO_3 \bullet (H_2O)$ (?)
1.540(60.02)	100	2.660(33.67)	60	2.350(38.27)	60	Mcgovernite	$Mn_9Mg_4Zn_2As_2Si_2O_{17}(OH)_{14}$
1.540(60.02)	100	15.400(5.73)	100	2.670(33.54)	100	Sauconite	$NaO,3Zn_3(Si,Al)_4O_{10}(OH)_2 \bullet 4(H_2O)$
1.544(59.85)	100	2.992(29.84)	100	2.597(34.51)	60	Glagolevite	$NaMg_6[Si_3AlO_{10}](OH,O)_8 \bullet H_2O$
2.45(35.42)	75	2.70(33.53)	100	4.13(21.51)	80	Goethite	$Fe{+}{+}{+}O(OH)$

Appendix 7: (continuation)

X-Ray Diffraction Table of Minerals Arranged by X-Ray Powder Diffraction, by John Weinrich Minerals Auctions

D_1 Å (2Θ)	I_1 %	D_2 **Å (2Θ)**	I_2 %	D_3 **Å (2Θ)**	I_3 %	**Mineral**	**Formula**
1.548(59.68)	100	2.940(30.38)	100	1.813(50.28)	100	Lewisite	$(Ca,Fe++,Na)_2 (Sb,Ti)_2O_7$
1.550(59.60)	100	2.522(35.57)	100	1.805(50.52)	92	Sabelliite	$Cu_2Zn(As,Sb)O_4 (OH)_3$
1.552(59.51)	100	2.950(30.27)	100	1.818(50.14)	100	Uranmicrolite	$(U,Ca)_2(Ta,Nb)_2 O_6(OH)$
1.574(58.60)	100	2.620(34.20)	100	2.920(30.59)	90	Calderite	$(Mn++,Ca)_3 (Fe+++,Al)_2(SiO_4)_3$
1.582(58.27)	100	1.433(65.03)	100	2.850(31.36)	100	Batisivite	$(Ti,V,Cr)_{14} Ba[Si_2O_7]O_{22}$
1.587(58.07)	100	3.040(29.36)	100	1.840(49.50)	100	Cesstibtantite	(Cs,Na)SbTa4O12
1.590(57.95)	100	2.130(42.40)	100	1.800(50.67)	100	Lindsleyite	$(Ba,Sr)(Ti,Cr,Fe,Mg)_{21} .O_{38}$
1.593(57.83)	100	1.487(62.40)	100	2.900(30.81)	90	Shuiskite	$Ca_2(Mg,Al)(Cr,Al)_2 (SiO_4)(Si_2O)(OH)_2 \bullet(H_2O)$
1.606(57.32)	-	2.901(30.80)	-	3.414(26.08)	-	Dessauite	(Sr,Pb)(Y,U) (Ti,Fe+++)20O38
1.609(57.21)	100	3.159(28.23)	100	2.633(34.02)	80	Cobaltau-stinite	$CaCo(AsO_4)(OH)$
1.610(57.17)	100	2.950(30.27)	100	**2.520(35.60)**	100	**Maghemite**	**gamma-Fe+++2O3**
1.618(56.86)	100	2.645(33.86)	100	1.873(48.57)	100	Zavaritskite	BiOF
1.69(54.11)	100	2.59(35.30)	100	**2.69(33.51)**	100	**Hematite**	**Fe_2O_3**

Appendix 8: Percentage Composition of Silica, Alumina, Iron (III) oxide and Iron in Raw, Tailing and Concentrate after Beneficiation

Level A

Treatment	SiO_2 Mean±SE	Al_2O_3 Mean±SE	Fe_2O_3 Mean±SE	Fe Mean±SE
Before concentrating	22.32±0.46	13.75±0.38	42.52±0.27	29.77±0.19
Magnetic Separation- concentrate	8.21±0.20	4.88±0.14	90.23±0.55	63.16±0.33
Magnetic separation-tailing	43.30±0.49	23.79±0.28	15.17±0.39	10.62±0.27

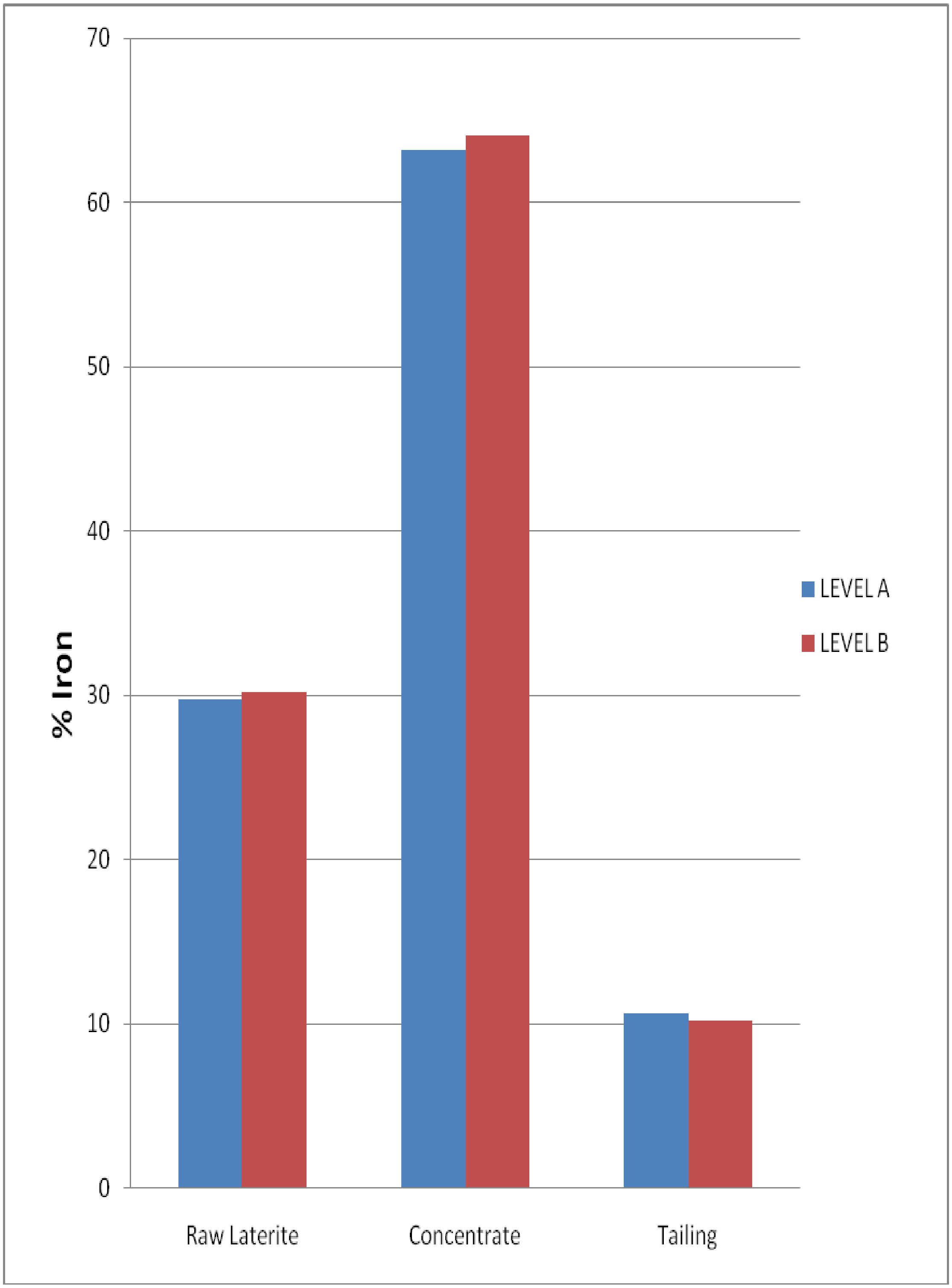
Level B

Treatment	SiO_2 Mean±SE	Al_2O_3 Mean±SE	Fe_2O_3 Mean±SE	Fe Mean±SE
Before concentrating	22.46±0.54	13.84±0.42	43.15±0.29	30.20±0.21
Magnetic Separation-concentrate	8.43±0.18	5.41±0.15	91.47±0.32	64.03±0.32
Magnetic separation-tailing	42.60±0.64	23.14±0.35	14.61±0.30	10.23±0.21

Note: In appendix 8 each value is Mean±SE of 90 replicates

Appendix 8 (continuation)

A Comparison of Percentage Iron in Raw, Concentrate and in the Tailing for Both Level A & B



Appendix 9: Map of Kenya showing the Sampling Area