UNIVERSITY OF MINES AND TECHNOLOGY TARKWA

FACULTY OF MINING AND MINERALS TECHNOLOGY

DEPARTMENT OF MINERALS ENGINEERING

A THESIS REPORT INTITLED

# PRODUCTION OF METALLIC IRON FROM MBALAM IRON ORES USING CARBON FROM END-OF-LIFE VEHICLE TYRE AND PLASTICS AS A REDUCING AGENT

**BY**

**OUM OUM II PAUL STEPHANE**

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ENGINEERING.

TARKWA, GHANA

SEPTEMBER 2021

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THESIS SUPERVISORS:

……………………….. ………………………..

ASSOC PROF JAMES RANSFORD DANKWAH

DR GEORGE M. TETTEH

TARKWA, GHANA

SEPTEMBER 2021

# DECLARATION

I declare that this thesis is my own work. It is being submitted for the degree of Master of Science in Minerals Engineering in the University of Mines and Technology (UMaT), Tarkwa. It has not been submitted for any degree or examination in any other university.

……………………..

(Signature of candidate)

……. Day of September 2021

# ABSTRACT

Four samples of iron ores were collected from Mbalam, which is located in the South-East of Cameroon where there are many rich iron ore deposits. In this work, investigation on the nature of Mbalam iron ores and the potential for production of premium grade metallic iron from them is studied using end-of-life tyres (ELTs) and end-of-life plastics (PET) as carbonaceous materials. The ores were characterised by mineralogical analysis, X-ray fluorescence analysis (XRF), X- ray diffraction (XRD) and Scanning Electron Microscopy Energy Dispersive Spectroscopy, (SEM/EDS). The mineralogical analyses of the ores show a correlation between magnetite, sphalerite and hematite. The results from the XRF, XRD and SEM/EDS analyses reveal that iron ore 1 (M1), iron ore 2 (M2) and iron ore 5 (M5) exhibit high hematite ($Fe_2O_3$) content of 96.56 wt.%, 97.35 wt.% and 96.83 wt.% respectively with correspondingly low levels of silica of 0.46 wt.%, 1.58 wt.% and 1.58 wt.%. Iron ore 3 (M3) showed a medium hematite content of 55.10 wt.%, with relatively high $SiO_2$ content 44.37 wt.%. Composite pellet was formed either with ELT or PET as reducing agents. M1 and M3 were mixed with ELT while M2 and M5 were mixed with PET. They were fired at different times (20, 30, 40, 50, 60 minutes) in a domestic microwave oven and after the irradiation, the extent of reduction was calculated. With ELT as reducing agent, the extent of reduction of M1 and M3 range from 54.36% to 60.37%. With PET as reducing agent, extent of reduction range from 78.48% to 93.04%. This clearly show that Mbalam iron ores have the potential to produce metallic iron using end-of-life polymers (PET) and end-of –life tyre (ELT) as reductants.

# ACKNOLEGDGEMENTS

I express my profound and heartfelt gratitude to the Almighty God, without whom nothing would be possible.

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|This work would be imkpossible without the guidance of my supervisors Assoc Prof James Ransford Dankwah and Dr George Mensah Tetteh, who assisted me in this work.

I am also greatful to my parents, Oum II Joseph and Ngo Nemy Bernadette Patience for their support, advises and prayers.

Lastly, I thank friend such as Kwaku Ohene Nimako and Anthony Forson for their assistant.

# DEDICATION

This thesis work is humbly dedicated to the family member Oum II and his newcomer Oum Oum II Joseph Twins-Faycal.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 **Problem Statement**

Metallic iron is formed from gas-solid reduction of iron ore by various reduction technologies. It is used mainly to manufacture steel and also used in engineering. Recently the production of iron and steel has significantly expanded, particularly in developing countries such as China, Australia, and India. The current mainstream iron making process technology is the blast furnace process, which is considered as first-generation process of ironmaking. It is estimated that the steel industry produced between 3 to 4% of total world greenhouse gas emissions. However, owing to its negative impact on the environment, three new iron making processes (fastmet, fastmelt, and ITmk3) have been developed. These processes are based on the coupling reaction between the reduction of iron oxide and gasification of carbon (Hidetoshi *et al.*, 2007). Generally, iron ore is reduced by carbon, carbon monoxide and hydrogen which are constituents of various reducing agents in the production of iron. Today, there exist one method to enhance the reducibility of iron ore include, microwave technology. Microwave heating is a phenomenon that combines electromagnetic waves and heat transfer. It is just lately that microwave have being applied to metals (Aguilar *et al.*, 1997).

Carbon is a nonmetallic chemical element found in organic molecules, in the atmosphere as carbon dioxide, in the lithosphere as fossil fuel and sedimentary rocks, and in some man-made materials. Among man-made elemental combination there are some materials which have the potential to wholly or partially replace coal and/or natural gas, these include: End of life tyre (ELTs) and waste polymeric plastics. Waste disposal of these polymeric products seem unattractive due to their negative impact in environment, and their resistance to biodegradation in environment (Sahajwalla *et al.*, 2011). In Cameroon, about 9 million tons of tyres enter the territory each year, but almost 95% are not recycled (Belibi *et al.*, 2020). ELT's are made of vulcanised rubber and various reinforced materials such as textile and steel fibers. They are compounds of both natural and synthetic rubber which are the main constituents of tyre materials. Waste plastics are materials consisting of any of a wide range of synthetic or semi-synthetic organic compounds that are malleable and can be molded into solid forms. As carbon and hydrogen are major constituents of these waste polymeric materials, these clearly have the potential to be cheap and readily available auxiliary source of carbon. In Europe, to alleviate this environmental problem, there is co-operation between steelworks and the pneumatic industries to supply used tyres for raw materials have been made (Sahajwalla *et al.*, 2011).

The scarcity of iron ore deposits and increasing demand for iron have made Banded Iron Formation (BIF) as important source of iron. Most of the world's iron ore resources occur in iron rich sedimentary rocks know as Banded Iron Formation which represents one of the most distinctive rock types that occured in the earlier part of Precambrian in most of the shield areas of the world.

In Cameroon, past works have led to the discovery in Precambrian greenstones terrain, several iron ore deposits like the Mbalam iron ore deposit, which is at the advanced stage of exploration, and development. Mbalam area has a deep weathering profile. The iron deposit is hosted in Archaean Banded Iron Formation recrystallised to ferruginous quartzite, which is associated with supergene hematite enrichment (Nforba *et al.*, 2011). The iron concentration increases from average of 46.18 wt % in the depositional soil material to as much as 79.18 wt% in the regolith zone (Nforba *et al.*, 2011). This project therefore seeks to study the potential for producing metallic iron using end-of-life tyres (ELTs) and waste polymeric plastics as reducing agents.

## 1.2 Project Objectives

The objectives of this work are to:

- Examine the mineralogy and chemical composition of Mbalam iron ore.
- Identify the suitable reducing agents in ELT and PET
- Investigate the potential for producing metallic iron from various grades of Mbalam iron ore using the identified reducing agents (ELT and PET),
- To Assess the efficiency of reduction of the Mbalam iron ore using ELTs
- Test the quality of the produced premium grade metallic iron.

## 1.3 Methods Used

The methods used include:

- Petrography and mineralogy of the ore,
- Mineral chemistry of the ore,
- Efficiency analysis of the reduction process,

- Quality analysis of the produced metallic iron

## 1.4 Facilities Used

The facilities used for this work include:

- Internet and library facilities at UMaT
- Mineral processing facilities at Minerals Engineering laboratory UMaT
- Polarising microscope at petrology laboratory at Department of Geological Engineering UMaT,
- XRF, XRD, SEM/EDX, QMSCAN at analytical center, school of chemical science and Engineering, UNSW, Sydney, Australia.

## 1.5 Organisation of Work

This work is organised and presented in five chapters. Chapter one is the general introduction to research conducted. It describes the problem from which the thesis is based on, the objectives of this work and the method used. Chapter two presents a brief description of the mine area and the review of relevant literature. Literature review explains briefly iron ore deposit in Cameroon, characterisation of waste polymeric materials (ELTs and plastics), microwave technologies and some of the new ironmaking processes. Chapter three presents the raw materials, preparation of different analyses and the methodology used in the experimental work. Chapter four presents the results of analysis (petrology and mineralogy), chemical composition of the ore and chapter five is conclusions and recommendations.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Iron and iron ore deposits

Iron is a chemical element with symbol, Fe and atomic number 26. It is by mass the most common element on earth. Most of the iron in the crust is combined with other elements to form many iron bearing minerals but five are the primary sources of iron ore minerals such as: hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), pyrite ($FeS_2$), siderite ($FeCO_3$), and goethite ($Fe_2O_3.H_2O$). Generally, a deposit must contain at least 25% iron to be considered economically recoverable (Weiss et *al.*, 1985). It is estimated that annual world production of iron ore is about one billion tonnes (Dankwah, 2016).

Most large deposits of iron ore are associated with iron formations which are found in all Precambrian shields (Simonson *et al.*, 2011). According to the Sub Commission on Precambrian Stratigraphy of the International Union of Geological Sciences, the Precambrian can be divided into Proterozoic and Archean.

In Cameroon, the Precambrian crust has been divided into an Archean cratonic and Neoproterozoic belt (Nforba *et al.*, 2012). It is also divided into two units: the Nyong unit and the Ntem unit which is very well exposed in southern Cameroon (Maurizot *et al.*, 1986). It is showing in figure 2.1 below.

The Ntem unit complex constitutes the northwestern part of Congo craton and is very well exposed in southern Cameroon (Maurizot *et al.*, 1986). It extends over 500 km from Mbalam in the south east to Kribi in Atlantic cost in the west with a lithological units such as schist, amphibolite, quartzite, gneiss, greenstone rocks and itabirite like rocks (Toteu *et al.*, 2004). Situated in equatorial forest where the geology is favorable to mineralisation of many substances as base metal and rare metal, the region is characterized by two types of iron mineralization such as:  One is a near-surface, high-grade hematite mineralisation, and the other is an itabirite-style mineralisation (Anon. 2005).

The Nyong unit is located in the western edge of Congo craton between Edea and Eseka cities. The area is dominated by laterite which is essentially made up of kaolinite, goethite, gibbsite, hematite, anatase and illite (Bayiga *et al.*, 2011). The weathered materials contain moderate to high $SiO_2$ from11.84 to 65.91%, Fe from 1.73 to 35.71% and, Al from 18.49 to 31.77% (Bayiga *et al.*, 2011).

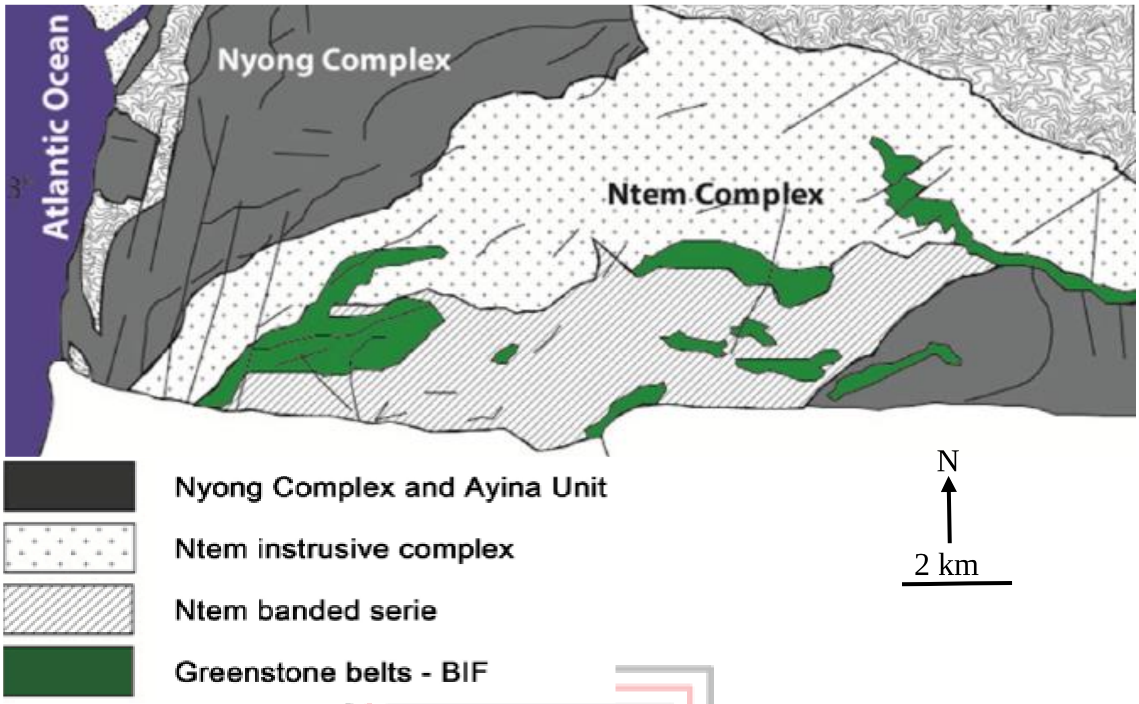


**Figure 2.1: Simplified Geological Map of South, South-East of Cameroon (Bonda *et al.*, 2017).**

In this different division, there are some iron projects which are in their advanced stages of exploration and development and include: Mbalam, Mamelles, and Ndjoum-Nkout. Mbalam mine is located about 300 km southeast of the capital city, Yaoundé. It is a deep weathered area located in south east Cameroon in the Eastern Region border with the Republic of Congo where they are significant deposits of iron ore. Figure 2.2 below show iron ore deposits in Cameroon

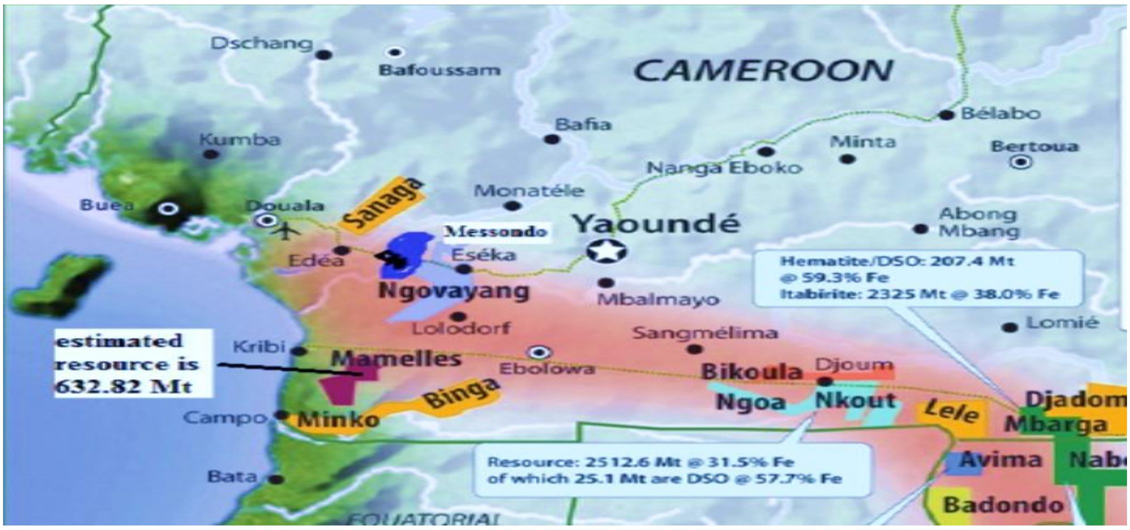


**Figure 2.2: Iron Ore Belt showing Iron Ore Deposits in Cameroon (Fuh, C., 2013).**

Exploration activities in this area have been developed by an Australian company, Sundance Resources Limited (SRL) which is active at the cross border between Cameroon and Congo through its subsidiaries Cam Iron s.a and Congo Iron s.a. The region is characterised by two types of iron mineralisation such as: near-surface, high-grade hematite mineralisation, and the other is an itabirite-style mineralisation (Longley *et al.*, 2012). High grade hematite mineralisation includes those found in the surficial zone, the supergene zone, and the transitional zone. Its estimated total 775.4Mt at grade of 57.2% Fe. As for itabirite hematite reserves it is estimated at about 2,325 billion tonnes at grade of 38% Fe, 44.4% $SiO_2$, 0.5% $Al_2O_3$, and 0.04% P (Longley *et al*., 2012). The Mbarga deposits north-South cross section and some iron ores collected from there are showing in figure 2.3 and figure 2.4.

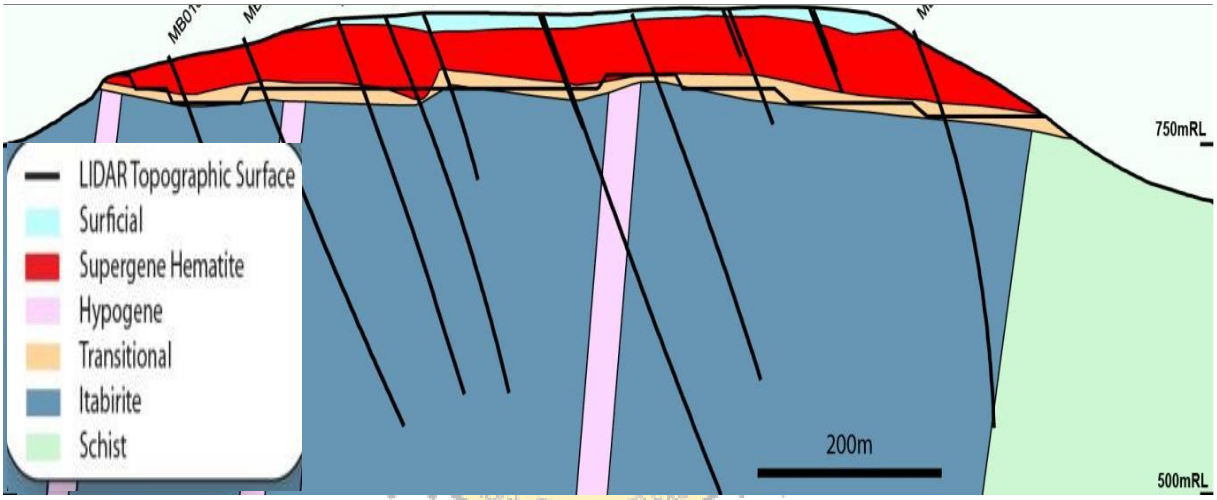


**Figure 2.3: Mbarga deposit north-south cross section (Longley *et al*., 2012).**

AFFERO subsidiary of Africa Aura Mining, Inc. estimated Ndjoum-Nkout around 1.2Bt for 32.9% Fe. In the Akon hills the grade of iron is up to 55.9% Fe (Fuh , C., 2013).

Mamelles: SINOSTEEL is a company which has an iron project in Mamelles. Prefeasibility study shows that the estimated resources is about 632.82 Mt and annual production around 4Mt. The grade of iron is around 35%Fe (Fuh, C., 2013).

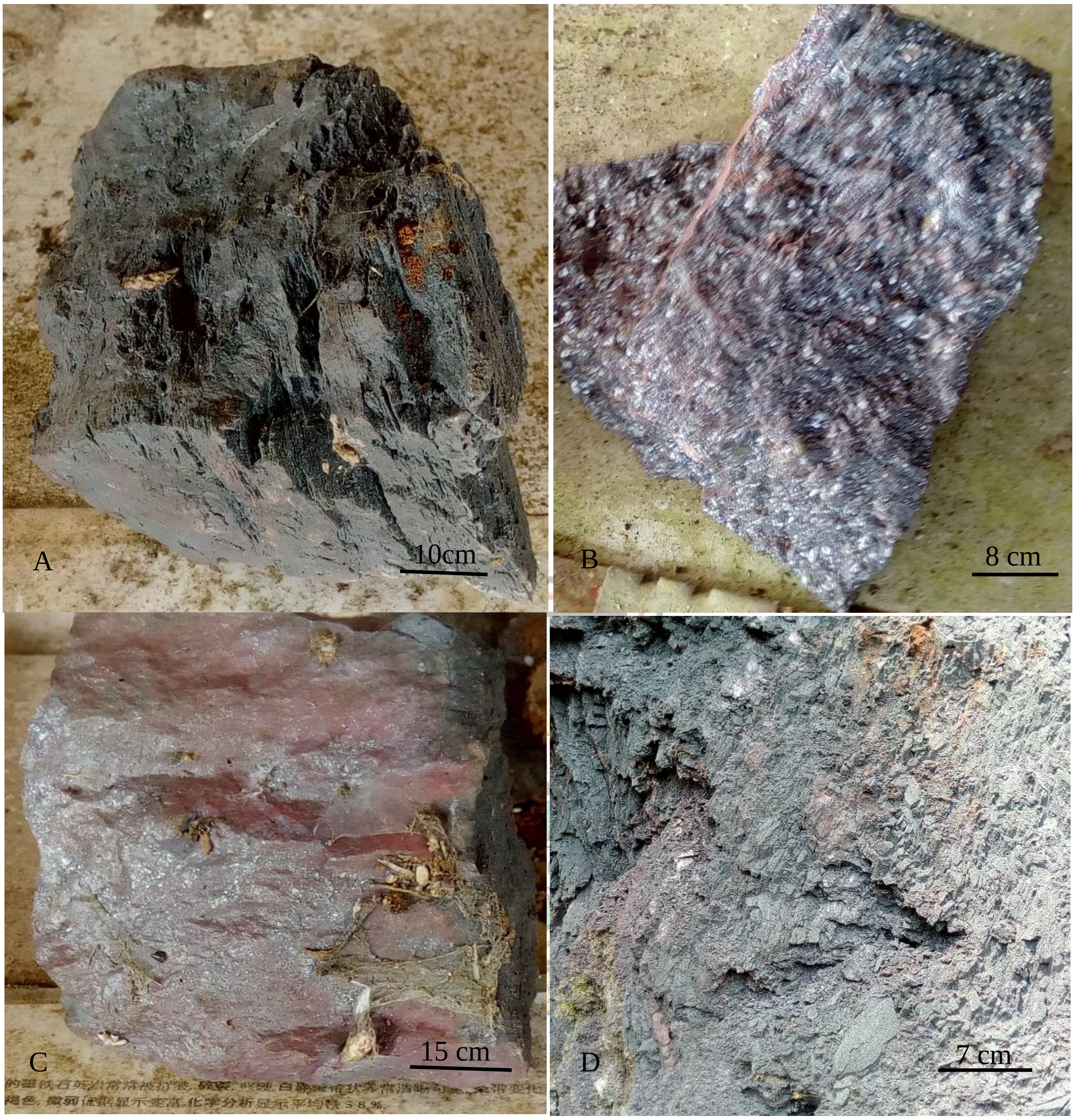


**Figure2.4: Photographs of Some Iron Ores from Mbalam. A) Iron ore 3 (M3) shows high lustre with hematite showing pseudo-micaceous forms. B) Iron ore 2 (M2) is very hard with metallic lustre. C) Iron ore 1 (M1) is a reddish grey rock showing folds. D) Friable rock with high sugary quartz, it is iron ore 5 (M5).**

### 2.2 characterisation of iron ores

Mineral characterisation involves the study of minerals in terms of their size, habit, chemical, composition, morphology, textural position association and others attributes. There is a well know and progressively need for this type of study applied to deposits of minerals. It is an important step to perform before its processing. The grade or quality, densities, shape, and physical characteristics are determinated to allow for suitable application of technical and economic parameters to upkeep production planning and evaluation of the economic viability of deposits. It is therefore very important to perform chemical, physical, and mineralogical characteristics of the ore.

### 2.2.1 Chemical Characterisation of Iron Ores

Identified the major and minor species or element of an ore sample, is the need to conduct chemical characterisation. There are two main methods for chemical characterisation, the destructive and the non- destructive methods. The destructive method used in chemical characterisation of ore minerals is the wet chemical methods. Example of these chemical methods include volumetric, gravimetric, and colorimetric analysis. Higher concentration of various elements are determined using volumetric or gravimetric. For trace element, colorimetric method is used (Amikiya, 2014).

X-ray fluorescence analysis (XRF) and X-ray diffraction analysis (XRD) are normally the non- destructive chemical characterisation method. XRF is used to determine major and minor elements of ore minerals. The XRD is used to determine peaks of major species in an ore. A typical iron ore analysis should include a loss of igmition( LOI). LOI is due to the loss of water from hydrated minerals, decomposition of carbonates and volatilisation of organic compounds.

### 2.2.2 Physical Characterisation of Iron Ores

The degree of liberation of an iron ore is not enough to predict its behaviour during its processing. The physical characteristics and properties of the iron ores are very important because they help to understand the ore’s behaviour during mining, handling, charging and descent in the mode of iron making processes (Muwanguzi, 2010). Physical characterisation methods include particle size, abrasion, and specify gravity.

## 2.3 Iron-making Technologies

Iron making is a process of reducing iron ore (solid oxidised iron) into metallic iron through the removal of its oxygen. This process is highly capital intensive in relationship to the added value to the input materials. Several modern methods for manufacturing steel have evolved significantly since industrial production began in the late 19th century, but most of them are based on the same premise as the original Bessemer process, which uses oxygen to lower the carbon content in iron. Today, ironmaking makes use of recycled materials as well as traditional raw materials, such as iron ore, coal, and limestone. In order to overcome the environmental issues, alternative ironmaking processes have been proposed or developed to replace the conventional ironmaking process. These processes are based on the coupling reaction between the reduction of iron oxide and gasification of carbon, which can produce high quality iron units from iron ore fines and coal that exist in abundance all over the world. Alternative iron making process are required to satisfy the criteria used in different coals, simplified material preparation, metal with little impurities, independent process steps, closed energy system, efficient pollution control and no waste generation (Hidetoshi *et al.*, 2007).

### 2.3.1 Blast furnace

The current mainstream ironmaking technology is blast furnace process which is considered as the first generation of iron production. Figure 2.5 is an illustration of blast furnace which is a vertical shaft furnace that produces liquid metals by the reaction of a flow of air introduced under pressure into the bottom of the furnace with a mixture of metallic ore, coke, and flux fed into the top. Blast furnaces produce pig iron from iron ore by reducing action of carbon (supplied as coke) at a high temperature in the presence of a fluxing agent such as limestone.

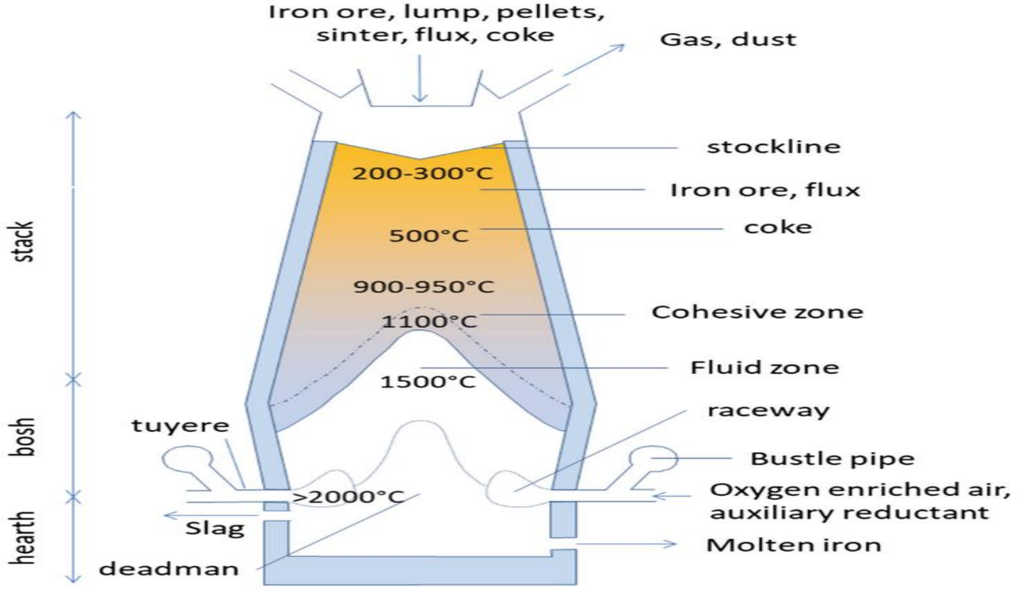


**Figure 2.5: Illustration of the Blast Furnace for Reducing Iron Ore (Anon., 2018).**

### 2.3.2 Direct reduction process (DRP)

The DR process is a solid-state reaction process in which removable oxygen is removed from the iron oxide, using coal or reformed natural gas as reductants, below the melting and fusion point of the lump ore or agglomerates of fine ores. It is considered as alternative ironmaking process that provides valuable options to steel company and deal with some current issues. Based on the types of reductant used, the DR processes can be classified into two groups: gas-based and coal/oil based.

Gas-based DR processes, account for about 92% of worldwide production of Direct Reduction process (DRP), the reducing gas is produced by chemically reforming a mixture of natural gas and off-gas from the reducing furnace to produce a gas that is rich in hydrogen and carbon monoxide. Among them are MIDREX, HYL, FINMENT, CIRCORED (Hidetoshi *et al., 2008).*

MIDREX process is the most successful gas-based DR process which reduces iron ore using a reforming gas from natural gas. Raw materials (lump ores, or pellets) are reduced by reductant gas from about the middle of the shaft furnace to metallic iron. Current MIDREX operating plants have been designed for $H_2/CO$ ratio ranging from 0.5 to 4.0 (Cheeley *et al.*, 1999). The quantity of gas required tend to be inversely related to $H_2/CO$ ratio.

For the coal/oil-based process, reducing gas is generated from hydrocarbons (primarily coal, but sometimes oil and natural gas) in the reduction zone of the furnace, which is typically a rotary kiln. In this process, the iron oxides in the agglomerate are reduced to metallic iron by the composite carbon within the agglomerate. Among the most common coal-based DR processes, there are FASTMET, FASTMELT, and ITmk3 processes, which have also been developed (Hidetoshi *et al.*, 2007)

FASTMET process is a unique process using a Rotating Heart Furnace (RHF) to reduce agglomerates containing coal with a high reduction ratio and high productivity. These agglomerates are fed into the RHF in one or two layers and heated rapidly to a maximum 1,350° C in the RHF by radiation heat. A schematic representation of this process is illustrate in figure 2.6.

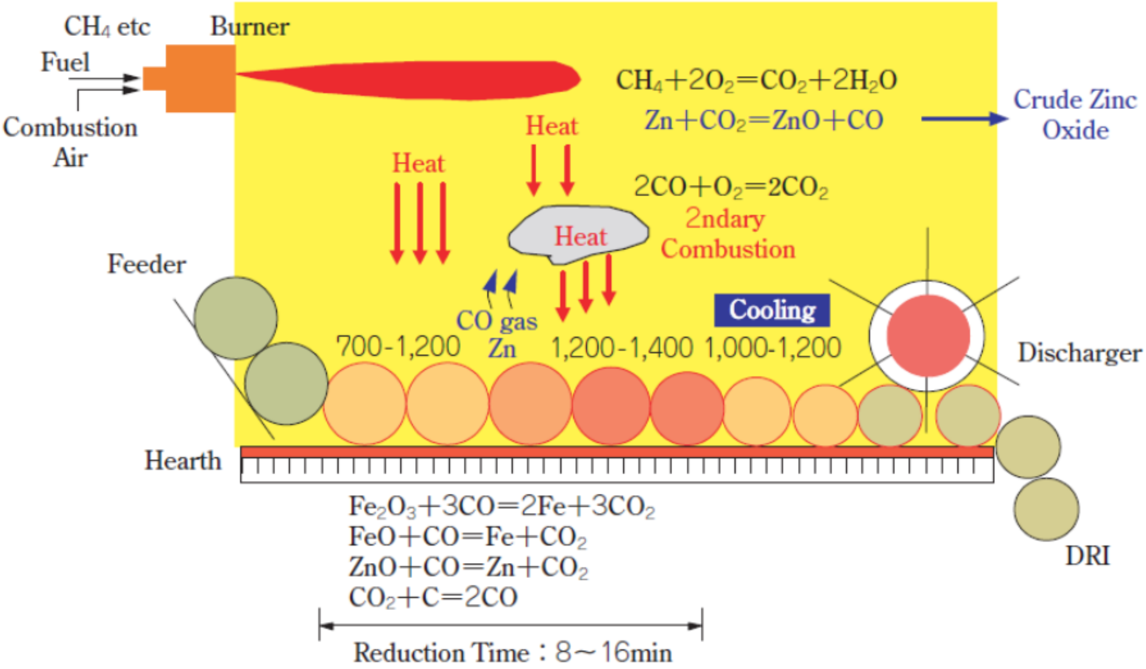


**Figure 2.6: Schematic drawing of reduction in FASTMET furnace (Hirofumi *et al.*, 2010).**

- ITmk3 process is a rapid iron making process that includes reducing ore, carburising and melting iron and separating slag, all at relatively low temperatures. This process utilises non-coking coal as the reductant. It seems that in the ITmk3 process, the reaction occurs must faster than BF and DRI. This reaction occurs within about 10 minutes (Kobayashi *et al.*, 2010). The main features of the process are:

  - Non coking coal is used as a reductant.
  - The process utilises low grade iron ore fines which are grounded in fine particles and beneficiated in order to produce high grade iron ore concentrate. This concentrate is converted into green pellets
  - The pellets are charged into a rotary hearth furnace (RHF), heated to 1350 ºC reduced, melted and separated into metal and slag.
  - The molten iron is solidified into nuggets inside the furnace, discharged after cooling and separated from the slag.

- The process is simple and uses conventional equipment. Further, the small retention time also facilitates the startup and stopping of the plant. Iron ore fines and pulverised coal are agglomerated into composite pellets.

In this process the reactions which occur are:

Fe xOy + yCO = xFe + y$CO_2$ ………………… (1)
$CO_2$ + C = 2CO ………………………………… (2)
C(s) = C (carburised) …………………………. (3)
Fe(s) = Fe (l) (melt) …………………………… (4)

Note that, reactions (1) and (2) occur in FASTMET and ITmk3, but reactions (3) and (4) are additional in ITmk3 processes (Kobayashi *et al.*, 2010).

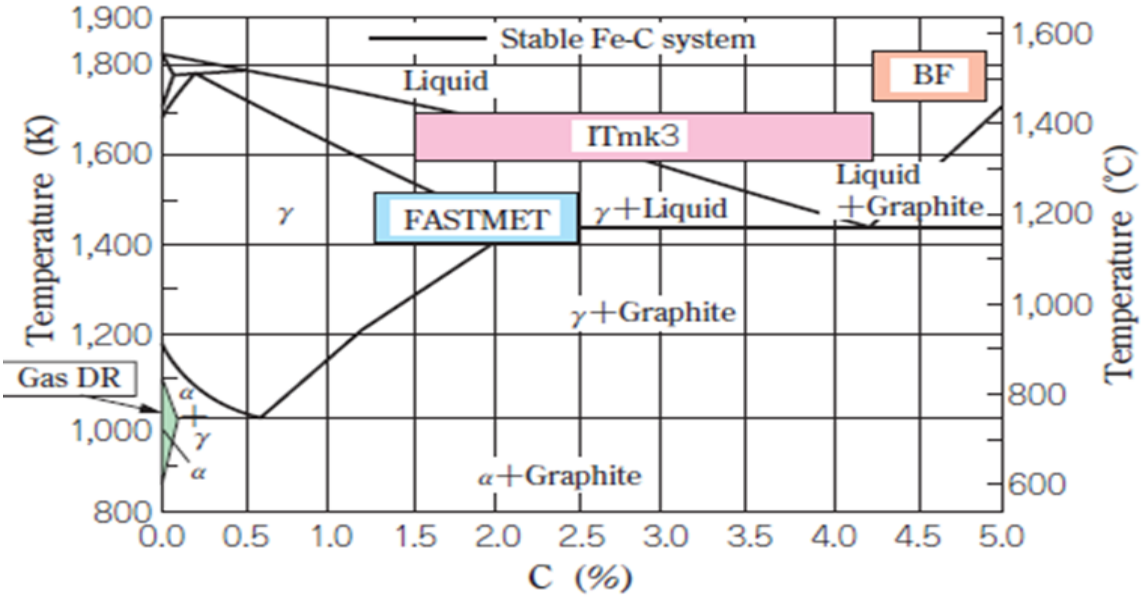


**Figure 2.7: Operational region of Iron Making Process (Hidetoshi *et al.*, 2010).**

## 2.4 Microwave Technologies

Microwave is a very fast heating oven emitting electromagnetic waves with length between 1m and 1mm. it is also a form of electromagnetic energy, which falls at the lower end of the electromagnetic spectrum and is defined in a measurement of frequency as 300 to 300,000 MHz (Adam, 2003). It is widely used in modern technology include: television industry, national and local security applications, communication, domestic house, hospital etc. Recently, microwave heating serves as new form of providing energy instead of the conventional sources and microwaves have been applied to the production of metals. This form of use is called microwave chemistry which is the science of applying microwave radiations to chemical reactions wherein microwaves act as high frequency electric fields and will heat any material containing mobile electric charges (Chaitanya *et al.*, 2001).

Among the many applications of microwave processing investigated in minerals treatment, there are: microwave assisted ore grinding, carbothermic reduction of metal oxides, minerals leaching, roasting and smelting of sulphide concentrates, pre-treatment of refractory gold concentrates, spent carbon regeneration and waste management. Generally, it appears that carbon materials are very good absorbents of microwave radiation. Studies have been done on microwave reduction of iron ore pellets from Brazil, and the report revealed that about 99 % of the microwave energy furnished to a carbon reduction reaction is lost by heat transfer to surrounding and only 1% does the job of reduction (Chaintaya, *et al.*, 2001).

Work done on the reduction of the magnetite ore using a domestic microwave oven showed that the extent of reduction ranges from about 47.4% to about 95.6% producing premium grade metallic iron which can be fed to the local steel industry when commercialised (Dankwah *et al.*, 2016).

**Table 2.1: Microwave Heating of Some Oxide Compounds**

| **Compounds** | **Heating time (min)** | **Max temperature (°C)** |
|---|---|---|
| $AL_2O_3$ | 24 | 1900 |
| CaO | 40 | 200 |
| $CO_2O_3$ | 3 | 900 |
| CuO | 4 | 800 |
| $Fe_2O_3$ | 6 | 1000 |
| $Fe_3O_4$ | 0.5 | 500 |
| MgO | 40 | 1300 |
| $MoO_3$ | 0.46 | 750 |
| $Ni_2O_3$ | 3 | 1300 |
| $UO_2$ | 0.1 | 1100 |
| PbO | 13 | 900 |

**(Source: Walkiewicz *et al.*, 1988)**

## 2.5 Alternative reducing agents of iron ore

The reduction of low-grade iron oxide is achieved by some reductants such as carbon monoxide and hydrogen through direct reduction process. For those countries which are limited in resources of coal or natural gas, the idea of replacing coke with carbonaceous materials or biomass seem to be a future minded alternative reducing agent. For most of them, the major composition is carbon and hydrogen.

Rubber or caoutchouc is fluid that is obtained from the sap of the rubber tree. It was during the end of 18th century that the properties of rubber as obtained from the tree were known throughout Europe (Rehan *et al.*, 1996).

Today, natural rubber is commercially produced in Indonesia, Thailand, Brazil, Nigeria, Cote D'Ivoire, and Ghana. There are two types of rubbers: natural rubber and synthetic rubber. Natural rubber is called poly-isoprene and is built up by long chains of molecules. It has very good mechanical properties, and good resistance to tearing, flexing and abrasion. Natural rubber exhibits a tensile strength of 250-350 kg/cm2 (= 25-35 MPa = Mega Pascal) and a modulus of elasticity of 10-30 kg/cm2 (1-3 MPa) at 300% elongation (when compounded with 25% carbon black, the modulus can increase to 50-100 kg/cm2 (5-10 MPa) (Rehan *et al.*, 1996).

Synthetic rubber is a type of rubber which is made from oil and characterised by high number of elastic materials closely resembling natural rubber but with different properties. Compared to natural rubber, synthetic rubbers offer better resistance to abrasion and the effects of aging. Among the different types of synthetic rubber which can be produced from mineral oil, there are: styrene-butadiene-rubber (SBR), ethylene-propylene (EP), nitrile (NBR) and butyl rubbers (BR).

### 2.5.1 Plastic

These are polymeric materials that have the capability of being moulded or shaped, usually by the application of heat and pressure. Polymers are chemical compounds whose molecules are very large, and constituted of interconnected links of carbon atom. Polymers that are classified as plastics can be divided into two categories: thermoplastics and thermosets. Table 2.2 show the properties and applications of commercially important plastics.

Thermosets are plastics which can be melted and shaped. On the other hand, it cannot be reprocessed upon reheating. In thermosetting process, a chemical reaction occurs that results in an insoluble network. The main thermosetting plastics are: epoxy resin (EP), melamine formaldehyde (MF), polyester resin (PR), urea formaldehyde (UF), phenol formaldehyde (PF).

Thermoplastics are plastics that can be softened and formed using heat, and when cool, will take up the shape that they have been formed into. The polymer structure associated with thermoplastics is that of individual molecules that are separated from one another and flow past one another. The molecules may have low or extremely high molecular weight, and may be branched or linear in structure, but the essential feature is that of separability and consequent mobility (Ferdinand Rodriguez, 2019).

**Table 2.2: Properties and Applications of Commercially Important Plastics**

| Polymer family and types | Density | Degree of crystallinity (%) | Glass transition temperature | Tensile | Type products and applications |
|---|---|---|---|---|---|
| Thermoplastics | | | | | |
| High density polyethylene (HDPE) | 0.95-0.97 | High | -120 | 137 | milk bottles, wire and cable insulation |
| Low density polyethylene (LDPE) | 0.92-0.93 | Moderate | -120 | 110 | Packaging film, grocery bags. |
| Propylene (PP) | 0.90-0.91 | High | -20 | 176 | Bottles, food containers |
| Polystyrene (PS) | 1.0-1.1 | Nil | 100 | - | Eating utensils |
| Acrylonitrile-butadiene-styrene (ABS) | 1.0-1.1 | Nil | 90-120 | - | Appliances housing, helmets |
| Polyvinyl chloride | 1.3-1.6 | Nil | 85 | - | Pipe, conduit, home siding |

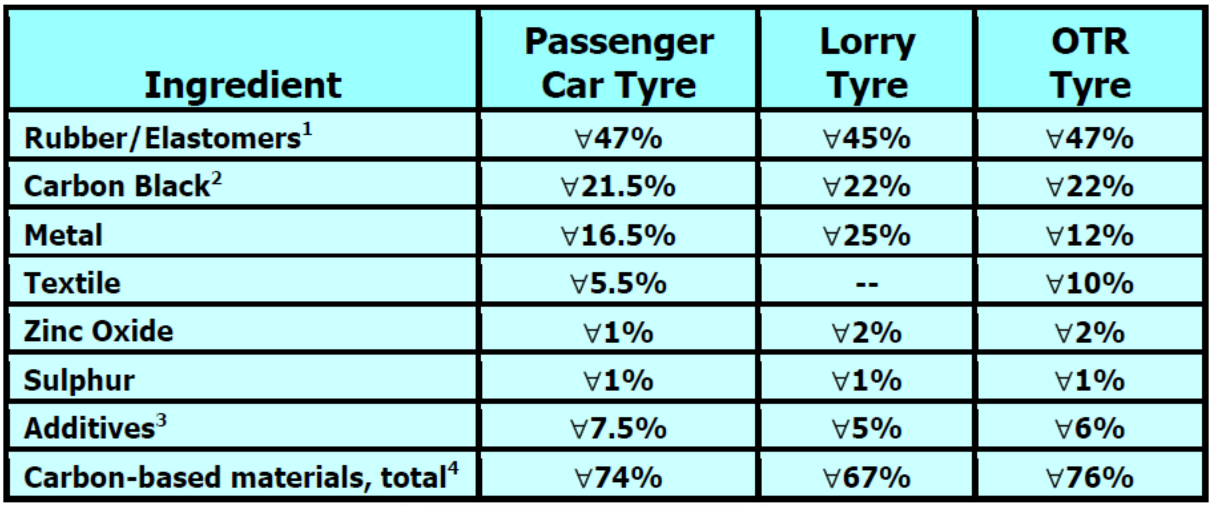
| | | | | | |
|---|---|---|---|---|---|
| unplasticised (PVC) | | | | | |
| Polyethylene terephthalate (PET) | 1.3-1.4 | Moderate | 69 | 265 | Transparent bottles, safety glasses |
| Polycarbonate (PC) | 1.2 | Low | 145 | 230 | Compact disc, |
| Polyacetal | 1.4 | Moderate | -50 | 180 | Bearing, gears |
| Polyphenylene sulphide (PPS) | 1.35 | Moderate | 88 | 288 | Machine parts, appliances |
| Cellulose diacetate | 1.3 | Low | 120 | 230 | Photographic film |
| Polycaprolactam(nylon,6) | 1.1-1.2 | Moderate | 50 | 210-220 | Bearings, pullets |
| Thermosets | | | | | |
| Polyester unsaturated | 1.3-2.3 | Nil | | | Boat hulls. Automobile panels |
| Epoxy | 1.1-1.4 | Nil | | | Flooring, aircraft parts |
| Phenol formaldehyde | 1.7-2.0 | Nil | | | Appliance handles |
| Urea and melamine formaldehyde | 1.05 | Low | | | Countertops, dinnerware |

**Source: (Fernandez Rodriguez, 2019).**

### 2.5.2 Tyres

Tyres are bands of rubber either solid or hollow and inflated placed over the rim of a wheel to provide traction of a displacement machine. It is obtained by mixing rubber with other chemicals to form thermoset material. This process is commonly known as vulcanisation. They are made up of numerous different rubber compounds, many different types of carbon black, fillers like clay and silica, and chemicals and minerals added to allow or accelerate vulcanisation.

**Table 2.3: Estimated Composition of Tyres**



| Ingredient | Passenger Car Tyre | Lorry Tyre | OTR Tyre |
|---|---|---|---|
| **Rubber/Elastomers[1]** | ∀47% | ∀45% | ∀47% |
| **Carbon Black[2]** | ∀21.5% | ∀22% | ∀22% |
| **Metal** | ∀16.5% | ∀25% | ∀12% |
| **Textile** | ∀5.5% | -- | ∀10% |
| **Zinc Oxide** | ∀1% | ∀2% | ∀2% |
| **Sulphur** | ∀1% | ∀1% | ∀1% |
| **Additives[3]** | ∀7.5% | ∀5% | ∀6% |
| **Carbon-based materials, total[4]** | ∀74% | ∀67% | ∀76% |

**Source: (Russ Evans et *al*., 2006).**

### 2.5.3 End of Life Tyres (ELT)

End of life tyre is tyre which cannot be reused for its originally intended purpose, but may have a further use as a raw material for other processes. According to the World Bank's 2018 report “What a waste 2.0”, Africa generated 174 million tonnes of waste in 2016, 69% of this waste was dumped in the open and often burned but Only 7% of them are recycled. In Cameroon, almost 9 million used tyres enter the territory each year, 95% of which are not recycled (Belibi *et al*., 2020).

Waste disposal options to alleviate this polymeric product are highly unattractive due to their resistance to biodegradation and the formation of polycyclic aromatic hydrocarbon upon combustion at incineration temperature (Sahajwalla *et al.*, 2011).

A survey has shown that about half of the total mass in tyre wear sample was composed of organic compound with the sixth being elemental carbon (Hildermann *et al.*, 1991). The net calorific value of a tyre is between 26 -34 GJ/tonnes, which is similar to that of common fuel sources such as wood. It burns almost completely at 650°C.

In Europe a joint effort between two industrials partners, the tyre partners and steel making plants, have been initiated for better co-operation on environmental issues such as raw material supply. In addition to being rich in carbon and hydrogen, this waste polymeric material has also the potential to be cheap and readily available auxiliary source of carbon, to partially replace conventional carbon material and reduce greenhouse effects.

# CHAPTER THREE

# METHODS EMPLOYED

## 3.1 Methods Used

In this work, four iron ore samples (iron ore 1, 2, 3, and 5) were selected from Mbalam, around the Mbarga hill where the mine is situated. Iron ore 1 (M1), is a massive rock with reddish grey colour. Iron ore 2 (M2), is a compact rock with metallic lustre. Iron ore 3 (M3), is a hard rock showing pseudo micaceous forms. Iron ore 5 (M5), it is friable rock with high sugar quartz. Carbonaceous materials, plastic bottles (PET) and end of life tyres (ELTs), were collected around the University of Mines and Technology (UMaT), Tarkwa. As bindering agent, flour was used in the formation of pellets. Magnet and hand lens were used to assess the efficiency of reduced material. The practical study of this work was carried out at Petrology-Mineralogy laboratory and Minerals Engineering laboratory of the University of Mines and Technology, Tarkwa. The analysis of this work was carried out in an external laboratory in Australia. The equipment used for this research consist of:

- Slides,
- Magnifying lens and,
- Polarising microscope.

In the Minerals Engineering laboratory, the equipment used are:

- The Jaw and Cone Crusher: to reduce the samples size to a range of 15 mm to -5 mm.
- Ball Mill of diameter 30 cm and length 23 cm.
- ASTM-E11 Screens: a 250 µm sieve was used to attain an undersize of -250 µm.
- Electronic Balance
- A Domestic 2400MW, 50Hz, SHARP Microwave oven
- Handheld magnet
- Roll crusher

Chracterisation of ores is an important step in material research before and after processing. It has an important implication on its metallurgical behaviour. In this work, elements present in sample were investigated using X-ray fluorescence (XRF) analysis, X-ray diffraction (XRD) was used for the identification of mineral phases. Scanning Electron microscopy and energy dispersive X-ray (SEM/EDS) was used to obtain information about the surface topography and composition. For each rock sample, polished and thin section were prepared and described using polarizing microscope.

### 3.2 Iron Ore Preparation

Separately, samples were broken first using a hammer and then sent to a jaw crusher for reduction of particles in order to obtain sizes ranging from 12 mm to 5 mm. The secondary reduction of particles was carried out by the cone crusher to a particle size below 5 mm. From the cone crusher, the ores were sent to a roll crusher to obtain particle size between 2.4 mm to1.5 mm and then to milling which was accomplished by the ball mill for about 15 minutes per samples. The product of milling was passed through sieving of 250µm to attain an undersize of -250µm. each iron ores were bagged and labelled M1, M2, M3, and M5 for iron ore 1, iron ores 2, iron ore 3 and iron ore 5 respectively. Figure (3.1) shows the powdered of iron ore 2 and 3.

**Figure 3.1: Powdered Iron Ores of a) M2 and b) M3.**

### 3.3 Carbonaceous materials preparation

The thermoplastics PET collected was shredded and cleaned. It was melted into liquid and then poured in a metallic container to allow it to cool. It was pulverised and screened to obtain particles size of – 250 µm, using standard sieve of 250 µm. Figure (3.2) is a representative of PET samples of the pulvirised to -250 µm.

The ELT used in this work was a type of Brigestone 4*4 tyres, which contain approximately 47% of rubbers, 5.5% of textile and the rest for other elements (Russ Evans *et al.*, 2006). The material was shredded, cleaned and dried for a day. A whole tyre of weight 13500 g was charred in a metallic container in normal air. Charing was done to upgrade the carbon content by expelling the volatile components of ELT using fire. The charred product was pulverised using a laboratory ball mill. The pulverised ELT were screened using standard sieve of 250 µm and the undersize was used for this work. Figure (3.2) show a representative of pulverised ELT.

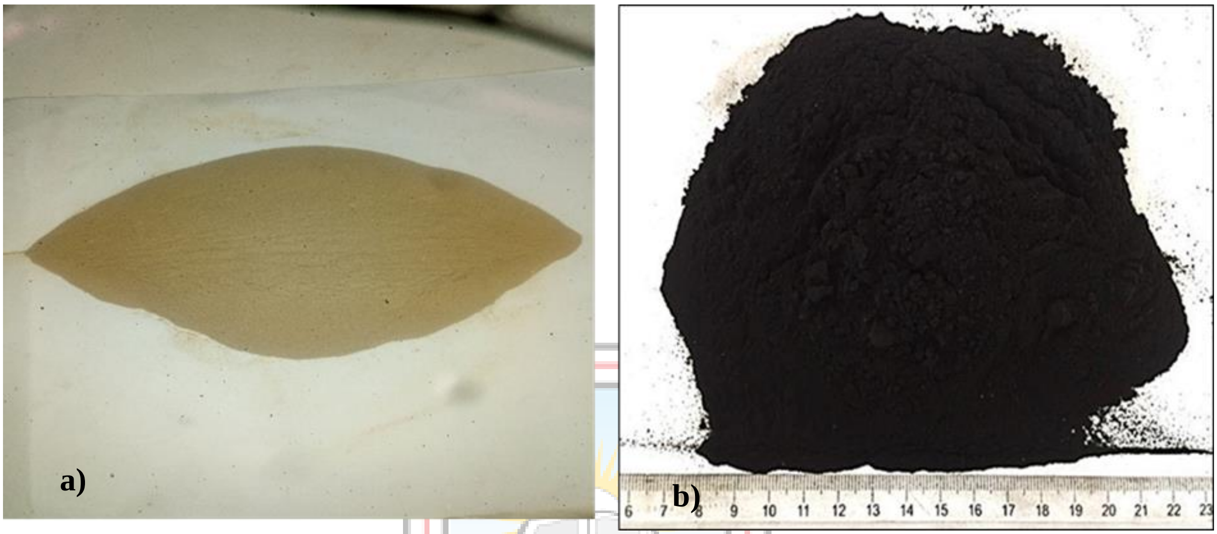


**Figure 3.2: Pulverised sample of Carbonaceous Materials generated from a) PET and b) ELT.**

## 3.4 Reducibility Procedure

### 3.4.1 Formation of pellets

Pellet is ore agglomerated by pelletising process. Pulverised sample of raw material is mixed with a binder and with the aid of water addition, is rolled into spherical ball, which is then dried, preheated, fired and cooled to become product pellets (Nomura *et al.*, 2015). In this work, pulverised iron ores (M1, M2, M3, M5) was mixed with pulverised sample of ELT or PET and flour and the mixture were pelletised into spherical form, then dried. For each iron ore, 10 pellets were produced. Sample M1 and M3 were mixed with ELT. Sample M2 and M5 were mixed with PET.

The total mass of each pellet was 30 g, which comprised 21 g of the iron ore, 8.4 g of carbonaceous materials, and 0.6 g of flour as the binding agent. The iron ore represents 70% of the whole pellet, whereas the reducing agent (ELT and PET) constituted 28% of the pellet. The rest (2%) is flour for pellet making. With aid of a bowl and water the iron ore-reducing agents, and flour were homogenized and shaped into a spherical ball. Figure (3.3) is a representative of Iron-Ore polymer composite pellet produced

### 3.4.2 Drying and weighing of pellets

In this work the method used to dry the pellets was natural air drying. It was done for 96 hours in open air to eliminate the water and further the moisture content. The mass of each pellet was determined before and after the reduction process using an electronic balance. After the reduction, a low intensity handheld magnet was used to separate the reduced metal from the associated slag and residual portions, the magnetic portion was weighed and recorded to calculate the weight loss and the extent of reduction of the different pellets.

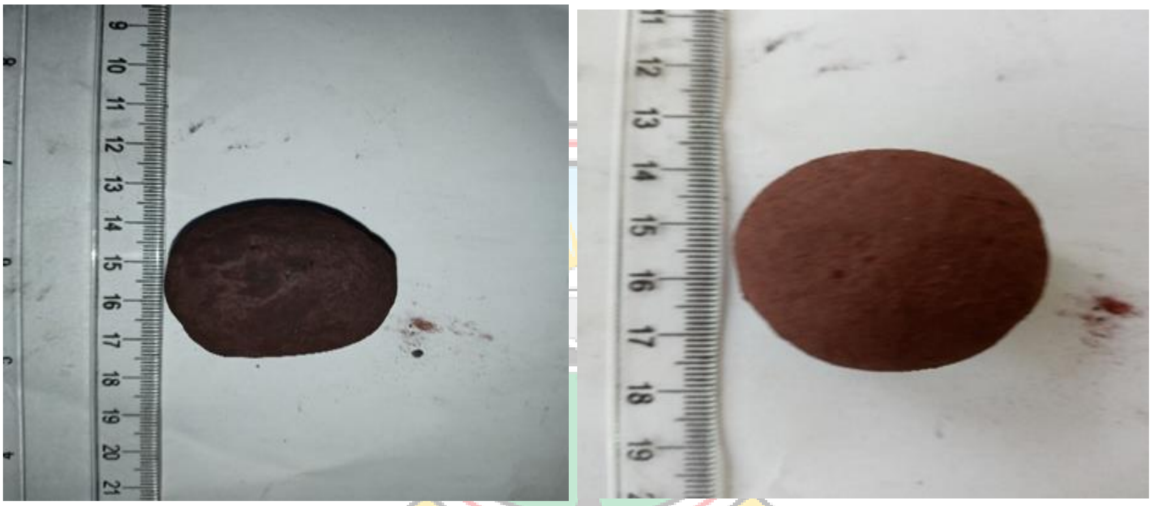


**Figure 3.3: Samples of Iron Ore-Polymer composite Pellets Produced from M5 and M1**

## 3.5 Microwave Reduction

Carbothermic reduction with microwave were conducted with a conventional microwave oven using 2450 MW, 50Hz Binatone as show in figure above.

The reduction of pellet was carried out at different times such as 15, 20, 30, 40, 50, and 60 minutes. At different time, single pellet of ore mixed with ELT or PET was placed into different crucible and then inside the microwave oven. It appears that during the reduction of iron ore pellet, some CO produced inside the microwave covers the pellet (mainly hematite), which leads to reduction from hematite to magnetite (Aguilar *et al.*, 1997). This magnetite is then reduced to wustite and finally to metallic iron. Figure 3.4 showing a firing of Iron Ore-polymer composite pellet in a domestic microwave.

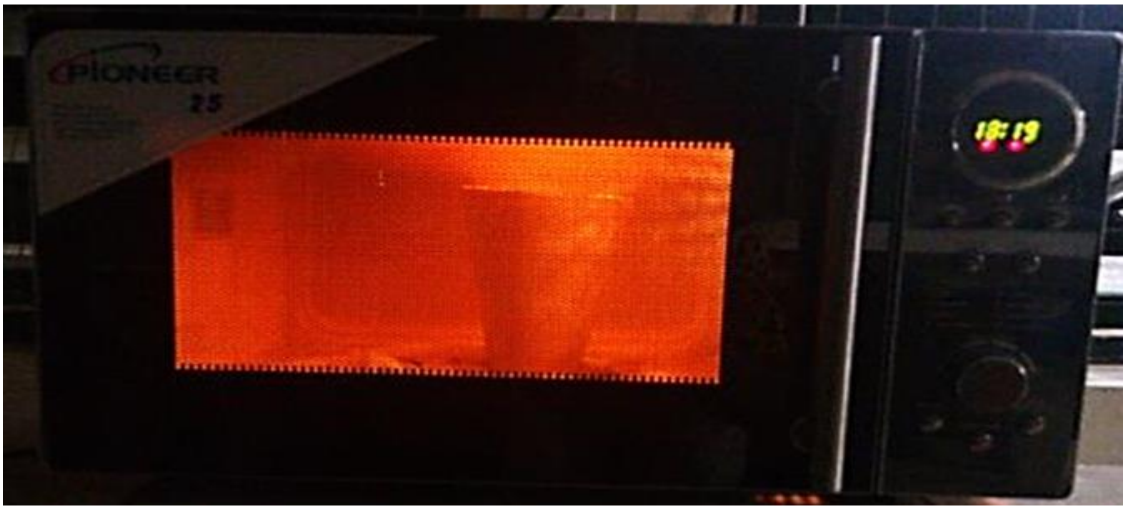


**Figure 3.4: Firing of Iron Ore-Polymer Composite Pellets in a Domestic Microwave Oven**

# CHAPTER FOUR

## RESULTS AND DISCUSSION

### 4.1 Microscopy of Mbalam Iron Ore

Iron ore from Mbalam are massive and banded. Figures 4.1 to 4.4 show photomicrographs of polish section of four different iron ore from Mbalam under plane polarised light. Figure 4.1 is the representation of iron ore 3 (M3) which shows a medium grained botryoidal texture. Under plane polarised light, figure 4.2 shows that the ore is rusty-red, with greyish tint and partially replaced by yellowish tint hematite. In Figure 4.3, third generation of tabula spharelite is partially replaced by hematite. Figure 4.4 the ore is clear white to bluish tint with ex-solution of bluish grey hematite which is also and ex solution of laminate spharelite.

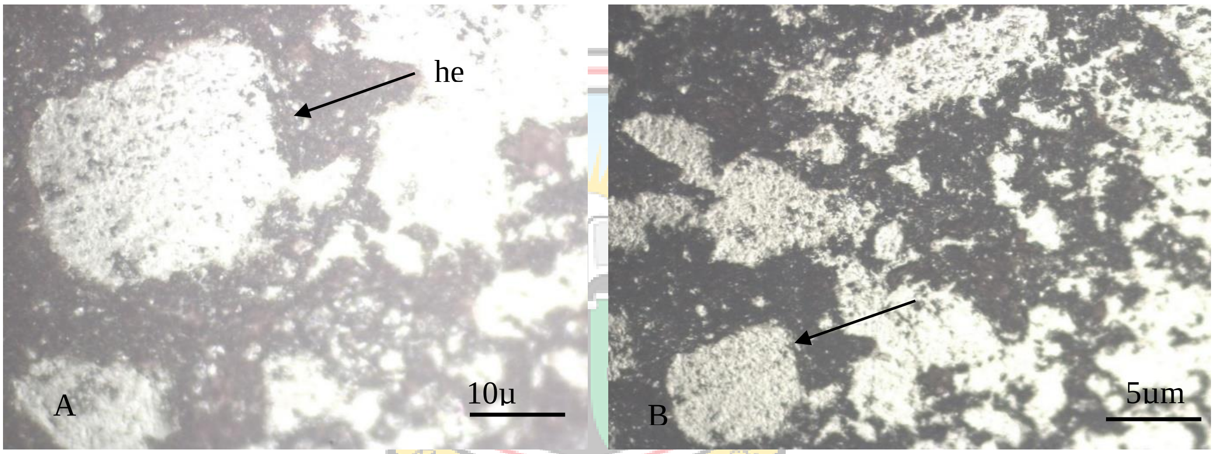


**Figure 4.1: Photomicrographs of Iron Ore 3 in A) Plane polarised light showing coarse grained with botryoidal texture. B) Crossed nicols.**

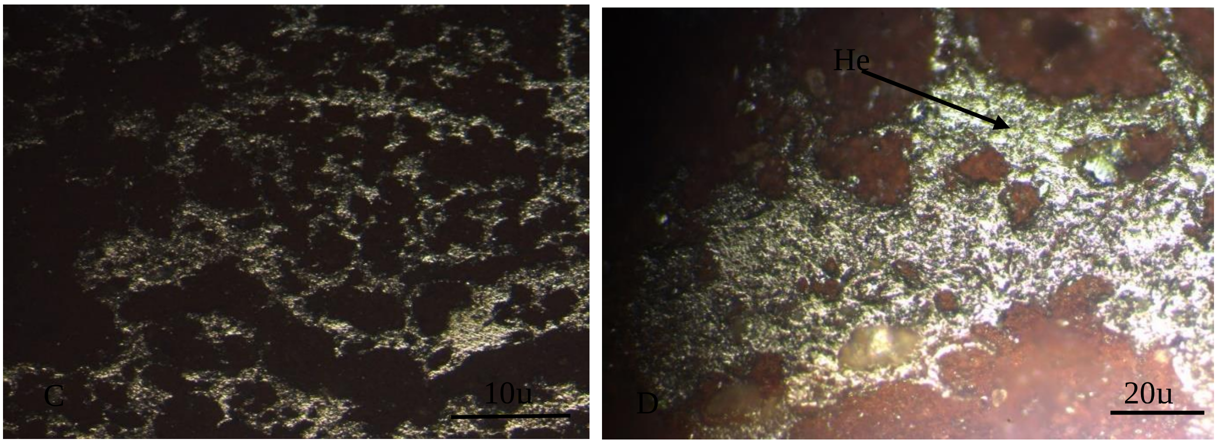


**Figure 4.2: Photomicrographs of Iron Ore 1 under C) Crossed polarised light, D) under Plane Polarised Light showing the replacement of reddish brown hematite by recrystallised hematite.**

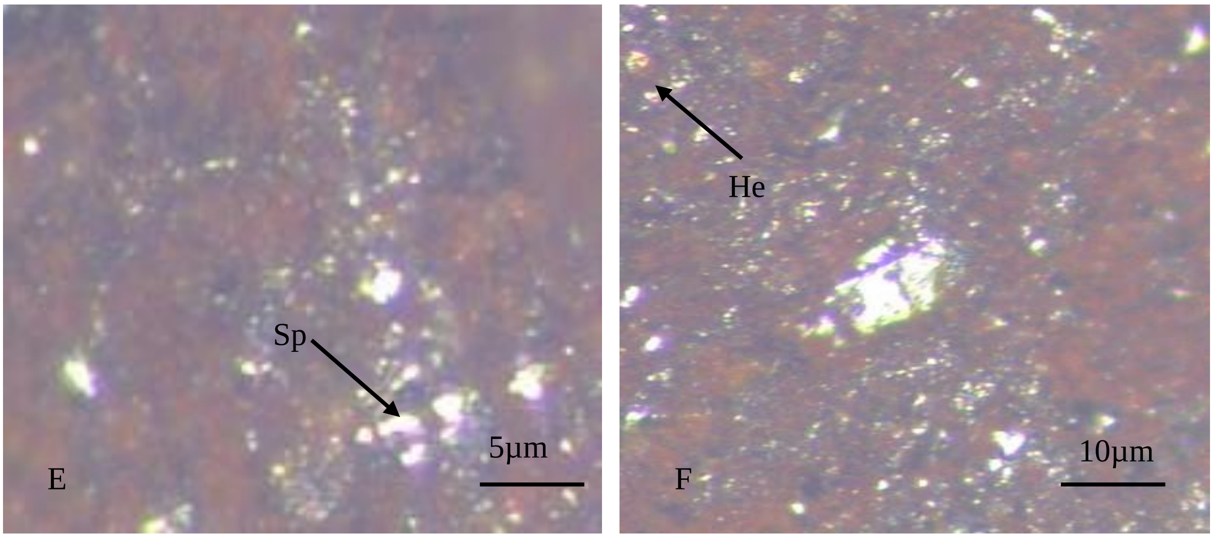


**Figure 4.3: Photomicrograph of Iron Ore 2 under Plane Polarised Light E and F) showing the spharelite partially replaced by reddish brown hematite**

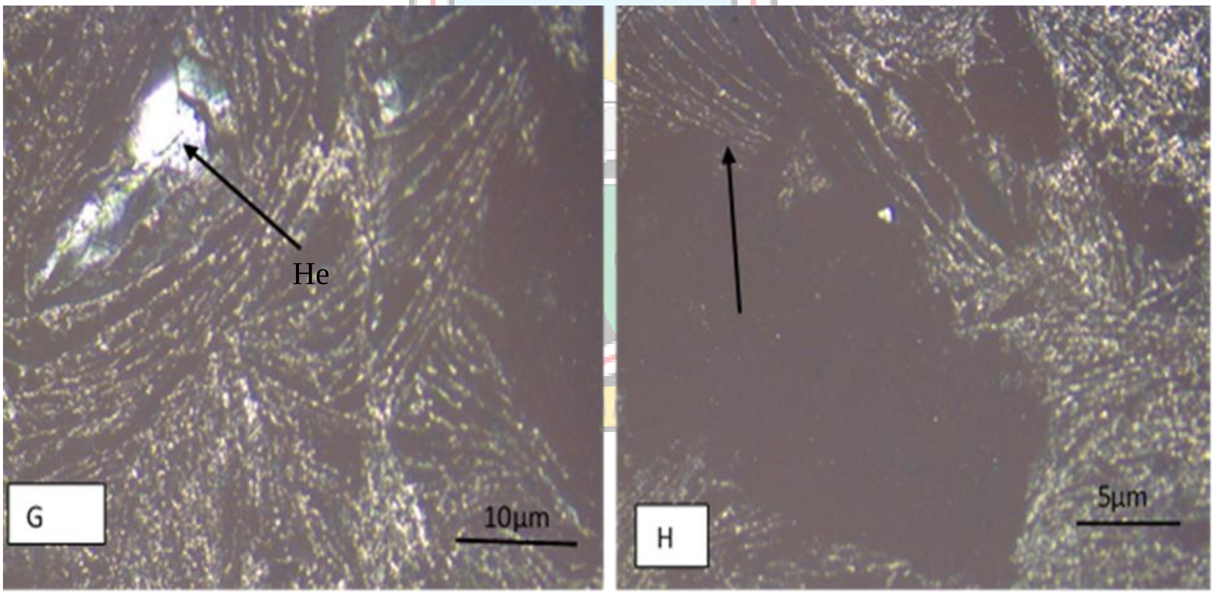


**Figure 4.4: photomicrograph of iron ore 5 under G) Plane Polarised Light, showing folds. H) Crossed polarised light.**

Petrography modal percentage analyses of Mbalam iron ores with polarising microscope is shown in Table 4.1. Meanwhile the ore present magnetite aspects and less correlation with hematite ore.

**Table 4.1: Modal Percentage of Mbalam Iron Ores using Polarising Microscope**.

| Mineral | Samples ID | | | |
|---|---|---|---|---|
| | Iron ore 1 | Iron ore 2 | Iron ore 3 | Iron ore 5 |
| Opaque oxide | - | - | - | 60 |
| Chlorite | - | - | - | 3 |
| Plagioclase | - | - | - | 5 |
| Quartz | - | - | - | - |
| Magnetite | 34 | 70 | 89 | 15 |
| Hematite | Trace | 5 | 1 | 10 |
| Sphalerite | 65 | 25 | 3 | |
| Pentlandite | 1 | - | - | - |
| Valleriite | - | - | 5 | - |
| Goethite | - | - | - | 7 |
| Total | 100 | 100 | 100 | 100 |

### 4.2 Geochemistry of Mbalam Iron Ores

Table 4.2 shows the results of the geochemical analysis of the Mbalam iron ores in weight percentages. The Mbalam iron ores 1, 2 and 5 exhibit high total iron oxide ($Fe_2O_3$) content of 96.56 wt.%, 97.35 wt.% and 96.83 wt.% respectively with corresponding low levels of silica of 0.46 wt.%, 1.58 wt.% and 1.58 wt.%. The Mbalam iron ores 1, 2 and 5 have alumina content of 0.46 wt.%, 0.23 wt.% and 0.28 wt.% respectively. The ores have low CaO and MgO content of < 0.01 wt.%.

Mbalam iron ore 3 has a medium iron oxide content of 55.10 wt.%, with relatively high $SiO_2$ content 44.37 wt.%, $Al_2O_3$ content 0.20 wt.% and with CaO < 0.01 wt.% and MgO of < 0.01 wt.% respectively.

In addition, the ores contain other impurities such as, $Na_2O$, $K_2O$, $TiO_2$, $V_2O_5$, $Cr_2O_3$, NiO

CuO, ZnO, SrO, $ZrO_2$, BaO, $HFO_2$, PbO and $Mn_3O_4$ which exist in considerably negligible amounts. The presence of high amount of silica in the Mbalam iron 3 poses great concerns because silica requires higher temperature for reduction. Hence the higher the silica content the higher the temperature required for reduction thus negative impact on reduction of hematite.

According to the results obtained from XRF analysis, it can be pointed out that the $SO_2$ and phosphorate contents in the Mbalam iron ores are considerably negligible. There is extremely low content of sulphur and phosphorus which are deleterious elements in the Mbalam iron ores. In iron and steel making, these elements have a great importance because a small amount can cause the iron to be brittle when hot or cold respectively.

According to Muwanguzi *et al.* (2012), phosphorate lowers the solidification temperature, increases fluidity, and renders the metal very fluid indirectly through the production of a low melting constituent in iron and steel making.

Generalised contents of $SiO_2$ and $Al_2O_3$ required in commercial iron ores are shown in Table 4.3.

It can be observed that the silica and alumina contents of the Mbalam iron ores 1, 2 and 5 are within the acceptable limits for commercial ores.However, Mbalam iron ore 3 has high silica content, which is above the acceptable level as contents of $SiO_2$ and $Al_2O_3$ in commercial ores should be less than 6 and 4%, respectively (Kiptarus *et al.*, 2015).

**Table 4.2: XRF Composition of the Mbalam Iron Ores**

| Component oxides | Composition (wt.%) | | | |
|---|---|---|---|---|
| | Iron Ore1 | Iron Ore 2 | Iron Ore 3 | Iron Ore 5 |
| $Na_2O$ | 0.05 | 0.03 | 0.08 | 0.1 |
| MgO | <0.01 | <0.01 | <0.01 | <0.01 |
| $Al_2O_3$ | 0.46 | 0.23 | 0.20 | 0.28 |
| $SiO_2$ | 0.46 | 1.58 | 44.37 | 1.57 |
| $P_2O_5$ | 0.12 | 0.05 | 0.03 | 0.06 |
| $SO_3$ | <0.01 | <0.01 | <0.01 | <0.01 |
| $K_2O$ | <0.01 | <0.01 | <0.01 | <0.01 |
| CaO | <0.01 | <0.01 | <0.01 | <0.01 |
| $TiO_2$ | <0.01 | <0.01 | <0.01 | <0.01 |
| $V_2O_5$ | <0.01 | <0.01 | <0.01 | <0.01 |
| $Cr_2O_3$ | <0.01 | 0.01 | <0.01 | 0.05 |
| $Mn_3O_4$ | <0.01 | <0.01 | <0.01 | 0.01 |
| $Fe_2O_3$ | 96.56 | 97.35 | 55.1 | 96.83 |
| NiO | <0.01 | <0.01 | <0.01 | 0.03 |
| CuO | 0.01 | 0.01 | <0.01 | 0.01 |
| ZnO | 0.03 | 0.03 | 0.02 | 0.01 |
| SrO | <0.01 | <0.01 | <0.01 | <0.01 |
| $ZrO_2$ | <0.01 | <0.01 | <0.01 | <0.01 |
| BaO | 0.01 | <0.01 | <0.01 | <0.01 |
| $HfO_2$ | <0.01 | <0.01 | <0.01 | <0.01 |
| PbO | <0.01 | <0.01 | <0.01 | <0.01 |
| L.O.I. | 0.41 | 0.18 | 0.24 | 0.46 |

The loss on ignition values 0.41 wt.%, 0.18 wt.%, 0.24 wt.% and 0.46 wt.% for the iron ores 1, 2, 3 and 5 respectively indicate low volatile matter (organic matter) in the ores. The silica content of the iron ore 3 can be removed or reduced to its barest minimum by pre-treating (washing and preheating) the ore before subjecting it to reduction process to minimise the energy required.

**Table 4.3: Average Percentages of Elements and Major oxides in Iron Ore**

| Components | Total Iron Content | | | $SiO_2$ | $Al_2O_3$ | P | S |
|---|---|---|---|---|---|---|---|
| | Low | Medium | High | | | | |
| Content Mass % | <58 | 62-64 | >65 | 6 | 3-4 | 0.05-0.07 | 0.1 |

**(Source: Kiptarus *et al.*, *2015*)**

### 4.3 X-Ray Diffraction (XRD) Analyses of Mbalam Iron Ores

Samples of the Mbalam iron ores were analysed by XRD analysis. The results in (Figures 4.5 to 4.8) showing that, the ore are predominantly composed of hematite in M1, M2, and M5. Figure 4.7 showing that, M3 has a high silica content.

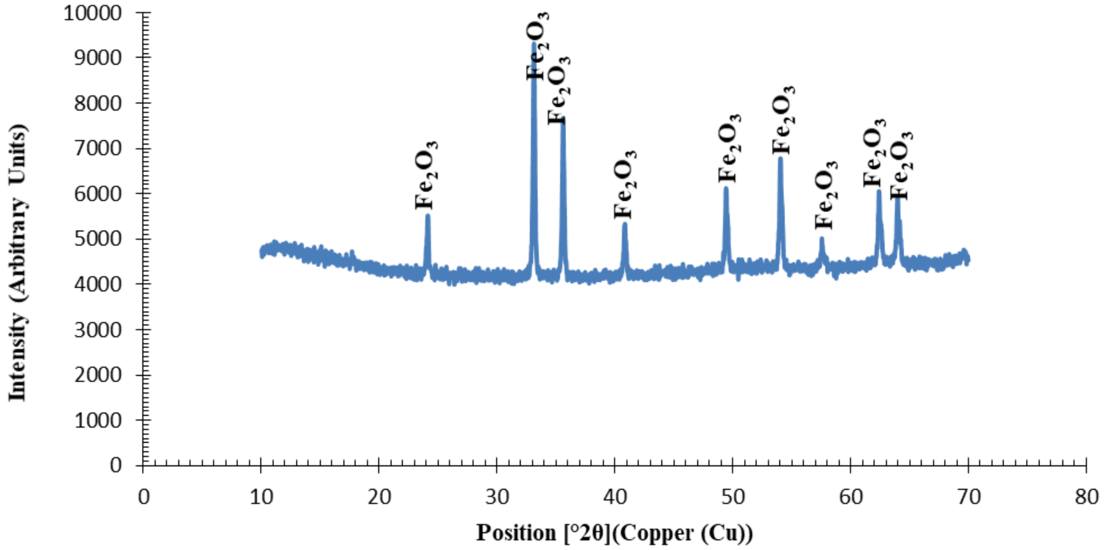


**Figure 4.5: XRD of Mbalam Iron Ore 1**

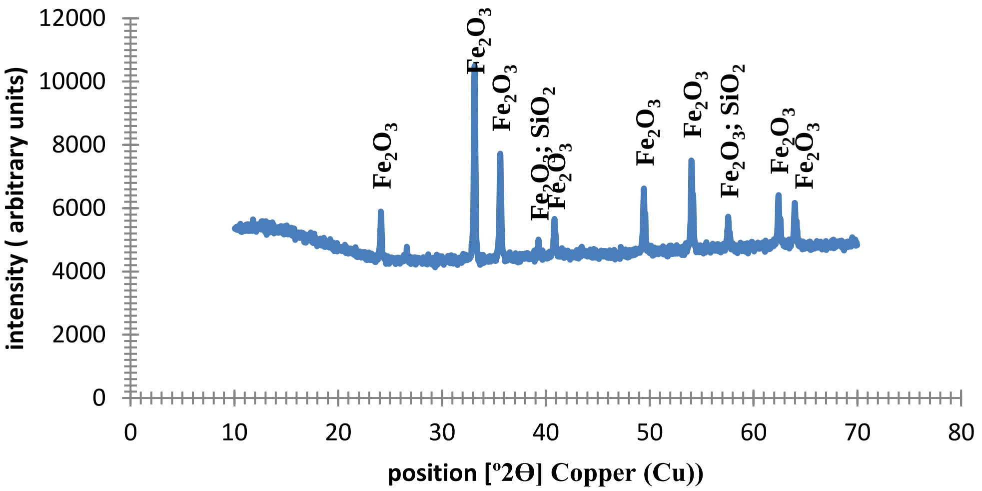


**Figure 4.6: XRD of Mbalam iron ore 2**

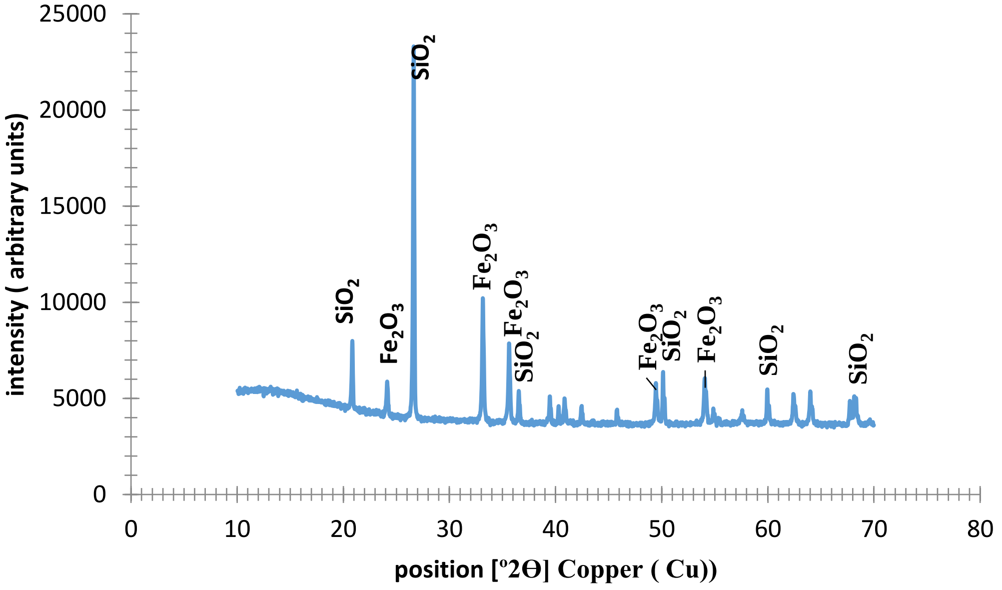


**Figure4.7: XRD of Mbalam iron ore 3**

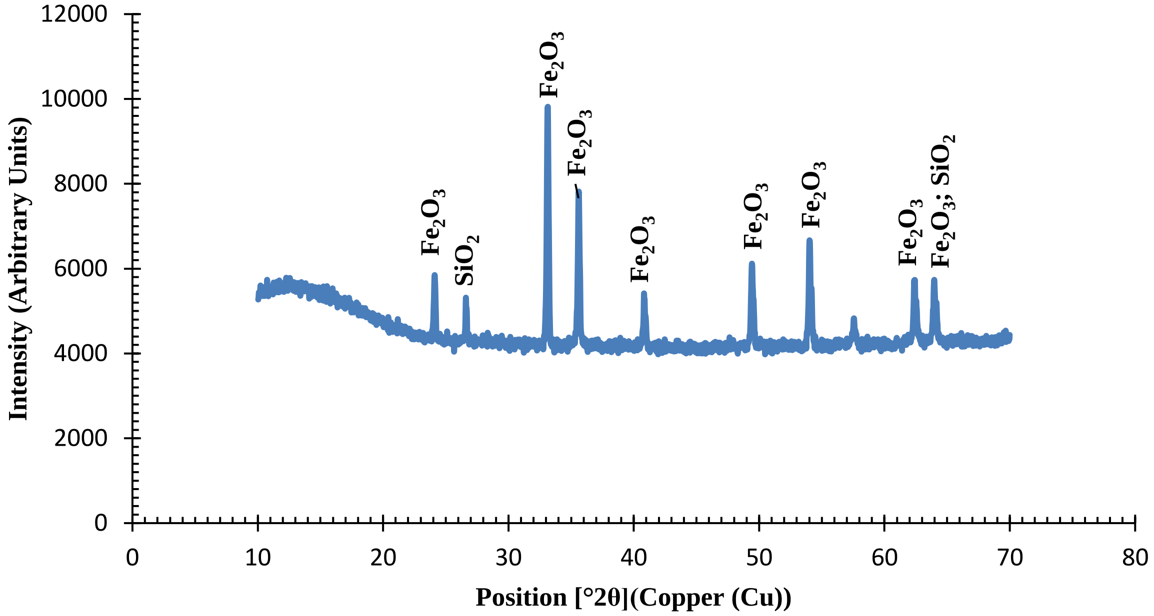


**Figure 4.8: XRD of Mbalam iron ore 5**

Grades of Iron ore are classified according to their Fe content. An iron ore is said to be of high grade when its Fe content is more than 65 wt.%, low grade when its Fe content is less than 58 wt.%, and medium grade when its Fe content is between 62 wt.% and 64 wt.% (Kiptarus *et al.*, 2015; Muwanguzi *et al*., 2012).

### 4.3.1 SEM/EDS Analyses of Mbalam Iron Ores

Results of SEM/EDS analyses of the Mbalam iron ores are shown in figures 4.9 to 4.12 and Tables 4.3, to 4.6 for the four iron ores 1, 2, 3 and 5 respectively and-indicated Fe content of 67.49 wt.%, 68.08 wt.%, 38.51wt.% and 67.72 wt.%, respectively for the ores. The potential for worldwide commercial exploitation of the Mbalam iron ores is very high. Comparing these values to the world's iron ore classification in Table 4.3, the Mbalam iron ores corresponds to high-grade iron ore (averagely 84 wt.% which is more than 65 wt.%).

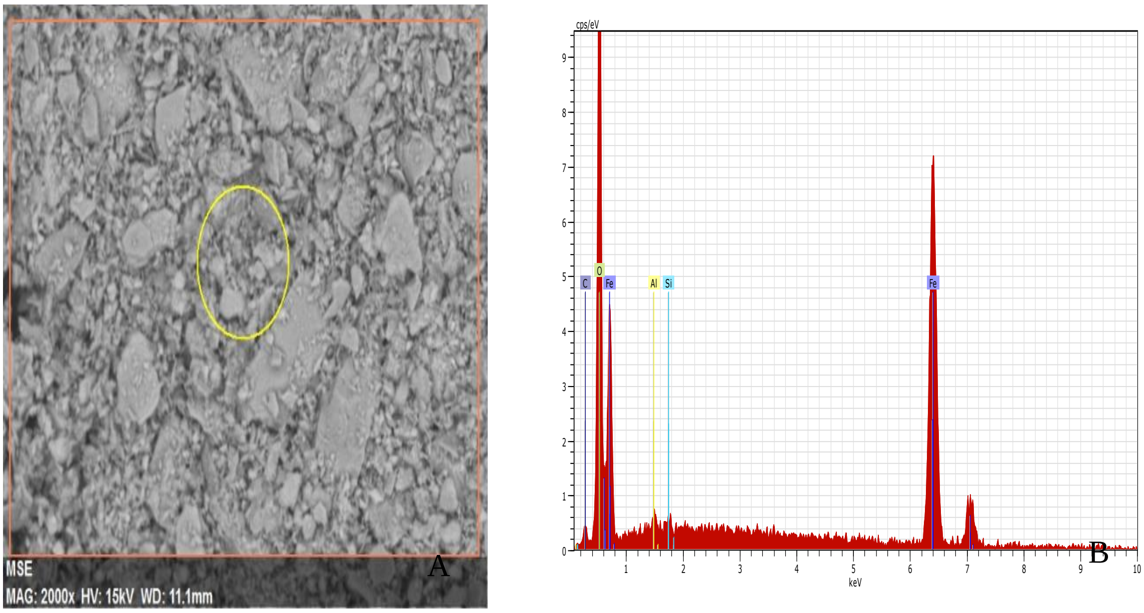


**Figure 4.9 SEM/EDS Analysis for Mbalam Iron Ore 1**.

The ore is subangular and moderately sorted. B) It presents high atomic percentage of oxygen followed by Fe and low intensity of carbon. Table 4.4 shows the elemental composition of Mbalam iron 1.

**Table 4.4: SEM/EDs Analysis for Mbalam Iron Ore 1**

| **Element (K-series)** | **Weight %** | **Atomic %** |
|---|---|---|
| Fe | 67.49 | 36.88 |
| O | 29.17 | 55.93 |
| C | 2.40 | 6.1 |
| Si | 0.33 | 0.35 |
| Al | 0.61 | 0.67 |
| **Total** | **100** | **100** |

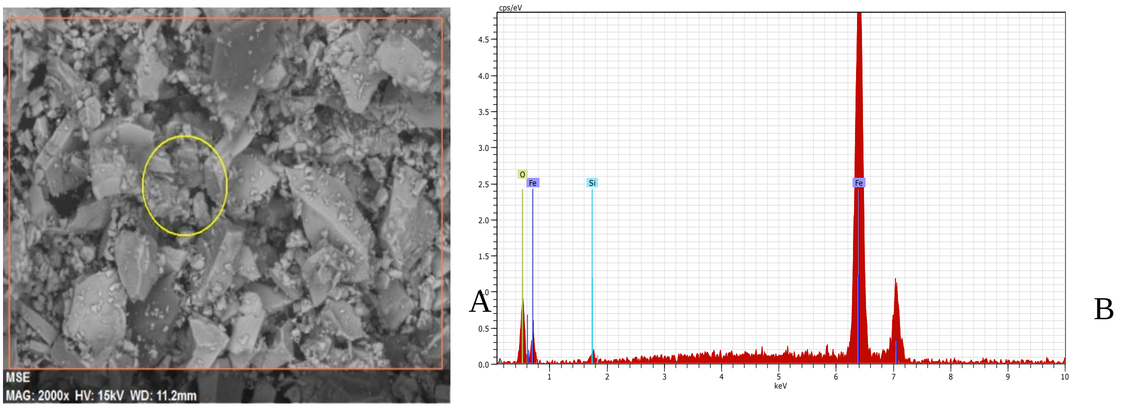


**Figure 4.10 SEM/EDS Analysis for Mbalam Iron Ore 2**

The ore is spherical and is composed of both coarse and fine grains. Table 4.5 shows the elemental composition of the ore.

**Table 4.5: SEM/EDS Analysis for Mbalam Iron Ore 2**

| **Element (K-series)** | **Weight %** | **Atomic %** |
|---|---|---|
| Fe | 68.08 | 38.90 |
| O | 28.68 | 57.55 |
| Si | 3.24 | 3.55 |
| **Total** | **100** | **100** |

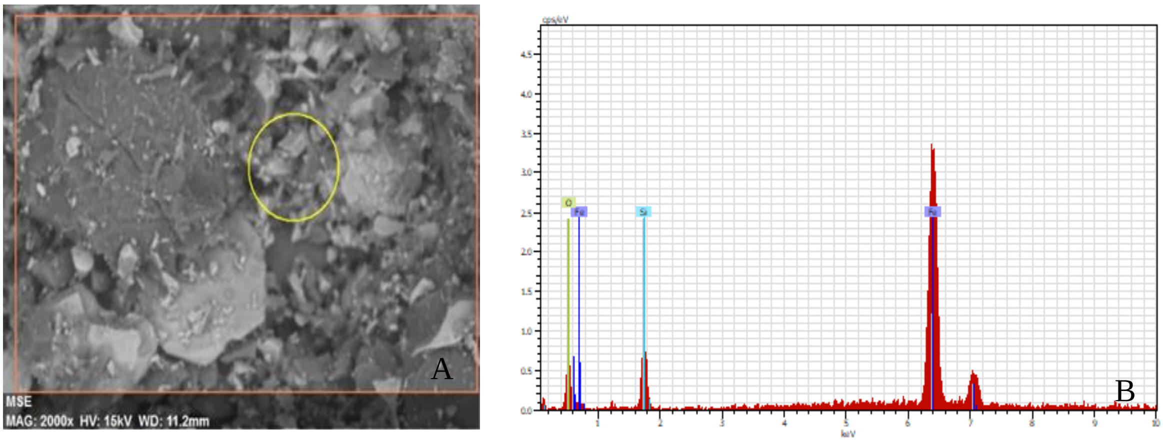


**Figure 4.11 SEM/EDS Analysis for Mbalam Iron Ore 3**

The ore presents an inequigranular textures with subangular shapes. Table 4.6 shows that it has a high amount of Fe and little amount of Oxygen and Silicon

**Table 4.6 SEM/EDS Analysis for Mbalam Iron Ore 3**

| **Element (K-series)** | **Weight %** | **Atomic %** |
|---|---|---|
| Fe | 38.51 | 15.81 |
| O | 53.54 | 77.67 |
| Si | 7.88 | 6.51 |
| **Total** | **100** | **100** |

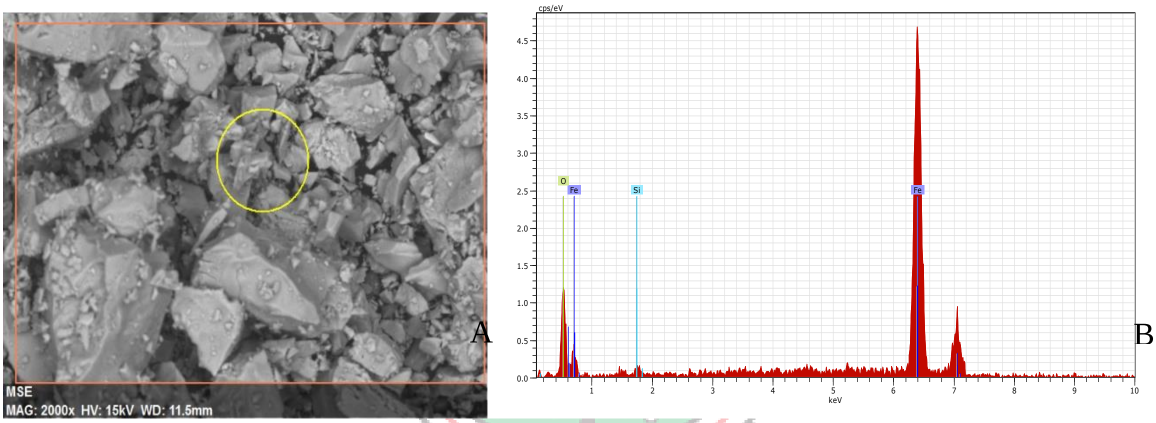


**Figure 4.12 SEM/EDS Analysis for Mbalam Iron Ore 5**

The ore presents both fine and coarse grained with spherical shape. Table 4.7 below shows elements in this ore.

**Table 4.7: SEM/EDS Analysis for Mbalam Iron Ore 5**

| **Element (K-series)** | **Weight %** | **Atomic %** |
|---|---|---|
| Fe | 67.72 | 37.93 |
| O | 31.14 | 60.81 |
| Si | 1.14 | 1.25 |
| **Total** | **100** | **100** |

Comparing the chemical composition of Mbalam iron ores to the commercial chemical composition requirement of various ironmaking process routes in Table 4.8, it is seen that the

Mbalam iron ores fall in all the various process routes. The XRF composition of FeO total in the Mbalam iron ores (1 to 5) are 65.67 wt%, 92.13 wt%, 86.69 wt% and 91.25 wt%, respectively. These, are all above the values of Fe content for Corex (65.0%), BF (62-65.0%), Midrex (67.0%), HYL (65.5%) and Rotary Kiln (64.0%).

The gangue and LOI of iron ores 1, 2 and 5 fall within the commercial process route requirement. This information indicates that Mbalam iron ores 1, 2 and 5 are suitable for any of the process routes stated above. However, the gangue content for the Mbalam iron ore 3 falls short of the commercial process route, indicating the Mbalam iron ore 3 is not suitable for any of the process routes stated.

**Table 4.8: Commercial Requirement for Various Ironmaking Process Routes**

| **Process** | **Fe Content (%)** | **Gangue ($SiO_2$+$Al_2O_3$) (%)** | **LOI (%)** |
|---|---|---|---|
| Corex | 65.0 min | 4.0 max | - |
| BF | 62-65 min | 6.0 max | 2.0 max |
| DRI-Midrex | 67.0 min | 3.2 max | 1.5 max |
| DRI-HYL | 65.5 min | 2.2 max | 1.5 max |
| DRI- Rotary Kiln | 64.0 min | 4.0 max | - |

**Source: (Dankwah, 218).**

### 4.4 Mechanism and Proposed Reactions of the Reduction Studies

In microwave heating, energy is delivered directly to the iron-carbon composite pellet through molecular interaction with the electromagnetic field. Heating of the iron carbon composite pellet is due to the transfer of electromagnetic energy to thermal energy. The mechanism is energy conversion rather than heat transfer. Microwaves transfer energy throughout the whole iron-carbon composite pellet volume. Heat is generated throughout the volume of the iron-carbon composite pellet resulting in volumetric heating. PET as reductant produces a mixture of gaseous hydrocarbons especially methane ($CH_4$) which is a gaseous reductant. The energy builds up at the core of the pellet and cause thermal decomposition of $CH_4$ into carbon and hydrogen and the reformation of carbon monoxide and hydrogen (Equation 4.2, 4.3 and 4.4) which causes subsequent reduction of the iron oxide.

PET which is a polymer is converted into methane and other hydrocarbons

$Polymer \rightarrow CH_{4\,(g)}$ (4.1)

The thermal decomposition of methane into carbon and hydrogen or reformation into CO and $H_2$

$CH_{4\,(g)} = C_{(s)} + 2H_{2\,(g)}$ (4.2)

$CH_{4\,(g)} + CO_{2\,(g)} = 2CO_{(g)} + 2H_{2\,(g)}$ (4.3)

$CH_{4\,(g)} + H_2O_{(g)} = CO_{(g)} + 3H_{2\,(g)}$ (4.4)

ELT(s) after charring mainly contains solid carbon. The reduction of iron ore by carbon is one of the most important reactions in iron making.

The volumetric heating occurs from the inner core to the outer of the composite pellets. Reduction begins at the core of the pellet by the solid carbon and gases of CO and $CO_2$ begin to evolve from the thermal decomposition of ELT in the iron ore-ELT composite pellet. These gases diffuse across the layers of the pellets and as this occurs unreacted carbon reacts with carbon dioxide ($CO_2$) through the Boudouard reaction ($CO_2 + C = 2CO$) to produce carbon monoxide (CO) which is also a reducing gas. This carbon is at the nano-scale and can easily be picked by the metal and subsequently causing melting and solidification of melt into spherical shapes. Charred ELT used in this work contains a fixed carbon of 29. 86% which is an important factor in the reduction of iron oxide. The reaction that occurs when iron oxide is reduced to metallic iron is detailed in equations (4.5-4.16). The possible reaction implies that solid form of reductant (C) and gaseous forms ($H_2$, CO, $CH_4$) all play major role in the reduction of Mbalam iron ore.

The reduction of $Fe_2O_3$ by carbon to produce Fe

$Fe_2O_3 + \frac{1}{3}C = \frac{2}{3}Fe_3O_4 + \frac{1}{3}CO$ (4.5)

$Fe_3O_4 + C = 3FeO + CO$ (4.6)

$FeO + C = Fe + CO$ (4.7)

The reduction of $Fe_2O_3$ by hydrogen to produce Fe

$Fe_2O_3 + \frac{1}{3}H_2 = \frac{2}{3}Fe_3O_4 + \frac{1}{3}H_2O$ (4.8)

$Fe_3O_4 + H_2 = 3FeO + H_2O$ (4.9)

$FeO + H_2 = Fe + H_2O$ (4.10)

The reduction of $Fe_2O_3$ by carbon monoxide to produce Fe

$Fe_2O_3 + \frac{1}{3}CO = \frac{2}{3}Fe_3O_4 + \frac{1}{3}CO_2$ (4.11)

$Fe_3O_4 + CO = 3FeO + CO_2$ (4.12)

$FeO + CO = Fe + CO_2$ (4.13)

Some side reactions that also occur

Water gas shift reaction: $H_2O_{(g)} + CO_{(g)} = H_{2(g)} + CO_{2(g)}$ (4.14)

Gasification of C by $H_2O$: $H_2O_{(g)} + C_{(s)} = H_{2(g)} + CO_{(g)}$ (4.15)

Gasification of C by $CO_2$ (Boudouard reaction): $CO_{2(g)} + C_{(s)} = 2CO_{(g)}$ (4.16)

## 4.5 Results of Studies on the Reduction of Mbalam Iron by PET and ELT

### 4.5.1 Introduction

In any reduction process, the rate at which the iron oxide can be reduced to metallic iron is the primary determinant of the rate of the production (Muwanguzi, 2012). Parameters used in this work are: mass of pellets (before and after), percent weight loss estimation and extent of reduction.

Before and after reduction, the mass of each pellet was measured and recorded. Determination of the weight loss and its corresponding percent reduction was calculated for each individual pellet. Table 4.8 shows the calculation of percent reduction for samples M1, M2, M3 and M5.

### 4.5.2 Extent of reduction

The extent of reduction depended on the redox potentials of the Fe (III) compounds (Bauer, I *et al.*, 2009). The kinetics of the reduction of iron ore generally involve a study of the rate of iron oxide conversion to metallic iron by the removal of oxygen. It is proportional to percentage weight loss and temperature. It was calculated for each pellet at different times

(20, 30, 40, 50, and 60 minutes). Independently of the reducing agents used, the extent of reduction ranges from 30.5% at 20 minutes to 93% at 40 minutes. Figures 4.13 and 4.14, illustrate the graph of extent of reduction of each samples M1 and M5, respectively.

**% Weight Loss = (Weight loss / Weight before)* 100**

**Extent of reduction = % Weight loss / 0.5481**

**Table 4.9: Extent of reduction values of sample with ELT and PET**

| Times(min) | Weight | | | | Extent of Reduction |
|---|---|---|---|---|---|
| | Weight Before | Weight After | Weight Loss | % Weight Loss | |
| M1+ ELT | | | | | |
| 20 | 27.1 | 19 | 8.1 | 29.89 | 54.53 |
| 30 | 26.7 | 14 | 12.7 | 47.57 | 86.78 |
| 40 | 25.5 | 13.5 | 12 | 47.06 | 85.86 |
| 50 | 27.2 | 16.5 | 10.7 | 39.34 | 71.77 |
| 60 | 30.2 | 14.8 | 15.4 | 50.99 | 93.04 |
| M2+ PET | | | | | |
| 20 | 29.5 | 16.8 | 12.7 | 43.05 | 78.55 |
| 30 | 28.4 | 15.8 | 12.6 | 44.37 | 80.95 |
| 40 | 28.9 | 15.3 | 13.6 | 47.06 | 85.86 |
| 50 | 29 | 14.2 | 14.8 | 51.03 | 93.11 |
| 60 | 29.3 | 14.4 | 14.9 | 50.85 | 92.78 |
| M3+ELT | | | | | |
| 20 | 30 | 24.9 | 5.1 | 17 | 31.02 |
| 30 | 28.1 | 23.4 | 4.7 | 16.73 | 30.52 |
| 40 | 29.9 | 20.8 | 9.1 | 30.43 | 55.53 |
| 50 | 27.2 | 18.7 | 8.5 | 31.25 | 57.02 |
| 60 | 27.8 | 18.6 | 9.2 | 33.09 | 60.38 |
| M5+PET | | | | | |
| 20 | 29 | 16 | 13 | 44.83 | 81.79 |
| 30 | 28.5 | 15.2 | 13.3 | 46.67 | 85.14 |
| 40 | 29.2 | 14.9 | 14.3 | 48.97 | 89.35 |
| 50 | 28.8 | 14.1 | 14.7 | 51.04 | 93.12 |
| 60 | 29 | 14.2 | 14.8 | 51.03 | 93.11 |

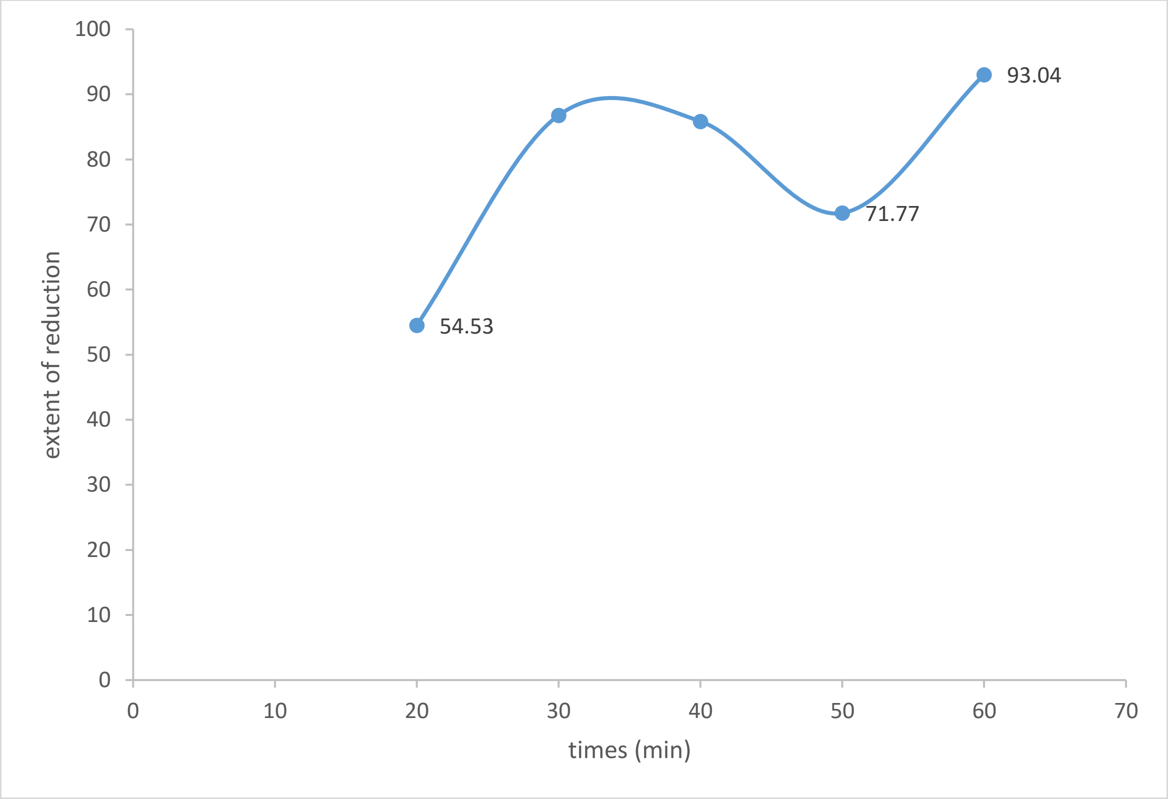


Figure 4.13: Extent of Reduction of M1 ore with ELT

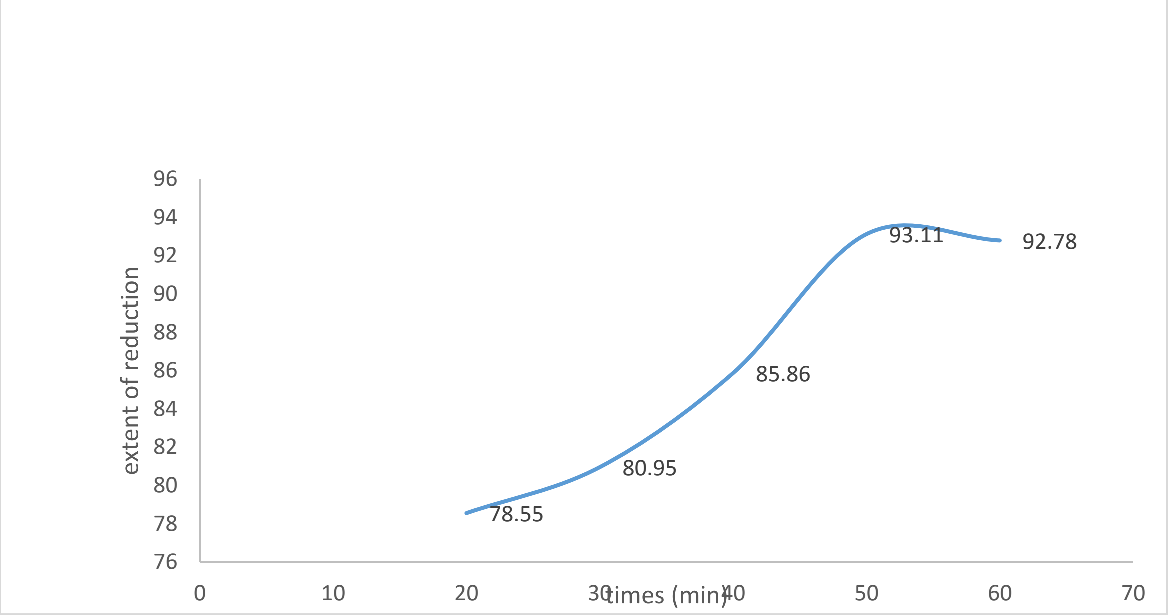


Figure 4.14: Extent of Reduction of M5 ore with PET

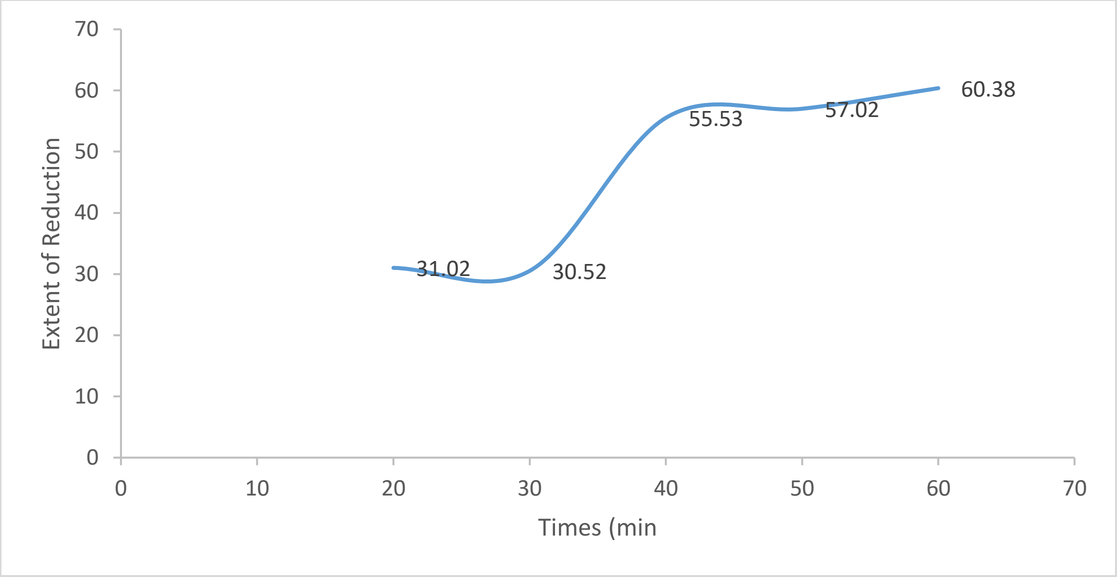


**Figure 4.15: Extent of Reduction of M3 with ELT**

### 4.5.3 Nature of Metal Produced

Reduced metals were obtained from various particle sizes deployed in the reduction studies. The reduced metal produced from the Mbalam iron ore using rubber tyre as a reducing agent were spherical. These spheres of metal were embedded in the slag phase of the reduced material and have to be subjected to breakage to free the spherical metals. Physical separation of the mixture of reduced metals and slag components was done using a low-intensity handheld magnet. The spherical nature of the reduced metal could be attributed to the excess carbonaceous material present in the iron ore-carbon mixture causing reduced iron to pick up or absorb these excess carbons causing the reduced iron to melt at a lower temperature into a molten mass that solidifies into a sphere when the microwave power is put off. According to the iron-carbon system (Figure 4.5) the melting point of iron changes from 1538 ˚C to about 1147 ˚C when the carbon content in iron is about 4.30 wt.%.

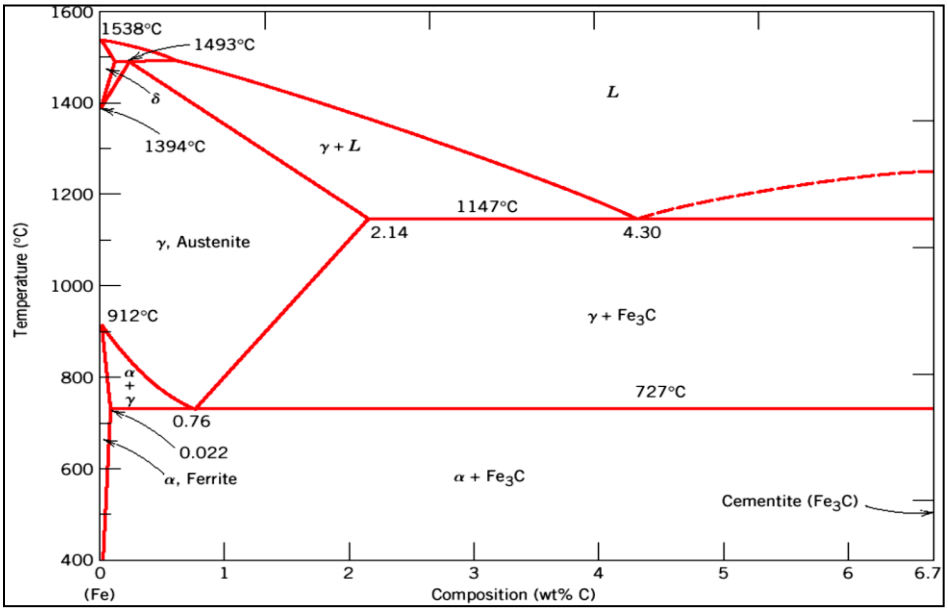


**Figure 4.16: Iron-carbon phase diagram. Source (Dankwah, 218).**

Reduced metals obtained from the Mbalam iron ore using PET were like iron filings in nature without any distinct difference between the reduced metal and slag component as observed in reduced metals of the Mbalam iron ore using rubber tyre as reductant. A low-intensity handheld magnet was used to separate the reduced metal from a pool of unreacted reductant. Figure 4.17 and 4.18 below show a photograph of metals produced from the Mbalam Iron ore using rubber tyre and PET as reductants respectively.

**Figure 4.17: Reduced Metal Produced from Mbalam Iron Ore 1 Using ELT as Reducing Agent**

**Figure 4.18: Reduced Metal Produced from Mbalam Iron Ore 3 Using PET as Reducing Agent.**

### 4.5.4 XRF and XRD analysis of the metal produced

XRF analysis of six iron ore samples produced with both ELT and PET at different times were carried out and the results shows that Fe is the major element with an average of 92.30%. The silica concentration of the metal produced ranges from 1.84 to 2.16%. Table 4.10 and 4.11 present the major and minor oxide percentage of some iron produced. From Figures 4.19 and 4.20, the XRD analysis showed that the reduction process is essentially complete. The $Fe_2O_3$ and $SiO_2$ contents in the ore decreased. Figure 4.22 showed that the carbon still remains associated with Fe.

**Table 4.10: Chemical Analysis for Major Elements (wt.%) of iron produced**

| | INSTRUMENT: EPSILON ED-XRF (MINIAN Software) | | | | | |
|---|---|---|---|---|---|---|
| Major Oxides | | | | | | |
| Sample ID | Sample17 | Sample18 | Sample19 | Sample20 | Sample21 | Sample22 |
| %Mg | 0.03 | 2.13 | 0.00 | 2.70 | 0.00 | 2.57 |
| %Al | 0.44 | 2.04 | 0.67 | 2.12 | 0.72 | 1.44 |
| %Si | 1.51 | 2.16 | 1.87 | 1.84 | 1.96 | 1.86 |
| %P | 0.10 | 0.07 | 0.02 | 0.13 | 0.03 | 0.13 |
| %S | 2.29 | 0.70 | 2.19 | 0.78 | 1.51 | 1.61 |
| %K | 0.04 | 0.20 | 0.00 | 0.08 | 0.00 | 0.13 |
| %Ca | 0.01 | 0.92 | 1.01 | 1.10 | 1.05 | 1.46 |
| %Ti | 0.01 | 0.39 | 0.00 | 1.64 | 0.00 | 0.00 |
| %Mn | 0.11 | 0.34 | 0.02 | 0.07 | 0.02 | 0.01 |
| %Fe | 95.33 | 89.37 | 94.21 | 89.46 | 94.69 | 90.77 |
| **SUM** | **99.88** | **98.34** | **99.98** | **99.92** | **99.98** | **99.98** |

**Table 4.11: minor Oxide Percentage in Mbalam iron produced**

| **Minor Oxides** | | | | | | |
|---|---|---|---|---|---|---|
| **Sample ID** | **Sample17** | **Sample18** | **Sample19** | **Sample20** | **Sample21** | **Sample22** |
| **$V_2O_5$** | 0.0825 | 0.0000 | 0.0000 | 0.0532 | 0.0000 | 0.0000 |
| **$Cr_2O_3$** | 0.0234 | 0.1043 | 0.0147 | 0.0132 | 0.0136 | 0.0054 |
| **Rb2O** | 0.0063 | 0.0050 | 0.0013 | 0.0063 | 0.0015 | 0.0090 |
| **SrO** | 0.0000 | 1.3597 | 0.0018 | 0.0000 | 0.0011 | 0.0009 |
| **$Y_2O_3$** | 0.0018 | 0.0000 | 0.0012 | 0.0000 | 0.0014 | 0.0000 |
| **$ZrO_2$** | 0.0000 | 0.0302 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **$Nb_2O_5$** | 0.0000 | 0.0028 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **$SnO_2$** | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **$WO_3$** | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **ThO2** | 0.0000 | 0.0145 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **$U_3O_8$** | 0.0055 | 0.0000 | 0.0014 | 0.0043 | 0.0015 | 0.0076 |
| **SUM** | **0.1222** | **1.6595** | **0.0215** | **0.0807** | **0.0209** | **0.0237** |

| | |
|---|---|
| **S17** | **M2+ ELT 40 min** |
| **S18** | **M2+ PET 50 min** |
| **S19** | **M3+ ELT 40 min** |
| **S20** | **M5+ PET 50 min** |
| **S21** | **M1+ PET 50 min** |
| **S22** | **M1+ ELT 60min** |

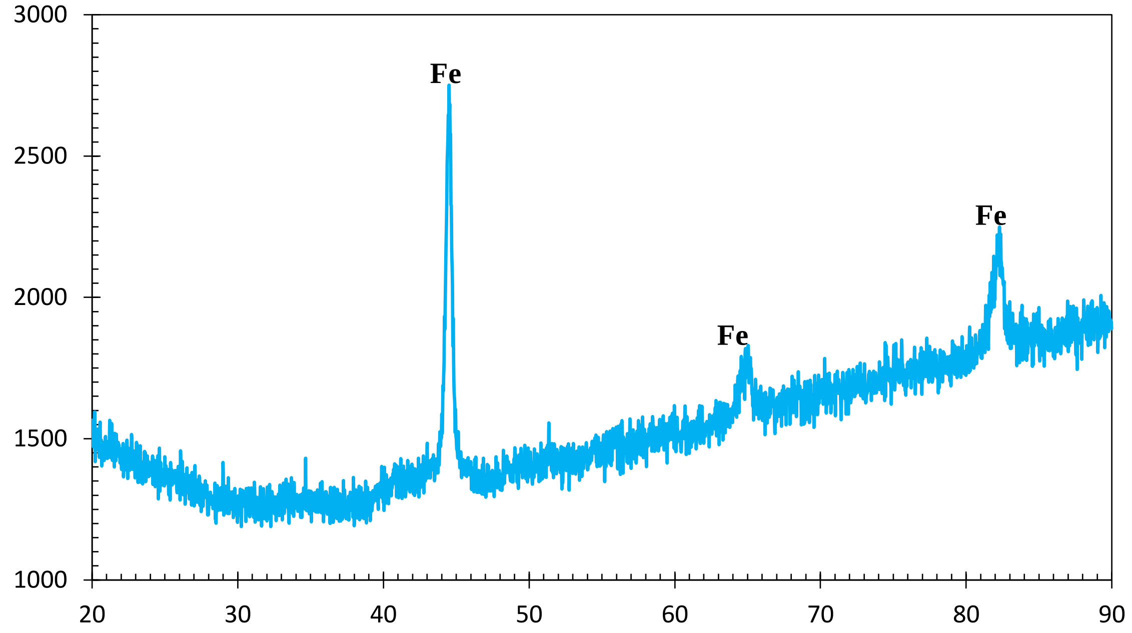


Figure 4.19: X ray diffractogram of metal 2 (sample 17)

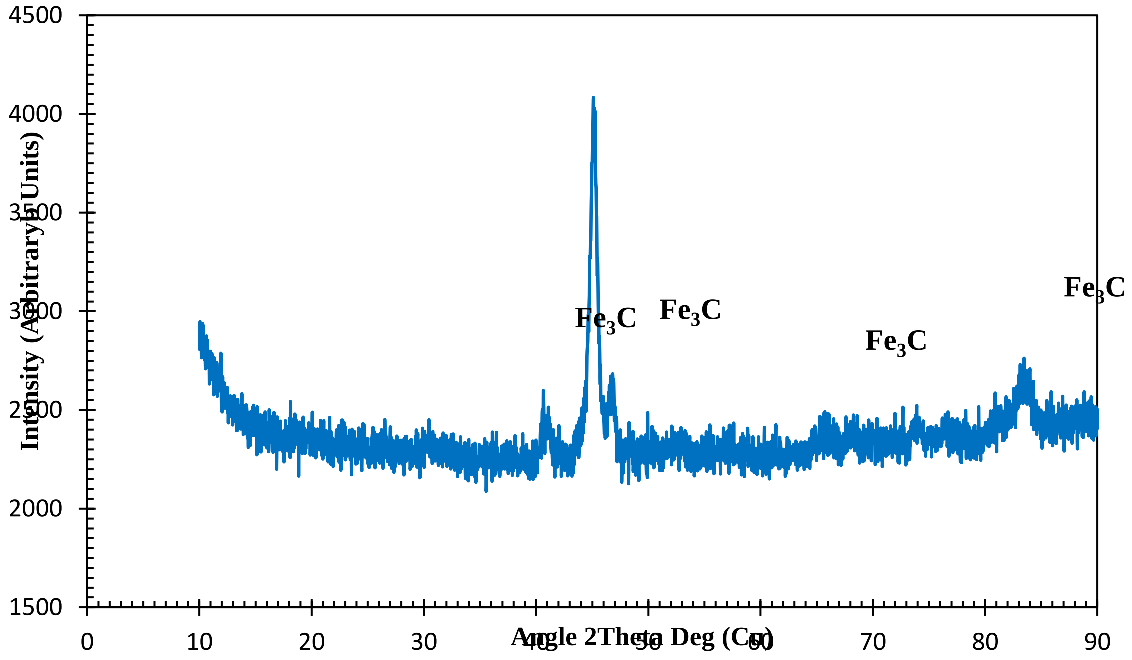


Figure 4.20: X-ray diffractogram of metal 1 (sample 22)

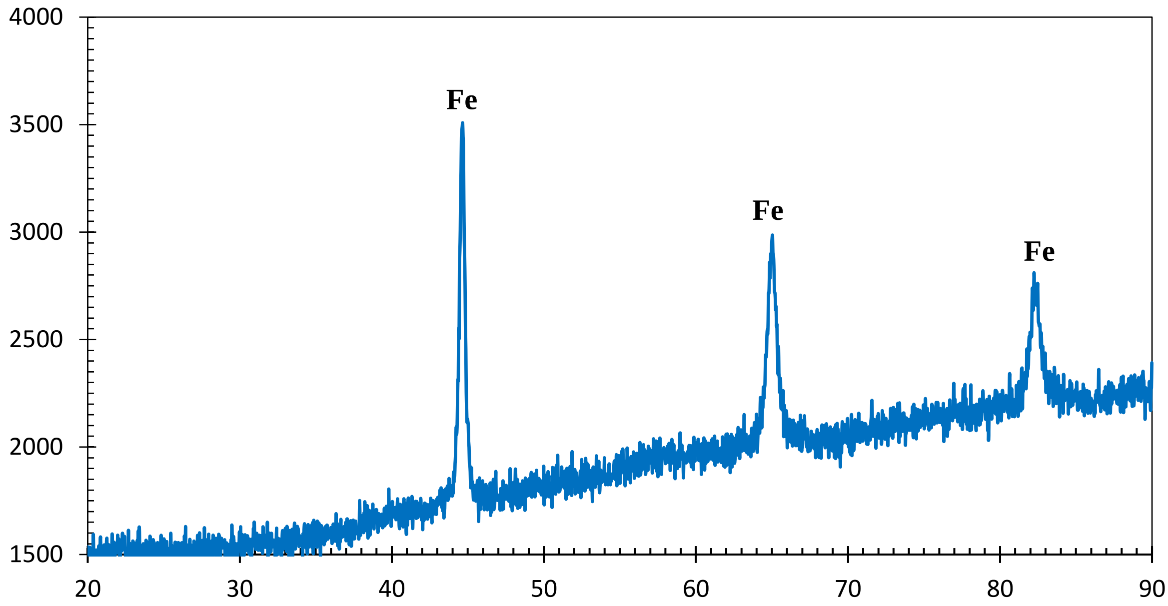


Figure 4.21: X-ray diffractogram of metal 5 (sample 21)

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Production of metallic iron from Mbalam iron ore has been investigated using end-of-life tyre (ELT) and End-of-Life plastics (PET) as reductants through microwave technology. Obtained results and the different aspects discussed permit the following conclusions:

- The mineralogical analyses of Mbalam iron ores comprise magnetite partially replaced by spharelite and/or hematite.
- The Mbalam iron ores contain total iron oxide ($Fe_2O_3$) content of iron 1, 2 and 5 96.56 wt.%, 97.35 wt.% and 96.83 wt.% respectively with correspondingly low levels of silica of 0.46 wt.%, 1.58 wt.% and 1.58 wt.% respectively. Iron ore 3 (M3) has a medium hematite content of 55.10 wt. %, with relatively high $SiO_2$ content 44.37 wt.%.
- ELT and PET are potential sources of carbonaceous materials for iron oxide reduction. Except that, the metal produced with ELT has a high sulphur content.
- With ELT as reducing agents, the metal produced content high sulphur. The extent of reduction of samples M1 and M3 ranged from 54.36% to 60.37%.
- The extent of reduction of samples with PET for samples M2 and M5 ranged from 78.48% to 93.04%.

## 5.2 Recommendations

The following are recommended to produce richer iron ores of the deposits.

- Further research should be done to ascertain the nature of iron produced through microwave technology.
- Work should be done to upgrade iron ore rich in silica in order to make it economically viable.
- There should be collaboration between iron mines and tyre industries in Cameroon to alleviate environmental problems associated with their operations as products.

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