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DEPARTMENT OF MINERALS ENGINEERING
A THESIS REPORT ENTITLED
STUDIES INTO THE NATURE OF THE PUDO IRON ORE AND ITS RESPONSE TO REDUCTION USING END-OF-LIFE TYRES
BY ABOTAR EMMANUEL
SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF PHILOSOPHY DEGREE IN MINERALS ENGINERRING
THESIS SUPERVISOR
ASSOC PROF JAMES RANSFORD DANKWAH
TARKWA, GHANA
MAY, 2019

DECLARATION

I declare that this thesis work is my own work. It is being submitted for the degree of Master of Philosophy 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 May, 2019.



ABSTRACT

In this work the nature of the Pudo iron ores in the Northern Region of Ghana and the potential for producing premium grade iron nuggets from the ores is investigated using carbonaceous materials generated from end-of-life rubber tyre (ELT) as reductant. Physical analyses such as, specific gravity, particle size distribution and Bond Work and Abrasion indices were performed on the as-received samples of the Pudo Titaniferous Magnetite ore. Pulverised samples of the ores (magnetite and non-magnetic) were then characterised by X-ray fluorescence (XRF) analysis, and Scanning Electron Microscopy-Energy Dispersive Spectroscopy, (SEM/EDS) analyses. The results from the XRF and SEM analyses of the representative sample showed that the Pudo non-magnetic iron ore is of a low-grade hematite with an average Fe content of about 10.17 wt%, but an excellent fluxing material since it has high amounts of magnesia and calcium oxide, with high amount of gangue material $(SiO_2 + Al_2O_3)$ and no deleterious elements (sulphur and phosphorus). The Pudo magnetite ore is a moderately high grade ore with an average grade of 80.918 wt% Fe₂O₃ (56.59 wt% Fe), with the presence of TiO_2 (10.140 wt %) and (0.018 wt%) sulphur. Values obtained from the abrasion and Bond Ball Mill Work Indices test showed that the Pudo Titaniferous magnetite ore is a very hard ore with values of 0.254 and 23.535 kWh/t, respectively. Carbonaceous materials were generated from ELT by pulverising charred crumbs of ELT in a laboratory ball mill to -106 µm. Proximate analysis conducted on ELT agrees with work done by previous researchers. Reduction studies were conducted on composite pellets of mixed variants of the iron ore containing charred ELT in a domestic microwave oven and the extent of reduction was calculated after microwave irradiation for 40 minutes. It was observed that premium grade metallic iron can be produced from appropriate blends of the Pudo iron ores using ELT as reductant, with a measured extent of reduction up to 103.8%.

DEDICATION

This thesis is dedicated to my parents,

Mr and Mrs John De-graft Abotar for their relentless and untiring support throughout my tertiary education.



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CHAPTER 1 INTRODUCTION

1.1 Statement of the Problem

The growing demand for automobiles and second-hand tyres has generated huge amounts of End-of-Life-Tyres (ELTs) in Ghana. In Ghana, unlike developed countries, ELTs are principally disposed in landfills or incinerated with little recycling approaches. Stockpiles of ELTs serve as ideal breeding grounds for mosquitoes and hiding places for reptiles such as snakes. This poses a significant health risk; fatal diseases such as malaria have been linked to such breeding grounds.

Moreover, stockpiles of these tyres can catch fire through lightning strikes or arson and such fires are notoriously difficult and costly to extinguish. Globally, about 1.5 billion ELTs make their way into the environmental cycle each year (Parthasarathy *et al.*, 2016).

The Pudo iron ore is one of the major iron deposits in Ghana. The deposit has iron content of about 80 wt% (Kesse and Banson, 1975). However, they still lay unexploited and little study has been done on them. Chemical analyses by Kesse and Banson (1975) revealed the absence of phosphorus and an extremely low sulphur content. This makes the Pudo iron deposit a promising source of iron oxide for the production of metallic iron and steelmaking plant in the country. Exploitation of the iron deposit at Pudo will create job opportunities for the local indigenes and the country as a whole.

In exploitation of any mineral, it is important to understand the main inherent properties and composition which determine their behaviour during processing. Moreover, the characteristics of minerals also often determine the economic aspect of commercial exploitation of deposits.

However, there are no coals in Ghana. It will be expensive to import coals or metallurgical coke for an Iron making industry in Ghana.

Therefore, the main purpose of this study is to evaluate the physical, chemical, mineralogical properties of the raw iron ore from Pudo deposits and how it responds to reduction using ELTs as reductant.

1.2 Thesis Objectives

This Research seeks to:

- I. Study the nature of the Pudo Titaniferous Magnetite ore, establish its physical, mineralogical, chemical properties and how it responds to reduction using ELTs;
- II. Present a more suitable alternative to ELTs disposal;
- III. Produce metallic iron nuggets from the Pudo iron ore.

1.3 Methods and Procedures Used

Methods and procedures used included:

- a. Review of relevant literature on the field of study
- b. Experimental work
 - i. Collection of ore sample;
 - ii. Sample preparation;;
 - iii. Proximate analysis on ELT
 - iv. Abrasion index,
 - v. Bond ball mill work index test;
 - vi. Particle size distribution (PSD);
 - vii. Loss on ignition (LOI);
 - viii. Specific gravity (s.g)
 - ix. X-ray fluorescence analysis (XRF);
 - x. Scanning electron microscope analysis (SEM); and
 - xi. Reduction studies.
- c. Analysis of the results
- d. Report writing

1.4 Facilities Used

Facilities used for this thesis included:

- a. Minerals Engineering Laboratory, University of Mines and Technology;
- b. University of Mines and Technology library; and
- c. Analytical Centre, School of Chemical Science and Engineering, UNSW, Sydney, Australia.

1.5 Chapter Outline

A brief description of the chapters is as follows: Chapter one is the general introduction to research conducted and it includes the problem statement, objective of the research and the methods used in this research.

In Chapter two, earlier works within the scope of the present study are reviewed. The literature is focused on the history of tyres, its composition, ELT(s), recycling of ELT(s), iron ore, characterisation methods, with a focus on applicability to iron ore, iron ore deposits, iron making, microwave utilisation in reduction of iron ores and the utilisation of End of life polymers in iron and steel making. Experimental work conducted, raw materials used and procedures are detailed in chapter three. Results obtained and the discussions of the result from the experimental work in previous chapter are outlined in chapter four. Chapter five draws conclusions based on the result and discussions made and suggest recommendations necessary to improve upon the research.



CHAPTER 2 LITERATURE REVIEW

2.1 Tyres

Tyre is a thermoset material that contains cross-linked molecules of Sulphur and other chemicals. The process of mixing rubber with other chemicals to form this thermoset material is commonly known as vulcanization. The development of tyres was based on improving the performance of natural rubber, which is obtained from the liquid latex secreted by certain plants (Maorwe, 2013).

Tyre is a complex and high-technology safety product representing a century of manufacturing inventions, which is still on-going. Tyre comprises many materials out of the very best that the metallurgical, textile and chemical industries can produce. From a materials' point of view, tyre is a mixture of synthetic and natural rubber, to which an array of specific substances are added to enhance its performance, durability and safety. The substances added include mineral oil, reinforcing fillers (carbon black and silica) and vulcanising agents (sulphur) which act as catalysts to accelerate the vulcanisation process. It is probably one of the best engineered, longest lasting products developed by man. It is designed for performance, aesthetics, comfort, control and safety (Karagiannidis and Kasampalis, 2009).

2.2 History of Tyres

During the 19th century, Charles Goodyear studied on making rubber more resistant to various chemicals. He started his working by mixing rubber with various dry powders, and aimed to find a way to make natural rubber stickier. In 1839, he achieved to obtain the best product by applying steam heat under pressure, for four to six hours at 132 °C (270 Fahrenheit) degrees. Following the discovery of vulcanization, manufacturers began producing tyres from solid rubber which yielded a strong material to resist cuts and abrasions. Although this was a great progress, the tyres were too heavy and rigid (Maorwe 2013).

2.2.1 Composition of Tyres

A typical passenger tyre contains 30 types of synthetic rubber, eight types of natural rubber, eight types of carbon black, steel cord, polyester, nylon, steel bead wire, silica and 40

different kinds of chemicals, waxes, oils and pigments. They typically contain 85% hydrocarbon, 10-15% iron (in the bead wire and steel belts) and a variety of chemical components. Figure 2.1 is a summary of the composition of a typical passenger car tyre. Vulcanization (a technique for hardening rubber, making it more durable), the introduction of radial tires in the 1950s and other advances, including compound revisions for greater durability and longer tread life, meant that by 1995 an estimated 2% of recycled material was being used in tires. Today, the use of recycled rubber is gradually decreasing as the properties of recycled rubber have a negative impact on performance (for example on fuel consumption) (Anon., 2008).



Figure 2.1 Composition of Tyres (Anon., 2008)

Tyres are made up of four main parts as follows:

- The tread; designed for contact with the ground and to ensure the proper friction;
- The carcass; the structural part of the tyre on which the tread is vulcanised;

- The shoulder; minimizes the effects of irregularities of the terrain and transfers the load due to braking and over steering under acceleration;
- The heels; to fit the casing to the rim.

Each compound contributes to the characteristics of the tyre, to promote longer life and a level of friction (Torretta *et al.* 2015).

2.3 End-of-Life-Tyres (ELTs)

An "end-of-life tyre", ELT, means that the tyre has ceased to perform its original function, that is, to complete the wheel of a vehicle to enable mobility in a safe condition. This does not mean that the material the tyre is made from can be immediately recycled and be reinserted into industrial production to produce other useful products.

On the other hand, disposal of the waste tyres all around the world is becoming higher and higher through time. This keeps on increasing every year with the number of vehicles, as do the future problems relating to the crucial environmental issues. (Groom *et al.*, 2005).

All tyres including passenger car, truck, airplane, two wheel and off-road tyres result in ELTs. However, because the bulk of ELTs results from passenger cars and trucks passenger car tyres were used in this work.

2.4 Recycling of ELT(s)

The recovery rates for ELT(s) have dramatically increased in Europe, Japan and the US over the last years. The recycling cost has decreased due to the efficiency increase in management structures and new recovery routes. This shift shows that ELT-derived products can legitimately be recognized as a valuable secondary raw material (ETRMA, 2011).

This may range from the products for the building industry, such as acoustic insulation and anti-vibration elements, to sport, with playgrounds, football pitches, and multi-purpose sports flooring. There is also the sector of roads and infrastructure where, next to silent and long lasting "modified" asphalts, we can find cycle lanes, street furniture and items for road safety.

Recycling of ELTs offers significant opportunities for achieving sustainable development objectives. Widespread use of ELTs in its Energy and Material recovery is a well-established as an alternative source to virgin materials such as coal.

2.4.1 Material Recycling

Applications for material recycling from end-of-life-tyres have significantly developed over the last decade. ELTs can be used either as a whole, or is shredded or as powdered rubber.

Whole tyres

Civil engineering applications are the main recovery route for whole tyres. The applications include coastal protection, erosion barriers, artificial reefs, breakwaters, avalanche shelters, slope stabilisation, road embankments and landfill construction operations, sound barriers and insulation material. Whole tyres are used also on farms as silage clamps (Karagiannidis and Kasampalis, 2009).

Shredded tyres

Whole tyres are mechanically sheared into shreds ranging in size from 25–300 mm. A large amount of crumb rubber is used in civil engineering projects, such as playground surfaces, parking lots, bank stabilization, fill under road surface and asphalt modifier, because the scrap tyre chips have properties that road builders find essential: light weight, low earth pressure, good thermal insulation and good drainage properties. Another important attribute is its better damping property which is good for running vehicles.

ELTs can be converted into rubber chips for use as attractive horticultural mulch that can assist in retaining nutrients and moisture, thereby helping plant growth and promoting the conservation of natural resources (Karagiannidis and Kasampalis, 2009).

Crumb and powdered rubber

After the removal of the steel and fabric components, the remaining rubber is reduced to granular rubber.

Applications include moulded rubber products such as wheels for caddies, dustbins, wheelbarrows and lawnmowers, urban furniture and signposts.

Crumb and powdered rubber are also to be found as flooring for playgrounds and sports stadiums, while a promising use of crumb rubber is in the construction of artificial turf, for example, in football fields.

Rubber-modified asphalt takes advantage of the elasticity and noise absorbing characteristics of the rubber and can finally be used also as a crack sealant and in repair

membranes (Karagiannidis and Kasampalis, 2009). Figures 2.2 and 2.3 showing some applications of ELTs as an anti-screen wall in France and as an artificial turf on a playing field respectively.



Figure 2.2 Anti-screen wall, France (Anon., 2008)



Figure 2.3 Artificial turf on playing field (Anon., 2008)

2.4.2 Re-use and Export

Many used tyres are transported world-wide and can be reused as second-hand tyres for their originally intended purpose. Currently, more than 9% of used tyres are reused locally or exported (Karagiannidis and Kasampalis, 2009).

2.4.3 Energy Recovery

With a calorific value equivalent to that of good quality coal, end of life tyres are used as an alternative to fossil fuels. The increase in the price of oil and the necessity to preserve resources could favour the development of this type of application (Rowhani and Rainey, 2016).

ELTs can be a low-cost source of fuel when located near a prominent fuel consumer. Tyre derived fuel (TDF) is one of the leading options for ELTs. TDFs are mainly used in cement kilns, but also in fuel intensive industries such as thermal power stations, pulp and paper mills, steel mills and industrial boilers as supplementary fuel. Tyres have high energy content and are an equal or better source of energy than many other solid fuels. This, alongside rising energy costs and increased environmental awareness in recent years, has led to an increase in use of TDF.

An alternative solution class for the thermal treatment of tyres is pyrolysis which is the thermal degradation of the tyre in an inert atmosphere. Pyrolysis of the tyres has been established for many years but is currently receiving renewed attention. Pyrolysis produces oil, char and gas products, all of which have the potential for use. The products of ELTs pyrolysis are lumped into four categories, namely aromatics, liquids, char and gases. The recovery of oil has a high calorific value. Increasingly, it is being used as a fuel, chemical feedstock or can be added to petroleum refinery feedstock (Wadhwa, 2016).

Kilns are increasingly being equipped to use ELTs as supplementary fuel and still be in compliance with the 2008 atmospheric emission standards. TDF is currently the biggest use for ELTs in the US and Japan, and energy recovery is about equal to material recovery in Western Europe and the US (Anon., 2008).

2.4.4 Retreading

Retreading is the process whereby selected and inspected worn tyres (called casings) receive a new tread. Truckers, airlines, construction companies, farmers and some car owners purchase retreads in order to save money. A retreaded tyre costs less to produce than a new tyre and sells for less, usually between 30 - 50% of the comparable new tyre price. However, there is a strong belief among people that retreaded tyres are less safe and have a higher failure rate than new tyres (Karagiannidis and Kasampalis, 2009).

2.4.5 Other Innovative and Emerging Uses for End-of-Life Tyres

Other innovative uses for ELTs are emerging as more research and development is carried out in this area. The following technologies are in development or already used in special circumstances.

Devulcanisation

Devulcanisation (the process of breaking down and recycling rubber) methods include thermal, mechanical, ultrasound and bacterial, and it can be used to make moulded rubber products from ELTs. Although devulcanisation is usually cost prohibitive, some applications have been developed and research is continuing (Maorwe 2013)

Pyrolysis

Tyre pyrolysis involves the thermal decomposition of ELTs into intermediate substances such as gas, oil and char. The economic viability of this alternative route for high temperature resource recovery from tyres is hampered by the fact that the prices obtained for the by-products often fail to justify the process costs.

Under current market conditions the economic viability of these options has yet to be proved (there are few or no large-scale plants currently in operation) but they have the merit to offer scope for increasing recovery rate (Anon., 2011).

Limited pyrolysis facilities currently exist and large-scale development is not currently economically viable (Anon., 2008).

Electric arc furnaces

Steelworks equipped with electric arc furnaces provide an almost closed loop recycling possibility for ELTs. The method involves applying a quantity of scrap metal into an electric arc furnace, followed by a quantity of tyres (shredded or whole), to convert carbon monoxide gas to carbon dioxide in the furnace. In the US, about 1.3 million ELTs are used in this way per year, and a market also exists in Japan. More recently this application has

been validated for industrial use in Belgium, France and Luxembourg, and it has the potential for growth in Europe (Sahajwalla, *et al.*, 2011).

This work seeks to recycle ELTs as a reducing agent in the iron making industry, since there is little research into ELTs in iron making.

2.4.6 Properties of Iron

Iron is a metallic element, a metal of transition group VIII of the periodic table with the symbol Fe, it is 26 on the periodic table. Iron has an atomic mass of 55.847 with a bulk density of 7.87 g/cm³ at 20 °C. Iron has a minimum and maximum melting point of 1534 °C and 1538 °C respectively. Iron has a boiling point of 2750 °C. Until 910 °C iron exist as α -iron. It is ferromagnetic but above 768 °C its magnetic properties disappear. Iron exists as γ -iron at 1400 °C and δ -iron above 1400 °C (Babich *et al.*, 2008).

2.5 Characterisation of Iron Ores

Mineral characterisation involves the study of minerals in terms of their size, habit, chemical composition, morphology, textural position, association and other attributes. There is a well-known and progressively need for this type of study applied to deposits of minerals. This is due to increasing specification requirements for raw materials and mineral products to compete in the marketplace and the realisation that mineral characterisation can ensure optimisation of mineral processing to maximise profit (Cook, 2000).

Characterisation of iron ores is an important step to perform before its processing. The grade or quality, densities, shape, and physical characteristics are determined to allow for suitable application of technical and economic parameters to upkeep production planning and evaluation of the economic viability of deposits (Kiptarus *et. al.*, 2015).

Characteristics of iron ores have implications on its metallurgical behaviour. Being it predictive metallurgy which determines the design of the process flow sheet and diagnostic metallurgy which is used in troubleshooting of reducibility problems during production (Sylvester, 2014). It is therefore very important to perform physical, chemical and mineralogical characteristics of the Pudo Iron ore to allow for suitable application of technical and economic parameters to support its evaluation of economic viability.

2.5.1 Physical Characterisation of Iron Ores

Basically, the physical characteristics or properties of the iron ores are very important because they highlight the ore's behaviour during mining, handling (transportation and screening), charging and descent in the mode of iron making processes (Muwanguzi, 2010).

The degree of liberation of an iron ore is not enough to predict its behaviour during its processing. Its different types of mixed particles present makes it behave in diverse ways. Therefore, it is important to understand how particles are generated. One can foretell the kind of particles to be generated when an ore undergoes comminution (Lund, 2013). Comminution models well-known are commonly used to predict product size distribution due to changes in feed size distribution, particle hardness, feed rate and design of mill (Lund, 2013).

Physical characterisation methods employed in these studies are particle size distribution, abrasion, and Bonds Ball Work indices as well as its specific gravity.

2.5.2 Chemical Characterisation of Iron Ores

Identifying the major and minor species or element of an ore sample, there 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 concentrations of various elements are determined using volumetric or gravimetric and 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 characterization method. XRF is used to determine major and minor elements of ore minerals. The XRD used to determine peaks of major species in an ore. A typical iron ore analysis should include a loss-on ignition (LOI). LOI is due to the loss of water from hydrated minerals, decomposition of carbonates and volatilisation of organic compounds. Table 2.1 shows the chemical composition of some iron ore sfrom various countries around the world. The chemical properties of the Pudo Iron ore used in this study were determined by subjecting it to XRF analysis.

COUNTRY ORE, DISTRICT		Fe	Mn	SiO ₂	Al ₂ O ₃	CaO	MgO	Р	S
Australia	Goldsworthy	63.2		4.90	1.60			0.035	
Belgium	Minette	38.7	0.3	15.70	6.10	5.6	1.60	0.90	
Brazil	Itabira	68.9	0.05	0.35	0.60			0.03	0.01
Canada	Labrador	64.7	1.03	6.30	1.10			0.08	0.01
India	Goa	57.8		2.50	6.50	0.7	0.30	0.04	0.02
India	Rajhara	64.5	0.01	3.58	2.46				
Kazakhstan	Kustanay	45.6	0.16	15.20	4.70	6.2	3.00	0.13	4.04
Liberia	Bomi Hills		0.15	0.10	0.20	0.02	0.15	0.05	
Peru	Peru Marcona		0.02	7.00	1.20	1	0.15	0.09	0.03
Russia	Olenegorsk	32.5	0.03	43. 0 0	0.25	2.41	1.52	0.04	0.04
Russia	Kursk 🚽	33.2	0.17	44. <mark>0</mark> 0	3.90	2.3	2.10	0.15	0.07
South Africa	Thabazimbi	66.6	0.2	3.50	0.50	0.1	0.10	0.025	
South Africa Pretoria		50	0.2	20.00	4.00	0.3	0.20	0.100	
Spain	Bilbao	51.83	0.84	11.76	1.70	0.05	0.14	0.048	0.025
Sweden	Kiruna	66.5	0.1	1.90	0.50	2.3	0.90	0.500	0.005
United Kingdom	Oxfordshire	31.3	0.27	11.44	9.79	0.74	0.51	0.33	0.028
Ukraine	Krivoi Rog	55	0.06	17.00	2.40	0.2	0.10	0.06	0.02
Ukraine	Kerch	40.8	2.21	19.20	5.10	2	1.10	1.06	0.13
USA	Mesabi	57.5	0.5	10.10	0.70	0.05	0.05	0.06	0.01
Venezuela	Cerro Boliver	63.7	0.02	0.75	1.00	0.3	0.25	0.09	0.03

 Table 2.1 Chemical Composition of Iron Ores from Various Countries Wt.%

(Source: Babich et al., 2008)

2.5.3 Mineralogical Characterisation of Iron Ores

Production of a high grade iron ore product requires a thorough knowledge of the mineralogical factors that might impact on the beneficiation of the ore. It is particularly important for low grade iron ores that require upgrading by comminution and other beneficiation processes. The mineralogical properties (for example, particle density and shape) of an iron ore influence significantly the efficiency of its upgrading processes (Amikiya, 2014).

Scanning Electron Microscopy (SEM/EDS) analysis was used in this study to determine the morphology and mineralogy of the Pudo Iron ores.

Cook (2000) has established that the use of SEM for mineralogical characterisation of ores allows detailed identification of individual minerals, either *in situ*, within a polished thinsection prepared from a rock sample, or a sample mount prepared from concentrate or other processing product. He also stated that SEM provides an optical image that can be processed and treated by image analysis techniques, permitting characterisation of size, morphology, and association. Table 2.2 shows a typical mineralogical characterisation on some important iron ores.



Туре	Ore Mineral	Chemical Formula	Colour	Streak	Density g/cm ³	Maximum Fe Content, Wt. %
Oxide	Magnetite	Fe ₃ O ₄	Iron black	Black	5.17	72.4
Oxide	Martite	Fe ₃ O ₄ and Fe ₂ O ₃	Black or dark red	Dark red	5.1-5.2	-
Oxide	Hematite	Fe ₂ O ₃	Steel grey or iron Red black		5.26	70
Hydroxide	Limonite	2Fe ₂ O ₃ .3H ₂ O	Brown, yellowish Yellowis brown, brown yellow		3.6-4.0	59.8
Hydroxide	Goethite	Fe ₂ O ₃ .H ₂ O	Brownish black	Brownish yellow or yellow	4.0-4.4	62.9
Hydroxide	Hydrohematite	Fe ₂ O ₃ .nH ₂ O	Rich Red	Red	4.2-4.6	69
Carbonate	Siderite	FeCO ₃	Pale yellow or brownish black or brownish red	White	3.9	48.3
Sulphide	Pyrite	FeS ₂	Bronze yellow to pale brass yellow	Greenish or brownish black	4.8-5.1	46.7

 Table 2.2 Mineralogical Characteristics of Iron ores

(Source: Babich et al., 2008)

2.6 Iron Bearing Minerals and their Associated Gangue Minerals

2.6.1 Iron Bearing Minerals

Every ore contains one or more minerals of an element to be extracted which is associated with gangue and impurities or tramp elements. The minerals are mainly oxides, hydroxides, and sulphides of the element to be extracted (Babich *et al.*, 2008).

Iron is usually found in the minerals of magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite (FeO(OH)) limonite ($FeO(OH).n(H_2O)$), siderite ($FeCO_3$), ilmenite ($FeTiO_3$) and pyrite (FeS_2). (Amikiya 2014).

The most commonly used iron-bearing minerals contain iron compounds as follows: hematite, Fe₂O₃ (70% Fe); magnetite, Fe₃O₄ (72.4% Fe) and of much less importance are: limonite, 2Fe₂O₃· $3H_2O$ (60% Fe); siderite, FeCO₃ (48.3% Fe); pyrite, FeS₂ (46.6% Fe)

(Muwanguzi et. al. 2012).

Magnetite (Fe_3O_4)

Magnetite is a compound of FeO.Fe₂O₃ (31% FeO in pure form) and contains about 72.4% Fe. It has magnetic properties at lower temperatures. Magnetite ores are characterised by high Fe content and relatively lower reducibility. FeO in the molecule of magnetite FeO.Fe₂O₃ can be oxidised by moisture and by oxygen in the atmosphere: $4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3$. As a result a mixture of hematite and magnetite is generated. This mixture is called martite. The value of $\text{k} = \text{Fe}_{\text{total}} / \text{Fe}_{\text{FeO}}$ determines the ratio of transition of magnetite to martite. This value is equal to 3 for pure magnetite and infinite for pure martite. It is assumed that ores with $\text{k} \leq 3.5$ are magnetite, with k ranging from 3.5 to 7.0 the ore is considered to be half martite, half magnetite and ores with k > 7.5 are purely martite (Babich *et al.*, 2008). The ore contains metallic minerals and impurities like silica, alumina and phosphorus, the gangue minerals are separated from the magnetite crushed ore by magnet (Yellishetty *et. al.*, 2012).

Hematite (Fe_2O_3)

Pure hematite ores contain about 70% Fe. Hematite iron ore is very widespread. It is characterised by high Fe-content and low content of harmful impurities (Babich *et al.*, 2008). It is considered as one of the most important sources of iron ore today (De Kock *et*

al., 2008). Hematite deposits are mostly sedimentary in origin. Its formation is not fully understood, but literature reveals that they were formed by the chemical precipitation of iron from shallow seas about 1.8 to 2.6 billion years ago, during the Precambrian period (Amikiya, 2014).

Hydrohematite, Goethite and Limonite

This group belongs to the brown ores Fe₂O₃.nH₂O which are chemically combined with varying number of water molecules:

Hydrohematite n ≈ 0.1 Goethiten = 1.0Limoniten = 1.5

Brown ores are characterised by lower iron content; high reducibility and porosity. They are often accompanied with manganese and phosphorous (Babich *et al.*, 2008). They are secondary minerals formed as a result of oxidation of Fe-carbonate, hematite and magnetite (Amikiya, 2014).

Siderite FeCO3

Is a carbonated ore which contains about 48.2% Fe. It is characterised by lower iron content due to both low iron content in the ore mineral and high gangue content and by high reducibility (Babich *et al.*, 2008). Siderite ores are just a fraction of the total world iron ore reserves (Amikiya, 2014).

Ilmenite (FeTiO₃)

It contains about 36.8% Fe and about 31.8% Ti in pure form. It is commonly associated with magnetite in the form of FeTiO₃.Fe₃O₄ and generates titano-magnetite ores. These ores have magnetic properties, low reducibility, high density and often accompanied by vanadium (Babich *et al.*, 2008).

Pyrite (*FeS*₂)

Pyrite contains about 46.7% Fe. It does not make up iron ore. Pyrite is used in chemical industry for sulphur extraction by means of burning (Babich *et al.*, 2008).

Pyrite is a good source of sulphur, but not a good source of iron because of the sulphur, which ruins iron and is hard to separate from it. When heated, sulphur is driven off and the iron is oxidised to magnetite (Amikiya, 2014).

2.6.2 Gangue Minerals

Iron ores contain impurities, collectively known as gangue. The presence of small amounts of some elements can have either bad or good effects on the characteristics of an iron ore. Most iron ores contain slag forming constituents, which include the acidic oxide silica (SiO₂), the basic oxides lime (CaO), magnesia (MgO) as well as the neutral alumina (Al₂O₃) (Amikiya 2014). The Pudo non-magnetic iron ore used in this study serves as a fluxing agent since it contains some amount of basic oxides lime (CaO), magnesia (MgO). Ratio of the percentage of ore mineral to gangue determines the richness of an ore.

Metal Oxides

Iron ores generally contain metallic oxides, which are reduced to metal in the process of iron making. Some of the metallic oxides, such as nickel, are easily reduced compared to oxides of iron, while others, such as manganese and chromium, are less easily. When the reduction of these metallic oxides occurs in the blast furnace, a proportion of the reduced metals contaminate the final steel produced. A manganese content of about 1% in steel is advantageous but small proportions of other metals, such as zinc, are undesirable (Amikiya 2014).

Deleterious Elements

Common deleterious elements in iron ores include phosphorus, sulphur, and titanium. Uncommon deleterious elements include vanadium, copper, zinc, chromium, nickel, arsenic, lead, and tin.

Phosphorus: Has four major effects on iron; it increases hardness and strength, lowers solidus temperature, increases fluidity and cold shortness. The strength and hardness of an iron increases with the increasing concentration of phosphorus. At concentrations higher than 0.2%, iron becomes increasingly cold short, or brittle at low temperatures (Rudyuk *et. al,* 1974).

Phosphorus lowers the liquidus temperature, allowing the iron to remain molten for longer, and increases fluidity. The additions of 1% can double the distance molten iron will flow.

Remedies for high phosphorus content in iron ores include avoiding high phosphorus content ores or oxidising the phosphorus during the fining process (removal of bubbles) by adding iron oxide (Amikiya 2014). Analysis done by Kesse and Banson (1975) revealed the absence of phosphorus in the Pudo Titaniferous Magnetite iron ore which is used in this investigation.

Sulphur: Is also present in small quantities in many ores. It dissolves readily in both liquid and solid iron at the temperatures of iron smelting. The effects of even small amounts of sulphur are immediate and serious. Iron with over 0.03% sulphur content is avoided (Amikiya 2014). Sulphur causes iron to be red or hot short. Hot short iron is brittle when hot (Anon 2018). Analysis done by Kesse and Banson (1975) revealed an extremely low sulphur content average of 0.01% of the iron ore used in this investigation.

2.7 Iron Deposits, Production and Consumption

Iron is considered to be the most important metal and almost omnipresent in our daily life. Its annual production exceeds by far that of all other metals combined. It comprises approximately 93% of the tonnage of all the metals used. It is estimated that worldwide there are 800 billion tonnes of iron ore resource, containing more than 230 billion tonnes of iron. These are reserves that can be extracted economically at the time of determination. China reserves are about 18% of the total global reserves. China's reserves are of low quality and grade. The world's best quality reserves are found in South Africa, Australia, and Brazil (Babich *et al.*, 2008).

An Iron deposit is referred to as a mineral body of reasonably size, iron content and definite chemical composition that can be mined and marketed at a profit under prevailing conditions of commodity, prices, costs and technology either immediately, or potentially (Arndt and Ganino, 2012). The major constraint to economics for iron ore deposits is not necessarily the grade or size of the deposits, because it is not particularly hard to geologically prove where enough tonnage of the rocks are. The main constraint is the position of the iron ore relative to market, the cost of rail infrastructure to get it to market and the energy cost required to do so (Anon 2018).

2.7.1 Iron Deposits in Ghana

Ghana is blessed with mineral deposits such as gold, bauxite, diamond, manganese, iron etc. Exploitation of these minerals is of great importance to the nation. Consideration is given to the exploitation of gold. Iron which is in high demand for steel production has to be given the same consideration.

Kesse and Banson, 1975 points out three main iron ore deposits of industrial or commercial importance in Ghana. These are;

- 1. The Pudo Titaniferous Magnetite Ore;
- 2. The Shieni Sedimentary Iron Ore;
- 3. The Opon Mansi Laterite Ore.

Moreover, (Kesse and Banson, 1975) mentioned the Akpafu Iron deposit as one of the minor Iron deposits. However, none of these iron deposits has been exploited. Exploitation of these major iron deposits even on a small-scale process to produce metallic iron using locally produced reductants will create employment opportunities for the local indigenes and will be a source of metallic iron for the steel industry in Ghana.

2.7.2 Location of the Study Area

The Pudo iron ore occurs in two distinct zones north and south of Pudo, a village in the Tumu District in the Upper West Region of Ghana. Pudo has geographical coordinates of 10° 56′ 11″ North, 1° 31′ 20″ West. Figure 2.4 shows the location of Pudo. The magnetite bearing zone outcrops on the Pudo-Wuru path 1.2 kilometers north-west of Pudo, running 5.6 km north-east and also on the Pudo-Bano, 2.0 km to the east.

Kesse and Banson, (1975), have established that the deposits were discovered by Sir Albert Kitson in April, 1927 when he was marching from Basisan to Pudo. The ore-body is apparently 30 feet wide - much wider at some places. It is continuous along the whole length of the hill and is visible in the plain at both ends of the hill.

The rocks in the area are classified by Kesse and Banson, (1975), as below:

- Quartz diorite
- Altered hornblende-biotite granodiorite
- Hornblende biotite granodiorite and tonalite
- Unfoiliated porphyroblastic biotite granodiorite, admelite and biotite gnesis
- Altered norite



Figure 2.4 Location of Pudo Hills (Kesse and Banson, 1975)

2.8 Iron making

Iron making is the process of reducing iron ore (solid oxidised iron) into metallic iron through the removal of its oxygen. It is the most energy-intensive stage of the steel process. In iron ore reduction processes, a reducing agent, based on carbon, hydrogen, carbon monoxide and methane, removes the oxygen from the iron oxides Dankwah (2014a).

Reducibility of an ore depends on its particle size, distribution and porosity. Gaviria *et al.* (2007) studied the reduction of hematite to magnetite by monitoring it with the help of Mössbauer spectroscopy and XRD. Reduction of hematite and magnetite to wüstite, and iron has been investigated over the years (Monazam et al., 2013; Huang et al., 2013, Mondal et al., 2004 and Yang et al., 2007). Although the reducibility of hematite and magnetite is widely investigated, there is little information on the reducibility of their blends.

2.8.1 Reduction of Iron Oxide by Carbon

The carbothermal reduction of iron oxides has been well investigated with documented research findings. The following reactions are known to occur sequentially as stated, although it is not a view shared by others.

$$Fe_2O_3 + \frac{1}{3}C = \frac{2}{3}Fe_3O_4 + \frac{1}{3}CO$$
(2.1)

$$Fe_3O_4 + C = 3FeO + CO \tag{2.2}$$

$$FeO + C = Fe + CO \tag{2.3}$$

As illustrated above, these reactions lead to significant build-up of CO which is capable of causing the solid-state reduction as

$$FeO_x + C \rightarrow FeO_{x-1} + CO_2$$
 (2.4)

$$C + CO_2 \to 2CO \tag{2.5}$$

The reaction of fixed carbon with iron ore is known to be the main reaction which follows the gaseous reduction (Sohn, 2005).

There have been several other literatures on the controlling mechanisms of iron oxides and various ores containing iron oxides (Sohn, 2005). Random nucleation and phase boundary mechanism have been suggested by Shimokawabe *et al.* (1979) and Sastri *et al.* (1982) respectively. El-Geassy (1998) concluded that a mixed reaction mechanism controlled the reduction of hematite (Fe₂O₃) to wustite (FeO) in the early stages of reaction which was followed by interfacial chemical reaction. The reduction of wustite to iron, however, was controlled by a mixed chemical reaction.

2.8.2 Reduction of Iron Oxide by Hydrogen

The reduction of hematite by H_2 is advantageous over reduction by carbon from the point of view of the environment and it follows the stepwise reaction:

$$Fe_2O_3 + \frac{1}{3}H_2 = \frac{2}{3}Fe_3O_4 + \frac{1}{3}H_2O$$
(2.6)

$$Fe_3O_4 + H_2 = 3FeO + H_2O \tag{2.7}$$

$$FeO + H_2 = Fe + H_2O$$
 (2.8)

Fruehan (1977) concluded that, the reduction of wustite (2.8) is the rate determining amongst the above equations. He expressed the rate of reaction by hydrogen as

$$R_{H_{2}} = K_{H_{2}} \left(\frac{P_{H_{2}}^{s} - P_{H_{2}O}^{s}}{K_{H_{2}}^{eq}} \right)$$
where $K_{eq} = \left(k_{f} / k_{r} \right) = a_{Fe}^{eq} P_{H_{2}O}^{eq} / a_{FeO}^{eq} P_{H_{2}}^{eq}$
(2.9)

is the equilibrium constant of the overall reaction in (2.8). Assuming a dominating chemical kinetics and as such a fast mass transfer,

$$P_{H_2}^S = P_{H_2}^{Bulk} and P_{H_2O}^S = P_{H_2O}^{Bulk}$$

He expressed the moles of oxygen removed $\frac{dno}{dt}$ as follows:

$$\frac{dno}{dt} = AK_{H_2} \left(\frac{P_{H_2}^s}{P_{H_2}^s} - \frac{P_{H_2O}^s}{K_{H_2}^{eq}} \right) = -S_{FeO_x} W_{FeO_x} K_{H_2} \left(\frac{P_{H_2}^{Bulk}}{P_{H_2}^{Bulk}} - \frac{P_{H_2O}^{Bulk}}{K_{H_2}^{eq}} \right)$$
(2.10)

2.8.3 Reduction of Iron Oxide by Carbon Monoxide

A reduction reaction similar to that of H_2 is observed for CO/iron oxide interfacial reaction with similar stepwise reduction reaction with hematite as indicated above. Similar rate equation is expressed as:

$$R_{CO} = K_{CO} \left(P_{CO}^{s} - \frac{P_{CO}^{s}}{K_{eq}^{eq}} \right)$$

$$where K_{eq}^{CO} = \left(k_{f} / k_{r} \right) = a_{Fe}^{eq} P_{CO_{2}}^{eq} / a_{FeO}^{eq} P_{CO}^{eq}$$

$$(2.11)$$

is the equilibrium constant. The moles of oxygen removed, dnodt/, and the equation for uniform internal reduction and topochemical receding interface are all expressed similarly by (2.12).

$$\frac{dno}{dt} = -S_{FeO_x} W_{FeO_x} \left(K_{H_2} \left(\frac{P_{H_2}^{Bulk} - \frac{P_{H_2O}^{Bulk}}{K_{H_2}^{eq}} + K_{CO} \left(\frac{P_{CO_2}^{Bulk} - \frac{P_{CO_2}^{Bulk}}{K_{CO}^{eq}} \right) \right)$$
(2.12)

2.8.4 Reduction of Iron Oxide with H₂/CO Mixture

Reduction of iron oxide with a mixture of CO and H_2 is well documented and aimed at the beneficial effect of H_2 on the reduction of iron oxide by CO and or solid carbon. The

evolution of both H_2 and CO may result in a competition with each other on the reaction sites or equal reaction of H_2 and CO (Sohn 2005). In the case of the later, Turkdogan (1980) used a linear combination of the individual reactions and established the total reaction rate, R_{total} and the moles of oxygen removed, dno/dt respectively as:

$$\mathbf{R}_{\mathrm{total}} = \mathbf{R}_{H_2} + \mathbf{R}_{CO} \tag{2.13}$$

$$\frac{dno}{dt} = -S_{FeO_x} W_{FeO_x} \left(K_{H_2} \left(\frac{P_{H_2}^{Bulk} - \frac{P_{H_2O}^{Bulk}}{K_{H_2}^{eq}} + K_{CO} \left(\frac{P_{CO_2}^{Bulk} - \frac{P_{CO_2}^{Bulk}}{K_{CO}^{eq}} + K_{CO} \left(\frac{P_{CO_2}^{Bulk}}{K_{CO}^{eq}} + \frac{P_{CO_2}^{Bulk}}{K_{CO}^{eq}} \right) \right)$$
(2.14)

It has however been found that, these reducing gases compete with each other to be adsorbed on the reaction site rather than a linear combination of the two independent reactions because the ability of the individual gases to be adsorbed is different at isothermal temperatures (Sohn 2005). Ishii et al (1986) concluded that the reduction of hematite was 10 times faster in H₂ atmosphere as compared to CO atmosphere, which was confirmed by Moon and Rhee (1997) where it was estimated that, the reduction of hematite with CO was 2 - 3 times lower than with H₂

2.8.5 Raw Materials Preparation

Coke Making

Coke is a product from metallurgical grade coal (coking coals). It is the primary reducing agent in the Blast Furnace (BF) process. Its combustion provides the reducing gases to reduce the iron ore, the heat to melt the iron ore and slag. In addition, coke physically supports the iron burden and provides a permeable medium through which the gases and liquid iron and slag flow. The process of coke making takes about 12–36 hr. This is done by heating blends of crushed coal in a coke oven at a temperature of 1000–1100 °C in the absence of air (O₂-deficient atmosphere) to drive off the volatile compounds (Carpenter, 2012).

However, as one of the most demanded and finite natural resources in the world, coal needs to be conserved and used as efficiently as possible. Moreover, currently, there are no known coal fields in Ghana. It will be expensive to import coals or metallurgical coke for an Iron making industry in Ghana. Thermally transformed ELTs can be an alternative source of locally produced effective reducing agent for an Iron making industry in Ghana.
Iron Ore Agglomeration

Iron ore in its natural state occurs as lump ore or fine ore. Lump ore is crushed and screened before shipment from the mine. It must meet certain quality restrictions (> 62% iron) and physical characteristics in terms of size and handling, since it is fed directly into the BF. The energy needs of the BF depend to some extent on the quality of the ore. Lump ore is more expensive than ore fines. About 25% of all iron ore is used directly, without agglomeration (Carpenter, 2012).

Fine ore must be converted into larger aggregates for use in BFs. These aggregates are often a better feedstock than lump ore. The two common ore agglomeration processes are sintering and pelletising. New iron reduction processes that can consume fine ore directly such as FINEX have an important cost advantage since they avoid the cost of agglomeration and the more expensive lump ore (Carpenter, 2012).

Pelletisation will be used in this work, since the use of pellets as feed in a furnace has several advantages such as their uniform size, known composition and strength.

2.8.6 Blast Furnace Iron Making Process

The purpose of a Blast Furnace (BF) is to chemically reduce and physically convert iron oxides into liquid iron called hot metal. The BF is a continuously operating shaft furnace based on its counter flow principle. At the top, coke and burden (sinter, pellets, lump ore and fluxes) are charged in different layers. Charged materials descend under the influence of gravity. The raw materials (charged materials) require 5 to 7 hours to descend to the base of the furnace where they become the final product. In the lower part of the furnace, hot blast (1000-1300 °C) is injected through tuyères. In front of each tuyère, the hot blast reacts with the coke to form carbon monoxide. Carbon monoxide formed ascends in the furnace and reduces the iron ores. At the bottom of the hearth, the molten metal is collected. Besides hot metal, slag is formed. The slag swims on the hot metal bath due to its low density. The products of the BF process are hot metal or pig iron, slag, top gas and flue dust. The slag produced has a well-defined composition. It is mainly used for road construction and in the cement industry (Babich *et al.*, 2008). Figure 2.5 shows a typical Blast Furnace Process for the reduction of iron oxide to metallic iron.



Figure 2.5 Blast Furnace Process (Dankwah, 2014)

2.8.7 Alternatives in Iron Making

Direct Reduction Process

DRI production is the most commonly used alternative to BF iron making. Direct Reduction (DR) is defined as any process in which metallic iron is produced (removal of oxygen) from iron ore or any iron oxide by avoiding the liquid melting phase and below the melting temperatures of any material involved with the use of solid, liquid or gaseous reductants. The product of DR process is called spongy iron or direct reduced iron.

The first iron workers in ancient times produced a spongy mass by reducing the iron ores with hot coals. Sponge iron was the principal source of supply for iron and steel for many centuries. The term sponge iron was common until the early 1980's when the more correct name "direct reduced iron" became generalised.

DRI is produced by passing hot reducing gases such as hydrogen, methane and carbon monoxide over iron ore (oxide), which is usually in the form of pellets or lumps. Although, the process is conducted at high temperatures, these are still substantially below the melting point of iron. This means that the lumps and pellets retain their original shape, but are considerably lighter owing to the removal of oxygen from the ore (Babich *et al.*, 2008).

Based on the types of reductant used, the DR processes can be broadly classified into two groups:

- Using solid reductant, that is, coal-based DR process
- Using gaseous reductant, that is, gas-based DR process

Coal-based Processes: In coal-based DR processes, non-coking coal is used as reducing agent. The iron oxides together with solid reductant (non-coking coal) are charged into the reactor. The generation of reducing gas (mainly CO) takes place in the reduction reactor, and the product has to be separated from excess reductant, ash, and sulphur (Dutta and Sah, 2016).

The main advantages of coal-based processes are as follows:

- a. They do not require high-grade coal that is scarcely available.
- b. They use non-coking coal.
- c. They can be installed at lower capacity.
- d. They can be easily installed at places where small reserves of coal and iron ore are available.
- e. Modules of small-scale operation are available.

Disadvantages of coal-based processes are as follows;

- a. Lower economy of scale.
- b. High energy consumption (16.0-21.0 GJ/t).
- c. Low carbon content in the product (< 1.0%).
- d. Lower productivity (0.5–0.9 t/m³/day).
- e. Hot feeding to the steelmaking furnace and hot briquetting are not possible due to the presence of residual char and ash in DRI.

Gas-based Processes: Reformed natural gas is used as a reducing agent. Iron ore lumps or pellets are reduced in the solid state and oxygen from iron oxide is removed by a gaseous reducing agent.

Natural gas is reformed at 950 °C (1223 K), in the presence of a catalyst (Ni or Al_2O_3), to produce reducing gases CO and H₂. The reducing gases H₂, CO, or mixture of H₂ and

CO, are introduced into the reactor at elevated temperatures up to 1000 °C and pressure up to 5 bar, (Dutta and Sah, 2016). If CH_4 is present in the reducing gas, it results in carburisation of the reduced product. The processes based on gaseous reduction are confined to the areas where natural gas is available in abundance at a reasonable price (Babich *et al.*, 2008). The processes discussed have both merits and demerits.

Gas-based processes have the following advantages of high productivity, lower energy consumption (10.5-14.5 GJ/t) and higher carbon content in the product (> 1.0%).

Midrex Process: Lump ore is reduced by gas with hydrogen content (about 55%) in flow shaft furnace. The reducing gas is produced by cracking (reforming) of natural gas (methane) in a reformer outside the reduction aggregate $CH_4 + CO_2 = 2CO + 2H_2$. Nickel is used as the catalyst in the reformer. The generated gas is then blown into the lower part of the shaft. The CO₂-rich gas is used for cracking as well as for heating the natural gas in the reformer. Produced DRI is either cooled in a separated zone or is extracted for hot briquetting (Babich *et al.*, 2008). Figure 2.6 shows a typical Midrex Reduction process for reducing iron oxide to metallic iron.



Figure 2.6 Midrex Reduction Flow Sheet (Hamadeh et al., 2018)

HYL process: The HYL process operates similar to the MIDREX process but with a higher pressure and amount of hydrogen in a reducing gas. It is characterised by steam reforming of natural gas to achieve a reducing gas high in hydrogen content (> 80%). Its operational pressure in the shaft is about 5 to 8 bar. Products are usually cold DRI. Equations 2.1 to 2.4

show the gas reforming process; it is performed after preheating and partial oxidation of natural gas in the shaft (Babich *et al.*, 2008).

Partial oxidation and reforming reactions as in the equations below:

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2$$
 2.15

$$CH_4 + H_2O = CO + 3H_2$$
 2.16

$$H_2 + \frac{1}{2}O_2 = H_2O$$
 2.17

$$CO + H_2O = CO_2 + H_2$$
 2.18

Fluidised Bed Processes: In the fluidised bed reactor, fine iron ore is blown from the bottom through a hole, nozzle or conical bottom as well as through single stream with fluidised flow substances (liquid or gas forms). The application of fluidised bed includes: FINMENT, CIRCORED and CIRCOFER processes (Babich *et al.*, 2008).

- *FINMENT process*: it is based on gas reduction of fine ores in a four-stage fluidising bed. Two trains are forming one module being supplied by one reformer with reducing gas, but each single stage train has its own recycle gas loop including CO₂ removal plant. A mixture of recycled top gas and fresh gas generated from natural gas in a steam reform provides a gas rich in hydrogen. In the final reactor of a train the temperatures are 700-800 °C and the pressure is up to 14 bar (Babich *et al.*, 2008).
- *CIRCORED process*: is also fine ore based gas reduction process. After preheating the fine ore (0.1 to 2 mm) to about 850 °C the two stage reduction unit couples a circulating fluidised bed for pre-reduction (metallisation 65-75% with about 630 °C, 4 bar) with a compartmentalised stationary fluidised bed for final reduction (metallisation > 95% with about 650 °C, 4 bar). Hydrogen as a pure reducing gas is selected because of the better low temperature reduction reaction characteristics due to reaction kinetics and sticking behaviour. The produced DRI does not contain any carbon due to the hydrogen reduction of the iron ore (Babich *et al.*, 2008).
- CIRCOFER process: is a coal based direct reduction process. Fine ore is pre-reduced to DRI in a CFB (Circulating Fluidised Bed) reactor. Char and hot reducing gases are produced as by-product. Coal injected into the heat generator, is partially oxidised at about 1050 °C. Unburned char enters the CFB reactor together with iron ore; carbon

reacts with CO₂ to generate CO according to the Boudouard reaction. Recirculated off gas is used for fluidisation of the solids in the reactors. Primarily, reduction occurs with carbon monoxide $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. After heat recovery in a boiler, the dedusted, quenched and CO₂ stripped gas is removed to the fluidised bed reactors. Iron ore enters the heat generator via one or two preheating stages (depending on desired off gas temperature), using sensible off gas heat. After preheating to reduction temperature, the ore is transferred into the CFB reactor together with char and the reaction gases from partial coal gasification; where pre-reduction takes place at about 950 °C. The pre-reduced ore is discharged in about 20 minutes, when a metallisation degree is approximately 85% (Babich *et al.*, 2008).

Rotary Hearth Furnace (RHF): in these processes green pellets incorporating carbon or a mixture of iron ore, oxides residue and carbon containing reducing agents like coal or coke is used. The charged materials are quickly heated up to about 1300 °C (Babich *et al.*, 2008).

The pellets are reduced and melted within approximately ten minutes, then discharged. The final step is separation of iron nuggets and slag. During reduction, volatiles from the coal and carbon monoxide (CO), produced from reduction, evolve into the gas space above the hearth and are combusted with air. Heat generated, plus heat from the burners, provides the energy required for reduction and melting. Off gas from the RHF is fully combusted but does contain considerable sensible heat. The off gas first passes through a heat recovery system to preheat combustion air. It then goes to a gas cleaning system to remove particulates before being discharged to the atmosphere (Dankwah, 2014a). Figure 2.7 is a typical Rotary Hearth Furnace Approach for reducing iron oxide to metallic iron.



Figure 2.7 Rotary Hearth Furnace Approach (Anon., 2010)

Smelting Process

Smelting reduction (SR) means group of processes which produce liquid hot-metal from iron ore without using coke as reductant. SR technology involves both solid state reduction and smelting. SR technology exploits the principle that coal can be gasified in a bath of molten iron. SR technology consists of two zones or vessels, *i.e.* a pre-reduction unit and a smelting vessel. The coal is fed into the smelting reduction vessel where it is gasified. This produces heat and hot gas containing carbon monoxide. The heat is used for melting of the iron in the smelting reduction vessel. The hot gas is transported to the pre-reduction unit and used for pre-reduction of the iron oxides (in the solid state). The pre-reduced iron is subsequently transported to the smelting vessel for final reduction.

SR technology is different from the BF as in non-coking coal is used, moreover, agglomeration of iron is avoided in most smelting reduction process (Babich *et al.*, 2008).

2.9 Microwave Utilisation in Iron Oxide Reduction

Microwaves are a form of electromagnetic energy with associated electric and magnetic fields. Microwave frequencies are in the range of 300 MHz to 300 GHz. In recent years, a growing interest in microwave heating in minerals treatment has emerged and a number of potential applications of microwave processing have been investigated (Koleini *et. al.* 2012).

Generally carbon materials are very good absorbents of microwaves; they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties, to be used as microwave receptors, in order to heat other materials indirectly, or to act as a catalyst and microwave receptor in different heterogeneous reactions (Menéndez *et. al.*, 2010).

The key factor for the emergence of microwave irradiation in carbothermal reduction of iron oxides has gained much attention because of its high potential for an essential reduction of carbon dioxide emission and its tendency to heat powders because of the possible volumetric heating (Takayama *et. al.*, 2008; Hayashi *et. al.*, 2013).

Koleini and Barani (2012) highlighted on the use of microwave in treatment of minerals. Table 2.3 shows the time in minutes and the maximum temperature in degree Celsius that each mineral attained during the treatment process.

Koleini and Barani (2012) stated that, earliest work on the microwaving of minerals began with a study of the high temperature processing of certain oxides and sulphides using a resonant cavity operating at 2.45 GHz and variable power up to 1.6 kW.

Aguilar and Gomez (1997) researched on the carbothermic reduction of iron oxides using microwaves energy as a heating source.

Ishizaki *et. al.* (2006) investigated the reduction of magnetite ore-coal composite in an inert atmosphere (nitrogen gas) using the microwave approach. They observed that reduction of the composite pellets started at 800 °C and pig iron was formed at a temperature of 1350 °C.

The selective absorption of microwave energy in the reduction of magnetite ore with carbon black in mixed powder was investigated by Ishizaki and Nagata (2007).

Junaidi *et al.*, 2014 used microwave irradiation process to reduce 60 g composite of high purity iron ore, using charcoal as a reducing agent and calcium oxide as a flux in the ratio 1:4:8. The homogeneous mixture was put in crucible and treated by microwave heating with a power supply 2000, 3000 Watts and irradiation time 40, 50, 60 min. Results from their studies showed that microwave irradiation increases the temperature behaviour in the reduction of composite iron, charcoal and calcium oxide mixture. They concluded that power supply and irradiation time were the main parameters in the reduction process. The optimum reduction process was observed at 3000 W power supply and 60 min irradiation time with an extent of reduction of 81.67%.

This study will employ the reduction of the Pudo Magnetite ore and blends of the Pudo magnetite and non-magnetic iron ores using ELTs as a potential reductant under microwave irradiation for 40 minutes.

Compound	Heating time	Max. Temperature
Compound	(min)	(°C)
Al ₂ O ₃	24	1900
С	0.2	1000
CaO	40	200
CO ₂ O ₃	3	900
CuO	4	800
CuS	5	600
Fe ₂ O ₃	6	1000
Fe ₃ O ₄	0.5	500
FeS	6	800
MgO	40	1300
MoO ₃	0.46	750
MoS_2	0.1	900
Ni ₂ O ₃	3	1300
PbO	13	900
UO ₂	ос, ластн 0.1	1100

Table 2.3 Microwave Heating of some Oxides and Sulphide Compounds

(Source: Koleini and Barani 2012)

2.10 Utilisation of End of Life Polymers in Iron and Steel Making Technology

Over the last years, research has been conducted to find alternatively cheap reducing agents for coals and metallurgical coke in ironmaking. As one of the most demanded and finite natural resources in the world, coals need to be conserved and used as efficiently as possible.

Reduction is mainly by carbon, and carbonaceous materials which are abundant in the environment are now used for reduction.

Waste polymer reduction technology is an emerging area in Metallurgy where carbonaceous materials generated from waste polymers are used in place of or in combination with other

carbonaceous materials as reductants for metal oxides reduction. (Dankwah *et al.*, 2016a). For countries like Ghana where commercial quantities of iron ores are available, but without the relevant source of carbonaceous materials, waste polymers offer a readily available alternative to high grade metallurgical coke as reductant for iron making (Dankwah *et al.*, 2016a). In the metallurgical field, the use of postconsumer plastics as reductants or as a source of energy is currently gaining the attention of various researchers (Dankwah *et al.*, 2016b).

The existing research in this area involves the use of thermoplastic polymers and or their blends with metallurgical coke, graphite, or biomass as reductants for the production of metallic iron from reagent grade iron oxides or electric arc furnace (EAF) slags containing iron oxide.

Dankwah (2014b) used blends of HDPE and coconut shells (CNS) as reducing agent for the production of metallic iron from iron oxide (Fe₂O₃). Several small droplets of metallic iron were seen distributed across the entire volume of the crucible after the reduction processes and he concluded that blends of postconsumer HDPE with waste CNS could be used effectively as reducing agents in iron making. Also, he conducted another experiment on reduction of FeO in EAF Steelmaking Slag by End-of-Life Polystyrene (PS) and its Blend with Metallurgical Coke'. The reduction done with the blend of polymer improved with the extent of reduction increasing from 51.9% for coke to 92.6% and 93.9% for the blends and he concluded that PS and blends of PS with coke could be used to partly or wholly replace the conventional coke used in iron and steelmaking as reductants (Dankwah, 2014c). Dankwah et al. (2015) used mixed plastics waste as reductant in ironmaking. These mixed plastic waste composed of 50 wt.% high density polyethylene (HDPE), 30 wt.% polypropylene (PP), 10 wt.% low density polyethylene (LDPE) and 10 wt.% polyethylene terephthalate (PET) were employed. Results from this research showed that iron oxide can be effectively reduced to produce metallic iron using mixed plastic waste as reductant. An improvement in extent of reduction was observed over metallurgical coke and the individual polymers when mixed plastics waste was used as reductant. This eliminates the need to sort out individual plastics from municipal solid waste for their effective utilisation as reductants in ironmaking.

Moreover, Dankwah *et al.*, (2016a), obtained an extent of reduction over 80% using waste electrical sockets (WES) as reductant.

Yunos *et al.*, (2016) used polypropylene (PP) to reduce iron oxide composite pellet for steelmaking processes. In their study, carbon from polymeric material such as the recycled PP was utilised as a reducing agent, which has not been extensively investigated especially in steelmaking processes. It was observed that hematite was the main phase present in the sample while a phase transformation from iron oxide to metallic iron occurred at high temperatures. They then concluded that reduction of iron oxide with recycled PP could be effectively used as an alternative carbon source and reducing agent in steelmaking.

Many investigations have also been conducted by many other researchers (Matsuda *et al.*, 2006; Nishioka *et al.*, 2007; Matsuda *et al.*, 2008; Ueki *et al.*, 2008; Dankwah *et al.*, 2011; Kongkarat *et al.*, 2011; Murakami *et al.*, 2009; Murakami and Kasai, 2011; Dankwah *et al.*, 2012b; Dankwah, 2013; Dankwah and Koshy, 2014; Dhunna *et al.*, 2014; Mansuri *et al.*, 2013; Dwumah *et al.*, 2016; Dankwah and Buah, 2017) trying to use different carbonaceous materials to effect reduction. These investigations have not only provided an alternative for metallurgical coke as a reductant but have also provided means of waste recycling since most of these carbonaceous materials are waste.

ELTs will be utilised as a potential reductant for the production of metallic iron nuggets from the Pudo Magnetite ore and blends of both the magnetite and non-magnetic Pudo Iron ores.



CHAPTER 3 EXPERIMENTAL WORK

3.1 Raw Materials

A quantified number of ELTs were collected from a tyre waste dump near a vulcanising shop opposite the main gate of the University of Mines and Technology (UMaT), Tarkwa. Magnetic and non-magnetic iron ores from Pudo in the Upper West Region of Ghana were the source of iron oxide used in this study. Flour served as a binding agent in the formation of pellets. A low intensity handheld magnet was used to separate the reduced material from a pool of unreacted reductant and slag.

3.2 Apparatus Used

A greater portion of this study was carried out in the Minerals Engineering Laboratory of the University of Mines and Technology and an external laboratory in Australia. The equipment used in the Minerals Engineering laboratory of the University of Mines and Technology.

- a. Crushers- Morse Jaw Crusher, Cone Crusher and Marcy GY-Roll Crusher;
- b. Ball Mill of diameter 30 cm and length 23 cm;
- c. Tumbling Mill;
- d. Riffle Sampler;
- e. ASTM-E11 Screens;
- f. Electronic Measuring Scale;
- g. MWM200 PIONEER Microwave Oven;
- h. Gas Fired Furnace also known as "Sika Bukyia" and;
- i. Ring of Magnet.

3.3 Sample Preparations

3.3.1 Carbonaceous Material

ELTs were shredded using various mechanical means. The shredded ELTs were rinsed with water in a metallic container to remove most of its associated debris. The cleaned ELTs were thereafter air dried for a day. 4.9 Kg of ELTs were charred. Charring was done to upgrade the carbon content by expelling the volatile components of ELTs using a gas fired

furnace ("Sika Bukyia"). Charring process was accompanied by the emission of thick smoke. The process charring got to completion at a point where no further smoke was detected from the furnace. The residence time for the charring process was 20 minutes. The charred ELTs was pulverised for 8 minutes using a ball mill.



Figure 3.1 Pulverised ELT(s)

The pulverised ELTs were screened using standard sieve of 106 μ m and the undersize was used for this research. Grinding and screening were done to enhance the bond contact during pellet formation. Figure 3.1 above is a sample of the pulverised -106 μ m used in the reducibility analysis.

3.3.2 Pudo Iron Ore

Samples of the Pudo Titaniferous Magnetite Ore were broken into various lumps using a hammer. Samples of the magnetite ore were taken for the Specific Gravity and Abrasion test. The magnetic and non-magnetic iron ore samples were crushed to 22 mm using a Morse Jaw Crusher. The particle size of the ore was further reduced using a secondary Cone Crusher. The product of the secondary crusher was screened with a 4 mm sieve size and the oversize was sent for tertiary crushing using the Marcy GY-Roll Crusher and this was done till all the material passed the 4 mm sieve. A representative sample of the stage crushed Pudo magnetite ore of -4 mm +106 μ m was taken for Particle Size Distribution (PSD) analysis and Bond ball mill work index (BBMWI) test. Part of the +106 μ m using a ball

mill. The product size of both the magnetite and non-magnetic ores were used for the reducibility studies. Figures 3.2 and 3.3 are samples of the pulverised Pudo Titaniferrous Magnetite and Non magnetic respectively used for the reducibility analysis.



Figure 3.2 Pulverised Sample of the Pudo Titaniferous Magnetite Iron Ore



Figure 3.3 Pulverised Sample of the Pudo Non Magnetic Iron Ore

3.4 Abrasion Index (AI)

With reference to this study abrasion index is said to be the relative measure of the resistance of an iron ore lump material to breakage by abrasion (Muwanguzi, 2012). Low energy

(abrasion) breakage is characterised using a tumbling test of selected single size fractions. The method used was adopted from the JK drop weight test. 3.00 kg of -55+38 mm particles size lump samples was used for the test. The samples were gently placed in a 305 mm by 305 mm laboratory tumbling drum fitted with 4×6 mm lifter bars. The drum was placed on a roller which rotated at 53 rpm for 10 mins. The resulting product was then sized using standard test sieves of 37.5 mm, 26.5 mm, 19.0 mm, 13.2 mm, 9.5 mm, 6.7 mm, 4.75 mm, 3.35 mm, 2.36 mm, 1.70 mm, 1.18 mm, 850 µm, 600 µm 425 µm. The Geometric mean particle size of the sample, the mass of the sample passing 1/10th of original particle size T₁₀ and abrasion parameter T_a values for the product were determined using equations 3.1, 3.2 and 3.3 respectively.

Geometric mean =
$$\sqrt[n]{x_1 x_2 \dots x_n}$$
 (3.1)

 $t_{10} = \frac{1}{10}$ (The Geometric mean particlesize of theoriginal size fraction) (3.2)

$$t_a = \frac{t_{10}}{10}$$
 (3.3)

3.5 Particle Size Distribution (PSD)

PSD is of great importance in determining the quality of grinding and in establishing the degree of liberation of the values from the gangue at various particle sizes (Wills and Napier-Munn, 2006). A representative sample of 500 grams of the -4 mm +106 μ m of the magnetic iron ore sample was sized using standard screens of 2.80 mm, 2.36 mm, 1.70 mm, 1.18 mm, 850 μ m, 600 μ m 425 μ m, 300 μ m, 212 μ m, 150 μ m and 106 μ m apertures to determine the feed particle size distribution 80% passing size of the feed in microns (F₈₀) of the ore. 90 μ m and 75 μ m screens were used to size a representative sample of product of the -106 μ m to determine the product particle size distribution (P₈₀) of the ore. Graphs of cumulative percent weight passing against log of sieve size for sample were drawn and the F₈₀ and P₈₀ estimated.

3.6 Bond Ball Mill Work Index (Wi) Determination

In this study the standard Bond Ball Mill Work Index (BBMWI) test procedure was used to determine the work index of the magnetic iron ore sample. BBMWI is known as the measure

of a material's or an ore's resistance to crushing and grinding. With reference to this study BBMWI will be defined as the kilowatt-hours per short ton needed to break an iron ore from an infinite size to a product size of 80% passing 106 µm (Haffez, 2012). The test was carried out in a closed circuit with a 106 µm laboratory sieve. The stage crushed magnetic iron ore sample of size -4 mm +106 µm was used for this test. A standard ball mill of size 0.305 m \times 0.23 m with rounded corners and running at 70 rpm was charged with feed weight equivalent to 700 mL and steel balls of a specified number, weighing approximately 20.1 kg. The sample was ground initially at 100 revolutions. The ground sample was screened with 106 µm sieve and the undersize sample was weighed and recorded. A representative amount of new feed was added to the test sieve oversize to bring the combined mass up to the initial mill charge. The number of revolution for the next period was determined from the previous period. This procedure was repeated five (5) times until the weight of undersize produced per mill revolution reached equilibrium. Average of net grams per revolution from the last three cycles was taken as the ball mill grindability (G_{bp}) in g/rev. A representative sample of product is sized to determine the P_{80} . Finally, the BBMWI is calculated using the Bond equation (1960) as in equation 3.4 below.

$$W_{i} = \underbrace{44.5}_{(A^{0.23} \times G_{bp}^{0.82} \left[\underbrace{10}_{\sqrt{P_{80}}} - \underbrace{10}_{\sqrt{F_{80}}} \right]}_{(A^{0.23} \times G_{bp}^{0.82} \left[\underbrace{10}_{\sqrt{P_{80}}} - \underbrace{10}_{\sqrt{F_{80}}} \right]}$$
(3.4)
Where, G_{bp} = average grams per mill revolution in g/rev;
 A = Test size sieve in microns (µm);
 P_{80} = 80% passing size of the product in microns; and

 $F_{80} = 80\%$ passing size of the feed in microns.

3.7 Specific Gravity

Specific gravity is the ratio of the density of a substance to the density of a reference substance; equivalently, it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume.

10 lump samples of the Pudo Titaniferous magnetite iron ore were used for this test. Each went through the method described hereafter. Each sample was weighed in air and thereafter

in water with an electronic weighing balance having a sensitivity of 0.1 grams. The weight in air for each lump was recorded as A_1 to A_{10} and their corresponding weight in water was recorded as W_1 to W_{10} . The specific gravity, (S.G.) of the specimen was derived by using the mathematical expression in equation 3.5.

Specific Gravity = $\frac{\text{Weight in Air (A)}}{\text{Weight in Air (A)} - \text{Weight in Water(W)}}$ (3.5)

3.8 XRF and SEM/EDS Analysis of the Pudo Iron Ore

 $30 \text{ grams} -106 \ \mu\text{m}$ of both Pudo Titaniferous Magnetite and non-magnetic iron ores were bagged and labelled as M_s and N_s for the magnetite and non-magnetic iron ore respectively. These samples were sent for XRF analysis (to determine the chemical composition) and SEM/EDS analysis (to determine the morphology and mineralogical composition of the samples) analysis at an external laboratory in Australia.

3.9 Proximate Analysis of ELT(s)

Analysis for moisture, volatile matter, ash and fixed carbon contents were carried out on samples of the shredded ELT(s).

3.9.1 Moisture

5 grams of air dried sample of ELT was placed in an air oven. The temperature of the oven was maintained at 110 °C for an hour. It was removed and weighed to determine its mass. The moisture content was calculated using equation (3.6).

% Moisture of ELT =
$$\frac{\text{Mass Before heating- Mass Afterheating}}{\text{Mass Before heating}} \times 100\%$$
(3.6)

3.9.2 Volatile Matter

5 grams of air dried ELT sample was taken in a crucible (made of silica) and covered with a lid. The crucible was introduced in a furnace and maintained at a temperature of 925 °C for 7 minutes. The crucible was then taken out and loss in weight of the ELT sample was determined by weighing it. The % loss in weight minus % of moisture content in the sample gives the value of percentage volatile matter in the sample on air dried basis as expressed in equation (3.7).

% VM of ELT = (
$$\frac{\text{Mass Before heating-Mass Afterheating}}{\text{Mass Before heating}} \times 100\%)$$
-% Moisture (3.7)

3.9.3 Ash

5 g of air dried sample was taken in a silica crucible and placed in the furnace maintained at a temperature of 775 °C, and kept there till complete burning. The percent weight of ash obtained is expressed as in equation (3.8).

% Ash of ELT =
$$\frac{\text{Mass Before Ashing - Mass After Ashing}}{\text{Mass Before Ashing}} \times 100\%$$
 (3.8)

3.9.4 Fixed Carbon

It was calculated as in equation (3.9) below:

% Fixed Carbon =
$$100 - \%$$
 (moisture + volatilematter + ash) (3.9)

3.10 Reducibility Studies

The reducibility determines the ease with which oxygen can be removed from the iron oxide in the ore by reducing agents. This influences the productivity and quality of the product.

The mass of each pellet prepared was 30 g with the ratio 70 to 85 wt.% iron ore to 13 to 28 wt.% carbonaceous materials and 2 wt.% of flour. The various blend ratios of the magnetic, non-magnetic iron ore and ELT(s) used in the reducibility studies are detailed in Table 3.1. In this work, the reducibility of naturally occurring magnetite and hematite ores and their blends are investigated into using locally generated carbonaceous material from ELTs.

3.10.1 Pelletising

Pelletising enables the conversion of iron ore fines into uniformly sized iron ore pellets, which can be charged into ironmaking furnaces or for the production of metal or direct reduced iron (DRI).

The total mass component used in forming the composite pellets was 30 grams. Pellets comprised of 21 grams of the iron ores, 8.4 grams of carbonaceous material (ELTs) and 0.6 grams of flour which served as the binding agent. These were placed in a plastic bowl. The iron ore-carbon mixtures were homogenised and moulded into a spherical pellet with the help of droplets of water. Maintaining the weights of the binding agent, carbonaceous

material (ELTs) and varying the various blends of the magnetic and non-magnetic iron ore, the above steps were repeated in forming the rest of the composite pellets and were labelled as DD, FD, GC, HB, HA and IA, M.



SAMPLE ID	IRON	ORE 70%	IRON OR	RE IN GRAMS	CARB MATI	ONACEOUS ERIAL 30%	CARBONACEOUS MATERIAL (G)			
CODE	MAGNETIC	NON MAGNETIC	MAGNETIC	NON MAGNETIC	ELTS	BINDER	ELTS	BINDER		
Μ	100%	0%	21.00	0.00	28%	2%	8.40	0.60		
IA	90%	10%	18.90	2.10	28%	2%	8.40	0.60		
НА	85%	15%	17.85	3.15	28%	2%	8.40	0.60		
HB	80%	20%	16.80	4.20	28%	2%	8.40	0.60		
GC	70%	30%	14.70	6.30	28%	2%	8.40	0.60		
FD	60%	40%	12.60	8.40	28%	2%	8.40	0.60		
DD	50%	50%	10.50	10.50	28%	2%	8.40	0.60		

 Table 3.1
 Blend Ratio of the Magnetic, Non-Magnetic Iron Ore and ELT(S) Used in the Reducibility Studies



3.10.2 Curing and Drying

The composite pellets were allowed to cure for 72 hours at room temperature to gain the requisite compressive strength needed for the firing process. It was further allowed to dry in open air for 96 hours to eliminate completely the moisture content. The choice of room temperature curing and air drying process was to ensure the preservation of the chemical composition of the iron ore - ELTs composite pellet before reduction. Figure 3.4 is a sample of the cured dried pellet.



3.10.3 Firing Process (Microwave Reduction)

The dry composite pellets were subjected to microwave heating using a 2400 MW, 50 Hz, PIONEER domestic microwave as shown in Figure 3.5. Using the method of finding the best spot for the highest energy input of a microwave described by Aguilar and Gomez (1997), the best spot was located to be 0.08 m from the entrance opening and 0.135 m from the aperture side of the microwave. The weight of a dry composite pellet was noted and recorded as mass of pellet (B_R). As a precautionary measure aimed at staving off metal loss through high temperature reaction with the crucible, direct contact between each composite pellet and the crucible was avoided. This was achieved by using a bed of the corresponding reducing agent as a seat for the composite pellet in the crucible. It was then placed in a fireclay crucible, which was then placed at the best spot determined earlier in the microwave

and heated for 40 minutes. The above procedure was repeated for the other composite pellets formed.



Figure 3.5 Reduction Process in a Domestic Microwave Oven



CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Abrasion Index (AI)

The geometric mean particle size of the original fraction size -55 mm + 38 mm is 45.7 mm. This was calculated using equation 3.1. The T_{10} sieve size was calculated to be 4.57 mm using equation 3.2. T_{10} is the % broken product passing the 4.57 mm sieve. This was estimated to be 2.54 by iterating between the cumulative percent passing for the sieves of 4.75 mm and 3.35 mm which were 2.55 and 2.47 respectively. A lower T_{10} value indicates that there is a lower percentage of material passing $1/10^{\text{th}}$ the original particle size.

The T_a value was calculated to be 0.254 using equation 3.3. The measure of the resistance of the Pudo Titaniferous Magnetite iron ore to milling by abrasion is 0.254. The lower the value, the greater the resistance of the ore to the abrasion breakage. The abrasion index of 0.254 falls within the range of 0.24 to 0.35 in Table 4.1 which indicates that the Pudo Titaniferous Magnetite iron ore is a hard ore.

Appendix B shows the Particle Size Distribution for the abrasion index and the Rosin Rammler model for the particle size distribution of the abrasion index.

 Table 4.1 Figures for the JKTech Drop Weight Test Abrasion Parameter and its

 Relative Measure

Property	Very Hard	Hard	Moderate Hard	Medium	Moderate Soft	Soft	Very Soft
Ta	< 0.20	0.24-0.35	0.35-0.41	0.41-0.54	0.54-0.65	0.65-1.38	> 1.38

(Source: Anon. 1992)

4.2 Bond Ball Mill Work Index (W_i)

The ball mill grindability (Gbp) in grams/revolution (g/rev) was calculated by averaging the results of the net mass per revolution from the last three cycles of the test. The average G_{bp} was calculated to be 0.7067 g/rev. The grindability is the ease at which a mineral particle is reduced to a predetermined size. F₈₀ of the feed and P₈₀ of the product were estimated to be 2177 µm and 86.65 µm respectively. The W_i of the Pudo Titaniferous Magnetite iron ore

was calculated to be 23.535 kWh/t using equation (3.4). Appendix C shows the feed and final product particle size analysis as well as the grindability test data.

A minimum of 23.535 kilowatts hour of energy is required to grind a ton of the Pudo Titaniferous Magnetite iron ore from an infinite size to 80% passing 106 μ m. The value of W_i obtained for the Pudo Titaniferous Magnetite iron ore sample was compared to typical values of hardness index (Table 4.2). It was deduced that Pudo Titaniferous Magnetite iron ore is very hard since its W_i falls above the index range of > 20 kWh/t. The Quartz diorite and altered hornblende–biotite granodiorite bearing rocks of the Pudo Titaniferous Magnetite ore could be the cause of its hardness. The value of the W_i is crucial in design of a metallurgical plant or circuit.

Table 4.2 Hardness Index for Various Bond Work Index Values

Property	Soft	Medium	Hard	Very Hard
Bond W _i (kWh/t)	7-9	9-14	14-20	>20

(Source: Shahani et. al., 2017; Bilal, 2017)

4.3 Specific Gravity

The ratio of the density of the Pudo titaniferous magnetite iron ore to the density of water and air is summarised in Appendix E. The average specific gravity of the ore was calculated to be 4.65 using equation (3.5). It had a standard deviation of 0.05. A specific gravity of 4.65 means the Pudo titaniferous magnetite ore is 4.65 heavier than water.

An SG of 4.65 is denser than water and will, disregarding surface tension effects, sink in water.

4.4 Nature of the Pudo Iron Ores

Table 4.3 shows the results of the chemical analysis of the Pudo iron ores in weight percentages. The Pudo Titaniferous magnetite iron ore exhibit high hematite (Fe₂O₃) content of (80.918 wt. %), with (10.140 wt. %) of TiO₂, with correspondingly low levels of silica (2.519 wt. %), alumina (3.864 wt. %), CaO (0.68 wt. %) and MgO of (1.679 wt. %) respectively.

However, the Pudo non-magnetic iron ore has a low hematite content of (14.958 wt. %), with relatively high SiO₂ content (47.244 wt. %), Al₂O₃ content of (11.844 wt. %) and with

CaO of (12.048 wt. %) and MgO of (9.059 wt. %) respectively. The high amounts of MgO and CaO in the Pudo non-magnetic ore make it an excellent fluxing agent with little amount of iron for the reduction of the Pudo Titaniferous Magnetite ore.

In addition, the ores contain other impurities such as, Na₂O, K₂O, TiO₂ and Mn₃O₄ which exist in considerably negligible amounts. Alumina represents contamination in the steel making process and is specific targets during iron ore beneficiation.

According to the results obtained from XRF analysis, it can be pointed out that the sulphur (S) and phosphorus (P) contents in the Pudo iron ores from the deposit are significantly low. The extremely low content of sulphur and phosphorus in the Pudo iron ores which are deleterious elements in iron and steel making is of 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), phosphorus 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 for SiO_2 and Al_2O_3 requirements in commercial iron ores are shown in Table 4.4

It can be observed that the silica and alumina contents of the Pudo Titaniferous magnetite ore (SiO₂ and Al₂O₃) are within the acceptable limits for commercial ores. However, the Pudo non-magnetic iron ore has high silica content, which is above the acceptable level. The contents of SiO₂ and Al₂O₃ in commercial ores should be less than (6 and 4) %, respectively according to Kiptarus *et. al.* (2015).

	Composition (wt %)									
Component	Non-Magnetic	Magnetic								
Na ₂ O	1.411	0.200								
MgO	9.057	1.679								
Al ₂ O ₃	11.844	3.864								
SiO ₂	47.244	2.519								
P ₂ O ₅	0.010	0.010								
SO ₃	0.000	0.018								
K ₂ O	0.107	0.007								
CaO	12.048	0.068								
TiO ₂	0.947	10.140								
Mn ₃ O ₄	0.456	0.409								
Fe ₂ O ₃	14.958	80.918								
LOI	1.96	1.16								
	ONLEDGE TRUTTLAND SCHURS									

Table 4.3 Chemical Composition (by XRF) of the Pudo Iron Ore used

The composition by XRF of the Pudo Titaniferous magnetite ore agrees with analysis conducted by Kesse and Banson (1975) on the ore.

The loss on ignition values 1.96 wt. % and 1.16 wt. % for both the non-magnetic and magnetic ore respectively is an indication of low volatile matter (organic matter) in the ores. Both the silica content and the volatile materials in the non-magnetic ore can be removed or reduced to its barest minimum by pre-treating (washing and preheating) the ore before subjecting it to reduction process to minimize the energy required.

Table 4.4 Generalized Percentages of Elements of Major Interest in Analysing Iron

Ore

Components	Т	otal Iron Cont	ent	SiO ₂	Al2O3	Р	S	
Components	Low	Medium	High	5102	11203	-		
Content Mass %	>58	62-64	>65	6	3-4	0.05-0.07	0.1	

(Source: Kiptarus et. al. 2015)

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 58 wt.% and 64 wt.% (Kiptarus *et. al.* 2015; Muwanguzi *et. al.* 2012).

Figures 4.1, 4.2 and Tables 4.5, 4.6 show the SEM/EDS analysis of the Pudo iron ores (magnetic and non-magnetic). The point by point surface analysis of the magnetite and non-magnetic ore exhibited an iron content of 49.20 wt% and 10.17 wt%, respectively. The complete analysis from the XRF showed an iron content of 56.597 wt%, and 10.462 wt% for the magnetite and non-magnetic ore respectively. The potential for worldwide commercial exploitation of the Pudo iron ores is low but it is possible to exploit it on small scale basis. Comparing these values to the world's iron ore classification in Table 4.4, the Pudo iron ore corresponds to the low-grade iron ore (approximately 57 wt.% which is less than 58 wt.%).





Figure 4.1 SEM/EDs Analysis for Pudo Titaniferous Magnetic Iron Ore

Element (K-Series)	Weight %	Atomic %
Fe	49.2	24.25
0	32.03	55.1
Ti	5.62	3.23
Al	4.15	4.23
С	3.13	7.18
Si	2.76	2.7
Mg	2.38	2.7
Mn	0.32	0.16
Na	0.31	0.37
Ca	0.1	0.07
Sum	100	100.0

Table 4.5 Values of SEM/EDs Analysis for Pudo Titaniferous Magnetic Iron Ore



Figure 4.2 SEM/EDs Analysis for Pudo Non Magnetic Iron Ore

Element (K-Series)	Weight %	Atomic %
Fe	10.17	3.86
0	43.51	57.64
Si	20.08	15.15
Ca	7.30	3.86
Al	5.91	4.65
Mg	5.28	4.60
с	4.60	8.13
Na	1.56	1.44
Mn	1.02	0.39
Ti	0.35	0.15
Cl	0.14	0.08
Κ	0.07	0.04
Р	0.01	0.01
Sum	100	100

Table 4.6 Values of SEM/EDs Analysis for Pudo Non Magnetic Iron Ore

4.5 **Proximate Analysis for ELT(s)**

The mass after heating the ELT sample for an hour at a steady temperature of 110 $^{\circ}$ C was 4.9575 grams. The percent moisture was calculated to be 0.85% using equation 3.6. The mass of the ELTs after subjecting it to heating for 7 minutes at a temperature of 925 $^{\circ}$ C to

expel the volatile matter was 1.9165 grams. The percent volatile matter was calculated to be 61.67% using equation 3.7. The ash content was calculated to be 7.6% using equation 3.8, the mass of the ELT sample after complete burning to produce ash at a temperature of 775 $^{\circ}$ C was weighed to be 4.62 grams.

The solid combustible residue of the ELT that remained after the shredded ELT were charred was its fixed carbon. This was calculated to be 29.88% using equation 3.9. The proximate analysis result of this study agrees with most of the analysis conducted by various authors, as illustrated in Table 4.7 below.

Author		Cor	nponent (wt	%)	
	Volatile	Fixed Carbon	Moisture	Ash	Steel
This investigation	61.67	29.88	0.85	7.6	-
Juma et al., (2006)	61.61	22.66	1.72	14.01	-
Rodrigues et al., (2001)	58.8	27.7	-	3.9	9.6
Lee et al., (1995)	67.3	28.5	0.5	3.7	-
Chang et al., (1996)	62.32	26.26	1.31	10.29	-
Gonzales et al., (2001)	61.9	29.2	0.7	8.0	-
Loresgoiti et al., (2004)	59.3	27.6	-	3.5	9.6
Orr <i>et al.</i> , (1996)	68.7	23.3	0.4	7.6	-
Williams and Bottrill, (1995)	66.5	30.3	0.8	2.4	-
Atal and Levendis, (1995)	58.7	33.6	-	7.7	-

Table 4.7 Proximate Analysis of ELTs by Various Authors

4.6 Reducibility Studies

Reducibility of an iron ore is the removal of oxygen combined with Fe from the iron ore. The rate at which the iron oxide can be reduced to metallic iron is the primary determinant of the rate of production in any reduction process (Muwanguzi, 2012).

4.6.1 Extent of Reduction

Figure 4.3 shows the extent of reduction for the magnetite ore and the various blends of the magnetite and non-magnetic ores utilising ELTs as reductant. The extent of reduction was

calculated from the oxygen content based on the weight loss of the composite pellet during the reduction process for 40 minutes.

The extent of reduction for the magnetic ore was 81.70%. The extent of reduction ranged a little over 87% to 103% for the various blends of the magnetic and non-magnetic ores. The extent of reduction for the various blends begins to increase with an increase in mass of the non-magnetic ore which served as a fluxing material for the reduction process since it contains high amounts of CaO and MgO. CaO fluxes the gangue in the iron ore to form a silicate melt phase as shown in equation 4.19. MgO either enters the magnetite lattice to form magnesio ferrite or dissolves in the slag phase. These melting phases interact with each other and dissolve a variable amount of iron oxides.

The observed extent of reduction in excess of 100% is attributed to the simultaneous reduction of SiO_2 and the blend of the magnetite and non-magnetic ore to form an alloy of ferrosilicon. Equation 4.21 shows the reduction of silica to silicon.

The magnetite ore had the lowest extent of reduction in comparison with the various blends of the magnetite and non-magnetic ores as shown in Figure 4.3 and Table 4.8.





Figure 4.3 Graph of Extent of Reduction for the Magnetite and Various Blends of the Magnetite and Non-Magnetic Ores

SAMPLE ID	Μ	IA	IA1	IA2	IA3	IA4	IA5	IA6	IA7	HA	HA1	HA2	HA4	HA5	HA6	HB	HB1	HB2	HB3	HB4	GC	GC1	GC2	GC3	GC4	FD	DD
WTG BEFORE																											
REDUCTION (G)	29.7	30.0	29.6	28.0	29.8	30.0	29.8	30.0	31.3	26.9	29.8	29.5	29.7	30	31.2	29.5	29.4	29.9	29.2	29.8	29.9	29.7	29.9	29.5	28.2	28.0	28.3
WTG AFTER																											
REDUCTION (G)	16.4	14.9	15.2	15.9	18.0	14.4	15.9	15.7	14.4	18.4	16.6	15.1	15.4	14.9	15.9	14.9	13.5	14.1	16.8	13.8	10.9	17.0	14.7	15.9	13.7	13.1	12.2
WEIGHT LOSS																											
(G)	13.3	15.1	14.4	12.1	11.8	15.6	13.9	14.3	16.9	8.5	13.2	14.4	14.3	15.1	15.3	14.6	15.9	15.8	12.4	16.0	19.0	12.7	15.2	13.6	14.5	14.9	16.1
AVERAGE																											
WEIGHT LOSS	13.3				14	1.3				-		13	3.5				-	14.9					15	.0		14.9	16.1
(G)																											
% WGT LOSS	44.78	50.33	48.65	43.21	39.60	52.00	46.64	47.67	53.99	31.60	44.30	48.81	48.15	50.33	49.04	49.49	54.08	52.84	42.47	53.69	63.55	42.76	50.84	46.10	51.42	53.21	56.89
AVERAGE %	44.70				47	70						40	12	11.				50.51					50	02		52.24	50.00
WTG LOSS	44.78	47.76					40.13				50.51					50.93					53.21	56.89					
% REDUCTION	81.70	91.83	88.76	78.84	72.24	94.87	85.10	86.97	98.51	57.65	80.82	89.06	87.85	91.83	89.47	90.30	98.67	96.41	77.48	97.96	115.94	78.02	92.75	84.11	93.81	97.09	103.80
BLEND	100 Magnetic				00 Momotio - 10 Non-momotio	70 Magneue + 10 Multimagneue					ron		oo Magneuc + 15 Mon magneuc					80 Magnetic + 20 Non magnetic					70 Magnetic + 30 Non magnetic			60 Magnetic + 40 Non Magnetic	50 Mag + 50 NonMag
AVERAGE % REDUCTION	81.70				87	.14						87	.81				9	92.0	6				92.	93		97.09	103.80

Table 4.8 Extent of Reduction Values for the Magnetite and Various Blends of the Magnetite and Non-Magnetic Ores after Reduction

4.6.2 Nature of the Metal Produced

Throughout the firing of the dried green iron ore-ELT composite pellets, for a residence time of 40 minutes, 3 chemically and physically different products were observed. These products are:

- I. Direct reduced iron (DRI);
- II. Transition Direct Reduced Iron (TDRI);
- III. Pure iron nuggets and slag;

It is observed from Figure 4.4 that a direct reduced iron was produced. It has an Irregular sponge like structure. The reduced metal was formed in the solid state. The metallized portion of the DRI did not melt. This reduced pellet was the 100% magnetite-ELT composite pellet. It has a low metallisation because magnetite ores are naturally difficult to reduce to metallic iron because of its porosity. Moreover, the Pudo magnetite ore is not a self-fluxing ore to enter into the molten state during reduction. DRI produced from the Pudo magnetite ore will be a good substitute for steel scrap for producing steel in EAF and BOF.



Figure 4.4 Samples of Reduced Material obtained after Reduction of 100% Magnetite Ore Iron Ores with ELT

From Figures 4.5 and 4.6 Transition Direct Reduced Iron (TDRI) are produced. The reduced pellets were 90% magnetite, 10% non-magnetic iron ores-ELT composite pellets and 85% magnetite, 15% non-magnetic iron ores-ELT composite pellets respectively. It can be observed that they have an irregular to spherical shape. They have higher metallisation than DRI due to the partial slag separation and reduced amount of pores. It can be observed that Figure 4.5 has higher pores but with a lower metallisation when compared to the Figure 4.6. This is because composite pellet of Fig. 4.6 had 5% more mass of the non-magnetic ore which served as a fluxing material than composite pellet of Fig. 4.5. TDRI was produced as more carbon dissolved in DRI and the metallised portion partially melted as a result of the addition of the non-magnetic iron ore which served as flux. As a result of this partial melting, partial slag separation was achieved.



Figure 4.5 Samples of Reduced Metal obtained after Reduction of 90% Magnetite and 10% Non-magnetic Iron Ores with ELT



Figure 4.6 Samples of Reduced Metal obtained after Reduction of 85% Magnetic and 15% Non-magnetic Iron Ores with ELT

The iron nuggets produced from Figures 4.7 to 4.10 are spherical in structure. These spheres of metal were embedded in the slag phase of the reduced material and were subjected to breakage to free the spherical metals. Slag separation was achieved due to the formation of two liquid products; slag and metal. This is due to the immiscibility and density difference.

The spherical shape of the metallic iron nuggets is an indication that they were solidified from the molten state. Physical separation of the mixture of reduced metals and slag components was effected using a low intensity handheld magnet. The spherical nature of the reduced metal could be attributed to the high CaO and MgO in the Pudo non-magnetic ore which served as an excellent fluxing agent in the reduction process and the excess carbon present in the iron ore-carbon composite causing the reduced iron to pick up these excess carbons causing the reduced iron to melt at a lower temperature into a molten mass that solidifies into sphere when the microwave power is put off.


Figure 4.7 Samples of Reduced Metal obtained after Reduction of 80% Magnetic and 20% Non-magnetic Iron Ores with ELT



Figure 4.8 Samples of Reduced Metal obtained after Reduction of 70% Magnetic and 30% Non-magnetic Iron Ores with ELT



Figure 4.9 Samples of Reduced Metal obtained after Reduction of 60% Magnetic and 40% Non-magnetic Iron Ores with ELT



Figure 4.10 Samples of Reduced Metal obtained after Reduction of 50% Magnetic and 50% Non-magnetic Iron Ores with ELT

4.6.3 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.

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 CO₂ 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 (CO₂) through the Boudouard reaction (CO₂ + C = 2CO) to produce carbon monoxide (CO) which is also a reducing gas. The syngas as they diffuse from the core to the outer of the pellet also achieve some form of reduction which together with the solid carbon contributes to the high extent of reduction achieved when microwave was used as a heating source.

The DRI, also called sponge iron, was produced from the direct reduction of the iron carbon composite by the reducing gas or elemental carbon produced from the ELTs

The Pudo non-magnetic iron ore contained high amounts of gangue materials such as silica (SiO₂), Alumina (Al₂O₃) along with high amounts of CaO and MgO. ELTs on the hand contain some amount of sulphur (S). Removal of these impurities was done by fluxing them by the CaO and MgO to form slag which consists of low melting point complex compounds such as calcium silicate, calcium aluminate etc. Further, CaO from the non-magnetic iron ore reacts with sulphur present in the ELT to form CaS which goes into the slag phase. Equations 4.1 to 4.23 show the possible reaction mechanisms for the reducing the Pudo magnetite ore and the various blends of the magnetite and non magnetic ore using ELTs as a source of reductant.

$Fe_2O_3 + 3C = 2Fe + 3CO$	(4.1)
$Fe_3O_4 + 4C = 3Fe + 4CO$	(4.2)

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$
 (4.3)

 $Fe_{3}O_{4} + 4H_{2} = 3Fe + 4H_{2}O$ (4.4)

The reduction of Fe₂O₃ by solid carbon (C) to produce Fe

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

$$Fe_3O_4 + C = 3FeO + CO \tag{4.6}$$

$$FeO + C = Fe + CO \tag{4.7}$$

The reduction of Fe₂O₃ by carbon monoxide (CO) to produce Fe

$$Fe_2O_3 + \frac{1}{3}CO = \frac{2}{3}Fe_3O_4 + \frac{1}{3}CO_2$$
(4.8)

$$Fe_3O_4 + CO = 3FeO + CO_2 \tag{4.9}$$

$$FeO + CO = Fe + CO_2$$
(4.10)

The reduction of Fe_2O_3 by carbon monoxide (H₂) to produce Fe

$Fe_2O_3 + \frac{1}{3}H_2 = \frac{2}{3}Fe_3O_4 + \frac{1}{3}H_2O$	(4.11)
$Fe_3O_4 + H_2 = 3FeO + H_2O$	(4.12)
$FeO + H_2 = Fe + H_2O$	(4.13)
Oxidation of solid carbon	
$C + 1/2O_2 = CO$	(4.14)
$C + O_2 = CO_2$	(4.15)
Gasification of C by CO ₂ (Boudouard reaction)	
$CO_2 + C = 2CO$	(4.16)
Water gas shift reaction:	
$H_2O + CO = H_2 + CO_2$	(4.17)
Gasification of C by H ₂ O	
$H_2O + C = H_2 + CO$	(4.18)

Slag forming reactions

$$CaO + SiO_2 = CaSiO_3$$

$$FeS + CaO + C = CaS + FeO + CO$$

$$SiO_2 + 2C = Si + 2CO$$

$$(4.19)$$

$$(4.20)$$

$$(4.21)$$

$$FeO + SiO_2 = FeSiO_3$$
 (4.22)



(4.23)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A laboratory investigation has been conducted on the nature of Pudo iron ore deposit and how it responds to reduction utilising End-of-Life Tyres (ELTs) as reducing agent. Iron ore was found to exist in two forms; thus the magnetite and non-magnetic. Based on the various test work carried out in these studies, the following are the major findings from the studies:

- a. The Pudo Titaniferous magnetite iron ore exhibit high hematite (Fe₂O₃) content of (80.918 wt. %), with Fe content of (56.59 wt.%) with the presence of TiO₂ (10.140 wt.%) with extremely low sulphur and phosphorus content.
- b. The Pudo magnetite ore is a very hard ore based on its BWI and abrasion index of 23.535 kWh/t and 0.254 respectively.
- c. The Pudo Titaniferrous magnetite ore has a specific gravity of 4.65
- d. Pudo non-magnetic iron ore has a low hematite content of (14.958 wt.%), with relatively high SiO₂ content (47.244 wt.%), Al₂O₃ content of (11.844 wt.%) with CaO of (12.048 wt. %) and MgO of (9.059 wt.%).
- e. The Pudo non-magnetic ore is an excellent fluxing material.
- f. ELTs are excellent potential source of carbonaceous material for iron oxide reduction.
- g. ELT utilised for this investigation has a fixed carbon content of 29.88% from its proximate analysis.
- h. The Extent of reduction for the 100% magnetite ore was 81.70%, its metal had an irregular spongy like structure.
- i. The extent of reduction rose little over 87% to 103% for the various blends of the magnetic and non-magnetic ores. The extent of reduction in excess of 100% is attributed to the complete reduction of the iron oxide and reduction of SiO_2 in the ore to form an alloy of ferrosilicon.

5.2 Recommendations

Due to various facts and observations obtained in this investigation, the following are recommendations made pertaining to this investigation;

- a. ICP-OES analysis should be conducted on the metals produced to determine their composition.
- b. LECO C/S analysis should be conducted on the metal produced to determine its carbon and sulphur content.
- c. Laboratory simulated process route should be carried out to develop a suitable and cost-efficient process route for reducing the Pudo iron ore.
- d. Charring of ELTs should be conducted in a fume chamber.
- e. Issues concerning ELTs in Ghana could be solved by using it in reduction processes.
- f. Metallic iron produced from this ore could serve as an alternative raw material to scraps for steel companies in the country.

Also further works should investigate on the time based reducibility analysis on the various blend ratios of the Pudo Iron ore and its kinetics. The effect of particle size distribution on the reducibility analysis of the various blends of the Pudo iron ores should be investigated.



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APPENDICES

APPENDIX A

ELTs ANALYSIS

Table A.1 Ultimate Analysis of ELTs

Author	Component (wt %)					
	С	Н	Ν	S	0	Ash
Rodrigues et al., (2001)	74.2	5.8	0.3	1.5	4.7	13.5
Juma et al., (2006)	81.24	7.36	0.49	1.99	8.92	-
Lee et al., (1995)	83.8	7.6	0.4	1.4	3.1	3.7
Chang et al., (1996)	74.4	6.96	0.21	1.6	5.02	10.21
Gonzales et al., (2001)	86.7	8.1	0.4	1.4	1.3	2.9
Chen et al., (2001)	81.16	7.22	0.47	1.64	2.07	7.44
Berrueco et al., (2005)	88.5	6.6	0.4	1.6	3.0	-
Arion <i>et al.</i> , (2001)	73.8	5.3	0.44	1.71	0.11	17.8
Loresgoiti et al., (2004)	74.2	5.8	0.3	1.5	5.1	13.1
Orr <i>et al.</i> , (1996)	81.3	7.3	0.3	1.5	-	1.4
Williams and Bottrill (1995)	85.8	8.0	0.4	1.0	2.3	2.4
Lanoir et al., (1997)	82.63	7.5	0.36	1.69	-	-
Senneca et al., (1999)	86.7	6.9	0.3	1.9	1.0	3.3
Roy et al., (1997)	86.6	8.1	0.5	0.8	2.2	-
Cunliffe and Williams (1998)	86.4	8.0	0.5	1.7	3.4	2.4

APPENDIX B

ABRASION INDEX

Table B.1 Particle Size Distribution for Abrasive Index

PARTICLE SIZE DISTRIBUTION FOR ABRASIVE INDEX						
Sieve Size (µm)	Mass Retained (g)	Percent Mass Retained (%)	Cumulative Percent Retained (%)	Cumulative Percent Passing (%)		
54500	0.0	0.00	0.00	100.00		
37500	2309.5	76.88	76.88	23.12		
26500	482.5	16.06	92.95	7.05		
19000	89.2	2.97	95.92	4.08		
13200	32.2	1.07	96.99	3.01		
9500	4.5	0.15	97.14	2.86		
6700	6.7	0.22	97.36	2.64		
4750	2.6	0.09	97.45	2.55		
3350	2.4	0.08	97.53	2.47		
2360	2.3	0.08	97.61	2.39		
1700	2.6	0.09	97.70	2.30		
1180	4.7	0.16	97.85	2.15		
850	7.2	0.24	98.09	1.91		
600	8.7	0.29	98.38	1.62		
425	13.7	0.46	98.84	1.16		
0	34.9	1.16	100.00	0.00		
	3003.8			-		

	Size (µm)	
D80	50077.81	
D60	45655.61	
D30	39022.32	
D10	28518.62	ABRASION INDEX (Ta)
T ₁₀ (4570 μm)	2.54	0.254
Uniformity Coefficient	1.60	
Coefficient of Gradation	1.17	
X	33184	
В	1	

Table B.3 Table Model for Abrasive Index

			R^2
		Rammler	K 2
77.41	3520000	100.00	510.305275
66.81	2489016	100.00	1909.023
56.62	1760000	100.00	2457.10934
47.27	1244508	100.00	1864.74928
38.00	880000	100.00	1224.30108
30.74	622254	100.00	777.559637
24.25	440000	99.96	467.310246
19.02	311127	99.75	271.127218
14.74	220000	98.94	150.614687
11.35	155563.5	96.81	80.2562232
8.85	110000	92.65	42.8381361
6.68	77781.75	86.16	20.5637878
5.18	55000.00	77.66	10.7085035
3.94	38890.87	67.87	5.41359452
3.01	27500.00	57.70	3.40635871
0.00	19445.44	47.89	0



Fig B.1 Model Log Graph of Particle Size Distribution for Abrasion Product

APPENDIX C

BOND BALL WORK INDEX AND PARTICLE SIZE DISTRIBUTION

PSD FOR BOND INDEX SAMPLE FEED						
Screen (mm)	Weight (g) Oversize	% Oversize	Cumulative % Oversize	Cumulative % Passing		
3.35	0	0.00	0.00	100.00		
2.8	43	8.60	8.60	91.40		
2.36	33.5	6.70	15.30	84.70		
1.7	84.7	16.94	32.24	67.76		
1.18	89.2	17.84	50.08	49.92		
0.85	60.5	12.10	62.18	37.82		
0.6	45.2	9.04	71.22	28.78		
0.425	33.3	6.66	77.88	22.12		
0.3	25.7	5.14	83.02	16.98		
0.212	19.3	3.86	86.88	13.12		
0.15	14.1	2.82	89.70	10.30		
0.106	11.9	2.38	92.08	7.92		
0	39.60	7.92	100.00	0.00		
Total	500.00		F80, mm	2.18		
		•	F80, µm	2177		

Table C.1 Particle Size Distribution (PSD) for Bond Index Sample Feed (F80)



Fig C.1 Graph of Particle Size Distribution for Bond Work Index Feed

 Table C.2 Particle Size Distribution (PSD) for Bond Index Product Sample (P80)

PSD FOR SAMPLE -106 µm					
	Weight (g)	9/ Oversize	Cumulative	Cumulative %	
Screen (µm)	Oversize	% Oversize	% Oversize	Passing	
106	0.0	0.00	0.00	100.00	
90	77.3	15.46	15.46	84.54	
75	101.7	20.34	35.80	64.20	
0	321.0	64.20	100.00	0.00	
Total	500.00		P80, μm	86.65	



Fig C.2 Graph of Particle Size Distribution for Bond Work Index Product

BOND BALL WORK INDEX										
Cycle No.	New Feed (g)	No. of Rev	Mass of +106 in product (g)	Mass of - 106 in Product (g)	Loss from Mill (g)	Total Refill (g)	Net gram/rev	Mass of - 106 in feed (g)	time in sec	time in mins
1	1925.1	100.0000	1753.2000	169.1000	2.8000	171.9000	0.1943	152.47	85.71428571	01:26
2	1925.1	2045.8986	596.6000	1325.9000	2.6000	1328. <mark>5</mark> 000	0.6427	13.61448	1753.627366	29:14
3	1925.1	834.6345	1276.3000	647.4000	1.4000	648. <mark>8</mark> 000	0.6513	105.2172	715.4010109	11:55
4	1925.1	682.9777	1374.0000	549.8000	1.3000	551.1000	0.7317	51.38496	585.4094441	09:45
5	1925.1	681.5133	1379.1000	545.0000	1.0000	546.0000	0.7371	43.64712	584.15428	09:44
					92 ~~					
IPP	550.0285714	3.5	70	60	86400		0.7067			
	100			WLEDGE,	RUTH AND	NORTH NO				
1756.0000										
						BOND	INDEX	23.535		

Table C.3 Data Sheet for Bond Ball Work Index

APPENDIX D

SPECIFIC GRAVITY

Table E.1 Summary of Specific Gravity Analysis on the Pudo TitaniferousMagnetite Iron Ore

SPECIFIC GRAVITY					
Weight In Air (g)	Weight in Water (g)	SG			
136.69	107.38	4.66			
94.59	74.2	4.64			
86.74	68.05	4.64			
101.45	79.53	4.63			
134.72	105.45	4.60			
26.05	20.57	4.75			
100.79	78.75	4.57			
57.2	44.9	4.65			
93.9	73.93	4.70			
102.6	80.61	4.67			
	Mean:	4.65			
	Standard Deviation	0.05			

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