THE REDUCTION OF CHINKOMBE
ILMENITE WITH GRAPHITE

BY

KODJO I. AF EWU B.Sc (ENG.)

A thesis submitted to the University of Zambia in
fulfilment of the requirements of the degree of Master
of Mineral Sciences in Metallurgy and Mineral
Processing. 236505

THE UNIVERSITY OF ZAMBIA

LUSAKA

1988
DECLARATION

This report is an account of research conducted by KODJO I. AFEWU in the laboratories of the School of Mines, University of Zambia, and other laboratories referred to, and the researcher attests that it is not a reproduction of work that has been submitted before for a degree at this or any University.

K.I. AFEWU

DECLARATION

This report is an account of research conducted by KODJO I. AFEWU in the laboratories of the School of Mines, University of Zambia, and other laboratories referred to, and the researcher attests that it is not a reproduction of work that has been submitted before for a degree at this or any University.

K.I. AFEWU

APPROVAL

This thesis of KODJO I. AFEWU is approved as fulfilling the requirements for the award of the degree of Master of Mineral Sciences in Metallurgy and Mineral Processing by the University of Zambia.

Signatures of Examiners

1. ........................................... ........................
   PROF. DR. ANDREJ PAULIN
   EXTERNAL EXAMINER

   ........................................... ........................
   17th July 1989

2. ........................................... ........................
   PROF. E.M.R. KIREMIRE
   CHAIRMAN
   BOARD OF INTERNAL EXAMINERS

   ........................................... ........................
   26th October 1989

3. ........................................... ........................
   IR. J.W. DEELDER
   MEMBER
   BOARD OF INTERNAL EXAMINERS

   ........................................... ........................
   19th October 1989

4. ........................................... ........................
   DR. J.B. MWALULA
   SUPERVISOR

   ........................................... ........................
   19th October 1989
DEDICATION

This thesis dedicated to my dear wife Gladys and our daughter Kekeli for their patience, tolerance and love.

TO GOD BE ALL GLORY, HONOUR AND PRAISE.
ABSTRACT

The proportion of the mineral phases in the Chinkombe ilmenite was estimated by point counting under a Reflected Light Microscope.

Reduction experiments were carried out on pellets made from mixtures of the ore and graphite in predetermined proportions, in the temperature range of 1173 to 1373 K. The experiments were conducted in an atmosphere of purified nitrogen gas and the isothermal weight loss sustained by the pellet formed from the mixture was determined and plotted as a function of time.

The effects of variables such as temperature, ore-graphite ratio in the mixture, ore particle size and the addition of a catalyst were also investigated.

The diffusion model \( f(R) = 1 - 2/3R - (1-R)^{2/3} \), fairly represented the kinetic data found in this investigation and an enthalpy of 482.0 kJ/mole (115.3 kcal/mole) was obtained in the temperature range of 1173 to 1373 K.
ACKNOWLEDGEMENT

With great pleasure, I wish to express my gratitude and thanks to the following persons:

- Dr. J.B. Mwalula, my Supervisor for his invaluable assistance, kindness and guidance at all stages of this work.

- Dr. J. Kaoma, Senior Scientist, and Head of the Industrial Minerals Section, at National Council for Scientific Research, Lusaka, for following this investigation at all its stages and his useful criticisms and constructive suggestions.

- Mr. Alfred Mumba, Senior Exploration Geologist, Minex-Zimco, Lusaka, who took me to the Petauke District in search of the sample for this research.

- Mr. H. Nugteren, for his cooperation and patience during the X-R-F and X-R-D analyses.

- Mr. Peter Hey, Head of Mineralogy, Technical Services, ZCCM, Kalulushi, for allowing me to complete the XRD analysis on their instrument when the diffractometer in School of Mines was out of order.

- Dr. N. Mtongo, Nuclear Chemist at National Council for Scientific Research, Lusaka, who led me through the analysis on their Mössbauer Spectrometer.

- Mr. Roy Morgan, Chief Technician, School of Mines, who has helped me so much and for putting his personal vehicle at my disposal on uncountable
number of occasions.
- Mr. Josh Kasengele, Senior Technician for the great
  love he has shown to me throughout this investigation.
- Messrs Shitimali, A. Yaluma, W. Nondwe, A. Munkhambwa,
  A. Mwansa and Mrs. L. Sichilima for their help.
- The entire academic staff in the School of Mines.
- My Christian brethren, Messrs A. Banda, A. Chimpashi,
  Ms S. Kamwanga, Dr M.B. Kamwanga, the Wotelas,
  Njapawus, Chilas and all members of the University
  Christian Fellowship and and the entire Christian
  community for their prayer support.
- My brothers who are also on the same programme, Messrs
  W. Assibey-Bonsu, Sam Frimpong, Temeng Amoako, H.
  Adjei-Sarpong, C. Akayuli, C. Sarpong for their
  encouragement and prayers.
- The Ghanaian community in Lusaka, especially the
  Agyemans, Tamakloes, Abotsis, Osei-Agyemans and Donkos
  for their encouragement.
- My mother, sister and brother for their care and love.
- My dear with Gladys and our daughter Kekeli for their
  patience, tolerance and to Gladys again for typing the
  final report in its present form.
- Ms Katulula for typing the initial manuscripts.
- ANSTI-UNESCO for giving me a study fellowship.

November, 1988

K.I. AFEWU
## CONTENTS

<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>i</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>CONTENTS</td>
<td>vii</td>
</tr>
</tbody>
</table>

### CHAPTER ONE

1.1 Introduction                            | 1

1.2 Geological Background and Mineralogy of Ilmenite | 2

1.3 Occurences of Ilmenite in Zambia           | 4

1.4 Market of Ilmenite and Rutile              | 5

1.5 Previous Work on Production of Titanium Dioxide from Ilmenite | 7

1.5.1 Concentration                           | 7

1.5.2 Chemical Processes of Reduction of Ilmenite | 8

1.6 Objectives of this Investigation           | 10

1.7 Scope of the Work                          | 10

### CHAPTER TWO

Theoretical Background                        | 11

2.1 Thermodynamics of Reduction of Ilmenite and Iron Oxides | 11

2.2 The Kinetics and Mechanisms of Reduction of Oxides with Carbon | 21

2.2.1 Introduction                            | 21
2.2.2 Mechanisms  
2.2.3 Effect of Temperature on the Kinetics of a Reaction  
2.2.4 Order of Reaction and Reaction Rate  
2.2.5 Evaluation of the Kinetic Data  

CHAPTER THREE  
MINERAL CHARACTERIZATION  
3.1 Ore Microscopy  
3.2 X - ray Diffraction  
3.3 Mössbauer Spectroscopy  
3.4 Chemical Analysis  
3.4.1 Qualitative Analysis  
3.4.2 Quantitative Chemical Analysis  
3.5 Summary and Conclusion of Mineral Characterization  

CHAPTER FOUR  
EXPERIMENTAL  
4.1 Materials  
4.2 Preparation of Samples  
4.3 Equipment Assembly  
4.4 Experimental Procedure  

CHAPTER FIVE  
RESULTS AND DISCUSSIONS  
5.1 RESULTS  
5.1.1 Effect of Temperature and Time  
5.1.2 Effect of Quantity of Carbon
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.3</td>
<td>Effect Ore particle size</td>
<td>51</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Effect of catalyst</td>
<td>57</td>
</tr>
<tr>
<td>5.1.5</td>
<td>Effect of Preoxidation</td>
<td>57</td>
</tr>
<tr>
<td>5.2</td>
<td>IDENTIFICATION OF THE PHASES IN THE REDUCED PRODUCTS</td>
<td>61</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Variation of Temperature</td>
<td>61</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Variation of Quantity of Carbon</td>
<td>72</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Effect of Catalysis</td>
<td>73</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Effect of Preoxidation</td>
<td>73</td>
</tr>
<tr>
<td>5.3</td>
<td>DISCUSSIONS</td>
<td>79</td>
</tr>
<tr>
<td>5.3.1</td>
<td>The Chemical Processes in the Reduction of the Chinkombe Ilmenite with Graphite</td>
<td>79</td>
</tr>
<tr>
<td>5.4</td>
<td>THE EFFECT OF THE VARIED PARAMETERS</td>
<td>87</td>
</tr>
<tr>
<td>5.4.1</td>
<td>The Effect of Temperature</td>
<td>87</td>
</tr>
<tr>
<td>5.4.2</td>
<td>The Effect of Variation of percent Carbon in the Mixture</td>
<td>88</td>
</tr>
<tr>
<td>5.4.3</td>
<td>The Effect Ore Particle Size</td>
<td>89</td>
</tr>
<tr>
<td>5.4.4</td>
<td>The Effect of Catalysis</td>
<td>89</td>
</tr>
<tr>
<td>5.5</td>
<td>PHASES IN THE REDUCED PRODUCTS</td>
<td>91</td>
</tr>
<tr>
<td>5.5.1</td>
<td>Variation of Temperature</td>
<td>91</td>
</tr>
<tr>
<td>5.5.2</td>
<td>Variation of Carbon</td>
<td>92</td>
</tr>
<tr>
<td>5.5.3</td>
<td>The Effect Catalysis</td>
<td>94</td>
</tr>
<tr>
<td>5.5.4</td>
<td>The Effect of Preoxidation</td>
<td>94</td>
</tr>
<tr>
<td>5.6</td>
<td>ANALYSIS OF THE KINETIC DATA</td>
<td>96</td>
</tr>
<tr>
<td>5.6.1</td>
<td>The Order of the Reaction at 1373 K</td>
<td>96</td>
</tr>
<tr>
<td>5.6.2</td>
<td>Modelling of the the Reaction Kinetics and Enthalpy of Activation</td>
<td>101</td>
</tr>
</tbody>
</table>
CHAPTER SIX
SUMMARY, CONCLUSION AND SUGGESTIONS 114
6.1 SUMMARY AND CONCLUSION 114
6.2 SUGGESTIONS 116
REFERENCES 118
APPENDICES 124
CHAPTER ONE

1.1 INTRODUCTION

Modern production of Titanium (Ti) and Titanium dioxide (TiO₂) is putting stress worldwide on natural reserves of rutile. In the late 1960's, it was forecast that there would be a worldwide shortfall of rutile supplies (1). This has not developed as quickly as expected but it could happen over a long period of time (1). Since ilmenite, another source of TiO₂ and Ti, is more relatively abundant in nature and cheaper than rutile (1,2), concerted effort, nowadays, is directed towards the development of beneficiation processes of ilmenite to produce synthetic rutile, a substitute of natural rutile, as a source of TiO₂ and Ti (1,3), thus reducing the dependence on the expensive and potentially scarce reserves of rutile.

Only about 5% of the world's annual production of titanium minerals goes to make Ti-metal and the remaining 95%, is primarily used to make white pigment of titanium dioxide (4,5). The interest in titanium dioxide shown by the pigment industry lies in its high refractive index (n = 2.55 - 2.71) (4). As a result of this property, TiO₂ imparts whiteness, opacity and brightness to paints and is suitable for use in varnishes and lacquers. Other useful properties of TiO₂ pigment include resistance to
chemical attack, good thermal stability and resistance to ultra-violet degradation. The same qualities of TiO₂ make it useful as a filler and coating in paper, plastics, textiles, asbestos, enamels, toilet soaps etc. Other uses of TiO₂ are glazing on ceramics and glass and as fluxing coat on electric welding rods.

Titanium (Ti), obtained from either ilmenite or rutile, has several applications in industry. The high strength-to-weight ratio of its alloys and their resistance to corrosion, make titanium a strategic metal. It is used in both frame and engine for high performance military and civilian aircraft, in electric generating plants and for the manufacture of a wide range of chemical processing and handling equipment (5).

1.2 GEOLOGICAL BACKGROUND AND MINERALOGY OF ILMENITE

Ilmenite is the most abundant titanium mineral (5) with the chemical formula FeTiO₂ and theoretical composition of 52.7% TiO₂ and 47.3% FeO. However, the term 'ilmenite' is also used to include material that has been oxidised and leached during weathering, containing up to 70% TiO₂, about 25% to 30% iron oxides and about 5% oxides of other elements (5). When the alteration is extreme, the residual material is essentially amorphous to finely crystalline TiO₂, and is called leucoxene (2).
Ilmenite has a Mohs' hardness of 5-6 and specific gravity of 4.3-5.5 (2). It is usually black and paramagnetic and has black streak. It occurs in hard rock deposits and beach sands.

Nearly all of the known commercially important rock deposits of titanium minerals are associated with anorthositic or gabbroic rocks (5) and are of three main types viz:

(a) ilmenite - magnetite (titano-ferrous magnetite)
(b) ilmenite - hematite (hemo-ilmenite), and
(c) ilmenite - rutile (titano-rutile).

Ilmenite-magnetite deposits usually contain ilmenite and magnetite as granular intergrowths that can be separated rather readily to yield concentrates of ilmenite and magnetite that may be essentially homogeneous minerals, or may consist of intimate intergrowths of one mineral in the other.

Ilmenite-hematite deposits usually contain these minerals as intimate intergrowths and yield an ilmenite-hematite (hemo-ilmenite) concentrate rather than a separate concentrate of each mineral. Ilmenite-rutile deposits contain rutile and ilmenite either as separate phases or as solid solution.
1.3 OCCURRENCES OF ILMENITE IN ZAMBIA

A deposit of ilmenite has been located around Chinkombe in the Petauke District of the Eastern Province of Zambia. The details of the site of the outcrops are contained in the O'Brien report (6). However, there is no evidence of any further geological study to know the origin of the deposit and its reserves (7,8), though it has been reported that the deposit in this area could be large and fairly consistent in chemical composition (6).

Another deposit which is a complex iron, uranium and titanium mineral called Davidite has been reported found west of Lusaka with an assay value of 17% TiO$_2$ (9). Its reserves have not been estimated yet.

Zambia currently depends on imported TiO$_2$ for her paint industry and other industries that make use of titanium dioxide as a raw material. It is imported from South Africa, West Germany, Swaziland, Spain and the United Kingdom (10).

The cost per tonne of titanium which is ever-increasing as shown graphically in Figure 1.1, and this calls for Zambia to exploit its own resources. Its local exploitation would save foreign exchange for the country and create job opportunities for the people.
1.4 MARKET OF ILMENITE AND RUTILE

Figure 1.1 shows the trend in the average annual price of rutile and ilmenite between 1981 and 1987. The expected short-fall (1,4) coupled with an increase in demand for Ti, TiO₂ and other non-metallic forms of titanium, has resulted in the price increase of these products.

The world demand for titanium-metal by the year 2000 has been forecast to range between 130,000 to 300,000 short tons, with the most probable demand estimated at 210,000 short tons, corresponding to an annual growth rate of 6.2% from 1983 (5).

The world demand for titatium dioxide and other non-metallic forms of titanium by the year 2000 has been estimated to be in the range of 2.2 to 3.8 million short tons (of titanium content), representing an annual average growth of 2.8% from 1983 (5).

Table 1.1 gives the consumption and the cost of titanium dioxide imported into Zambia from 1984 to 1986. The cost of titanium dioxide increased about eight-fold from 1984 to 1986 for about the same quantity of the commodity. This is very likely to continue till the economy of the country improves. Hence the production of TiO₂ from local resources would be a great relief to its users - mainly the paint industry.
Figure 1.1 Average annual London prices of rutile and ilmenite from 1981 to 1987

SOURCE: Average prices/year computed from Mining Journal - LONDON
Table 1.1  Quantity and Cost of import of Titanium Dioxide into Zambia from 1984 to 1986.

<table>
<thead>
<tr>
<th>YEAR</th>
<th>1984</th>
<th>1985</th>
<th>1986</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity (kg)</td>
<td>202122</td>
<td>295896</td>
<td>184249</td>
</tr>
<tr>
<td>Cost (Kwacha)</td>
<td>418612</td>
<td>1411459</td>
<td>3027441</td>
</tr>
</tbody>
</table>

Source: Central Statistics Office, Lusaka.

1.5  PREVIOUS WORK OF PRODUCTION OF TITANIUM DIOXIDE FROM ILMENITE

1.5.1  Concentration

The mode of occurrence and the mineralogical composition of ilmenite determine the upgrading processes. Usually, ilmenite is concentrated by:

(i) Gravity separation techniques using Humphreys spirals, pinched sluice, jigs (especially for stream type deposits)
(ii) flotation
(iii) magnetic and electrostatic separation, and/or a suitable combination of all or some of the above mentioned beneficiation techniques.
1.5.2 Chemical Processes of Reduction of ilmenite

Ilmenite is a spinel of iron oxide and titanium dioxide. Thus it is not possible to separate iron from the titanium in ilmenite by physical methods. Hence intensive chemical treatment has invariably been applied to the mineral to effect this separation. Materials from ilmenite that have a TiO₂ as synthetic rutile are beneficiated ilmenite. Processes to produce rutile substitutes from ilmenite fall into three general classes:

(i) those in which the iron oxide is completely reduced to metallic iron which is either physically or chemically separated from the reaction mass,

(ii) those in which the iron oxide is reduced to the ferrous state and is chemically leached out from the titanium dioxide.

(iii) those in which ilmenite is selectively chlorinated to remove iron and other impurities.

Since 1968, Associated Minerals Consolidated Ltd in Capel, Australia has been engaged in the reduction of the iron content of ilmenite to the metallic state, followed by accelerated oxidation of the iron to rust-like particles in an aqueous environment. The process, originally known as the Becher Process, involves oxidation, reduction and
aeration (2,5).

At Richards Bay in South Africa, ilmenite (approximately 50% TiO₂) is reduced with coal in electric furnace to yield 85% TiO₂ slag (2,5). Quebec Iron and Titanium in Canada and Osaka Titanium in Japan also produce high grade titania slag from the smelting of high grade titanium concentrates (2,5).

Notable places where the solid state partial reduction to the ferrous state is practised include Colombia, Southern Murso, and Laporte Industries Ltd in the United Kingdom. In the vast majority of the proposed and commercially practised synthetic rutile production techniques, hydrochloric acid is the leachant upon partial reduction of ilmenite (1,2,5).

Consideration has also been given to the inclusion of an oxidation pretreatment of the concentrates before the reduction step by Laporte Industries Ltd (1). Ishihara Sangyo Kaisha Ltd at Yokkaichi in Japan uses sulphuric acid leaching after partial reduction of the ilmenitic iron to the ferrous state (2,5,11).

Another process called the Summit Process, patented by Shah (2) involves the reduction of preoxidised ilmenite to the metallic state followed by leaching in iron (III) (ferric) chloride solution. This process is still at the pilot-plant stage.
1.6 THE OBJECTIVE OF THIS INVESTIGATION

The objective of this research is to recover titanium dioxide from Chinkombe ilmenite ore. The reduction of the ore with graphite has been investigated.

1.7 THE SCOPE OF THE WORK

The study encompasses:

(i) background information,
(ii) theoretical analysis - Thermodynamics and Kinetics of the reduction of the ore,
(iii) experimental work which includes mineral characterization and the reduction of the ore with graphite,
(iv) results and discussions, and
(v) conclusions and recommendations.
CHAPTER TWO

THEORETICAL BACKGROUND

In this chapter, the discussions concern thermodynamics and kinetics of reduction of ilmenite with carbon.

2.1 THE THERMODYNAMICS OF REDUCTION OF ILMENITE AND IRON OXIDES

To determine the conditions of reducing ilmenite and hematite to metallic iron and titanium dioxide, the thermodynamics of reduction of the materials is analysed in terms of the thermodynamics of formation of the compounds that are likely to be formed.

The values of free energy of formation, \( \Delta G \), for the oxides of carbon, iron, and titanium dioxide are given in Appendix 1.1. The plots of the free energies of formation against temperature are given in Figures 2.1 and 2.2.

In these considerations, attention has been given to developing processes for the selective reduction of the hematite and ilmenite to metallic iron. Thus the following reactions have been considered:

\[
\text{FeTiO}_3 + C \rightarrow \text{Fe} + \text{TiO}_2 + \text{CO} \]

\[
\text{2.1}
\]
Figure 2.1 Free energy relationships
Figure 2.2 Free energy relationships
whose $\Delta G^0$ is obtained from Equations (iv) and (viii) in Appendix 1.1, as

$$\Delta G^0_{2.1} = 158463.8 - 141.62 \ T \ \text{joules.}$$

Thus ilmenite could be reduced at approximately 1120 K when the pressure of carbon monoxide is 1 bar (1 atmosphere).

$$2\text{FeTiO}_3 + C = 2\text{Fe} + 2\text{TiO}_2 + \text{CO}_2 \quad (2.2)$$

whose $\Delta G^0$ is obtained from Equations (iv) and (vii) as in Appendix 1.1.

$$\Delta G^0_{2.2} = 146383.6 - 108.93 \ T \ \text{joules.}$$

Thus ilmenite could be reduced by carbon at 1344 K when the pressure of carbon dioxide is 1 bar.

From reaction Equations 2.1 and 2.2, another reaction equation could be developed as:

$$2\text{FeTiO}_3 + 3/2C = 2\text{Fe} + 2\text{TiO}_2 + 1/2\text{CO}_2 + \text{CO} \quad (2.3)$$

whose $\Delta G^0$ is given by:

$$\Delta G^0_{2.3} = 231655.6 - 196.08 \ T \ \text{joules}$$

Thus ilmenite could be reduced by carbon at 1181 K at a pressure of $\text{CO}_2 + \text{CO}$ of 1 bar.

The reaction:

$$\text{FeTiO}_3 + \text{CO} = \text{Fe} + \text{TiO}_2 + \text{CO}_2 \quad (2.4)$$
whose $\Delta G^0$ is obtained from Reactions (iv) and (ix) in Appendix 1.1 as:
\[ \Delta G^0_{2.4} = -2890 + 7.82 \text{ T joules}. \]

The thermodynamic feasibility of this reaction has been discussed with respect to the effect of the ratio of the partial pressures of CO to CO$_2$ in the presence of solid carbon, on the reduction of ilmenite. This has been dealt with under the discussion on Figure 2.3, below. From the above thermodynamic considerations, solid carbon was found to be suitable for use as a reductant for ilmenite, hence graphite was used throughout for the reduction experiment.

Moreover, there are large deposits of coal and graphite (some of which are being mined at the moment) in Zambia so they could be readily obtained locally.

The reducibility of ilmenite by means of carbon depends on the carbon monoxide to carbon dioxide partial pressure ratio and the temperature in the system. These are shown in Figure 2.3 by applying the equations developed in Appendix 1.2.

At high temperatures, above 1273 K, a carbon dioxide-carbon monoxide mixture in equilibrium at 1 bar with solid carbon, is virtually carbon monoxide. Hence the reducing capacity of the gas mixture is increased with
Figure 2.3: Variation of equilibrium $\log_{10} P_{\text{CO}}/P_{\text{CO}_2}$ values with temperature for some reactions of interest in the reduction of ilmenite
increase in temperature. It follows that reduction of ilmenite should be effective at temperatures higher than 1273 K.

As evident in Figure 2.3, a comparison of the calculated equilibrium values of $P_{CO}/P_{CO_2}$ with temperature at a total pressure of CO and CO$_2$ of 1 bar, for Reactions (3) and (1), it is thermodynamically not feasible below 1743 K for CO in the presence of solid carbon to reduce ilmenite to metallic iron and titanium as the values generated by $P_{CO}/P_{CO_2}$ for Reaction (1) are less than those for Reaction (3). (These reaction numbers are shown on the curves in Figure 2.3). However, above 1743 K, the values of $P_{CO}/P_{CO_2}$ due to Reaction (1) are greater than those for Reaction (3), and so metallic iron and titanium could be produced. This does not necessarily mean that metallic iron and titanium would be products, as other reactions are possible which under a particular condition might be thermodynamically more favourable.

The standard free energies of Reactions (1) and (2) and the variation the calculated equilibrium $P_{CO}/P_{CO_2}$ values for them at a total pressure of CO and CO$_2$ of 1 bar, show that at temperatures above 1120 K Reaction (1) is thermodynamically more favourable than Reaction (2).

Thus above 1120 K, ilmenite could be reduced by CO to iron and TiO$_2$. 
The variation of $P_{\text{co}}/P_{\text{co}_2}$ values for Reaction (4) at $P_{\text{co}} + P_{\text{co}_2} = 1$, shows that these values are lower than those for Reaction (1) at all temperatures and hence the formation of cementite (Fe$_3$C) is thermodynamically feasible in this investigation. Thus the iron produced around 1120 K by Reaction (2), if given enough time could be transformed to Fe$_3$C, in which case the iron initially produced is an intermediate reaction product. This could occur if the rate of carburization of iron by Reaction (4) is substantially slower than the rate of reduction of ilmenite to metallic iron by Reaction (2).

From the thermodynamic analysis, the minimum temperature at which ilmenite is reduced by carbon to Fe and TiO$_2$ is 1120 K. For substantial rates of the reaction, the temperature should be higher than 1120 K. The experimental work was therefore conducted from 1173 to 1373 K.

From Figure 2.2, titanium dioxide could be thermodynamically reduced to the lower oxides of titanium.

Thus TiO$_2$ could be reduced to Ti$_3$O$_5$ and Ti$_2$O$_3$ at about 1390 K and 1446 K respectively. These products were found in some previous investigations (20,22,24) that were conducted at temperatures around and above 1473 K. All these products are predictions from the thermodynamic
point of view, their formation is subject to the kinetics of those reactions producing them.

The equations of the reactions are:

\[ 3\text{TiO}_2 + C = \text{Ti}_3\text{O}_5 + \text{CO} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.5 \]

whose \( \Delta G^0 \) is given by:

\[ \Delta G_{2.4}^0 = 601084 - 432.63 \, T \, \text{joules}. \]

Thus at temperatures above 1390 K, \( \text{TiO}_2 \) could be reduced to \( \text{Ti}_3\text{O}_5 \), and

\[ 2\text{TiO}_2 + C = \text{Ti}_2\text{O}_3 + \text{CO} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 2.6 \]

whose \( \Delta G^0 \) is given by:

\[ \Delta G_{2.6}^0 = 554100.8 - 383.31 \, T \, \text{joules} \]

Thus at temperatures above 1446 K, \( \text{TiO}_2 \) could be reduced to \( \text{Ti}_2\text{O}_3 \).

Any reduction of the \( \text{TiO}_2 \) would lead to loss of reductant as \( \text{TiO}_2 \) is the desired material. The control of the process to prevent the formation of the reduced forms of rutile would be advantageous as the extra cost of handling and re-oxidation would be saved.
Another possible means of loss of reductant is the likelihood of the formation of Fe₃C, by Reaction (4) in Figure 2.3.

Preoxidation of ilmenite has been reported to be generally beneficial in the reduction of ilmenite (1,2,20-24). When ilmenite is heated under neutral and oxidising conditions at temperatures around and above 1173 K, pseudobrookite (Fe₂TiO₅) is formed (1). The oxidation is complete in oxidising atmospheres while it is incomplete in neutral atmospheres (1).

The oxidation reaction is represented by the equation:

\[
2\text{FeTiO}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2 + \text{TiO}_2 \quad \text{2.7}
\]

ilmenite \hspace{1cm} \text{pseudobrookite} \hspace{1cm} \text{rutile}

From the thermodynamic analysis in Figure 2.2, it could be observed that the reduction of pseudobrookite with carbon is thermodynamically more favourable than that of ilmenite, as carbon could reduce pseudobrookite to metallic iron and titanium dioxide, producing carbon monoxide at temperatures higher than about 890 K to metallic iron, titanium dioxide and carbon dioxide at temperatures higher than 930 K. Both temperatures are lower than the corresponding temperatures for the reduction of ilmenite as observed from Figure 2.1
2.2 THE KINETICS AND MECHANISMS OF REDUCTION OF OXIDE WITH CARBON

2.2.1 Introduction

The thermodynamic data considered above, only determine the occurrence of the reactions but not how the reactions proceed. To understand the way the a reaction occurs and proceeds, its kinetics and mechanisms should be evaluated. The following factors determine the kinetics of a reaction:

a. the concentration of the reactants involved
b. the temperature of the reaction
c. the degree of blending
d. the physical state of the reactants e.g. solids, liquids or gases, if solid, then the particle size, solubility, melting, sublimation and boiling points etc. are important considerations.

The study of the kinetics of a reaction is essential for the following reasons:
- for understanding how chemical bonds are made and broken, and for estimating their energies and stability,
- for efficient design of equipment to effect the reaction on a technical scale.
In this investigation the solid-state reaction involves carbon in the form of graphite and ilmenite ore.

2.2.2 Mechanisms

Kolchin (12) has proposed four possible mechanisms regarding the reduction of metallic oxides with carbon, viz:

Scheme 1:
The oxide is reduced by carbon monoxide, that is formed by gasification of carbon dioxide reduction product:

\[
\text{MeO}_{(s)} + \text{CO}_{(g)} = \text{Me} + \text{CO}_2(g) \quad \cdots \cdots \cdots \cdot 2.8
\]

\[
\text{CO}_2(g) + \text{C}_{(s)} = 2\text{CO}(g) \quad \cdots \cdots \cdots \cdot 2.9
\]

Scheme 2:
The oxide dissociates into metal and oxygen with subsequent oxidation of carbon:

\[
2\text{MeO}_{(s)} = 2\text{Me} + \text{O}_2(g) \quad \cdots \cdots \cdots \cdot 2.10
\]

\[
\text{C}_{(s)} + n\text{O}_2(g) = m\text{CO}_2(g) + r\text{CO}(g) \quad \cdots \cdots \cdots \cdot 2.11
\]

Scheme 3:
Direct contact between the oxide and carbon
leads to the formation of a metallic layer by diffusion of carbon into the oxide through this layer:

\[ \text{MeO}_{(s)} + \text{C}_{(s)} = \text{Me} + n\text{CO}_{(g)} + m\text{CO}_{(g)} \ldots .2.12 \]

Scheme 4:
The metal oxide initially vapourises and the then reacts with solid carbon:

\[ \text{MeO}_{(s)} = \text{MeO}_{(g)} \ldots .2.13 \]
\[ \text{MeO}_{(g)} + \text{C} = \text{Me} + m\text{CO} + m\text{CO}_2 \ldots .2.14 \]

where Me is the metal; m, n and r the number of moles; subscripts (s) and (g) refer to solid and gas respectively.

According to Kolchin (12), there is no universal theory to explain oxide reduction since even for a single metal oxide, different mechanisms may control the reaction at different stages and under different conditions, but the slowest one is the rate controlling reaction for the whole process.

Scheme 3, for example, describes direct reduction (12) and carbon is presumed to react directly with the oxides, producing CO and CO\(_2\). The direct reduction may be visualised as
beginning at the points of contact between the oxides and carbon particles. As the reaction proceeds, the metallic phase formed appears on the surface of the oxide and may fuse together to form a continuous layer or shell around the still unreduced oxide and thus inhibiting the progress of the reaction since the oxide and the carbon particles are no longer in contact.

Further reduction is assumed by diffusion of carbon atoms through the reduced metallic phase (13) to the oxide-metal interface. In recent years, however, Scheme 1 has become widely accepted as the most likely mechanism of reduction for the majority of oxides (12,15). Reaction 2.9 in Scheme 1 proceeds at a slower rate (13) than Reaction 2.8 and it is therefore the rate controlling step of the overall reduction process.

Chemical compounds which can exchange oxygen with carbon in a reversible manner at the temperatures of interest are capable of enhancing the rate of the solution loss reaction (Reaction 2.9) and consequently enhancing the overall reaction rate of the oxide reduction (13).
2.2.3 Effect of Temperature on the Kinetics of a Reaction

For many reactions and, in particular, elementary reactions, the rate expression can be represented by the Arrhenius Law:

\[ k = A e^{\frac{-E}{RT}} \]  

where \( k \) is the rate constant at a temperature, \( T \) in Kelvin,
\( A \) is the frequency factor
\( E \) is the activation energy, and
\( R \) is the general gas constant equal to 8.31 J/mole K (17).

The expression fits experiment well over a wide temperature range and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency (18).

Significant departures of data from the Arrhenius Law are usually instances of complex reaction mechanisms or changes in the dominant mechanism over the temperature range under study (19).
There are two other views on the dependency of kinetics on temperature viz: the Collision Theory and the Transition State Theory (18,21).

The Collision Theory assumes that $A$ (the frequency factor in Equation 2.15 is equal to the frequency of collisions between the reacting molecules. The actual rate is usually much lower than predicted by this theory and this indicates that only a small fraction of the collisions results in a reaction. These collisions involve energies in excess of the activation energy $E$, and hence such collisions lead to reactions.

The Transition State Theory assumes that the reactants combine to form unstable intermediates called activated complexes which then decompose spontaneously into products.

The Collision Theory views the rate to be governed by the number of energetic collisions between the reactants and disregards what happens to the unstable intermediate, and suggesting that the intermediate breaks down rapidly enough into products that it does not influence the rate of the overall process.
The Transition State Theory on the other hand, views the reactions rate to be governed by the rate of decomposition of the intermediates, and assumes the rate of formation of the intermediate to be too rapid to affect the reaction rate.

Arrhenius Law is a good approximation to the temperature dependency of both the Collision and Transition State Theories.

2.2.4 Order of Reaction and Reaction Rate

The Order of a Reaction

The manner in which a reaction varies with the concentrations of the reacting substances can be indicated by stating the order of the reaction. In general, if it is found experimentally that the rate of a reaction is proportional to the \( \alpha \)th power of the concentration of one the reactants, e.g. A, and to the \( \beta \)th power of the concentration of reactant B etc; for a hypothetical reaction:

\[ A + B + \ldots = \ldots \quad \ldots \ldots \quad 2.16 \]

then \[ \mathcal{R} = k C_A^\alpha C_B^\beta \quad \ldots \ldots \quad 2.17 \]
and the overall order of the reaction is simply:

\[ n = \alpha + \beta \]  \hspace{1cm} 2.18

where \( \mathcal{R} \) is the rate of the reaction

\[ k \] is the rate constant

\[ C_A \] is the concentration of reactant A

\[ C_B \] is the concentration of reactant B

\[ n \] is the overall order of the reaction, and

such a reaction is said to be of \( \alpha \)th order with respect to A and \( \beta \)th order with respect to B.

In many cases the relationship between the rate and the concentration is much more complicated than that represented by Equation 2.17, for example, frequently a concentration appears in the denominator of the rate expression. Such complex situations arise as a result of the fact that the reaction occurs by a complex mechanism involving a number of steps (17). The order of a reaction does not necessarily bear any relationship to the stoichiometric coefficients in the reaction, the former are determined from experiment.

**The Rate Constant of a Reaction**

The rate constant (or specific rate constant), \( k \), in Equation 2.17, is equal to the rate, \( \mathcal{R} \), when the concentration of the reactants are
present at unit concentrations. Its units depend upon those employed for the concentration of and the order with respect to each of the reactants or products that form part of the rate equation.

**Determination of the Order and Rate of a Reaction**

There are a number of methods of determining these quantities from experimental data. The differential method suggested by Van't Hoff (17) deals with the actual rates of reactions as determined by measuring the slopes of tangents to concentration-time curves.

The rate of a reaction may be related to the concentration of a product or a reactant by the expression:

\[ V = k C^n \]  \hspace{1cm} 2.19

where \( V \) is \( \text{d}C/\text{d}t \), the rate of formation of a product or the rate of disappearance of a reactant.

\( k \) is the rate constant

\( C \) is the concentration of the substance (reactant or product) under consideration, at time \( t \);

\( n \) is the order of the reaction with respect to
the substance whose concentration is being varied.

Equation 2.19 could be put in the form:

\[ \ln V = \ln k + n \ln C \quad \ldots \quad 2.20 \]

Plotting ln V against ln C, yields a straight line with its slope equal to n, and its intercept on the ln V axis equal to ln k.

2.2.5 Evaluation of the Kinetic Data

Several methods are in use for measuring the rate at which a reaction proceeds. The adoption of a particular method depends on the nature of the reaction under consideration.

For the kind of reaction in this investigation (solid - solid type) solid reactants yielding solid and gaseous products, in an inert atmosphere, the weight loss method provides a convenient method to measure the extent to which the reaction has occurred. Representing the reduction of a metal oxide with carbon by the reactions:

\[
\text{MeO}_2 + C = \text{Me} + \text{CO}_2 \quad \ldots \quad 2.21 \\
\text{MeO}_2 + 2C = \text{Me} + 2\text{CO} \quad \ldots \quad 2.22
\]

and given that MeO₂ and Me are not volatile in
the temperature range of interest, the weight loss in the reaction mixture represents the weight of CO$_2$ and CO evolved. The oxygen component of the evolved CO$_2$ and CO would be that derived from MeO$_2$ as it is reduced to Me. Hence a knowledge of the rate of evolution of CO$_2$ and CO would facilitate a study of the rate of Me formation from MeO$_2$.

Since Reactions (2.21) and (2.22) are written from the thermodynamic viewpoint, they do not indicate the mechanism by which the reduction of the oxides takes place, but as the thermodynamic analysis depends only on the initial and final states of the system under view, the two equations are sufficient to obtain the amount of products formed.

In the case of reduction of ilmenite with graphite, the solid products of the reduction reaction (Fe and TiO$_2$) are not volatile as for example the vapour pressure of iron at 1373 K is $8.74 \times 10^{-9}$ bars (21). Hence, it is possible to study the reduction of ilmenite with graphite by the weight-loss method.
CHAPTER THREE

MINERAL CHARACTERIZATION

Due to the lack of information on the mineralogy of the Chinkombe ilmenite, mineral characterization of the ore sample was undertaken.

Five different methods were adopted to physico-chemically characterize the Chinkombe ilmenite sample viz:

1. Ore microscopy
2. X-ray diffraction
3. Mössbauer Spectroscopy
4. X-ray fluorescence
5. Wet chemical methods

Items 1 to 3 are physical methods used for qualitative and quantitative identification of minerals present in an ore sample. Items 4 and 5 are for elemental analysis of the mineral.

3.1 ORE MICROSCOPY

Ore microscopy is valuable in determining the mineral composition of an ore sample. It provides information on the various ore minerals in terms of size, dissemination, intergrowths and relative proportions.
Figure 3.1: Optical Micrograph of Chinkombe Ilmenite, showing Hematite (light lenslites) and secondary iron oxides (black spots) in Ilmenite matrix.
(magnification x 50).
The ore microscopic analysis of the Chinkombe ilmenite was conducted on a polished section of a representative sample, using a Leitz reflected light microscope model HM-POL. The light micrograph of the sample is shown in Figure 3.1. The analysis of the polished section shows that the Chinkombe ilmenite ore is composed mainly of ilmenite as the matrix which exhibited a well-developed lamellae twinning. All the ilmenite grains exhibited lenslite exsolution lamellae of hematite. The crystallographically aligned hematite lamellae were up to several hundred microns in length but rarely exceeded ten microns in width. Secondary iron oxides occur along the fractures.

The relative proportions of ilmenite and hematite (together with other secondary oxides of iron) determined using Jones and Horton (20) method are listed below:

<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>Relative Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ilmenite</td>
<td>67.24 ± 3.48</td>
</tr>
<tr>
<td>hematite and secondary</td>
<td></td>
</tr>
<tr>
<td>oxides of iron</td>
<td>32.76 ± 7.13</td>
</tr>
</tbody>
</table>

The evaluation of the result using the Jones and Horton method is given in Appendix 2.1.
3.2 X-RAY DIFFRACTION

Finely disseminated mineral phases cannot be easily identified with Light microscope using polished section. The limitation of the ore microscopic analysis is associated with the sensitivity of the equipment of the microscope i.e. the magnification. To overcome this limitation, X-ray diffraction is usually applied to determine all the mineral phases present in the ore sample.

A Philips X-ray diffractometer model PW 1050/80, (at School of Mines, University of Zambia), equipped with Lithium Fluoride (LiF) monochromator was used to obtain X-ray diffractograms from finely ground samples for the identification of the mineral phases. The radiation was Mo Kα. The diffractogram was obtained at a scanning rate of 2° 2θ per minute. Figure 3.2 shows the diffractogram.

The analysis of the X-ray diffractograms of the Chinkombe sample reveals that ilmenite and hematite are the mineral phases.

3.3 MÖSSBAUER SPECTROSCOPY

The advantage of Mössbauer Spectroscopy over X-ray diffraction is that the former reveals the crystal structure of the phases present in a solid or sample i.e. whether the minerals are mixed or are in a solid
Mössbauer Spectroscopy is the name given to a technique of studying the absorption of gamma rays by the nuclei of atoms.

A constant acceleration Mössbauer Spectrometer at National Council for Scientific Research, Lusaka, was used to obtain Mössbauer Spectra of the mineral phases containing iron. This spectrometer consisted of a 2 kilobyte Canberra series 35 Plus multichannel analyser model 3501 with the external control wiring option 3521; a Canberra spectroscopy amplifier model 2006E, a transducer MA 250; a function generator F G 351; a Driving Unit MR 250; a Reuter stokes RS-P3-1603-261 proportional counter; Canberra H.V. power supply 3002; and a 10mCi Co-57 source in a rhodium matrix. The driving and synchronization units are from CMTE Electronik GmbH.

The spectra obtained from the ore samples are shown in Figure 3.3. The mineral phases observed are ilmenite and hematite as the iron containing minerals present. The relative proportions of the ilmenite and hematite are 67.8% and 32.2% respectively.

The observed internal magnetic field for the alpha-
Figure 3.2: X-ray diffractogram of Chinkoebbe Ilmenite Ore

KEY
I = Ilmenite
H = Hematite

0.86 I, H
0.89 H
0.91 H
0.95 H
0.96 H
0.98 I

1.07 H?
1.12 H
1.16 H
1.18
1.21 I, H
1.27 I, H
1.32 H
1.34 I, H
1.37 I
1.45 H
1.46 I
1.49 I
1.50 I
1.61 I
1.63 I
1.69 H
1.86 I
2.10
2.22 I
SLIT \( \lambda^0 = 0.2 \text{ mm}^{-1} \)
2.53 I
2.75 I

3.73 I
SLIT \( \lambda^0 = 0.2 \text{ mm}^{-1} \)
Figure 3.3: Mössbauer Spectra of Chinkombe Ilmenite

- a. General Head Sample
- b. -212 + 150 size fraction
- c. -150 + 106 size fraction

For all Mössbauer Spectra:
- H = Hematite
- P = Pseudobrookite
- I = Ilmenite
- Fe = alpha Iron
hematite in Chinkombe ilmenite ore from Mössbauer Spectroscopic analysis was 509 kOe, a value somewhat lower than the typical value of 516 kOe for alpha-hematite. This discrepancy is the evidence that the hematite and the ilmenite in the Chinkombe ilmenite sample are in a solid solution (9); of composition about 32% Fe₂O₃ - 68% FeTiO₃.

3.4 CHEMICAL ANALYSIS

3.4.1 Qualitative Analysis

Mineralogical investigation does not tell us of all the elements present in the ore.

Qualitative chemical analysis reveals almost all of the elements present. In the absence of emission spectroscopy, X-ray fluorescence was used for this purpose. A Philips X-ray fluorescence - model spectrometer PW 1410 (at School of Mines, University of Zambia) was used to obtain a spectrogram as shown in Figure 3.4.

The elements identified in the spectrogram are:

Major elements: Iron and Titanium

Minor elements: Niobium, Manganese, Magnesium, Chromium, Silicon, Calcium, Cobalt, Nickel, Zinc
and Copper.

3.4.2 Quantitative Chemical Analysis

X-ray fluorescence model PW 1410, Atomic Absorption Spectrophotometer - model 1200 Varian Techtron, and titration with potassium dichromate solution gave the results summarized in Table 3.1.

Table 3.1: The Chemical Composition of the Chinkombe ilmenite ore, percent by weight:

<table>
<thead>
<tr>
<th>Compound</th>
<th>TiO₂</th>
<th>Fe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>37.68*</td>
<td>39.28*</td>
<td>32.48#</td>
<td>20.06</td>
<td>5.34</td>
<td>1.12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>CoO</th>
<th>CaO</th>
<th>MnO</th>
<th>Cr₂O₃</th>
<th>NiO</th>
<th>CuO</th>
<th>Nb₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.99</td>
<td>0.45</td>
<td>0.33</td>
<td>0.25</td>
<td>0.15</td>
<td>0.03</td>
<td>0.02</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

Total - 98.90 weight per cent.

n.a - not analysed;

* - analysed on X-ray fluorescence

# - analysed by titration using potassium dichromate standard solution;
The value of Fe₂O₃ was found by difference, with the assumption that:

\[ \text{total iron} = \text{Iron (II)} + \text{Iron (III)} \]

the unmarked ones were analysed by Atomic Absorption Spectrophotometry.

3.5 SUMMARY AND CONCLUSION OF THE MINERAL CHARACTERIZATION

From the characterization analysis carried out on the samples, it was found that the Chinkombe ilmenite sample is probably a solid solution of ilmenite and hematite of the approximate proportion of 2.1:1. Oxides of Aluminium, Magnesium, Manganese, Niobium and Chromium form about 10% by weight of the sample.

Due to the fact that the Chinkombe ilmenite is a solid solution, that the hematite is finely disseminated in the ilmenite matrix, no concentration was done. The sample was therefore considered a concentrate of ilmenite and hematite, which form about 90% by weight of the sample.
CHAPTER FOUR

EXPERIMENTAL

4.1 MATERIALS

The materials used in the present investigation for the reduction were:

- The ilmenite ore sample from the bulk taken from Chinkombe, and whose chemical composition has been given in Table 3.1.

- The graphite and Lithium carbonate were of Analytical grade supplied by Hopkin and Williams. They were in a finely divided form and hence no attempt was made to separate them into size fractions.

- Nitrogen (high grade, 99.9% purity) was supplied by Zambia Oxygen (ZAMOX) Ltd., Lusaka.

- Certified Titanic oxide (TiO₂) T-315 supplied by Fisher Scientific Company whose Lot analysis given in Table 4.1, was used to prepare standards for X-ray fluorescence analysis.

- Iron (III) oxide supplied by Merck of minimum assay of 99.0% Fe₂O₃, used to prepare standards for X-ray fluorescence analysis.

- Sodium carbonate (minimum assay 99.5% Na₂CO₃) supplied by Central Chemical and Educational supplies Limited, Lusaka, was mixed with the samples for
**X-ray fluorescence analysis.**

**Table 4.1:** Certificate of Actual Lot Analysis of the Fisher Scientific Titanic Oxide T-315.

<table>
<thead>
<tr>
<th>Water soluble salts</th>
<th>0.03%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.003%</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.002%</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.003%</td>
</tr>
</tbody>
</table>

### 4.2 PREPARATION OF SAMPLES

The handpicked broken outcrops of ilmenite samples were handsorted and crushed, ground and split into eight different components on a rotating bottle sampler. One of the eight components was taken as a head sample and the other seven were thoroughly mixed and separated into size fractions viz: +300, -300+212, -212+150, -150+106, -106+75, -75+53 and -53 micrometers. A sizeable amount of ilmenite sample fraction and graphite were mixed to give the desired composition. The mixing was done in a dry bottle for approximately 2 hours to ensure thorough mixing of the mixture. The proportions of the ilmenite sample to graphite and the size fraction of the ilmenite sample were varied from mixture to mixture.
For each pellet that was made, a sample weighing about 3g was taken from the prepared mixture and pressed on a Speca hand press to a force of 10 tonnes for between 1 to 1.5 minutes.

Precautionary measures were taken to prevent any contamination and distortion of pellet shape during the preparation of the pellet by cleaning the mould with acetone-moistened cloth, always before making a new pellet.

4.3 EQUIPMENT ASSEMBLY

A schematic diagram of the apparatus used for the reduction experiment is shown in Figure 4.1. The main elements of the set-up are a horizontal tube furnace rated from 0 to 1473 K, fitted with a silica tube, 27mm internal diameter and 100 cm long, a cylinder containing nitrogen gas, and a gas flowmeter.

A Pt/Pt-10% Rh thermocouple was used to monitor the temperature inside the silica tube where the sample boat was placed. Its measurements were within ± 5°C range.

The nitrogen before entering the silica tube was passed through a solution of alkaline pyrogallol to remove any traces of oxygen, and then through concentrated sulphuric acid and a column of silica gel for drying and finally
Figure 4.1 A Schematic Diagram of the Apparatus used for the Experiment

1. Nitrogen cylinder
2. Solution of alkane pyrolysis
3. Concentrated sulphuric acid
4. Silica gel covered with glass wool
5. Reaction gas lowwamer
6. Silica tube (reactor)
7. Tube furnace
8. Capillar stand
9. Flexible rubber tube
10. P/I/PH 10 % rh thermocouple

Exit gases to fume cupboard
through the flowmeter which measured the volume flow rate. The ends of the silica tube were closed with rubber stoppers in which holes were centrally drilled to permit the inflow and outflow of gas and for a thermocouple sheath for temperature measurement.

The heating of the furnace and temperature control were achieved with an Eurotherm temperature control unit rated from 298 to 1473 K and with a calibrated scale on Pt/Pt-10% Rh, an ammeter of range 0 to 10 A; a contactor model PNE - 113950 and a Variac model T N ⊕ PHO-2505 (USSR).

4.4 EXPERIMENTAL PROCEDURE

The reduction experiment was conducted as follows:
A pellet of ilmenite sample - graphite of known proportion was put in a preweighed boat and reweighed.

Purified nitrogen gas was flushed through the silica tube for ten minutes after the furnace had attained the working temperature.

From the right end side the boat containing the pellet was pushed into the middle of the silica tube where a uniform temperature was maintained. The tube was then tightly closed with the rubber stopper, with the thermocouple sheath adjusted accordingly to allow it to
be very close to the boat.

After the desired reaction time had expired, the pellet and boat were allowed to cool down, in the incoming nitrogen atmosphere, in the left end side of the tube protruding outside the furnace for 20 minutes. From the silica tube, the boat with the pellet was transferred into a dessicator for further cooling. After it has cooled down to the temperature in the dessicator it was removed and weighed. The boat was weighed empty to adjust for any weight changes sustained by it. This sequence of operations was repeated for each set of experiment.

The sample weight measurements were carried out on a Sartorius Electronic Analytical Balance of sensitivity of 0.1 mg. The same procedure was followed for the reduction of the preoxidised samples. The oxidation was carried out on the sample of -150+106 micrometres size fraction in an oxidising atmosphere (air was pumped from a compressor into the furnace at 1273 K for 1 hour). The oxidised sample was stored in a dessicator after cooling.

The reduced samples were subjected to X-ray diffraction and Mössbauer Spectroscopy analyses.

The parameters investigated include, the effects of
temperature, ore-graphite ratio in the mixture, ore particle size, and the effect of a catalyst, in the temperature range 1173 to 1373 K. The calculations for the stoichiometric weight of carbon required for the reduction of unit mass of the Chinkombe ilmenite ore is given in Appendix 3.1.

The percent metallic iron produced from the sample after reduction was determined from the stoichiometric calculation based on weight loss with the assumption that the amount of carbon dioxide in the product gas was negligible and that carbon monoxide was predominantly the gas responsible for weight loss. The calculation has been outlined in Appendix 3.2.

The exit gases (CO and CO₂) could not be measured due to the breakdown of the gas orsat apparatus - the only means of doing so at the time of this investigation. Attempts to determine the amount of metallic iron formed in the presence of the oxides of iron in the reduced pellets failed, most probably due to over simplification of the apparatus.
CHAPTER FIVE

RESULTS AND DISCUSSIONS

5.1 RESULTS

Most of the results are presented as isothermal plots of percent weight loss against time. The percent weight loss was computed from the experimental weight loss data as:

\[
\text{percent weight loss} = \frac{W_0 - W}{W_0} \times 100
\]

\[
= \frac{\Delta W}{W_0} \times 100
\]

5.1

where \( W_0 \) is the initial weight of the pellet, \( W \) is the weight of the pellet after reduction, and \( \Delta W = W_0 - W \)

The time \( t \), used in the experimental data is exclusive of the time of heating the furnace to the appropriate temperature, time of acclimatization of the sample in the reactor (two minutes for each sample) and the time of cooling the sample at the left end of the reactor tube protruding outside the furnace (close to the point of entry of the nitrogen gas).
The data used for the plots of Figures 5.1 to 5.8 are tabulated in Appendix 4.1. A summary of the results deduced from the graphs follows:

5.1.1 **Effect of Temperature and time**

The experiments were conducted at 1173 K, 1223 K, 1273 K, 1323 K and 1373 K to study this effect. The results as shown in Figure 5.1 indicate that in the temperature range used, the higher the temperature, the higher the percent weight loss. Thus the rate of reduction increases with increase in temperature. Figure 5.2 shows that the rate of reduction of the Chinkombe ilmenite is slow between 1173 K and 1223 K, but thereafter, the rate increases approximately linearly from about 1250 K to 1373 K.

5.1.2 **Effect of Quantity of Carbon**

This study was conducted at 1373 K for a period of 1 hour. As shown in Figure 5.3, the percent weight loss increases up to 20%C in the mixture, and then falls off with further increase in carbon content beyond 20%. Figure 5.4 confirms this trend.

5.1.3 **Effect of ore particle size**

The experiments for this study were conducted on samples of size ranges -150 + 106, -212 + 150 and -300 + 212 micrometres for one hour at 1373 K and at
Figure 5.1 The effect of temperature and time on the reduction of Chinkombe ilmenite
Figure 5.2  The effect of temperature on the reduction of Chinkombe ilmenite
Figure 5.3 The effect of varying carbon content on the reduction of Chinkombe ilmenite.
Figure 5.4 The effect of varying carbon content in the mixture at 1373 K
Figure 5.5 The effect of particle size of Chinkombe ilmenite on its reduction.
the optimum carbon content of 20% in the mixture. These results, shown in Figure 5.5, indicate that the rate of reduction of the samples increases with decreasing particle size.

5.1.4 Effect of a Catalyst

Two sets of experiments were run for this investigation:

a) for ore particle size of \(-150 + 106\) micrometres at 1373 K with 20% carbon in the mixture and 5% Lithium carbonate \((\text{Li}_2\text{CO}_3)\) of the mixture.

b) For ore particle size of \(-212 + 150\) micrometres at 1273 K with 15% carbon in the mixture and 5% \(\text{Li}_2\text{CO}_3\) of the mixture. The results shown in Figure 5.6 clearly show that \(\text{Li}_2\text{CO}_3\) enhances the rate of reduction of the Chinkombe ilmenite samples.

5.1.5 Effect of Preoxidation

The results of the reduction experiment conducted with a preoxidised ore are shown in Figures 5.7 and 5.8. Figure 5.8 shows a comparison of the direct reduction and the reduction of the preoxidised Chinkombe ilmenite ore. These figures show that with about the same percent excess carbon and ore sample particle size of \(-150 + 106\) micrometres:

a. at 1273 K the reduction rate was enhanced for the preoxidised sample, but
Figure 5.6 The effect of catalytic agent (Li\textsubscript{2}CO\textsubscript{3}) on the reduction of Chinkombe ilmenite
Figure 5.7 The effect of temperature and time on the reduction of preoxidised Chinkombe ilmenite
Figure 5.8 Comparison of reduction of Chinkombe ilmenite with and without preoxidation
b. at 1373 K the reduction rate was retarded.

Figure 5.7 further supports Figures 5.3 and 5.4 on the claim of an optimum carbon content in the mixture for an effective reduction of the Chinkombe ilmenite ore, as 33.4% carbon content in the mixture gave a lower loss in weight over the two-hour period of reduction than 11.4% carbon content.

5.2 IDENTIFICATION OF THE PHASES IN THE REDUCED PRODUCTS

The reduced products were examined with the following techniques to identify the phases present:

a. Mössbauer Spectroscopy, at National Council for Scientific Research, Lusaka, with a Co-57 source of gamma rays to identify the phases that contain iron.

b. X-ray diffractometry, using Philips X-ray diffractometer model PW 1390 at Technical Services Division of Zambia Consolidated Copper Mines, Kalulushi, Zambia. The radiation was Cu Kα.

Both Mössbauer spectra and X-ray diffractograms are reported in Figures 5.9 to 5.24.

5.2.1 Variation of Temperature

Figure 5.9 is the diffractogram of the Chinkombe ilmenite reduced at 1173 K with 20%C in the
Figure 5.9: X-ray diffractogram of Chinkombe ilmenite reduced at 1173 K with 20% C for 2 hours.

For all X-ray diffractograms:
I = Ilmenite  P = Pseudobrookite
H = Hematite  R = Rutile
Fe = Iron      C = Carbon
Figure 5.10: X-ray diffractogram of Chinkombe ilmenite reduced at 1273K at 20%C for 2 hours.
Figure 5.11: X-ray diffractogram of Chinkombe Ilmenite reduced at 1373K with 20% CO for 1 hour.
Figure 5.12: Mössbauer Spectra of Chinkombe ilmenite reduced at:
a. 1173 K for 2 hours
b. 1273 K for 2 hours
c. 1373 K for 2 hours
mixture for a period of 2 hours. The product phases shown are carbon (graphite), iron and ilmenite. The corresponding Mössbauer spectra is shown in Figure 5.12a. No peaks for hematite were detected on both Figures 5.9 and 5.12a.

The diffractogram and the Mössbauer spectra shown in Figures 5.10 and 5.12b respectively are for the sample reduced at 1273 K with 20% C for 2 hours. They show a similar trend to those recorded for the reduction at 1173 K but with higher weight loss which is confirmed by the heights of the products formed, showing that a higher reduction had taken place at 1273 K than at 1173 K.

The diffractogram and the Mossbauer spectra of the run at 1373 K with 20% C for 1 hour are shown in Figures 5.11 and 5.12c respectively. The latter shows only metallic iron as the iron mineral phase present. Figure 5.11 shows weak peaks at 3.49, 2.47, 2.43 and 1.88 Å, indicating the presence of traces of pseudobrookite. The presence of titanium in the reduced sample was determined using X-ray fluorescence techniques and a value of 42.51% TiO₂ was obtained after the elemental analysis.
Figure 5.13: X-ray diffractogram of Chinkombe Ilmenite heated in an inert atmosphere without carbon (0%C) at 1373K for 1 hour.
Figure 5.14: X-ray diffractogram of Chikombe ilmenite reduced at 1373K with 5% C for 1 hour.
Figure 5.15: X-ray diffractogram of Chinkombe ilmenite reduced at 1373K with 10%C for 1 hour.
Figure 5.16: X-ray diffraction pattern of Chnkondo limonite reduced at 1173K with 30% CO for 1 hour.
Figure 5.17: Mössbauer Spectra of Chinkombe ilmenite reduced at 1373 K for 1 hour with:

a. 0% C    b. 5% C    c. 10% C
5.2.2 Variation of Quantity of Carbon

Figures 5.13 and 5.17a are the diffractogram and Mössbauer spectra respectively of the sample run without the addition of carbon (thus 0% C) for 1 hour in an atmosphere of nitrogen gas. Figure 5.17a shows that all the hematite peaks disappeared and pseudobrookite grew with diminished ilmenite peaks. Figure 5.13 shows peaks for pseudobrookite, rutile and ilmenite. For 10% C (used as the stoichiometric carbon requirement) at 1373 K for 1 hour, the Mössbauer spectra in Figure 5.17c gave longer α-Fe peaks and shorter ilmenite peaks than those recorded in Figures 5.17b. The peaks labelled X in Figure 5.17c were not identified. Peaks for rutile and pseudobrookite are found in Figure 5.12.

The results of the reduction at the optimum carbon content- 20% C at 1373 K have been stated above. The Mössbauer spectra and the diffractogram for sample with 30% C reduced at 1373 K for 1 hour are shown in Figures 5.18a and 5.16 respectively. The figures for 20% C and 30% C show the same phases but the weight loss obtained for 20% C was higher than that obtained for 30% C.
5.2.3 The Effect of Catalysis

The diffractogram and Mössbauer spectra for the catalysed sample (catalysed with 5% Li₂CO₃ of the 20%C ore-graphite mixture) reduced at 1373K for 30 minutes are shown in Figures 5.19 and 5.20b. The same mineral phases are indicated in these figures and the corresponding ones for 20%C mixture reduced at 1373 K for 1 hour.

5.2.4 The Effect of Preoxidation

Figure 5.21 shows the diffractogram of the Chinkombe ilmenite which has been oxidised for 1 hour at 1273 K in air. It shows peaks for pseudobrookite, rutile, hematite. Figure 5.22a shows the corresponding Mössbauer spectra - with peaks for only hematite and pseudobrookite, as the iron containing phases. The hematite peaks were shorter than those in the original samples shown in Figure 3.3. This oxidised sample then became the sample for the reduction experiment - referred to as the reduction of the preoxidised sample.

Figure 5.23 is the diffractogram on the preoxidised sample with 25%C, reduced at 1273 K for 2 hours, showing peaks for metallic iron, ilmenite, carbon, rutile and pseudobrookite. The Mössbauer spectra on the sample is shown in Figure
Figure 5.18: Mössbauer Spectra of Chinkombe ilmenite reduced at 1373 K for 1 hour with:

a. 20% C  b. 30% C
Figure 5.19: X-ray diffractogram of Chinkombe Ilmenite catalysed with Li$_2$CO$_3$ and reduced at 1373 K with 20°C for 30 minutes.
Figure 5.20: Mössbauer Spectra of Chinkombe ilmenite reduced at 1373 K with 20% C and:

a. without a catalyst for 1 hour,
b. with a catalyst Li₂CO₃ - 5% by weight of the mixture, 30 minutes.
Figure 5.21: X-ray diffractogram of Chinkombe ilmenite heated in air (oxidised) at 1273K for 1 hour.
Figure 5.22: Mössbauer Spectra of Chinkombe ilmenite

a. heated in air (oxidised) at 1273 K for 1 hour
b. oxidised at 1273 K for 1 hour and then reduced with 25% C at 1273 K for 1 hour
c. oxidised at 1273 K for hour and then reduced with 25% C at 1373 K for 1 hour
5.22b, showing peaks for ilmenite and peaks labelled Y which are probably Fe$_2$TiO$_4$ (ferrous pseudobrookite).

Figures 5.24 and 5.22c show the diffractogram and the Mössbauer spectra for the preoxidised sample with 25% C, reduced at 1373 K for 2 hours. The former shows peaks for metallic iron, pseudobrookite and weak peaks for rutile being slightly covered by graphite peaks at 3.33 Å and 1.67 Å. Figure 5.22c shows peaks for only metallic iron, as the only iron containing phase present.

5.3 DISCUSSIONS

5.3.1 The Chemical Processes in the Reduction of the Chinkombe Ilmenite with Graphite

The chemical reactions that were taking place in the reduction of the Chinkombe ilmenite ore with graphite are:

a. Solid state reaction:

\[
\text{Fe}_2\text{O}_3,\text{FeTiO}_3 + C \rightarrow \text{Fe} + \text{TiO}_2 + \text{CO} \quad \ldots 5.2
\]
Figure 5.23: X-ray diffractogram of Oxidised Chinkombe ilmenite reduced at 1273K with 25%C for 1 hour.
Figure 5.24: X-ray diffractionogram of oxidised Chinkoobe Tinite with Cu Kα, reduced at 1373K with ZnO for 1 hour.
b. Gaseous reduction:

\[ \text{Fe}_2\text{O}_3.\text{FeTiO}_3 + \text{CO} \rightarrow \text{Fe} + \text{TiO}_2 + \text{CO}_2 \quad \ldots \ldots 5.3 \]

c. The in-situ generation of CO (Boudouard reaction):

\[ \text{CO}_2 + \text{C} = 2\text{CO} \quad \ldots \ldots \ldots \ldots 5.4 \]

The experimental procedure used in this investigation (i.e. reduction of the ore with graphite), Reaction 5.2 would be expected to initiate the process of reduction at the points of contact between the particles of the ore and the graphite. Reaction 5.2 continues until the contact between the ore and the carbon particles disappears as a result of the build up of products at the interface.

The degree of contribution of Reactions 5.3 and 5.4 to the reduction process would depend on the regeneration of carbon monoxide in the system as well as its diffusion towards and outwards the reaction site. The regeneration of carbon monoxide also depends on the amount of carbon present and the temperature of the system. Rao (13) proposed the following mechanisms of
formation of CO initially in an oxide-graphite system:

a. oxygen of the entrapped air combining with carbon particles.
b. carbon reacting with oxygen released by the dissociation of the oxides, if any,
c. oxygen chemisorbed on carbon surfaces liberated as CO, and
d. direct reduction taking place at the points of contact between the oxide and carbon particles.

In this investigation, only method (d) is important and likely to occur. Ilmenite is a stable oxide which does not decompose on heating, so method (b) is not likely. If method (c) was important source of carbon monoxide, the reduction would be expected to start at even low temperatures. Previous work (31) has shown that the reduction of ilmenite with carbon starts around 1133 K which is just about the equilibrium temperature for Reaction 2.1, as shown in Figures 2.1 and 2.2.

Hence, since CO is absent from the initial reactants, it is expected to be generated by Reactions 5.2 and 5.4, implying that the reduction
process would be initiated by Reaction 5.2.

Reaction 5.4 is endothermic and previous kinetic studies on it confirm that it has significant rate only around and above 1273 K (13,14,28,29), thus below this temperature, the solid-solid interaction would be the main contributor to the process. These could be inferred from Figure 5.1 showing a low rate of reduction of the sample at 1173 K and 1223 K. This is an evidence of solid-solid reaction mechanism as the vapour pressure of solids is extremely low and implying a negligible rate of diffusion. Such reactions stop soon after starting without going to completion, due to the build up of products at the reactants' interface.

With high temperatures, especially above 1273 K, the rate of generation of CO via Reaction 5.4 and consequently the rate of Reaction 5.3 increases. Since gas-solid reactions are faster than solid-solid reactions, the overall effect would be an increase in the reaction rate, though the accumulation of product at the ore-graphite interface is still a hindrance to Reaction 5.2. Hence, further reaction is expected to proceed via the gaseous reaction involving the cyclic process formed by Reactions (5.3) and (5.4).
The in-situ formation of CO by Reaction (5.4), tends to restore the reducing potential of the gas phase as excess carbon (above the stoichiometric amount) was used. A number of mechanisms have been proposed as being responsible for the gasification of carbon by carbon dioxide.

Walker et al (13), proposed among others the following mechanisms:

i. Chemisorption of CO$_2$ onto a free reaction site on carbon:

$$\text{CO}_2(g) + \text{C}_f \rightarrow \text{CO}_2(g) + \text{C}_o \quad \text{......5.5}$$

and

ii. Liberation of chemisorbed oxygen:

$$\text{C}_o \rightarrow \text{CO}_2(g) \quad \text{.........................5.6}$$

where $C_f$ is a free reaction site on carbon and $C_o$ is oxygen chemisorbed on carbon.

The gasification rate of carbon by CO$_2$ is directly proportional to the number of occupied sites (14) and is retarded by CO adsorption on the reaction site that could be occupied by oxygen (13,14). The explanation of the retardation due to the presence of CO is the reaction between the chemisorbed oxygen ($C_o$ and CO) (the reverse of Reaction 5.5) (13,14) takes place producing CO$_2$. 
The catalytic effects of small amounts of metals and metal oxides on the gasification of carbon are known (13,16).

There are generally two categories of theories proposed to explain this catalytic effect (13) viz:
i. oxygen transfer mechanism involving a oxidation reduction cycle, and
ii. electron transfer mechanism which assumes transfer between the \( \Pi \)-electrons of graphite and vacant orbitals of the metallic catalyst.

Metallic iron is a well known catalyst (13,16) of the gasification of carbon by \( \text{CO}_2 \), but it becomes inactive when it has undergone oxidation to \( \text{FeO} \).

Vastola and Walker (30) proposed the following chemical mechanism for Fe-catalysed \( \text{C} - \text{CO}_2 \) reaction:

\[
\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 5.7
\]

Adding \[
\text{FeO} + \text{C} = \text{Fe} + \text{CO} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 5.8
\]

\[
\text{C} + \text{CO}_2 = 2\text{CO} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 5.4
\]

Hence the catalyst-metallic iron does not actually take part in the reaction at the end.

The metallic iron formed from the Chinkombe
ilmenite during the reduction of the later would act as a catalyst to enhance the reaction of the ore with graphite, through the accelerated generation of CO. The catalysis occurs at the iron-carbon contacts, and the availability of such iron catalytic centres strongly depends on the temperature.

5.4 THE EFFECT OF THE VARIED PARAMETERS

5.4.1 The Effect of Temperature

The results in Figure 5.1 show that in the temperature range considered in this investigation, the reaction rate increases with increasing temperature. The reaction rate was very low at 1173 K. From Figure 2.1, ilmenite could be thermodynamically reduced by carbon at about 1123 K. The higher rates obtained with increasing temperature are consistent with the Arrhenius equation:

\[ k = Ae^{-E/RT} \]

2.15

Another reason for the higher reduction rate with increasing temperature is that at temperatures close to and above 1272 K, CO₂ in the product reacts with excess carbon, leading to an increased rate of formation of CO because of the endothermic
nature of the C – CO₂ reaction. The increase in the production of CO increases the reducing potential of the system and the CO being gas diffuses efficiently within the pellet, thus increasing the reduction rate.

Metallic iron produced from the reduction of the hematite portion of the ore at relatively lower temperatures – about 873 K could also catalyse the CO₂ – C reaction to produce more CO.

From Figure 5.2, it was found that the reaction rate was quite low between 1173 to 1260 K and then became sharply high (approximately two times higher) between 1260 and 1373 K.

5.4.2 The Effect of variation of percent carbon in the mixture.

As could be observed from Figures 5.3 and 5.4 the percent weight loss increased with increasing carbon content in the mixture to 20% and then gradually decreased with further increase in the carbon content beyond 20%. The initial increase in the rate of the reduction (from 0 to 20%C) in the mixture is due to the fact that with increasing carbon content the generation of CO by the Boudouard reaction (Reaction 5.4) is enhanced
and hence the reduction atmosphere becomes more reducing. This is further increased because CO being a gas, diffuses at a fast rate within the pellet causing the reduction rate to increase.

The drop in reduction after further additions of graphite beyond 20%, is due to the decreased surface of the ore to carbon and the generated CO. EI Gruindy and Davenport’s work (31) corroborates these findings.

5.4.3 The Effect of ore particle size

The increase in the reduction rate with decreasing particle size in the 300 to 106 micrometres range should be expected due to the increased surface area of the ore exposed to the reducing atmosphere.

5.4.4 The Effect of Catalysis

Purpose: The catalyst, Lithium carbonate (Li₂CO₃) was used to substantiate the contribution of the Boudouard reaction (Reaction 5.4) in the reduction of the Chinkombe ilmenite ore, as it has been reported that LiCO₃ and Li₂O (13,32) catalyse the Boudouard reaction.
The reduction rate has been considerably enhanced on the addition of 5% weight Li₂CO₃ to the mixture. This goes to support the fact that Li₂CO₃ actually does catalyse the Boudouard reaction. Since C - CO₂ reaction is also catalysed by the iron formed during the reduction process, the net effect should be regarded as synergistic, being more than the sum of the individual catalytic effects of Li₂CO₃ and Fe. A number of theories have been put forward to explain the catalytic action of Li₂O and Li₂CO₃ on the Boudouard reaction. Taylor and Neville (13) were of the view that oxygen-carbon complexes (chemisorbed oxygen formed on carbon surfaces) are more readily decomposed in the presence of such alkali-metal carbonates and that the cleared surface is then much more reactive toward CO₂. The mechanism of the catalytic effect of Li₂CO₃ may be represented by the equation involving an intermediate oxide (32):

\[
\text{Li}_2\text{CO}_3 \text{(l)} + \text{C} \text{(s)} = \text{Li}_2\text{O} \text{(s,l)} + 2\text{CO} \text{(g)} \ldots \text{5.14}
\]

adding

\[
\text{Li}_2\text{O} \text{(s,l)} + \text{CO}_2 \text{(g)} = \text{Li}_2\text{CO}_3 \text{(l)} \ldots \ldots \ldots \text{5.15}
\]

\[
\text{C} \text{(s)} + \text{CO} \text{(g)} = 2\text{CO} \text{(g)} \ldots \ldots \ldots \text{5.4}
\]

Adding Reactions (5.14) and (5.15), Reaction 5.4 which is the Boudouard reaction is obtained.
Li$_2$CO$_3$ (melting point = 999 K) (32) being molten at the temperatures employed in this investigation would uniformly wet the carbon particles, hence the catalytic action occurs over the entire carbon surface.

5.5 PHASES IN THE REDUCED PRODUCTS

5.5.1 Variation of Temperature

The graphite peaks that showed in all the diffractograms mentioned in the results, are peaks due to unreacted graphite. The titanium phase is most probably rutile, since there are no confirmed peaks containing Ti – Fe complexes in such figures as Figures 5.8 and 5.12c. The proximity of the graphite (carbon) and titanium dioxide (rutile) peaks to each other explains the reason rutile could not be detected. It is observed that the rutile peaks on the X-ray diffractogram might be obscured by the prominent graphite peaks. For instance graphite peak at 3.33 Å covers the space for the 100% relative intensity peak for rutile at 3.25Å and also the graphite peak of 1.67 Å covers the rutile peak at 1.69Å.

Jones (20) found out that the reduction path for ilmenite above 1423 K was:
ilmenite $\rightarrow$ pseudobrookite $\rightarrow$ Fe + TiO$_2$,
this could be the case for the Chinkombe ilmenite,
that the traces of pseudobrookite persist after
reduction at 1373 K. Such traces were not found
in the diffractograms on samples run below this
temperature. No pseudobrookite peaks were also
seen in the Mössbauer spectra - Figure 5.12c,
consequently the claim that the weak peaks shown in
Figure 5.8 are just evidences of traces of it, and
not enough to show in Figure 5.12c.

The sample with 20% C run at 1373 K was analysed by
X-ray florescence and found to be 42.51% TiO$_2$
after converting for the elemental analysis.
Since there are no peaks for reduced rutiles or
Fe – Ti complexes, it was inferred that Ti would
be existing in the reduced product as rutile but
are being covered by the carbon peaks as discussed
above. Upon careful look at some of the
diffractograms, around the d-spacing of 3.25Å,
slight discontinuity shows suggesting a weak peak
over there for rutile.

5.5.2 Variation of Carbon

In the absence of carbon, after reduction at
1373 K for an hour, pseudobrookite and rutile
peaks show. These results confirm the previous
works (1,20) that pseudobrookite is formed when ilmenite is heated in an inert atmosphere. A complete transformation of all ilmenite to pseudobrookite is attained only when the heating is done in an oxidising atmosphere (1).

The reactions taking place in the Chinkombe ilmenite in this particular case could be:

\[ \text{Fe}_2\text{O}_3 + \text{FeTiO}_3 \rightarrow \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 \quad \text{.........5.9} \]

Part of the rutile would react with any free hematite to form more pseudobrookite:

\[ \text{Fe}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Fe}_2\text{TiO}_5 \quad \text{.................5.10} \]

With 5% C, at 1373 K for 1 hour, there is a limited degree of reduction as shown in the spectra in Figure 5.17b - showing peaks for metallic iron, pseudobrookite and ilmenite. The products of the 10% C reduced at 1373 K for 1 hour lend support to the proposition that the reduction of ilmenite proceeds through the formation of pseudobrookite or the pseudobrookite formation reaction occurs along side that of the reduction in a limited way since the quantity of pseudobrookite might be very small, and too small to show on the Mössbauer
5.5.3 The Effect of Catalysis

Though the same phases are shown here for catalysed sample reduced for 30 minutes and uncataylsed for 1 hour, the catalysed reactions are generally faster than the uncataylsed ones. The increased rate is due to the higher rate of generation of CO which causes a higher rate of reduction than solid carbon due to its ease of diffusion through the product layers to the reaction front.

5.5.4 The Effect of Preoxidation

The products detected in the Mössbauer Spectra (Figure 5.22a) and the diffractogram (Figure 5.21) for the oxidation of the Chinkombe ilmenite could be expressed in the following equation:

\[
\text{Fe}_2\text{O}_3 \cdot \text{FeTiO}_3 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 \quad \cdots \quad 5.11
\]

The reduction products of this oxidised ilmenite ore with 25%C for 2 hours at 1273 K are shown in Figures 5.23 and 5.22b. A probable reaction at this temperature could be:

\[
\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 + 4\text{C} \rightarrow 2\text{Fe} + 2\text{FeTiO}_3 + 4\text{CO} \quad \cdots \quad 5.12
\]
At a higher temperature of 1373 K with the same 25% C, the reduction products after 2 hours are metallic iron and rutile which could be expressed in the following equation:

\[ \text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 + 6\text{C} \rightarrow 4\text{Fe} + 2\text{TiO}_2 + 6\text{CO} \ldots .5.13 \]

Reaction 5.13 probably moved through Reaction 5.12 to the final products which could explain the presence of residual pseudobrookite and ilmenite in the diffractograms in Figures 5.23 and 5.24.

The fact that reduction processes in which relatively low amount of carbon was used, as shown in Figures 5.15 and 5.24 with clearly defined peaks for rutile, corroborates its presence as a reduction product in this investigation. The absence of peaks for it in Figures 5.13 and 5.14 could be attributed to the very low carbon content which could not reduce all the hematite and so residual hematite reacts with any rutile formed as a reaction product, according to reaction 5.10, above, to form pseudobrookite.
5.6 ANALYSIS OF THE KINETIC DATA

5.6.1 The order of the Reduction Reaction at 1373 K

The order of the reduction of the Chinkombe ilmenite with respect to iron produced was determined for the sample of particle size -150 + 106 micrometres in a mixture of 20%C at 1373 K using the Equation 2.18:

\[ V = kC^n \] ...........................................2.18

\[ \ln V = \ln k + n\ln C \] ..........................2.19

The values of the percent iron produced from the samples at different times and temperatures were calculated from the stoichiometry of the reaction using the weight loss determinations. The derivation of the formula for these calculations for iron is shown in Appendix 3.1 and the values are in Table 5.1. Here the variables in Equation 2.18 can be expressed as; \( V \) is the rate of formation of Fe from the ore and carbon mixture; \( k \) the rate constant, \( C \) the percent conversion of Fe formed and \( n \) the order of the reaction.

These values were plotted as shown in Figure 5.25. Tangents were drawn at various points along the curve for 1373 K in Figure 5.25 and their
gradients, \( V \), were determined for the evaluation of the order of the reaction at that temperature.

Table 5.1: Percent iron produced as function of time and temperature (determined by calculation according to the equation \( \%Fe = 4.319 \times \% \) weight loss)

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>1173 K</th>
<th>1223 K</th>
<th>1273 K</th>
<th>1323K</th>
<th>1373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.61</td>
<td>4.68</td>
<td>6.83</td>
<td>12.11</td>
<td>27.03</td>
</tr>
<tr>
<td>10</td>
<td>4.23</td>
<td>5.92</td>
<td>8.21</td>
<td>19.35</td>
<td>48.25</td>
</tr>
<tr>
<td>30</td>
<td>5.83</td>
<td>7.77</td>
<td>16.15</td>
<td>39.26</td>
<td>79.78</td>
</tr>
<tr>
<td>45</td>
<td>6.56</td>
<td>8.85</td>
<td>16.54</td>
<td>50.36</td>
<td>94.41</td>
</tr>
<tr>
<td>60</td>
<td>7.04</td>
<td>9.46</td>
<td>22.63</td>
<td>70.32</td>
<td>98.17</td>
</tr>
<tr>
<td>120</td>
<td>9.07</td>
<td>11.66</td>
<td>35.68</td>
<td>86.60</td>
<td>99.73</td>
</tr>
</tbody>
</table>

Table 5.2 shows the values so determined.
Figure 5.25 The percent iron formed by calculation based on the weight loss during reduction of Chinkombe ilmenite with graphite.
Table 5.2: The values of the gradients of the tangents to the points of conversion of the ore to iron in Figure 5.26.

<table>
<thead>
<tr>
<th>C (%)</th>
<th>20</th>
<th>30</th>
<th>48</th>
<th>50</th>
<th>60</th>
<th>79.78</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>4.444</td>
<td>4.026</td>
<td>3.000</td>
<td>1.762</td>
<td>1.400</td>
<td>1.333</td>
</tr>
</tbody>
</table>

The natural logarithms of V and C were found and plotted as in Figure 5.26. Two distinct straight lines 1 and f were obtained, with the following information established about them as stated in Table 5.3.

Table 5.3: The measured parameters from Figure 5.26.

<table>
<thead>
<tr>
<th>Line/measured parameter</th>
<th>l</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of correlation, r</td>
<td>-0.9986</td>
<td>-0.92</td>
</tr>
<tr>
<td>Slope (n)</td>
<td>-0.445</td>
<td>-0.95</td>
</tr>
<tr>
<td>Intercept (k)</td>
<td>16.76</td>
<td>4.44</td>
</tr>
</tbody>
</table>

Hence the order of the first part (up to about 50% reduction to iron) from the Chinkombe ilmenite ore is about 0.45 with rate constant of 16.76 mol^{-0.55} min^{-1} with respect to the formation of metallic
Figure 5.26: Reduction rate data for the Chinkombe ilmenite at 1373 K with 20% carbon fitted to van't Hoff's Equation.
iron.
The line which represents the whole reduction process up to about 80% reduction to metallic iron has an order of 0.95 which is approximately 1, and a rate constant of about 4.44 min⁻¹, with respect to the metallic iron. The reaction might be taking place, with hematite reduction preceeding that of ilmenite or at least the reduction of hematite begins and later the ore is reduced uniformly.

5.6.2 Modelling of the Reaction Kinetics and Enthalpy of Activation

The expirimental rate data obtained under isothermal conditions of 1173, 1223, 1273, 1323, and 1373 K were fitted to Crank, Ginstling and Brounshtein's simplified diffusion model (33), and it was found satisfactory in representing the results.
The equation is:

\[ f(R) = 1 - 2/3R - (1 - R)^{2/3} = \frac{kt}{r_0^2} = K't \quad \ldots \ldots 5.16 \]

where \( R \) is the fraction or percent of the reaction completed in time \( t \),
\( k \) is the specific rate constant,
\( r_0 \) is the initial radius of the reactant particles, and
\[ k = K^1 \times r_0^2 \]

The following precautions were taken to carry out and to obtain as representative a result as possible:

a. The same particle size of the ore (-150 + 106 micrometres) was used,

b. The same percent carbon (20\%) in the mixture,

c. Each pellet was approximately 3g and the time counting starting after 2 minutes of positioning in the equi-temperature zone in the reactor,

d. The timing procedure remained the same, as stated in the Experimental Procedure.

The data used in this determination were based on the calculated values of iron formed from the weight loss determinations. These values are shown in Table 5.4.

The \( f(R) \) vrs time graphs are shown in Figures 5.27 to 5.29. The values for \( f(R) \) at 1373 K for 60 and 120 minutes were not included in the plot in Figure 5.29, because their \( f(R) \) values are too high above 90\% iron formed. Habashi (33) says that the \( f(R) \) vrs time graphs cease to be linear after about 90\% reaction due to the fact that the correction for change in volume of the sphere
Table 5.4: The f(R) values as a function of temperature and time based on the percent iron formed as stated in Table 5.1

<table>
<thead>
<tr>
<th>Time/Temp (K) (mins)</th>
<th>1173</th>
<th>1223</th>
<th>1273</th>
<th>1323</th>
<th>1373</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4717 x 10^{-4}</td>
<td>2.486 x 10^{-4}</td>
<td>5.347 x 10^{-4}</td>
<td>1.720 x 10^{-3}</td>
<td>9.290 x 10^{-3}</td>
</tr>
<tr>
<td>10</td>
<td>2.0264 x 10^{-4}</td>
<td>4.002 x 10^{-4}</td>
<td>7.78 x 10^{-4}</td>
<td>4.560 x 10^{-3}</td>
<td>0.034</td>
</tr>
<tr>
<td>30</td>
<td>3.8779 x 10^{-4}</td>
<td>6.9508 x 10^{-4}</td>
<td>3.130 x 10^{-4}</td>
<td>0.021</td>
<td>0.1240</td>
</tr>
<tr>
<td>45</td>
<td>4.9262 x 10^{-4}</td>
<td>9.0635 x 10^{-4}</td>
<td>3.290 x 10^{-4}</td>
<td>0.037</td>
<td>0.2240</td>
</tr>
<tr>
<td>60</td>
<td>5.6866 x 10^{-4}</td>
<td>1.0386 x 10^{-4}</td>
<td>6.350 x 10^{-4}</td>
<td>0.086</td>
<td>0.2761</td>
</tr>
<tr>
<td>120</td>
<td>9.5298 x 10^{-4}</td>
<td>1.5947 x 10^{-4}</td>
<td>0.017</td>
<td>0.161</td>
<td>0.3157</td>
</tr>
</tbody>
</table>
Figure 5.27: Isothermal reduction rate data fitted to the diffusion model.
Figure 5.28: Isothermal reduction rate data fitted to the diffusion model.
Figure 5.29: Isothermal reduction rate data fitted to the diffusion model.
Table 5.5: Parameters measured from $f(R)$ vs time graphs in Figure 5.27 to 5.29

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>1173</th>
<th>1223</th>
<th>1273</th>
<th>1323</th>
<th>1373</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope ($K^1$)</td>
<td>$6.8772 \times 10^{-6}$</td>
<td>$1.1327 \times 10^{-5}$</td>
<td>$1.4322 \times 10^{-4}$</td>
<td>$1.4406 \times 10^{-3}$</td>
<td>$5.2510 \times 10^{-3}$</td>
</tr>
<tr>
<td>Correlation Coefficient, $r$</td>
<td>0.995</td>
<td>0.986</td>
<td>0.981</td>
<td>0.986</td>
<td>0.995</td>
</tr>
</tbody>
</table>
Figure 5.30: Arrhenius plot of the rate constant data obtained from the diffusion model.
during reaction was not taken into account in the derivation of Equation 5.16.

Since \( k = K^1 r_0^2 \) it implies that:

\[
\ln k = \ln K^1 + 2 \ln r_0, \quad \text{and}
\]

\[
\frac{d(\ln k)}{d(1/T)} = \frac{d(\ln K^1)}{d(1/T)} + \frac{2 \cdot d(\ln r_0)}{d(1/T)}
\]

but \( r_0 \) is constant, so \( \frac{d(\ln r_0)}{d(1/T)} = 0 \)

and hence the gradient of the line in Figure 5.30 is given by:

\[
- \frac{d(\ln k)}{d(1/T)} = - \frac{d(\ln K^1)}{d(1/T)} = + \frac{E}{R}
\]

Using \( R = 8.31 \text{ J/mol K} = 1.986 \text{cal/mol K} \) (17), the enthalpy of activation of 482.0 kJ/mol (or 115.3 kcal/mol) was found for the formation of metallic iron from the Chinkombe ilmenite in the temperature range of 1173 to 1373 K.

A second method used to determine the enthalpy of activation of the Chinkombe ilmenite in this investigation was based on the initial reaction rates \( R_i \), evaluated as the slopes of the initial parts (0 to 2 minutes) of the curves in Figure
5.25. Table 5.6 shows the initial rates so evaluated and the associated data needed for the Arrhenius plot as shown in Figure 5.31. The straight line has a correlation coefficient of -0.966. The enthalpy of activation obtained by this method in the temperature range of 1173 to 1373 K is 131.7 kJ/mol (or 31.5 kcal/mol).

Table 5.6 Percent iron formed initially as determined from Figure 5.25

<table>
<thead>
<tr>
<th>Temp, T (K)</th>
<th>10^4/T</th>
<th>Slope, R_i</th>
<th>ln R_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173</td>
<td>8.525</td>
<td>0.722</td>
<td>-0.3257</td>
</tr>
<tr>
<td>1223</td>
<td>8.177</td>
<td>0.936</td>
<td>-0.0661</td>
</tr>
<tr>
<td>1273</td>
<td>7.855</td>
<td>1.336</td>
<td>0.3119</td>
</tr>
<tr>
<td>1323</td>
<td>7.559</td>
<td>2.422</td>
<td>0.8846</td>
</tr>
<tr>
<td>1373</td>
<td>7.283</td>
<td>5.406</td>
<td>1.6875</td>
</tr>
</tbody>
</table>

It could be concluded from the kinetic data the value of the enthalpy of activation of 131.7 kJ/mol obtained is that of the reduction of mainly the hematite portion of the the Chinkombe ilmenite to metallic iron.
Figure 5.31: Arrhenius plot of the initial rate constant data for the reduction of the Chinkombe ilmenite ore with graphite in the temperature range 1173 to 1373 K.
Different values have been reported in the literature for the enthalpy of activation of hematite with solid carbon. Srinivasan and Lahiri (34) gave a range of 56.10 to 416.16 kJ/mol in the temperature range of 1208 to 1333 K, Rao (12) obtained 102.10 kJ/mol between 1230 and 1360 K as the enthalpy of activation of hematite reduction with carbon.

Furthermore, the Mössbauer spectra in Figures 5.12a, 5.12b and 5.17a show that the reduction of the hematite precedes that of the ilmenite. The standard free energy relationships for the reduction of oxides of iron and ilmenite in Figures 2.1 and 2.2 also show that ilmenite and titanium dioxide (TiO₂) are far less easily reduced than the simple oxides of iron.

The enthalpy of activation of 482.0 kJ/mol could include the activation energy of the reduction of the Chinkombe ilmenite as solid solution of hematite and ilmenite to metallic iron and titanium dioxide using carbon (graphite) as the reductant in the temperature range of 1173 to 1373 K.

The two straight lines, l and f in Figure 5.26
further support the fact that the hematite reduction probably precedes the ilmenite reduction. The initial reduction could be represented by line 1 which is the reduction of the hematite and then the ore as solid-solution being reduced to metallic iron and titanium dioxide is represented by line f.
CHAPTER SIX

SUMMARY, CONCLUSION AND SUGGESTIONS

6.1 SUMMARY AND CONCLUSION

The present investigation has been on Chinkombe ilmenite ore. The ore was composed of exsolution lamellae of hematite in ilmenite as a solid-solution. The ore assayed 37.68% TiO₂ and 39.29 total iron.

Reduction experiments were carried out on the ore with graphite between 1173 and 1373 K. The results show a pronounced effect of temperature on the overall reduction process, with the reduction being enhanced by increase in temperature. It was found that the rate of reduction was low between 1173 and 1260 K, but became sharply high (approximately two times higher) between 1260 and 1373 K. A similar effect (increase in the reduction rate) was observed with decreasing ore particle size and the addition of a catalyst. There was an optimum carbon content, of 20% for effective reduction, above which the extent of the reduction fell.

The reduction reaction of the ore with graphite is governed to a large extent by the availability of carbon monoxide. The Boudouard (solution-loss) reaction taking
place between the carbon particles and the carbon dioxide product gas was the chief means of generating carbon monoxide within the ore-graphite pellet. The effect of the catalyst lithium carbonate on the reduction substantiates this fact.

The reduction of the preoxidised ore did not increase the rate or the extent of the reduction reaction. The direct reduction of the ore at 1373 K with 20% carbon in the mixture for one hour was effective in reducing almost all the iron oxides in the ore the metallic iron.

The products formed during the reduction were metallic iron and rutile. The observations show that the hematite portions of the ore were reduced prior to the reduction of ilmenite. The kinetic data obtained from reduction experiment approximately fitted the diffusion model developed by Crank et al (33):

\[ f(R) = 1 - 2/3R - (1-R)^{2/3} = K^t \]

The enthalpy of activation found using this model was 482.0 kJ/mol (115.3 kcal/mol) for the Chinkombe ilmenite ore in the temperature range of 1173 to 1373 K.

In any industrial process, the reaction could be stopped after all the iron oxides are reduced to metallic iron and the product could be leached using dilute hydrochloric acid or dilute sulphuric acid or iron
(III) (ferric) chloride solution, depending on the economics of the process, to remove the metallic iron into solution, leaving the titanium dioxide residue for the paint industry.

6.2 SUGGESTIONS

Further work is required to clarify and substantiate the present results, such as:

i. determination of such impurities mainly manganese and magnesium; and their distribution and effects on the reduction of the Chinkombe ilmenite,

ii. effect of preoxidation on the reduction, on the morphology of the metallic iron produced and on the subsequent removal of the metallic iron from the synthetic rutile, and

iii. conditions under which reduced rutile would be produced and how this could be minimised or reoxidised to get titanium dioxide, suitable for the paint industry or any other use.

More X-ray diffraction analyses are needed to identify the solid-solution series of ilmenite during reduction as reported in the literature (21-24) and their effects, if any, on the Chinkombe ilmenite ore. The precise chemical composition of these transition compounds may also be
confirmed by electron probe microanalysis.
REFERENCES


7. Discussions held with Mr A. Sliwa, Chief Geologist, Minex - ZIMCO, Lusaka.

8. Discussions held with Mr J.A. Tether, Assistant Director, Geological Survey Department, Lusaka.

9. Discussions held with Dr J. Kaoma, Senior Scientific Research Officer, Industrial Minerals Research Unit, National Council for Scientific Research, Lusaka.


19. Hullett J.R. Deviation from the Arrhenius Equation, Quaterly Reviews of Chemical Society, 18, 1964, p 227


23. Peterson M.C.L. and Cameron J. Limitations in gaseous reduction, oxidation and upgrading of Allard Lake ilmenite.

M Sc Thesis 1979 Univ. of Strathclyde.


33. Habashi F. Principles of Extractive Metallurgy

APPENDICES
APPENDICES

1.1 The Thermodynamic data used for Figures 2.1 to 2.3.
1.2 Determination of values for plotting Figure 2.3.
2.1 Determination of the number grains to be counted.
3.1 Determination of the stoichiometric carbon requirements for the reduction of the Chinkombe ilmenite.
3.2 Determination of the theoretical percent iron formed during the reduction, based on the weight loss data.
4.1 Weight loss data at different temperatures, times and percent carbon in the mixture.
**APPENDIX 1.1**

The thermodynamic data used in drawing Figures 2.1 - 2.3

| i  | 2Fe + O₂ = 2FeO  | -126620 + 31.24T | 298 - 1642 | 26  |
| ii | 6FeO + O₂ = 2Fe₂O₄ | -149240 + 59.8T | 298 - 1642 | 26  |
| iii | 4Fe₂O₃ + O₂ = 6Fe₂O₃ | -119240 + 67.24T | 298 - 1460 | 26  |
| iv | 2Fe + O₂ + 2TiO₃ = 2FeTiO₃ | -129220 + 25.86T | 1173 - 1400 | 26  |
| v  | Ti + O₂ = TiO₂  | -217703 + 41.39T | 298 - 2000 | 26  |
| vi | 4/3Fe + O₂ + 2/3TiO₂ = 2/3Fe₂TiO₃ | -136166 + 47.0T | 1140 - 1470 | 24  |
| vii | C + O₂ = CO₂ | -94200 - 0.2T | 298 - 2000 | 26  |
| viii | 2C + O₂ = 2CO | -53400 - 41.9T | 298 - 2500 | 26  |
| ix | 2CO + O₂ = 2CO₂ | -135000 + 41.5T | 298 - 2000 | 26  |
| x  | 3Fe + C = Fe₃C | -2475 - 2.43T | 1073 - 1773 | 12  |
| xi | 2Ti₂O₃ + O₂ = 4TiO₂ | -185960 - 49.8T | 298 - 2000 | 24  |
| xii | 2Ti₃O₇ + O₂ = 6TiO₂ | -197200 + 61.6T | 298 - 2000 | 24  |
The thermodynamic equations used in the plotting of the curves in Figure 2.3 were determined as follows:

For equation:

\[ \text{CO}_2 + \text{C} = 2\text{CO} \] \hspace{2cm} A.1

\[ \Delta G^0_1 = 40800 - 41.7 T \text{ cal} \] \hspace{2cm} A.1.1

the equilibrium constant \( K_1 = \frac{P_{\text{CO}}^2}{a_c P_{\text{CO}_2}} \),

where \( P_{\text{CO}} \) and \( P_{\text{CO}_2} \) are the partial pressures of carbon monoxide and carbon dioxide respectively, and \( a_c \) is the activity of carbon. The standard state of carbon is assumed and hence \( a_c = 1 \), therefore,

\[ K_1 = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \] \hspace{2cm} A.1.2

Since the reactions are taking place at one atmosphere pressure (approximately one bar), the total pressure of CO and \( \text{CO}_2 \) is 1; thus

\[ P_{\text{CO}} + P_{\text{CO}_2} = 1 \] \hspace{2cm} A.1.3

Solving Equations A.1.2 and A.1.3 simultaneously,

\[ (P_{\text{CO}})^2 + K_1 P_{\text{CO}} - K_1 = 0 \] \hspace{2cm} A.1.4

Considering only the positive values of \( P_{\text{CO}} \) at the various temperatures, after determining \( K_1 \) from the equation:

\[ K_1 = e^{-\Delta G^0_1/RT} \] \hspace{2cm} A.1.5
where $R$ is the general gas constant = 8.31 J/mol K = 1.986 cal/mol K (17). The values of $P_{co2}$ could be found from Equation A.1.2 or Equation A.1.4 and the results are expressed in Table A.1.2

Table A.1.2: Equilibrium log$_{10}$ $P_{co}/P_{co2}$ values with temperature for Equation A.1.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>log$<em>{10}$P$</em>{co}/P_{co2}$</td>
<td>0.17</td>
<td>0.87</td>
<td>1.51</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1200</td>
<td>1300</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>3.05</td>
<td>3.40</td>
<td>3.78</td>
</tr>
</tbody>
</table>

For the equation:

FeTiO$_3$ + CO = Fe + CO$_2$ + TiO$_2$ .................A.2

$\Delta G^0_z = 2890 + 7.82 T$ cal ..................A.2.1

$$K_2 = \frac{a_{Fe}.a_{TiO_2}.P_{co2}}{a_{FeTiO_3}.P_{co}}$$

but the activities of pure solids (assumed to be in their standard states) are unity and hence:

$$a_{Fe} = a_{TiO_2} = a_{FeTiO_3} = 1$$

and $K_2 = P_{co2}/P_{co}$ ..................A.2.2
\[ P_{co} + P_{co2} = 1 \] .................A.1.2

\[ K_2 = e^{-\Delta G_2^{0}/RT} \] .........................A.1.5

The values for Table A.1.3 have been obtained using these equations and varying the absolute temperature, \( T \)

**Table A.1.3:** Equilibrium \( \log_{10} P_{co}/P_{co2} \) values with temperature for Equation A.2.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log_{10} P_{co}/P_{co2} )</td>
<td>1.06</td>
<td>1.12</td>
<td>1.17</td>
<td>1.21</td>
</tr>
<tr>
<td>1100</td>
<td>1.25</td>
<td>1.28</td>
<td>1.31</td>
<td>1.33</td>
</tr>
</tbody>
</table>

For the equation:

\[ Fe + Ti + 3CO_2 = FeTiO_3 + 3CO \] ...............A.3

\[ \Delta G_3^{0} = -79633.92 - 7.98T \text{ cal} \] .................A.3.1

\[ K_3 = \frac{a_{FeTiO_3} \cdot P_{co}^3}{a_{Fe} \cdot a_{Ti} \cdot P_{co2}^3} \]
for the same reason as above, \( a_{Fe,103} = a_{Fe} = a_{Ti} = 1 \)

hence \( K_3 = (P_{co})^3 / (P_{co2})^3 \) .......................... A.3.2

and \( K_3 = e^{-\Delta G^*/RT} \) .......................... A.3.3

\( P_{co} + P_{co2} = 1 \) .......................... A.1.3

Using Equations A.1.3, A.3.2, A.3.3 the following values as stated in Table A.1.4 were obtained.

Table A.1.4: Equilibrium \( \log_{10} P_{co}/P_{co2} \) values with temperature for Equation A.3.

<table>
<thead>
<tr>
<th>Temp(°C)</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>log_{10} P_{co}/P_{co2}</td>
<td>6.55</td>
<td>5.99</td>
<td>5.33</td>
<td>5.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.81</td>
<td>4.52</td>
<td>4.27</td>
<td>4.05</td>
<td>3.86</td>
<td></td>
</tr>
</tbody>
</table>

For the equation:

\[
3Fe + 2CO = Fe_3C + CO_2 .......................... A.4
\]

\[
\Delta G_{4}^{o} = -43275 + 39.27 T  \text{ cal}  .................. A.4.1
\]

\[
K_4 = \frac{a_{Fe,3C} \cdot P_{co2}}{a_{Fe,3} \cdot P_{co}^2}
\]
and for pure Fe₃C and Fe, \( a_{Fe} = a_{Fe3C} = 1 \)

\[
K_4 = \frac{P_{\text{co}2}}{(P_{\text{co}})^2} \quad \text{..........................A.4.2}
\]

\[
K_4 = e^{-\Delta G^\circ /RT} \quad \text{..........................A.4.3}
\]

For total pressure of 1 bar (atmosphere):

\[
P_{\text{co}} + P_{\text{co2}} = 1 \quad \text{..........................A.1.3}
\]

From Equation A.4.2, \( K_4 (P_{\text{co}})^2 = P_{\text{co2}} \)

substituting it into Equation A.1.3,

\[
K_4 (P_{\text{co}})^2 + P_{\text{co}} - 1 = 0,
\]

and solving the quadratic equation for \( P_{\text{co}} \) by using:

\[
P_{\text{co}} = \frac{-1 \pm \sqrt{(1 + 4K_4)}}{2K_4}
\]

The values for \( P_{\text{co2}} \) are found by substituting for \( P_{\text{co}} \)
in Equations A.1.3 or A.4.2; and these are shown in Table A.1.5.
Table A.1.5: Equilibrium $\log_{10} \frac{P_{\text{CO}}}{P_{\text{CO}_2}}$ values with temperature for Equation A.4

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log_{10} \frac{P_{\text{CO}}}{P_{\text{CO}_2}}$</td>
<td>-0.51</td>
<td>0.046</td>
<td>0.614</td>
<td>1.18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.71</td>
<td>2.17</td>
<td>2.57</td>
<td>2.93</td>
<td>3.24</td>
</tr>
</tbody>
</table>
APPENDIX 2.1

DETERMINATION OF NUMBER OF GRAINS TO BE COUNTED

Using Jones and Horton formula:

\[ N = \frac{4q}{pE^2} \]

where \( N \) is the number of grains to be counted on the polished section,
\( p \) is the proportion of the desired mineral phase (ilmenite in this case),
\( q = 1 - p \), and
\( E \) is the specified relative error on \( p \).

The value of \( p \) is not usually known at the start of the investigation so it is necessary to arrive at the correct value of \( N \) and \( p \) by a series of iterative calculations performed during the course of the counting procedure.

From rough inspection made on the polished section,
\( p = 0.5 \), implying \( q = 1 - p = 0.5 \);

Fixing the relative error \( E \) at a maximum of 5%,

\[ N = \frac{4(0.5)}{(0.5)(0.05)^2} = 1600 \text{ counts} \]

The polished section was then traced on an ordinary graph.

133
paper and 83 squares were covered by the sample. The number of counts per square is therefore 1600/83 which is 19.27 (which to next whole number is equal to 20. Rotating the stage on which the sample was mounted, to cover a uniform area in each square, the angle per square is $360^\circ/20 = 18^\circ$.

Hence for each square on the polished section, 20 grains were counted at intervals of $18^\circ$.

RESULTS
At the end of the point counting, the result arrived at are:

Number of points covered by ilmenite = 1098
Number of points covered by hematite and its hydrated forms = 515
TOTAL = 1613

for the relative error in the point counting for ilmenite: $N = 1613, \; p = 1098/1613 = 0.6724$
$q = 1 - p = 0.3276$

$E^2 = \frac{4 \times (0.3276)}{1613 \times (0.6724)} = 1.2082 \times 10^{-3}$

$E = 0.03476 = 3.48\%$
Hence the ilmenite proportion observed under the microscope on the polished section is 67.24 ± 3.48%.
The relative error E for hematite and its hydrated forms:
p = 0.3276, q = 0.6724, E^2 = 5.0899 x 10^{-3};
E = 7.13%

Hence the proportion of hematite and its hydrated forms is 32.76 ± 7.13% as observed from the polished section.
APPENDIX 3.1

Determination of stoichiometric carbon requirement for the reduction of Chinkombe ilmenite ore to metallic iron and titaniom dioxide. Carbon monoxide was assumed to be the only product gas. The Chinkombe ilmenite ore used in the investigation contained 20.05% Fe₂O₃ and 32.48% FeO. These two oxides of iron would be reduced to metallic iron.

\[ \text{Fe}_2\text{O}_3 \cdot \text{FeO} \rightarrow \text{TiO}_2 + \overset{\text{%O}_2}{\text{in the Chinkombe ilmenite}} \]

\[ \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 30 \]

159.7  117  48 (molar masses)
0.2005  0.1402  0.06

For 1 g of the Chinkombe ilmenite ore, 0.2005g of it would be Fe₂O₃ and would require 0.06g of oxygen to be removed by carbon.

\[ \text{FeO} \rightarrow \text{Fe} + 0 \]

71.85  55.85  16 (molar masses)
0.3248  0.2525  0.0723

For 1 g of the Chinkombe ilmenite ore, 0.3248g of it would be FeO and would require 0.0723 g of oxygen to be removed by carbon.

Total weight of oxygen to be removed = 0.06 + 0.0723 = 0.1323g = Total weight of oxygen to be removed per gram of the ore.
\[ C + O = CO \]

\[
\begin{array}{ccc}
12 & 16 & 28 \\
0.0992 & 0.1323 & \\
\end{array}
\] (molar masses)

The 0.1323 g of oxygen would require 0.0992 g of carbon to be removed to form carbon monoxide.

Percent weight of carbon in the mixture

\[
\frac{\text{Wt of carbon}}{\text{wt of carbon} + \text{wt of ore sample}} \times 100
\]

\[
= \frac{0.0992 \times 100}{0.0992 + 1}
\]

\[ = 9.02 \]

10% was chosen for the stoichiometric case.
APPENDIX 3.2

Determination of the theoretical percent iron formed from the weight loss data.

From Appendix 3.1, it was found that:

The total weight of oxygen per gram of the ore that is to be removed = 0.1323 g; and the total weight of iron per gram of the ore = 0.1402 + 0.2525

= 0.3927 g of iron associated with oxygen per gram of the ore.

For 1 g of oxygen removed

\[
\text{For 1 g of oxygen removed = } \frac{0.3927 \text{ g of Fe}}{0.1323 \text{ g of Oxygen}} = 2.9683 \text{ g of Fe formed.}
\]

\[
\begin{array}{c}
C + O = CO \\
12 & 16 & 28 \text{ (molar masses)}
\end{array}
\]

z \ y \ (weight per gram of sample)

\[
y \text{ gram of weight loss} = z = \frac{16y \text{ gram of oxygen loss}}{28}
\]

1 g of oxygen loss = 2.9683 g of iron formed

\[
\frac{16y \text{ g oxygen loss}}{28} = \frac{2.9683 \times 16y}{28} \text{ g of iron formed}
\]

= 1.69617y g of iron formed

percent Fe formed

\[
\text{percent Fe formed} = \frac{\text{Total Fe formed} \times 100}{\text{Total Fe contained in sample}}
\]

\[
= \frac{1.69617y \times 100}{0.3927}
\]

= 4.319 y \times 100

but y \times 100 = percent weight loss, hence

% theoretical Fe formed = 4.319 \times \% weight loss.
APPENDIX 4.1

Table A.1: Weight loss data 20% carbon in ilmenite-graphite mixture of ilmenite particle size of -150 + 106 microns

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Time (min)</th>
<th>Sample Initial (W₀)</th>
<th>Weight (g) Final (W)</th>
<th>Weight loss (ΔW)</th>
<th>% Weight loss (ΔW/W₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173</td>
<td>5</td>
<td>3.0021</td>
<td>2.9770</td>
<td>0.0251</td>
<td>0.84</td>
</tr>
<tr>
<td>1173</td>
<td>10</td>
<td>3.0046</td>
<td>2.9753</td>
<td>0.0293</td>
<td>0.98</td>
</tr>
<tr>
<td>1173</td>
<td>30</td>
<td>3.0038</td>
<td>2.9632</td>
<td>0.0406</td>
<td>1.35</td>
</tr>
<tr>
<td>1173</td>
<td>45</td>
<td>3.0080</td>
<td>2.9624</td>
<td>0.0456</td>
<td>1.52</td>
</tr>
<tr>
<td>1173</td>
<td>60</td>
<td>3.0082</td>
<td>2.9693</td>
<td>0.0489</td>
<td>1.63</td>
</tr>
<tr>
<td>1173</td>
<td>120</td>
<td>3.0107</td>
<td>2.9474</td>
<td>0.0633</td>
<td>2.10</td>
</tr>
<tr>
<td>1223</td>
<td>5</td>
<td>3.0081</td>
<td>2.9755</td>
<td>0.0326</td>
<td>1.08</td>
</tr>
<tr>
<td>1223</td>
<td>10</td>
<td>3.0065</td>
<td>2.9653</td>
<td>0.0412</td>
<td>1.37</td>
</tr>
<tr>
<td>1223</td>
<td>30</td>
<td>3.0094</td>
<td>2.9553</td>
<td>0.0541</td>
<td>1.80</td>
</tr>
<tr>
<td>1223</td>
<td>45</td>
<td>3.0077</td>
<td>2.9461</td>
<td>0.0616</td>
<td>2.05</td>
</tr>
<tr>
<td>1223</td>
<td>60</td>
<td>3.0076</td>
<td>2.9417</td>
<td>0.0659</td>
<td>2.19</td>
</tr>
<tr>
<td>1223</td>
<td>120</td>
<td>3.0052</td>
<td>2.9241</td>
<td>0.0811</td>
<td>2.70</td>
</tr>
<tr>
<td>1273</td>
<td>5</td>
<td>2.9909</td>
<td>2.9436</td>
<td>0.0473</td>
<td>1.58</td>
</tr>
<tr>
<td>1273</td>
<td>10</td>
<td>3.0246</td>
<td>2.9672</td>
<td>0.0574</td>
<td>1.90</td>
</tr>
<tr>
<td>1273</td>
<td>30</td>
<td>3.0176</td>
<td>2.9048</td>
<td>0.1128</td>
<td>3.74</td>
</tr>
<tr>
<td>1273</td>
<td>45</td>
<td>3.0320</td>
<td>2.9158</td>
<td>0.1162</td>
<td>3.83</td>
</tr>
<tr>
<td>1273</td>
<td>60</td>
<td>3.0278</td>
<td>2.8690</td>
<td>0.1588</td>
<td>5.24</td>
</tr>
<tr>
<td>1273</td>
<td>120</td>
<td>3.0185</td>
<td>2.7692</td>
<td>0.2493</td>
<td>8.26</td>
</tr>
</tbody>
</table>
### Table A.1 continued

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Time (min)</th>
<th>Sample weight (g)</th>
<th>Weight loss ($\Delta W$)</th>
<th>% Weight loss ($\Delta W/W_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1323</td>
<td>5</td>
<td>2.9994</td>
<td>0.0841</td>
<td>2.80</td>
</tr>
<tr>
<td>1323</td>
<td>10</td>
<td>3.0138</td>
<td>0.1350</td>
<td>4.48</td>
</tr>
<tr>
<td>1323</td>
<td>30</td>
<td>3.0205</td>
<td>0.2745</td>
<td>9.09</td>
</tr>
<tr>
<td>1323</td>
<td>45</td>
<td>3.0044</td>
<td>0.3502</td>
<td>11.66</td>
</tr>
<tr>
<td>1323</td>
<td>60</td>
<td>3.9185</td>
<td>0.4915</td>
<td>16.28</td>
</tr>
<tr>
<td>1323</td>
<td>120</td>
<td>3.0219</td>
<td>0.6059</td>
<td>20.05</td>
</tr>
<tr>
<td>1373</td>
<td>5</td>
<td>3.0222</td>
<td>0.1891</td>
<td>6.26</td>
</tr>
<tr>
<td>1373</td>
<td>10</td>
<td>3.0244</td>
<td>0.3378</td>
<td>11.17</td>
</tr>
<tr>
<td>1373</td>
<td>30</td>
<td>3.0197</td>
<td>0.5577</td>
<td>18.47</td>
</tr>
<tr>
<td>1373</td>
<td>45</td>
<td>3.0210</td>
<td>0.6604</td>
<td>21.86</td>
</tr>
<tr>
<td>1373</td>
<td>60</td>
<td>3.0314</td>
<td>0.6890</td>
<td>22.73</td>
</tr>
<tr>
<td>1373</td>
<td>120</td>
<td>3.0287</td>
<td>0.6993</td>
<td>23.09</td>
</tr>
</tbody>
</table>
Table A3: Particle size of -300+212 microns and -212+150 microns with 20°C at 1373 K

<table>
<thead>
<tr>
<th>Particles Size (microns)</th>
<th>Time (min.)</th>
<th>Sample Initial (W₀)</th>
<th>Weight (g) Final (W)</th>
<th>Weight loss (g) (∆W)</th>
<th>% Weight loss (%) ∆W/W₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>-300+212</td>
<td>5</td>
<td>3.0789</td>
<td>3.0050</td>
<td>0.0739</td>
<td>2.40</td>
</tr>
<tr>
<td>&quot;</td>
<td>10</td>
<td>3.0470</td>
<td>2.8965</td>
<td>0.1505</td>
<td>4.94</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>3.0144</td>
<td>2.7326</td>
<td>0.2818</td>
<td>9.35</td>
</tr>
<tr>
<td>&quot;</td>
<td>45</td>
<td>3.0206</td>
<td>2.5986</td>
<td>0.4220</td>
<td>13.97</td>
</tr>
<tr>
<td>&quot;</td>
<td>60</td>
<td>3.0187</td>
<td>2.5267</td>
<td>0.4920</td>
<td>16.30</td>
</tr>
<tr>
<td>&quot;</td>
<td>120</td>
<td>3.0197</td>
<td>2.4617</td>
<td>0.5580</td>
<td>18.48</td>
</tr>
<tr>
<td>-212+150</td>
<td>5</td>
<td>3.0215</td>
<td>2.8399</td>
<td>0.1816</td>
<td>6.01</td>
</tr>
<tr>
<td>-212+150</td>
<td>10</td>
<td>3.0225</td>
<td>2.8164</td>
<td>0.2061</td>
<td>6.82</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>3.0175</td>
<td>2.5964</td>
<td>0.4211</td>
<td>13.96</td>
</tr>
<tr>
<td>&quot;</td>
<td>45</td>
<td>3.0115</td>
<td>2.5313</td>
<td>0.4802</td>
<td>15.95</td>
</tr>
<tr>
<td>&quot;</td>
<td>60</td>
<td>3.0124</td>
<td>2.4212</td>
<td>0.5912</td>
<td>19.63</td>
</tr>
<tr>
<td>&quot;</td>
<td>120</td>
<td>3.0105</td>
<td>2.3645</td>
<td>0.6479</td>
<td>21.46</td>
</tr>
</tbody>
</table>
Table A4: Particle size of -150+106 microns for 10% C and 30% C at 1373K

<table>
<thead>
<tr>
<th>Percent carbon</th>
<th>Time (min)</th>
<th>Sample</th>
<th>Weight(g)</th>
<th>Weight loss(g)</th>
<th>% Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C</td>
<td>Initial ($W_i$)</td>
<td>Final(W)</td>
<td>($\Delta W$)</td>
<td>($% \Delta W/W_0$)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>3.0169</td>
<td>2.8680</td>
<td>0.1489</td>
<td>4.94</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.0119</td>
<td>2.7542</td>
<td>0.2577</td>
<td>8.56</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.0206</td>
<td>2.5929</td>
<td>0.4277</td>
<td>14.16</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>3.0137</td>
<td>2.5023</td>
<td>0.5114</td>
<td>16.97</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.0314</td>
<td>2.4706</td>
<td>0.5608</td>
<td>18.50</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.0125</td>
<td>2.3967</td>
<td>0.6158</td>
<td>20.44</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>3.0064</td>
<td>2.6172</td>
<td>0.3892</td>
<td>12.95</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.0062</td>
<td>2.4510</td>
<td>0.5552</td>
<td>18.47</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.0089</td>
<td>2.4199</td>
<td>0.5890</td>
<td>19.58</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.0203</td>
<td>2.3803</td>
<td>0.6400</td>
<td>21.19</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.0051</td>
<td>2.3363</td>
<td>0.6688</td>
<td>22.26</td>
</tr>
</tbody>
</table>
Table A5: Weight loss data for the catalysed reactions with 5% L\textsubscript{2}CO\textsubscript{3} at 1373K or particle size of 150+106 microns with 20%C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Initial ($W_0$)</th>
<th>Weight (g) Final ($W$)</th>
<th>Weight loss (g) ($\Delta W$)</th>
<th>% Weight loss (% $\Delta W/W_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.0090</td>
<td>2.6298</td>
<td>0.3792</td>
<td>12.60</td>
</tr>
<tr>
<td>10</td>
<td>3.0079</td>
<td>2.5172</td>
<td>0.4907</td>
<td>16.31</td>
</tr>
<tr>
<td>15</td>
<td>3.0125</td>
<td>2.4083</td>
<td>0.6042</td>
<td>20.06</td>
</tr>
<tr>
<td>20</td>
<td>3.0117</td>
<td>2.3706</td>
<td>0.6411</td>
<td>21.29</td>
</tr>
<tr>
<td>30</td>
<td>3.0120</td>
<td>2.3307</td>
<td>0.6813</td>
<td>22.62</td>
</tr>
</tbody>
</table>

at 1273K for particle size of -212+150 microns with 15%C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Initial ($W_0$)</th>
<th>Weight (g) Final ($W$)</th>
<th>Weight loss (g) ($\Delta W$)</th>
<th>% Weight loss (% $\Delta W/W_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.0287</td>
<td>2.7802</td>
<td>0.2485</td>
<td>8.20</td>
</tr>
<tr>
<td>30</td>
<td>3.0261</td>
<td>2.7335</td>
<td>0.2926</td>
<td>9.66</td>
</tr>
<tr>
<td>45</td>
<td>3.0212</td>
<td>2.6575</td>
<td>0.3637</td>
<td>12.04</td>
</tr>
<tr>
<td>60</td>
<td>3.0237</td>
<td>2.6062</td>
<td>0.4175</td>
<td>13.81</td>
</tr>
<tr>
<td>120</td>
<td>3.0188</td>
<td>2.5411</td>
<td>0.4777</td>
<td>15.82</td>
</tr>
<tr>
<td>180</td>
<td>3.0238</td>
<td>2.4463</td>
<td>0.5775</td>
<td>19.10</td>
</tr>
</tbody>
</table>
Table A6: Weight loss data for particle size of -212+150 microns reduced at 1273K with 15°C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample Initial (W₀)</th>
<th>Weight (g)</th>
<th>Weight loss (g) (ΔW)</th>
<th>% Weight loss (% ΔW/W₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.0217</td>
<td>2.9651</td>
<td>0.0566</td>
<td>1.87</td>
</tr>
<tr>
<td>30</td>
<td>3.0233</td>
<td>2.9516</td>
<td>0.0717</td>
<td>2.37</td>
</tr>
<tr>
<td>45</td>
<td>3.0259</td>
<td>2.9299</td>
<td>0.0960</td>
<td>3.17</td>
</tr>
<tr>
<td>60</td>
<td>3.0166</td>
<td>2.8908</td>
<td>0.1258</td>
<td>4.17</td>
</tr>
<tr>
<td>120</td>
<td>3.0007</td>
<td>2.7940</td>
<td>0.2130</td>
<td>7.08</td>
</tr>
<tr>
<td>180</td>
<td>3.0202</td>
<td>2.7279</td>
<td>0.2923</td>
<td>9.68</td>
</tr>
</tbody>
</table>
Table A7: Weight loss data on Reduction of the Preoxidised ilmenite of particle size -150+106 microns

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>%C</th>
<th>Time (min.)</th>
<th>Sample Weight (g)</th>
<th>% Weight loss (% ΔW/WW0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial (W0)</td>
<td>Final (W)</td>
</tr>
<tr>
<td>1373</td>
<td>11.4</td>
<td>10</td>
<td>3.0195</td>
<td>2.7930</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>3.0152</td>
<td>2.5386</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>3.0107</td>
<td>2.4340</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>3.0056</td>
<td>2.3940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>3.0017</td>
<td>2.3218</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>10</td>
<td>3.0034</td>
<td>2.7036</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>3.0033</td>
<td>2.5267</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>3.0035</td>
<td>2.4244</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>3.0057</td>
<td>2.3589</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>3.0192</td>
<td>2.3354</td>
</tr>
<tr>
<td>33.4</td>
<td></td>
<td>10</td>
<td>2.9916</td>
<td>2.6748</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>2.9962</td>
<td>2.5496</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>3.0004</td>
<td>2.4812</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>2.9943</td>
<td>2.4199</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>2.9993</td>
<td>2.3316</td>
</tr>
<tr>
<td>1273</td>
<td>25</td>
<td>10</td>
<td>3.0070</td>
<td>2.8491</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>3.0067</td>
<td>2.8174</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>3.0103</td>
<td>2.7745</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>3.0140</td>
<td>2.8007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>3.0105</td>
<td>2.7462</td>
</tr>
</tbody>
</table>