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GASEOUS REDUCTION OF NICKEL CALCINES IN $H_2$ AND CO BETWEEN
400° C AND 850° C

by

Christopher John Bleecker Crowe

A thesis submitted in conformity with the requirements for the degree of
Doctor of Philosophy
Graduate Department of Metallurgy and Material Science
University of Toronto

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GASEOUS REDUCTION OF NICKEL CALCINES IN H₂ AND CO BETWEEN 400°C AND 850°C

Ph.D. Thesis 1998
Christopher John Bleecker Crowe
Department of Metallurgy and Material Science
University of Toronto

ABSTRACT

The behaviour of two roasted nickel sulphide concentrates when heated in argon, hydrogen and carbon monoxide atmospheres was characterized by combining thermogravimetric analysis with off-gas analysis. Mass changes in inert atmospheres were attributed to sulphur dioxide evolution from solid state reactions between pyrrhotite and iron oxides (above 300°C) and from the decomposition of sulphates (above 550°C). In reducing atmospheres, sulphate decomposition was achieved at lower temperatures (250°C in H₂; 350°C in CO; reduction of the hematite phase prevented SO₂ emissions from the solid state reactions. Direct reduction of metal sulphides yielding H₂S and COS was detected above 500°C.

The rate of oxygen removal from two roasted nickel concentrates by H₂ and CO reductants was measured using thermogravimetric analysis. Non-isothermal and isothermal techniques were applied. It was found that hydrogen reduction obeyed a uniform internal reduction model. The temperature dependence of the rate constant obeyed an Arrhenius expression. Using isothermal analysis, different rate constants expressions were measured for the two calcines, however their activation energies were statistically the same (55 kJ/mol). The difference between the two expressions was attributed to the difficulty in measuring the degree of conversion in complex solids.

Isothermal and non-isothermal thermogravimetric analysis failed to provide consistent rate expressions for CO reduction of calcines. The reduction rate was noticeably retarded above 600°C. In addition the deposition of carbon on the calcine pores was observed.
It was concluded that carbon deposition had interfered with access of the gaseous reductant to the solid oxide, and hence lowered the reaction rate.

Reoxidation of deeply reduced calcines in air was measured. Above 500° C, reoxidation caused samples to gain mass at a rate of \( = 8\% \text{/min} \). Calcines pre-reduced in \( \text{H}_2 \) reoxidized approximately 20\% faster than calcine pre-reduced in \( \text{CO} \). From the relatively low activation energy of 12 kJ/mol, it was concluded that oxidation was diffusion controlled. This was in agreement with other researchers.
Acknowledgements

Thanks go to Dorr for making me start this research, Prof. Utigard and the staff at Falconbridge for helping me along the way and to & for making me finish.
## Nomenclature - English

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<th>Symbol</th>
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<td>Gas Concentration</td>
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### Nomenclature - Greek

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<td>Density</td>
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<td>σ</td>
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<tr>
<td>τ</td>
<td>Tortuosity of pores</td>
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# Table of Contents

1.0 **INTRODUCTION** ........................................... 1-1

1.1 Partial Roast / Electric Smelting of Nickel Sulphides ....... 1-2

1.2 Flash Smelting of Nickel Sulphides .............................. 1-5

1.3 Comparison of Flash Smelting and Roast/Electric Smelting .... 1-7

2.0 **LITERATURE REVIEW** ........................................ 2-1

2.1 Roasting Ni/Cu Concentrates ...................................... 2-1

2.2 Reductive Smelting of Calcines at Falconbridge .......... 2-3

2.3 Reduction of Metal Sulphides ...................................... 2-8

2.4 Gaseous Reduction of Iron Oxides ................................. 2-9

2.4.1 Reduction of Hematite ......................................... 2-9

2.4.2 Reduction of Magnetite ......................................... 2-13

2.4.3 Reduction of Wustite ........................................... 2-14

2.4.4 Effect of Trace Elements on Iron Oxide Reduction .... 2-15

3.0 **THEORY** ...................................................... 3-1

3.1 Thermodynamics ................................................... 3-1

3.1.1 Iron Oxygen System ........................................... 3-1

3.1.2 The Fe-C-CO-CO\_2 System ...................................... 3-4

3.1.3 The Fe-O\_2-H\_2 System ......................................... 3-6

3.1.4 Fe-O\_2-S System .............................................. 3-6

3.1.5 Sulphide Reduction ............................................. 3-9

3.2 Kinetics of Gas-Solid Reactions .................................. 3-9

3.2.1 Shrinking Un-reacted Core Model ............................. 3-10

3.2.2 Reaction Modulus ............................................... 3-16

3.2.3 Effect of incomplete reaction on controlling regimes .... 3-17
3.2.4 Effect of an Inert Core on the Shrinking Un-reacted Core Model ........................................ 3-18
3.2.5 Porosity and the Grain Model ...................... 3-19
3.2.6 Effect of Grain Size Distribution on Conversion/Time Relationships ..................... 3-20
3.2.7 Uniform Internal Reduction ..................... 3-20
3.2.8 Higher Order Reaction Kinetics ..................... 3-21
3.2.9 Nucleation and Growth Kinetics ..................... 3-22
3.3 Classifying the Rate Controlling Step by the Activation Energy ........................................ 3-22

4.0 EXPERIMENTAL METHOD ........................................ 4-1
4.1 Calcine Samples ........................................ 4-1
4.2 Reducing Gas Compositions ..................................... 4-1
4.3 Thermogravimetric Balance .............. 4-2
4.4 Experimental Procedure ............................... 4-5
4.4.1 Non-isothermal Experiments ............................. 4-5
4.4.2 Isothermal Experiments ..................... 4-6
4.5 Standardization of sample size ..................................... 4-7
4.6 Procedure for Analyzing Gravimetric Data ... 4-11
4.6.1 Isothermal Methods ..................................... 4-11
4.6.2 Non-isothermal Methods ..................................... 4-13
4.6.3 Thermodynamic Driving Force ..................... 4-14
4.6.4 Comparison of Isothermal and Non-isothermal Analysis ........................................ 4-17
4.7 Cyclone Reactor ..................................... 4-19

5.0 RESULTS - THERMOGRAVIMETRIC ANALYSIS ............. 5-1
5.1 General Behaviour of Calcines ..................... 5-1
5.2 Isothermal Reduction and Re-oxidation ............. 5-15
5.2.1 Generation of samples for microscopic study ...... 5-25
5.2.2 Behaviour of Pre-reduced Calcines in Inert
Atmospheres ........................................ 5-33
5.2.3 Sources of Error ............................... 5-37

6.0 GENERAL BEHAVIOUR OF CALCINES .............. 6-1
6.1 Heating Calcines in Inert Atmospheres .......... 6-1
6.2 Heating Calcines in Hydrogen .................. 6-5
6.3 Heating Calcines in Carbon Monoxide ........... 6-11

7.0 KINETIC STUDY OF GASEOUS REDUCTION OF
CALCINES ............................................ 7-1
7.1 Suitability of Uniform Internal Reduction Model .. 7-1
7.2 Non-isothermal Thermogravimetric Reduction of
Calcines ............................................. 7-2
7.2.1 Hydrogen ...................................... 7-3
7.2.2 Carbon Monoxide ............................... 7-10
7.3 Isothermal Studies ............................... 7-16
7.3.1 Isothermal Study in H₂ ........................ 7-16
7.3.2 Isothermal Study in CO ....................... 7-19
7.4 Summary of Thermogravimetric Kinetic Study .... 7-22
7.4.1 Calcine Reduction in Hydrogen ................ 7-22
7.4.2 Calcine Reduction in CO ....................... 7-22
7.5 Industrial Significance ............................ 7-24

8.0 BEHAVIOUR OF PRE-REDUCED CALCINES .......... 8-1
8.1 Re-oxidation of Pre-reduced Calcines ............. 8-1
8.2 Heating Pre-reduced Calcines in Inert Atmospheres ... 8-6

9.0 CONCLUSIONS ....................................... 9-1
REFERENCES ............................................ R-1

APPENDIX A NON-ISOTHERMAL DATA ..................... A-1
List of Figures

Figure 1.1 Falconbridge Partial Roast/Electric Smelting of Nickel Sulphide Concentrate ................................................................. 1-3
Figure 1.2 Cross-section through the Falconbridge Furnace .................. 1-4
Figure 1.3 Flash Smelting of Nickel Sulphides (Western Mining) ............ 1-6
Figure 2.1 Reactions when calcine/coke mixtures were heated in N₂ (From Celmer et al., 1987) ......................................................... 2-5
Figure 2.2 Comparative mass losses Fe₉S₁₀, CuFeS₂, and mixtures of Fe₉S₁₀ with Fe₂O₃ and Fe₃O₄ were heated in N₂ (From Celmer et al., 1987) .... 2-6
Figure 2.3 Calcine reactions as a function of temperature in inert atmospheres (From Celmer et al., 1987) ................................................... 2-7
Figure 2.4 Mechanisms for gas-solid reactions .................................... 2-10
Figure 3.1 Fe-O binary phase diagram from (Ehlers, 1972) .................... 3-2
Figure 3.2 Fe/Wustite/Magnetite/Hematite/CO/CO₂ stability fields ............ 3-4
Figure 3.3 Fe/Wustite/Magnetite/Hematite/H₂/H₂O stability fields ............ 3-7
Figure 3.4 Activities of the liquid Fe-S-O system at 1200° C, according to Stofko et al. ................................................................. 3-8
Figure 3.5 Concentration profiles forming in a spherical particle reacting with a fluid ................................................................. 3-11
Figure 3.6 Effect of particle size distribution on conversion profile for N(4,1) grains undergoing a chemically controlled process ........... 3-21
Figure 3.7 Nucleation and growth conversion profile .......................... 3-23
Figure 4.1 Setaram TGA 92 Thermogravimetric Analyzer ..................... 4-4
Figure 4.2 Effect of sample size on weight loss profile: top C97 in 40% H₂; bottom C97 in 100% CO ......................................................... 4-9
Figure 4.3 Effect of reaction on the reducing gas strength: C92, 40% H₂ at 10K/min. ................................................................. 4-10
Figure 4.4 Comparison of integral and differential analysis for determining the kinetics of multiple reactions: top rate constants; bottom activation energies. ................................................................. 4-15
Figure 4.5 Thermodynamic Driving Force for CO/CO₂ and H₂/H₂O in Fe-FeO
systems ............................................ 4-18

Figure 4.6 Cyclone reactor used for isothermal batch experiments ............... 4-20

Figure 4.7 Flow-sheet incorporating cyclone reactor. .................................. 4-22

Figure 5.1 Mass change when calcines are heated to 850° C in argon: top C92, bottom C97 .................................................. 5-5

Figure 5.2 Analysis of gases evolved when calcines heated in Ar: top C92, bottom C97 .................................................. 5-6

Figure 5.3 Mass change when calcines were heated in 40% H₂ at different heating rates: top C92, bottom C97 .................................................. 5-8

Figure 5.4 Analysis of gases evolved when calcines heated in 100% H₂: top C92, bottom C97 .................................................. 5-9

Figure 5.5 Mass change when calcines were heated in 100% CO at different heating rates: top C92, bottom C97 .................................................. 5-11

Figure 5.6 Analysis of evolved gases from heating calcines in 100% CO: top C92, bottom C97 .................................................. 5-12

Figure 5.7 Mass change when calcines heated at 10° C/min at different H₂ concentrations: top C92, bottom C97 .................................................. 5-13

Figure 5.8 Mass change when calcines heated at 10° C/min at different CO concentrations: top C92, bottom C97 .................................................. 5-14

Figure 5.9 Gas switching in isothermal reduction/re-oxidation experiments ........ 5-15

Figure 5.10 Isothermal (H₂) reduction and oxidation of calcines at 600° C: top C92, bottom C97 .................................................. 5-20

Figure 5.11 Isothermal reduction (CO) and re-oxidation of calcines at 600° C: top C92, bottom C97 .................................................. 5-21

Figure 5.12 Isothermal reduction of calcines in CO% H₂: top C92, bottom C97 .................................................. 5-22

Figure 5.13 Isothermal reduction of calcines in 40% H₂: top C92, bottom C97 5-23

Figure 5.14 Isothermal re-oxidation of calcines pre-reduced in 40% H₂: top C92, bottom C97 .................................................. 5-24

Figure 5.15 Topochemical structure of calcine particles: top C92, bottom C97. Field of view = 71μm x 47.5μm .......................... 5-28

Figure 5.16 Oxidized pyrhotite particles, top C92, bottom C97. Field of view
Figure 5.17 Calcines reduced 50% in the TGA at 600° C in 40% H₂: top C92, bottom C97. Field of view = 71µm x 47.5 µm ........................................ 5-29
Figure 5.18 Calcines reduced 50% in the TGA at 600° C in 100% CO: top C92, bottom C97. Field of view = 71µm x 47.5 µm. ........................................ 5-30
Figure 5.19 Calcines reduced in the cyclone reactor: 600° C, 60s. Field of view = 71µm x 47.5 µm ........................................ 5-31
Figure 5.20 Example of experiments performed to determine the effect of limited pre-reduction on subsequent SO₂ evolution ........................................ 5-32
Figure 5.21 Effect of pre-reduction in H₂ on subsequent mass change in Ar: top C92, bottom C97. ........................................ 5-33
Figure 5.22 Effect of Pre-reduction in CO on subsequent mass change in Ar: top C92, bottom C97 ........................................ 5-34
Figure 5.23 Effect of temperature error on rate constant determination: based on non-isothermal TGA - C97, 10° C/min, 40% H₂ ........................................ 5-35
Figure 5.24 Effect of weight bias on rate constant determination: based on non-isothermal TGA, C97, 10° C/min, 40% H₂ ........................................ 5-36
Figure 5.25 Effect of alternating bias on rate constant determination based on non-isothermal TGA, C97, 10° C/min, 40% H₂ ........................................ 5-37
Figure 5.26 Effect of error in reducing gas strength on non-isothermal thermogravimetric analysis. ........................................ 5-38
Figure 6.1 Weight loss profiles of calcine heated to 850° C at 10° C/min in argon ........................................ 6-1
Figure 6.2 Rate of mass loss and evolution of SO₂ when calcines heated in Ar: top C92, bottom C97 ........................................ 6-2
Figure 6.3 Reactions of calcine in inert atmospheres ........................................ 6-3
Figure 6.4 Weight loss profiles of calcine heated to 850° C at 10° C/min in 40% H₂ ........................................ 6-4
Figure 6.5 Rate of mass loss and evolution of H₂O when calcines heated in H₂ ........................................ 6-5
Figure 6.6 Reduction of CuSO₄, NiSO₄, and FeSO₄ in H₂ ........................................ 6-6
Figure 6.7 Summary of reactions when calcine is heated to 850° C in H₂ ........................................ 6-7
Figure 6.8 Weight loss profiles for calcines heated in 100% CO. ........................................ 6-8
Figure 6.9 Analysis of evolved gases from heating calcines in 100% CO.

Figure 6.10 Reactions undergone by calcine when heated to 850° C in CO.

Figure 6.11 Comparison of SO2 evolution from calcines heated in Ar, H2 and CO: top C92, bottom C97.

Figure 7.1 Isothermal reduction of C97 in H2 at 500° C, 550° C, 600° C, and 650° C.

Figure 7.2 C92 reduced in H2 at different heating rates: top Arrhenius plot; bottom conversion.

Figure 7.3 C97 reduced in H2 at different heating rates: top Arrhenius plot; bottom conversion.

Figure 7.4 Non-Isothermal Arrhenius plot of calcines in 15%, 20%, 40% H2: Top C92; bottom C97.

Figure 7.5 Linear portions of Arrhenius plots on a single graph: top C92, bottom C97.

Figure 7.6 Comparison between actual and calculated weight loss profiles: top C92; bottom C97.

Figure 7.7 C92 reduced in CO at different heating rates: top Arrhenius plot; bottom conversion.

Figure 7.8 C97 reduced in CO at different heating rates: top Arrhenius plot; bottom conversion.

Figure 7.9 Arrhenius plots of CO reduced calcines: top C92; bottom C97.

Figure 7.10 Confidence and prediction intervals for the isothermal reduction of calcines in H2: top C92, bottom C97.

Figure 7.11 Isothermal reduction of Calcines in 100% CO: top C92, bottom C97.

Figure 7.12 Rate Constants for H2 reduction of Ni/Cu calcines: "NI" from non-isothermal TGA, "I" from isothermal TGA.

Figure 8.1 Reduction of C97 calcine in 40% H2 at 600° C followed by re-oxidation in air.

Figure 8.2 Re-oxidation of calcines deeply reduced in H2 and CO: 10° C/min in air.

Figure 8.3 Isothermal re-oxidation of pre-reduced calcines: top C92, bottom
Figure 8.4 Arrhenius diagram for the re-oxidation of pre-reduced calcines 8-5
Figure 8.5 Effect of pre-reduction on subsequent weight loss - all data 8-7
Figure 9.1 Rate constants for the hydrogen reduction of nickel calcines 9-4
List of Tables

Table III.1 Reduction of iron oxides - reaction free energies (From Gaskell, 1990) ........................................... 3-5
Table III.2 Equilibrium H₂S/H₂ and COS/CO over base metal sulphides as a function of temperature ........................................... 3-10
Table IV.1 Mineralogy of the Sample Calcines ........................................... 4-1
Table IV.2 Gas Compositions used during thermogravimetric analysis ............ 4-2
Table IV.3 Pre-programmed Temperature For the Thermogravimetric Analyzer ........................................... 4-7
Table IV.4 Experiments to determine the effect of mass transfer on TGA ............ 4-8
Table IV.5 Parameters for the gaseous reduction of a hypothetical mixture of metal sulphates ........................................... 4-14
Table IV.6 Calculation of (C₆⁰ - C₆¹) for CO/CO₂/Fe/Fe₂O₃ and CO/CO₂/Fe/Fe₃O₄ systems ........................................... 4-17
Table V.1 Non-isothermal TGA Experiments - C97 Calcines. Performed by author except as noted. ........................................... 5-2
Table V.2 Non-isothermal TGA experiments - C92 Calcine. Performed by author, except as noted. ........................................... 5-3
Table V.3 Schedule of Isothermal Reduction/oxidation experiments ............... 5-17
Table V.4 Schedule of Isothermal reduction/oxidation experiments ............... 5-18
Table V.5 Calcines samples prepared for microscopic examination. ............... 5-26
Table V.6 Schedule of experiments to determine effect of pre-reduction on SO₂ evolution. ........................................... 5-34
Table VI.1 Equilibrium data for calcine reactions evolving a gas (From HSC) .... 6-3
Table VI.2 Standard Gibbs energies for the reduction of sulphates in H₂ and CO at 300° C ........................................... 6-8
Table VII.1 Activation energies for the hydrogen reduction of metal oxides ....... 7-10
Table VII.2 Calculation of rate constant from isothermal kinetic data: C97 in 40% H₂ ........................................... 7-17
Table VII.3 Analysis of variance for the isothermal reduction of C97 in 40% H₂ ........................................... 7-19
Table IX.1 Rate Constant Parameters for Isothermal Reduction of Calcines in
1.0 INTRODUCTION

Since its first commercial production from the Sudbury deposit in 1885, nickel has played a major role in the Canadian economy. Today, with nickel mined, smelted or refined in forty countries, Canada still dominates with 20-30% of worldwide production.

Nickel is extracted from two types of deposits: laterite or oxide deposits are usually found in tropical climates; sulphide deposits are mostly found in Canada, South Africa, Australia and Russia. There are greater reserves of laterites, but extraction from sulphides is more economical for the following reasons:

- conventional mineral dressing technologies can be applied to the ore to produce a high grade nickel concentrate (>10% Ni) and a low nickel tailings; in contrast, only limited upgrading of laterite to about 3% is possible and almost the entire ore must be treated to extract nickel;
- the heat from oxidizing metal sulphides partially fulfils the smelting energy requirements;
- sulphide deposits often contain secondary metal values such as copper, cobalt and platinum group metals.

As sulphide deposits were depleted, attention had been shifting towards exploiting laterites. The recent discovery of a large deposit in Labrador, however, has given sulphide processes new life.

The Sudbury ore body contains the nickeliferous minerals pentlandite ([Ni, Fe]_9S_8) and pyrrhotite (Fe,S_8 with minor nickel content) and copper bearing chalcopyrite (CuFeS_2). Pyrometallurgical processes for extracting nickel from nickel sulphide concentrates proceed by generating an intermediate product called Bessemer matte (Terry and others, 1985). Bessemer matte is a solution of Ni,S_2, Cu,S and Co,S with metals. The sulphur content of the matte is typically less than that required for the metals to be tied up as sulphides, therefore the matte is termed "sulphur deficient" or "metallized". Transforming concentrate into Bessemer matte consists of the following steps:

- thermal decomposition of the constituent minerals,
• oxidation of iron and sulphur,
• separation of the iron oxide phase from the matte phase.

The production of Bessemer matte is dominated by two processes - the Roast/electric Smelting Process practiced by Falconbridge in Sudbury, Ontario and INCO in Thompson, Manitoba; and the Flash Smelting Process, invented independently by INCO and Outokumpu (Ozberk and others, 1983).

1.1 Partial Roast / Electric Smelting of Nickel Sulphides
The Falconbridge flow-sheet, depicted in Figure 1.1, revolves around three process units: a fluid bed roaster; an electric furnace; and Peirce-Smith converters (McKague and Norman, 1984). Slurried nickel concentrate is oxidized in a fluid bed roaster to remove sulphur as SO₂. Iron sulphides react preferentially to form magnetite and hematite while nickel and copper remain as sulphides (Zamalloa, 1995). Silica, added as a flux in the furnace, is pre-heated in the roaster and acts to stabilize the fluid bed. The roasted product is fine (100% -100μm), such that 85% is elutriated with the roaster off-gas (McKague and Norman, 1984). The balance is discharged from the bed. The particulate is separated from the gas in high efficiency cyclones and an electrostatic precipitator. The conditions in the ESP (low temperatures and excess sulphur dioxide and oxygen) are conducive for the formation of metal sulphates. The cleaned off-gas contains approximately 14% SO₂ and is ducted to a single pass acid plant where the SO₂ is fixed as sulphuric acid (Hoffman and Kaiura, 1988).

The roaster bed overflow, cyclone catch and ESP dusts are blended with coke and smelted in an electric furnace. Coke and silica are added to reduce iron oxides to a faylite slag, and to improve metal yields. Figure 1.2 illustrates a cross-section through the smelting furnace. Banks of calcine, coke and flux float on a liquid slag layer which in turn floats on a liquid matte layer. A solid metallic heel forms which protects the hearth refractories. In the fusion zone, the calcine particles melt and coalesce. The matte initially wets the coke particles and is reduced, yielding a CO/CO₂ mixture. However, once a gas film surrounds the particle, further reduction must proceed through this layer. Evolved gas bubbles rise through the calcine banks and may react with the solid iron oxides and coke,
Figure 1.1  Falconbridge Partial Roast/Electric Smelting of Nickel Sulphide Concentrate
however this is not an efficient reaction zone. One important benefit of bubbles rising through the calcine banks is that, by fluidizing the calcine, the solid flow characteristics are improved (McKague and Norman, 1984).

The gas rising from the calcine bank is rich in carbon monoxide. The furnace is operated under draft to bring air into the freeboard, where it combusts the CO. Sufficient air is brought in to quench the resulting off-gas to below 800° C. The heat liberated from freeboard combustion does not contribute to the matte and slag heat content and is lost. This practice is wasteful of the reductant and causes large off-gas volumes and high solid elutriation rates. The low off-gas temperature, however, extends the roof refractory life.
The furnace off-gas is cleaned in electrostatic precipitators, and exhausted to a stack. SO₂ generated in the furnace therefore bypasses the acid plant and therefore represents a sulphur emission.

The reducing conditions in the furnace suppress the formation of nickel and cobalt oxides, therefore the pay metals tend not to dissolve in the slag, which can be discarded; the matte is tapped into ladles and transferred to the converter aisle. Electrical power is required to melt the slag and matte phases and to offset the endothermic reduction of iron oxides by coke.

In contrast to copper smelting, nickel cannot be converted economically from the sulphide to the metal. The purpose of nickel converting is to oxidize the remaining iron from the electric furnace matte. The resulting Bessemer matte is tapped, cast and shipped to a hydrometallurgical facility for refining. Converting drives off SO₂, especially during the final stages, however the intermittent operation of converters precludes economical treatment of the converter off-gases in an acid plant. Therefore SO₂ from the converters also represents a sulphur emission. Converter aisle emissions were dramatically reduced when Falconbridge increased the sulphur removal in the roaster from 50% to 65%. From an emissions control standpoint, higher degrees of roast are desirable, but have been prevented because of the detrimental effect on furnace operation.

1.2 Flash Smelting of Nickel Sulphides
In a flash smelter (Figure 1.3), roasting and smelting are performed in a single vessel. Dry nickel concentrate is dispersed in a jet of enriched air (Outokumpu) or technical oxygen (INCO). Solid and molten phases fall into a settling vessel, while the strong SO₂ stream is ducted to the gas cleaning systems. When technical oxygen is used, the roasting reactions are sufficiently exothermic to melt the products; in enriched air processes fuel in the form of coal is added. Silica flux is added to form a fayalite slag which separates from the sulphide bearing matte. The oxidizing conditions cause some nickel and copper to dissolve in the slag phase. The smelter slag should therefore be sent to a slag cleaning furnace to maximize copper and nickel recoveries.
Figure 1.3 Flash Smelting of Nickel Sulphides (Western Mining)
At INCO's Coppercliff facility, the matte is tapped, the iron slagged off in Peirce-Smith converters, and the converter matte is cast. Slow cooling causes nickel and copper sulphides to crystallize as distinct phases which are separated into a low nickel copper sulphide product and a low copper nickel sulphide product. The copper sulphide phase is sent to a copper flash converter to produce blister copper; nickel is recovered by a roast/chlorination/reduction process (Terry and others, 1987). All converter slags are recycled to the flash furnace.

1.3 Comparison of Flash Smelting and Roast/Electric Smelting
The perceived benefits of flash smelting over roast reduction centre around the use of enriched air or oxygen in the smelting furnace. Reacting the concentrate in oxygen means that little or no additional fuel is required. At the same time, sulphur is removed in a single strong SO₂ gas stream which can be ducted to an acid plant. As uncontrolled emissions of SO₂ from nickel smelters become more regulated, this is a significant advantage.

The oxidizing conditions in the flash process, however, generate high tonnages of slag which contain significant quantities of dissolved nickel oxides and entrained matte. This slag must be cleaned to recapture the metal values. Western Mining have appended an electric slag-cleaning furnace to their flash furnace at the Kalgoorlie smelter (Apelt and others, 1995); INCO Coppercliff dumps the smelter slag and loses the metal values; Noranda, a copper smelter, slowly cools their smelter slag and applies mineral processing techniques (crushing, grinding, flotation) to recapture entrained metal values. The slag from the Falconbridge electric furnace, in contrast, is discarded without treatment and with little pay metal loss.

While the roast-reduction process does not require an oxygen plant or a slag cleaning furnace for the smelter slag, there are other drawbacks. Electric smelting and the use of coke result in a higher power cost per tonne of metal (Ozberk and others, 1983) and emit CO₂, a greenhouse gas. The furnace off-gas represents a significant SO₂ source which cannot be economically treated in an acid plant.
This research studies the feasibility of reducing the calcine outside the furnace using a gaseous reductant, perhaps in a fluid bed or rotary kiln. The pre-reduced calcine would then be melted in the furnace. The benefits of this approach would be:

- The calcine may be sufficiently reduced to prevent the evolution of SO₂ in the furnace.
- The use of reformed natural gas will lower the emission of CO₂, a greenhouse gas whose emission is currently under scrutiny.
- Decreasing coke will proportionally decrease the furnace off-gas volume and the fraction of the feed carried out with the off-gas; the capacity of the furnace off-gas systems limits the throughput of the Falconbridge operation.
- The degree of roast can be increased without adversely affecting the furnace operation. High roast operation significantly decreases converter aisle emissions.
- Removing the endothermic coke reactions from the furnace would decrease the electrical load and hence the power requirements per tonne of metal.

This thesis investigates the kinetics of gaseous pre-reduction of nickel calcines using carbon monoxide and hydrogen.
2.0 LITERATURE REVIEW

2.1 Roasting Ni/Cu Concentrates

In Sudbury, nickel concentrate consists of pentlandite ([Fe, Ni]_{x}S_{8}), pyrrhotite (Fe_{x}S_{2}) and chalcopyrite. Concentrate was roasted under different conditions and examined microscopically, with phases identified using an electron microprobe (Zamalloa, 1995). All phases were oxidized topochemically, as evidenced by the formation of iron oxide rims surrounding sulphide cores.

Pentlandite particles (36% Ni) were converted to heazlewoodite (Ni_{x}S_{2}) via an iron-nickel monosulphide solid solution. The nickel content of the magnetite phase adjacent to the sulphide core was reported to reach 20%, while the average nickel content in the oxide rims was much lower. The average nickel content of the oxide rims was higher in high roast calcines¹ (4.2% Ni) than in a low roast calcine (1.3% Ni). It was concluded that nickel diffused into the magnetite locally, yielding nickel spinel NiO.Fe_{2}O_{3} (= 25 wt.% Ni). The conversion of pentlandite was concluded to occur by the following reactions:

\[ \text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{8} + \left( \frac{2}{3} \right) \text{O}_{2} = \text{Fe}_{(4.5-x)\text{Ni}_{4.5}\text{S}_{8}} + \left( \frac{x}{3} \right) \text{Fe}_{3}\text{O}_{4} \]  (2.1)

\[ 2\text{Fe}_{2}\text{O}_{4} + \frac{1}{2}\text{O}_{2} = 3\text{Fe}_{2}\text{O}_{3} \]  (2.2)

\[ \text{Fe}_{(4.5-x)\text{Ni}_{4.5}\text{S}_{8}} + \left( \frac{79.5-4x}{6} \right) \text{O}_{2} = 4.5\text{NiO} + \frac{(4.5-x)}{3}\text{Fe}_{2}\text{O}_{3} + \text{SO}_{2} \]  (2.3)

Cobalt represents a significant revenue stream to the Falconbridge nickel smelter. The nickel/cobalt ratio in Falconbridge concentrate is about 30:1; approximately half of the cobalt is lost with the smelter slag. The price ratio on the London Metal Exchange is 1:10 (Roskill, 1997), although cobalt prices are expected to soften as new sources, such as Voisey Bay, come on line (Falconbridge annual report, 1996). Cobalt occurred mostly

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¹ High roast calcine refers to > 80% S removal (referenced from the concentrate); low roast is typically below 65% S removal

2-1
in the pentlandite mineral. During roasting, cobalt migrated towards the sulphide core and away from the oxide rim. The highest cobalt concentration observed in the rims was 0.31 wt.%, suggesting that cobalt had not been converted into a spinel. This is somewhat surprising since, given its electronegativity cobalt would be expected to behave like iron. The low cobalt concentration may be due to the inability of an electron microprobe to accurately measure phases smaller than 3 μm x 3 μm x 3 μm.

The starting nickel content of the pyrrhotite particles is relatively small (0.62 wt%), hence producers attempt to reject as much pyrrhotite at the concentrate mills as possible. It was found that during the roasting process, nickel preferentially diffused inwards to the sulphide core, while iron counter-diffused to the oxidized rim. The main reactions of pyrrhotite oxidation can be written:

\[ 3Fe_{1-x}S + (5-2x)O_2 = (1-x)Fe_2O_4 + 3SO_2 \]  (2.4)

\[ 2Fe_2O_3 + \frac{1}{2}O_2 = 3Fe_2O_3 \]  (2.5)

Roasted chalcopyrite particles (34.6% Cu) were converted to chalcocite-diginite (Cu₂S) via bornite (Cu₄FeS₄). Nowhere was the copper content of the oxide rims found to exceed 5.2 wt.%, therefore it was concluded that cuprospinel was not formed. The average copper content of the rims for high roast calcine was 2.5 wt.%. The behaviour of chalcocite particles was in agreement with that previously observed in flash smelting experiments. The mechanism for chalcopyrite gave these following reactions:
A similar nickel/copper concentrate was deep-roasted (80% - 95% sulphur removal) and the calcine analyzed chemically (Diaz and others, 1994). The tendency for metals to be found in the sulphide core increased in the order Cu > Ni > Co > Fe at high roast; at low roast the Fe/Co order was reversed. The order Cu-Ni-Co-Fe reflects the thermodynamic stability of the metals as oxides and sulphides. As the degree of roast was increased, the fraction of the sulphur remaining as sulphate increased from 18% to 53%. Unfortunately, the calcine sampling method was not described, so it is not possible to rule out that the sulphate had formed when the calcine was cooled. The roaster operated at 830°C - 850°C, with 0.5% O₂ and 14% SO₂. At 850°C and under these gas conditions, NiSO₄ is the only stable sulphate; however if the calcine is cooled in an SO₂/O₂ atmosphere, iron (II) sulphate, iron (III) sulphate and copper sulphate can be stable.

2.2 Reductive Smelting of Calcines at Falconbridge

Electric smelting replaced blast furnace operations at Falconbridge in 1978. The intention was to melt the calcine in an oxidizing atmosphere. It was found that the calcine did not flow evenly in the furnace and the design throughput could not be achieved. The decision was made to operate the furnace in reductive mode by introducing coke with the feed. The gasification of coke in the fusion zone fluidized the calcine banks and improved the flow characteristics of the calcine (McKague and Norman, 1984). Coke additions also increased the nickel yield.
The smelting rate of calcine and calcine/coke mixtures has been measured thermogravimetrically (Celmer and others, 1987), (Zamalloa, 1995), (Diaz and others, 1994), (Crowe and others, 1997). Gasification of petroleum coke by CO₂ was negligible below 800° C, slow between 800° C and 900° C and vigorous above 900° C (Diaz and others, 1994). Calcine/coke mixtures heated in an inert (nitrogen) atmosphere were not found to react appreciably below 800° C (Zamalloa, 1995). It was concluded that calcine reduction occurred through CO/CO₂ gaseous intermediates, i.e. i) CO reduced calcine, yielding CO₂ ii) CO₂ reacts with coke particles, regenerating CO. It was also proposed that the rate of the gasification of coke controlled the overall rate of reaction. This has been confirmed by thermogravimetric analysis of calcines in pure CO, wherein calcine reduction proceeded vigorously at the relatively low temperature of 500° C (Crowe and others, 1997).

Celmer et al. (1987) combined thermogravimetric analysis with gas chromatography to determine the reactions which occur when calcine/coke mixtures are heated. In an effort to simulate the conditions in the electric furnace, a pre-weighed sample was suspended from a micro-balance and heated to 1250 °C at a rate of 5° C/min. The furnace atmosphere was controlled by flushing with nitrogen or air, meanwhile the off-gas was periodically sampled and analyzed by gas chromatography.

Figure 2.1 illustrates the gas species observed at different temperatures. The evolution of SO₂ when heated in an inert atmosphere supports the theory that SO₂ was evolved as a result of sulphate decomposition, thermal decomposition of under-roasted minerals, and reactions between iron sulphides and iron oxides. It was calculated that the equilibrium pressure of \((\text{SO}_2 + \text{SO}_3 + \text{O}_2)\) over \(\text{Fe}_2(\text{SO}_4)_3/\text{Fe}_2\text{O}_3\) reaches 1 atm. at 727° C.

The evolution of SO₂ was found to be less for highly roasted calcines due to the decreased levels of under-roasted minerals (i.e. unconverted chalcopyrite and pentlandite), and the decreased presence of iron sulphide. Solid state reactions between coke and calcine was insignificant below 900° C.
Figure 2.1 Reactions when calcine/coke mixtures were heated in N$_2$ (From Celmer et al., 1987)

In separate experiments, Celmer et al. (1987) observed that hematite/pyrite and magnetite/pyrite mixtures reacted vigorously at 450° C and 550° C respectively (See Figure 2.2). Their results were qualitatively summarized in Figure 2.3, which shows the reactions likely occurring in the calcine bank as a function of temperature, i.e. as the calcine descends).

Tests were repeated in air to determine the effect of oxygen in the furnace freeboard on the reactions. It was observed that when the calcine was heated to 450° C, the sample gained weight. This stored oxygen was released as SO$_2$ when the temperature was raised above 700° C. Increasing the coke ratio mitigated this effect sharply.

The experimental procedure described above is not representative of the Falconbridge furnace in a key sense: while coke reactions may not proceed below 900° C, the calcine banks reside in a CO/CO$_2$ atmosphere from the gases rising from the fusion zone.

2-5
Figure 2.2 Comparative mass losses Fe₉S₁₀, CuFeS₂, and mixtures of Fe₉S₁₀ with Fe₂O₃ and Fe₃O₄ were heated in N₂ (From Celmer et al., 1987)

Therefore it is likely that some hematite is reduced to magnetite and wustite before reacting with sulphides to evolve SO₂. This zone is similar to the reaction zone of a blast furnace, although the electric furnace is shallower and the gas/solid contact correspondingly less efficient than in the blast furnace.

The solubility of iron oxides in sulphide melts has led to the term "oxysulphide" melt being applied in non-ferrous smelting. The reduction of oxysulphide melts by coke has been investigated. In one approach (Zamalloa, 1995) low roasted calcine was mixed with coke and heated in a tube furnace at a constant heating rate to 1200° C. A constant flow of nitrogen was passed over the sample to convey evolved gases to CO, CO₂ and SO₂ analyzers. When no coke was added, 22% of the sulphur was removed from the calcine as SO₂. A sharp peak at 600° C was observed, followed by peaks at 900° C, 1100° C and 1200° C. The peak at 600° C was attributed to sulphate decomposition and reactions between hematite and pyrrhotite. Coke additions of 4% did not affect the peak at 600° C,
Figure 2.3 Calcine reactions as a function of temperature in inert atmospheres (From Celmer et al., 1987)

however subsequent peaks were sharply diminished and a total desulphurization of $\approx 10\%$ was recorded.

At 1050°C, the sulphide phase started to melt, dissolving the oxide rims. The temperature was confirmed by differential thermogravimetry. Magnetite has been shown to have a high solubility in sulphide melts (Kaiura and Toguri, 1974) and (Stofko and others, 1974), however the saturation limit may be reached in individual calcine particles, causing $SO_2$ evolution. The concentration of CO$_2$ rose steadily from 600°C and 1000°C during which time the CO level was negligible. This implies that significant solid state reduction of the calcine can occur prior to matte melting (1050°C).

The smelting behaviour of petroleum cokes and breeze cokes was compared (Zamalloa, 1995). Breeze coke was found to gasify more readily and, since gasification limited the smelting rate, was the preferred reductant. From experiments with different coke particle
sizes it was recommended that coke finer than 100 mesh be used. With 400 mesh coke, it was found that 70% of the ultimate reduction was achieved between 900° C and 1000° C. The higher the degree of reduction which can be achieved prior to melting, the lower the likelihood that a melting particle becomes magnetite saturated, hence SO₂ evolution above 1000° C will be suppressed. However other practical considerations restrict the particle sizes which can be used. The Falconbridge furnace operates with an oxidizing freeboard hence fine particles combust as they descend the freeboard. Finer particles settle at slower velocities, exacerbating the problem. Also, finer coke particles are more likely to be elutriated with the furnace off-gas.

2.3 Reduction of Metal Sulphides

The industrially preferred pyrometallurgical process for removing sulphur from a metal sulphide mineral is by oxidation. This removes sulphur as an SO₂ stream which can be fixed in an acid plant. An alternative method has been proposed wherein the sulphide is removed by hydrogen. The resulting H₂S stream can be treated to fix sulphur in its elemental form (Gaballah and others, 1994). The reduction of copper, iron, lead and zinc sulphides was investigated using non-isothermal thermogravimetric analysis in hydrogen and nitrogen atmospheres (Gaballah and others, 1994). Chalcopyrite was observed to steadily lose weight between 500° C and 800° C in nitrogen, and the following reactions identified from x-ray diffraction of the intermediate products:

\[ 4 \text{CuFeS}_2(\text{s}) = 2 \text{CuFe}_2\text{S}_3(\text{s}) + \text{Cu}_2\text{S}_3(\text{s}) + \frac{1}{2} \text{S}_8(\text{s}) \]  

\[ 2 \text{CuFe}_2\text{S}_3(\text{s}) + \text{Cu}_2\text{S}_3(\text{s}) = 0.8 \text{Cu}_2\text{Fe}_6\text{S}_8(\text{s}) + 3.2 \text{FeS}_2(\text{s}) + 0.3 \text{S}_8(\text{s}) \]  

These reactions proceeded at an accelerated rate in a hydrogen atmosphere. In addition a dramatic weight loss was observed at 900° C. X-ray analysis of the products determined that the chalcopyrite had been reduced to iron and copper via cubanite:

\[ 2 \text{CuFeS}_2(\text{s}) + \text{H}_2(\text{g}) = \text{CuFe}_2\text{S}_3(\text{s}) + \text{Cu}_2\text{S}_3(\text{s}) + \frac{1}{2} \text{Cu}(\text{s}) + \frac{1}{2} \text{H}_2\text{S}(\text{g}) \]
The conversion of pyrite ($\text{FeS}_2$) to pyrrhotite ($\text{FeS}$) proceeded in both nitrogen and hydrogen, again at an accelerated rate in hydrogen. When heated above 900° C in $\text{H}_2$, pyrrhotite was reduced to iron and $\text{H}_2\text{S}$, while no such decomposition occurred in an inert atmosphere. Although nickel bearing concentrates were not studied, they are expected to decompose quicker in hydrogen than in nitrogen.

2.4 Gaseous Reduction of Iron Oxides

An extraordinary amount of research has been performed characterizing the reactions between iron oxides and CO/CO$_2$(C) and $\text{H}_2/\text{H}_2\text{O}$ systems. To date, primary iron production is dominated by the blast furnace. This process relies on pellet sized iron ore larger than 10 mm diameter. Due to the relatively large size of the particles, diffusion through the product layer is an important, if not rate controlling, process.

2.4.1 Reduction of Hematite

A series of review articles (Turkdogan and Vinters, 1971a) (Turkdogan and others, 1971b), (Turkdogan and Vinters, 1972) and (Tien and Turkdogan, 1972) examined the physico-chemical processes in the hydrogen reduction of iron oxides. Isothermal TGA experiments were performed on crushed and sized high grade lump hematite ore (96% Fe$_2$O$_3$). Conditions were controlled to eliminate hydrogen starvation and gas film transport resistance. At 200° C and 300° C, a sigmoidal inflexion in the weight loss profile was observed, indicative of nucleation and growth kinetics where the rate of magnetite nucleation was slow below 400° C. An unusual temperature effect was reported in the temperature range 650° C and 800° C whereby the reaction rate decreased with increasing temperature. This phenomenon was more pronounced for smaller particles. This has since been explained to be due to the formation of a dense iron layer which hindered gaseous diffusion (Moukassi and others, 1983). It also coincides with temperature range at which dense magnetite is formed (Swann and Tighe, 1977). Hematite reduced in CO did not display this anomalous temperature behaviour (Turkdogan and Vinters, 1972).

\[ \text{CuFe}_2\text{S}_3(\omega) + 3\text{H}_2(\omega) = 2\text{Fe}^+(\omega) + \text{Cu}^+(\omega) + 3\text{H}_2\text{S}(\omega) \]
Three models were proposed to describe gaseous reduction of hematite (Turkdogan and Vinters, 1971a): Uniform internal reduction (UIR) described the situation where the particle was homogenously reduced. Small particles reacting at low temperatures were described by this model. This model applies to hematite particles smaller than 350μm reacting at temperatures below 800°C. The reaction rate is independent of particle size. During reduction, rosettes or platelets formed randomly throughout the particle. Large particles reacting at high temperature tended to assume topochemical structures, i.e. a hematite core surrounded by a porous magnetite layer itself surrounded by a wustite or iron shell. Limited mixed control described the reduction behaviour between these two extremes.

In UIR, the rate controlling step was the reaction on the pore walls. In contrast, for large particles, diffusion through the solid product or through the boundary layer controls the rate. Sharp boundaries between reaction phases, e.g. hematite/magnetite, result. The time to reduce hematite in this regime was found to be proportional to the square of the particle diameter, in accordance with shrinking core models (Szekley and others, 1976).

As the size of the pellet was reduced, the divisions between adjoining phases became less distinct and diffusion of the reducing gas into the porous reactant was observed while the reaction proceeded. In limited mixed control, chemical reaction can be thought of as proceeding in parallel with gaseous diffusion into the reactant. This was shown to give an interesting temperature dependence: as the reaction temperature was increased, the reaction rate increased exponentially; the reacting gas does not have the opportunity to diffuse into the solid reactant as far, therefore the reaction surface area decreased. Thus the effect of a temperature rise on the reaction rate would be less than that predicted from
intrinsic kinetics. It was shown that, overall, the reaction rate is proportional to \((k D_{\text{eff}})^{1/2}\), where \(k\) is the rate of the intrinsic chemical reaction and \(D_{\text{eff}}\) is the effective diffusivity through the porous reactant. This expression gives an apparent activation approximately half that of the intrinsic reaction (Szekely and others, 1976). It was also shown that in this regime, the time to convert the particle is proportional to its diameter (Turkdogan and Vinters, 1972).

Reduction of hematite pellets under limited mixed control was modelled on a computer (Matyas and Bradshaw, 1974). Following separate measurements of the intrinsic reaction rate from granular solids and the effective diffusivity of pellets, the concentration profile of the reactant gas was determined by numerically solving transport equations. The rate of conversion was assumed to be first order with respect to the gas. The model showed that for a 1.3cm diameter pellet, the boundary between hematite and magnetite became more distinct as the temperature increased from 600° C to 850° C, in accordance with microscopic examinations.

Microscopic examination of partially reduced hematite fines (-63µm) showed that the reduction occurred in two stages: reduction of hematite to magnetite was topochemical; further reduction to wustite and iron occurred uniformly throughout the particle (Monsen and others, 1995).

Use of "environmental cells" in transmission electron microscopes (Rau and others, 1987) and scanning electron microscopes (Finnstrom, 1976) have allowed the direct observation of nucleation and growth processes. In these experiments, the sample is placed in a furnace in the microscope. The microscope is pumped down and the sample heated and subjected to reducing gas pressures (eg. 0.15 Pa in SEM, 5300 Pa in TEM studies.) At low temperatures, where nucleation and growth dominated, little reaction was observed for up to three minutes after which the reaction proceeded rapidly. Nucleation sites were more often located where the surface had been damaged by the electron beam.

The different morphologies of magnetite was also studied by "in situ" reduction of hematite in a scanning electron microscope (Swann and Tighe, 1977). In general, high
temperature reduction of hematite produced dense magnetite referred to as lath magnetite; low temperature reduction generated a porous magnetite. There is a wide discrepancy in the reported transition temperatures. Swann et al. reported that below 800° C, magnetite was perforated by tunnels. The tunnels conveyed gas from the atmosphere to the reaction interface and obviated the need for solid state diffusion through the magnetite layer. The tunnels were homogenous in spacing and dimension. At low temperatures, magnetite was observed to grow from widely spaced nuclei. After an incubation period, a lath magnetite nucleus would 'suddenly appear' and porous magnetite would grow across the surface. Tunnel diameters increased ten-fold as the temperature was increased from 400° C to 700° C, and approximately halved in H₂/H₂O vs CO/CO₂ mixtures, also in agreement with Turkdogan and others (1971b). Between 700° C and 850° C magnetite nucleated as plates but grew into the tunnel morphology. Above 850° C, magnetite nucleated and grew as platelets, forming a dense cover. Matyas and Bradshaw (1974) reported that the transition temperature was 800° C, while Turkdogan reported a wider temperature range of 500 to 800° C.

The above studies were performed on industrial hematite minerals. Et-Tabirou and others (1988) studied the morphology of magnetite reduced from single hematite crystals prepared by chemical vapour deposition under a variety of reducing strengths (CO/CO₂) and temperatures. Three morphologies were seen: at low temperatures the hematite crystal was fractured and porous magnetite deposited along the surfaces; lath (non-porous, plate-like) magnetite dominated at high temperatures and porous magnetite at intermediate temperatures. They were also able to show that the transition temperature depended on the degree of reduction and the partial pressure of CO. The temperature region for porous magnetite formation could be extended by increasing the CO pressure.

Reduction of hematite to porous iron was characterized by connected pore volume studies (mercury penetration porosimeter), critical and smallest pore radii measurements and BET pore surface area studies as a function of reduction temperature (Turkdogan and others, 1971b). The results, in agreement with the images from scanning electron microscope images, showed that the pore structure coarsened with increased reduction temperature. The BET surface area decreased from a value of 25 m²/g for iron reduced at 400° C to

2-12
= 0 m²/g when the reduction temperature was 1000°C. High porosities coincided with an increasingly pyrophoric iron product. The pore structure of iron reduced in hydrogen from dense wustite was compared to iron reduced in carbon monoxide and found to be considerably finer (Turkdogan and Vinters, 1972).

Reduction of thin flat hematite specimens in H₂/He mixtures was found to be first order with respect to the hydrogen partial pressure and an activation energy of 60, 745 ± 1, 380 J/mol measured (Moinpour and others, 1988).

2.4.2 Reduction of Magnetite

Microstructural changes from the gaseous reduction of dense magnetite are highly dependent on reaction temperature and the gaseous environment (Matthew and Hayes, 1990). In situ observations of the gaseous reduction of dense magnetite was performed using an optical heating stage and a metallurgical microscope. Nucleation and growth of iron was photographed and the linear rate of growth measured. Below 570 °C (wustite eutectoid temperature) hydrogen reduction of dense magnetite yielded a porous iron product. The pore size increased markedly with decreasing reduction potentials, decreasing hydrogen partial pressure and decreasing temperature, with the temperature effect less pronounced.

Above the eutectoid temperature, wustite formed as an intermediate product. Porous iron only formed at either i) low temperatures and low reduction potentials or ii) high temperatures and high reduction potentials. Tunnels in the intermediate wustite layer were observed under the remaining conditions. The tunnels coarsened at low H₂ partial pressures and low reduction potentials. Under tunnel forming conditions, dense iron condensed at the tunnel openings, although a porous iron product was also observed at high hydrogen pressures. The wustite layer caused brittle fractures to occur parallel to the growth front. It was predicted that in CO/CO₂ mixtures slow reaction kinetics would allow a thicker wustite layer to form thereby preventing brittle fractures.

In situ experiments below the eutectoid temperature were performed in an environmental cell in a transmission electron microscope. Phases were identified from their electron
diffraction pattern (Rau and others, 1987). After exposure to a reducing gas at low temperature, faceted pits would appear. Iron would nucleate adjacent to the pits and grow to cover the magnetite surface. Decreased porosity was observed at higher temperatures. The volume change associated with iron formation caused fissures.

Reduction of magnetite concentrates (+63, -90μm) in H₂/CÖ/H₂O/CO₂ mixtures was reported to be accelerated by pre-oxidation to hematite (Monsen, 1992). It was found that the rate at which pre-oxidized grains were reduced back to magnetite was inversely related to the pre-oxidation temperature. Microscopic examination of the crystalline structure showed that grains pre-oxidized at low temperatures (800°C) consisted of individually oriented hematite crystals within the grain. At higher temperatures the hematite crystals grew until their size approached that of the grain. This was verified by measuring the ratio of sub-grain perimeter to sub-grain area using a videoplan image processing system (Monsen and others, 1995). The ratio was found to decrease from 3x10⁻⁵/m to 0.1x10⁻⁵/m as the pre-oxidation temperature was raised from 800°C to 1250°C. Upon reduction, the hematite to magnetite conversion proceeded topochemically. Magnetite was reduced to wustite uniformly with a rate inversely related to the pre-oxidation temperature. This was attributed to the increased porosity of the magnetite. Metallization was noticeably retarded when the pre-oxidation temperature was raised from 1050°C to 1150°C.

2.4.3 Reduction of Wustite

Its transformation to iron and magnetite below the eutectoid temperature proceeds so slowly that wustite can be regarded as metastable (Rau and others, 1987). In situ experiments in vacuum detected the formation of magnetite, but not iron. It was concluded that either the iron deposited interstitially and could not be detected, or that it had been incorporated into the remaining wustite which has a wide, albeit unstable, compositional range. Reduced wustite yielded iron with similar morphology to that produced from magnetite. Incubation periods and faceted pits were, however, not observed. Reducing wustite to iron was shown to also increase the disproportionation of wustite to magnetite. When samples undergoing simultaneous reduction and disproportionation were isolated from the reducing environment magnetite formation was seen to decline. It was therefore determined that disproportionation was promoted by the
reduction process, but that the presence of the iron product did not affect the rate of magnetite formation.

Iron from reduced wustite can assume three morphologies, i) porous iron, ii) porous wustite covered by dense iron, and iii) dense wustite covered by dense iron. It has been reported that, for all morphologies, the initial iron layer formed is always dense (St. John and others, 1982) and that reduction is initially controlled by solid state reduction across this layer. The breakdown of the dense iron layers by CO/CO₂ gas mixtures was attributed to the carburization of the iron, followed by solid state reaction between carbon and wustite, the explosive evolution of gas lifting the dense layer off the wustite (Edstrom, 1956). A similar mechanism has been reported in H₂/H₂O systems, with hydrogen dissolving in the dense iron layer, reacting with the wustite and explosively releasing water vapour (St. John and others, 1984). In this case, the volume change from desorbing water to the gaseous state lifted the dense iron from the wustite.

The effect of trace amounts of hydrogen sulphide and water vapour on the hydrogen reduction of wustite was reported by (Hayashi and others, 1983). At temperatures between 600° C and 1000° C, the reaction rate peaked when \( P_{\text{H₂}}/P_{\text{H₂O}} \) was ≈ 10⁻⁴. Examination of the iron product revealed that it was more porous. Increased gas diffusion through the iron product was concluded to increase the reaction rate, however it likely makes the reduced iron more pyrophoric. Addition of water vapour led to the formation of a dense iron phase, sharply lowering the rate of reduction. Coincident additions of water vapour and hydrogen sulphide did not lead to dense iron formation.

2.4.4 Effect of Trace Elements on Iron Oxide Reduction

Substitution of other ions for either the Fe³⁺ or the Fe²⁺ ion in the metal sublattice of iron oxides can affect the reaction characteristics of iron oxides by three mechanisms: changes in lattice geometry, phase stabilization, and catalytic effects.

The iron lattice can be opened up by substituting trace elements whose ionic radius is larger than Fe³⁺ (0.64Å) or by substituting ions with a lower valence. Alkali metals (K⁺, Na⁺ with ionic radii \( r_\text{K⁺} = 1.30\text{Å} \) and 0.99Å respectively) would therefore be expected to
increase reduction rate, while phosphorous and silicon (r=0.35Å and 0.42Å respectively) would decrease reduction rate.

Reduction of dense hematite plates, dense magnetite plates and dense wustite plates in CO/CO₂ atmospheres were accelerated by first dipping the plates in KCl solutions (Nakagawa and Ono, 1985). The reduction products were universally found to be more porous, which led to increased gas permeability. Potassium was never detected in the lattices of either the oxides or the metal. It was suggested that potassium catalyses the nucleation process (Roederer and others, 1987). Doping blast furnace pellets with KCl caused swelling and degradation while K₂CO₃ additions caused catastrophic failures (Stephenson and Smailer, 1980), so the industrial use of alkali metals is limited.

Earth metals, especially magnesium, increased reducibility and improved pellet strength, and form the flux in the blast furnace (Stephenson and Smailer, 1980). Modest lime additions to wustite extends the gas conditions which cause porous iron formation (Nakiboglu and others, 1986).

Silica retards reduction by stabilizing wustite as faylite (2FeO-SiO₂) and tridimite (FeO-SiO₂). The addition of alumina to sintered hematite pellets similarly retards reduction, stabilizing wustite as hercynite (FeO-Al₂O₃) (Suzuki and others, 1981).

Chromium tends to increase the reducibility of hematite in H₂/CO/H₂O/CO₂ gas mixtures because it is a catalyst for the regeneration of hydrogen by the water shift reaction:

\[
\begin{align*}
FeO + H_2(g) & = Fe + H_2O(g) \\
H_2O(g) + CO(g) & = H_2(g) + CO_2(g)
\end{align*}
\]

(2.15)

Since reduction proceeds quicker in hydrogen than carbon monoxide, reduction is accelerated by increasing the concentration of hydrogen at the reaction interface. Excessive chromium additions decreased the reduction rate of wustite (Chinje and Jeffes, 1989). This was explained by noting that Cr³⁺ is smaller than Fe²⁺ (cf. 0.63Å vs 0.74Å) and tends to close the metal sub-lattice.
Divalent nickel and cobalt have ionic radii of 0.69Å and 0.75Å respectively fall between the ionic radii of Fe$^{2+}$ and Fe$^{3+}$. From a lattice standpoint, nickel and cobalt would be expected to accelerate reduction of hematite, where they substitute for the Fe$^{3+}$, and retard later reductions, where they substitute for Fe$^{2+}$. 
3.0 THEORY

A study of chemical kinetics properly starts with a discussion of the thermodynamics of the system. The three familiar laws of thermodynamics can be summarized into the single axiom that all processes advance towards equilibrium. In general, the equilibrium state must be determined experimentally. The equilibrium state can be predicted with a high degree of precision if the system behaves in an 'ideal' fashion.

In contrast, reaction rates cannot (yet) be predicted from first principles; they must be measured. It has been determined that, under certain circumstances, sulphur catalyses the gaseous reduction of iron oxides (Hayashi and others, 1984). This could not have been predicted from first principles. Further, trace impurities which do not significantly affect the thermodynamics of the system, can profoundly change the reaction rate.

There is a unique connection between thermodynamics and kinetics. Theoretically, the only kinetic conclusion which can be drawn from thermodynamics is that the reaction will proceed towards equilibrium. It is incorrect to equate, for instance, large equilibrium constants to fast reaction kinetics.

This chapter summarizes the thermodynamics of the iron/nickel/oxygen/sulphur systems involved in the solid state reduction of roasted nickel calcine. Subsequently, gas/solid reaction mechanisms are developed along with their characteristic conversion/time profiles.

3.1 Thermodynamics

3.1.1 Iron Oxygen System

The binary phase diagram for the iron oxygen system is shown below in Figure 3.1. (Ehlers, 1972). The light broken lines represent $O_2$ isobars. Metallic iron exists in three phases: $\alpha$-iron is stable below 900°C; $\gamma$-iron is stable between 900°C and 1405°C; and from 1405°C to the melting point 1528°C $\delta$-iron is the stable phase. The solubility of oxygen in solid iron is negligible (less than 0.01 wt. %). In molten iron, oxygen solubility starts at 0.17 wt.% at the melting point and increases with temperature. (Bogdandy and von Engell, 1971)

Iron forms three solid stable oxides: wustite $Fe_1.4O$; magnetite $Fe_3O_4$ and rhombohedral
hematite $\alpha$-$\text{Fe}_2\text{O}_3$. A meta-stable cubic hematite $\gamma$-$\text{Fe}_2\text{O}_3$ forms under certain conditions (Bogdandy and von Engell, 1971). As seen from Figure 3.1, wustite is a metal deficient oxide with an equilibrium chemical composition of wustite between $x=0.04$ and $x=0.16$. Wustite crystallizes as a cubic NaCl lattice. The oxygen lattice is fully occupied while some lattice points on the iron sub-lattice are vacant. Charge neutrality requires that each
vacancy be compensated by two trivalent iron ions in the iron lattice. The vacancies and
electron holes make wustite electrically conductive. Iron ions can diffuse through the
lattice by jumping to a neighbouring vacancy, while the vacancy counter diffuses. The
high self diffusivity of iron in wustite has kinetic implications. Wustite is unstable below
570°C, decomposing eutectoidally to α-iron and magnetite. The melting point of wustite
varies between 1390°C and 1410°C depending on the oxygen content (or oxygen partial
pressure).

Solid magnetite (Fe₃O₄ or Fe⁴⁺Fe³⁺Fe²⁺O₄) crystallizes congruently at 1594°C into a cubic
inverse-spinel lattice which is stable at all temperatures below its melting point. The
oxide sub-lattice is full, while the iron sub-lattice consists of Fe⁺⁺, Fe⁺⁺⁺ and vacancies.
At higher temperatures, magnetite can accept an excess of the trivalent iron ions in the
lattice. The corresponding vacancies required by charge neutrality means that magnetite's
phase field incorporates a metal deficient region. At its most metal deficient, the oxide
can be represented by Feₓ₃₋ₓO₄ where x = 0.11. Magnetite melts congruently at an oxygen
partial pressure of ≈ 0.1 atm. In other words magnetite melts and decomposes in air at
approximately the same temperature. Magnetite is ferrimagnetic with a Curie temperature
of 627°C. This property is useful as it allows iron ores to be concentrated, for instance,
by reduction roasting of hematite followed by magnetic separation.

Two phases of hematite exist: γ-Fe₂O₃ is (meta)-stable below 400°C, while α-Fe₂O₃ is
stable at high temperatures. γ-Fe₂O₃ is a spinel structure (similar to magnetite with
additional vacancies in the metal sub-lattice) and is ferrimagnetic. It has been suggested
that this phase is only stable when oxidized in the presence of water (David and Welch,
1956). α-Fe₂O₃ is a rhombohedral, diamagnetic phase. The two phases behave differently
when reduced: since magnetite and γ-Fe₂O₃ have similar spinel lattices, reduced γ-Fe₂O₃
gives a dense magnetite product; in contrast magnetite formed by the reduction of α-Fe₂O₃
is porous and friable (Kirkaldy and Ward, 1964). α-Fe₂O₃ melts congruently at an oxygen
pressure above 1 atm. Therefore when heated in pure oxygen at 1 atm, hematite
decomposes to magnetite and oxygen before melting. α-hematite shows a narrow region
of oxygen deficiency, such that Fe₂O₃₋ₓ where x = 0.01. This has been ascribed to
vacancies in the oxygen sub-lattice and iron ions in additional interstitial positions
Systems which lower the equilibrium $p_{\text{CO}}$ can be used to reduce iron oxides. Industrially, $\text{H}_2/\text{H}_2\text{O}$, and $\text{CO}/\text{CO}_2$ are used in iron production (blast furnace, Midrex, Hyl); $\text{C}/\text{CO}/\text{CO}_2$ is used in direct smelting (Quebec Iron and Titanium) and slag cleaning (INCO, Western Mining); sulphide/$S_2/\text{SO}_2$ mixtures are used in non-ferrous slag cleaning (Falconbridge).

### 3.1.2 The Fe-C-CO-CO$_2$ System

Figure 3.2 illustrates the stability of iron and its oxides in a CO/CO$_2$ atmosphere at a total pressure of 1 atm. Superimposed on the diagram is the "sooting" line representing unit
carbon activity at a system pressure of 1 atm. for the Boudouard-Naumann reaction:

\[ 2CO(\text{g}) = C + CO_2(\text{g}) \quad \Delta G^\circ = -282400 + 86.81T \text{ [J/mol]} \quad (3.1) \]

Gas mixtures above the sooting line tend to precipitate carbon (sooting out). Appreciable decomposition of CO occurs between 400°C and 700°C (Soma, 1964). The rate at which sooting occurs is catalyzed by iron, nickel and other metals. Hydrogen also accelerates deposition (Walker and others, 1959). SO\textsubscript{2} and H\textsubscript{2}S are inhibitors whose action is irreversible, i.e. their poisoning effect continues after they are removed from the gas phase (Schenck and Maschankla, 1960).

Carbon and iron form a solid solution and an intermediate compound Fe\textsubscript{3}C (6.7wt.% C) is metastable. At temperatures above 700°C in the presence of iron, CO reacts according to (3.1) give an iron/carbon solution and CO\textsubscript{2}.

The CO/CO\textsubscript{2} ratio required to reduce wustite to iron increases with temperature, i.e. thermodynamically, CO loses its reducing strength at high temperature. The CO/(CO\textsubscript{2}) ratio required to reduce hematite to magnetite is too low to be represented on this diagram (6.3x10\textsuperscript{-3} at 800°C), indicating that hematite is readily reduced.

**Table III.1 Reduction of iron oxides - reaction free energies** (From Gaskell, 1990)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ/(\text{J/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2} \text{Fe}_3\text{O}_4 + \frac{1}{6}R = \frac{1}{3} \text{Fe}_2\text{O}_3 + \frac{1}{6} \text{RO} )</td>
<td>( R = \text{H}_2 ) -573-13.62T ( R = \text{CO} ) -5493-8.28T</td>
</tr>
<tr>
<td>( \frac{1}{3} \text{Fe}_3\text{O}_4 + \frac{1}{3}R = \text{FeO} + \frac{1}{3} \text{RO} )</td>
<td>22087-23.43T 9953-12.76T</td>
</tr>
<tr>
<td>( \frac{1}{3} \text{Fe}_3\text{O}_4 + \frac{4}{3}R = \text{Fe} + \frac{4}{3} \text{RO} )</td>
<td>35687-31.18T -12847+11.5T</td>
</tr>
<tr>
<td>( \text{FeO} + R = \text{Fe} + \text{RO} )</td>
<td>13600-7.75T -22800+24.26T</td>
</tr>
</tbody>
</table>

* T in K

The free energies for the reduction of iron oxides are summarized in Table III.1. In the
case of reduction by CO, reactions between adjoining phases are exothermic with the exception of the Fe$_3$O$_4$/FeO$_{1.5}$ boundary. Reduction of hematite to metallic iron is therefore also exothermic. The heat of reaction may be used to partially offset heat losses from a gas/solid reactor such as a fluid bed.

3.1.3 The Fe-O$_2$-H$_2$ System
The corresponding diagram for H$_2$/H$_2$O is reproduced in Figure 3.3. There is minimal H$_2$ solubility in iron, and no intermediate hydride is stable. As with the CO/CO$_2$ system, hematite can be reduced easily. According to Table III.1, stepwise hydrogen reduction of all iron oxides are endothermic, thus the net reduction of hematite to iron is also endothermic. The magnitude of the enthalpies involved is not great, however the heat requirement becomes significant when reactor heat losses are included.

In contrast to carbon monoxide, hydrogen is a thermodynamically more powerful reductant at higher temperatures than at low temperatures. The fact that low temperature reduction of wustite in pure H$_2$ is orders of magnitude faster than in pure CO, despite the latter being thermodynamically the stronger reductant, exemplifies the folly of predicting kinetics from thermodynamic data.

3.1.4 Fe-O$_2$-S System
Iron oxides can also be reduced by metal sulphides. For example hematite is reduced by pyrrhotite, such that finely divided mixed powders evolve SO$_2$ when heated to 450°C in an inert atmosphere (Celmer and others, 1987).

$$10Fe_2O_3 + FeS = 7Fe_3O_4 + SO_{2(g)}$$

The corresponding reduction of magnetite by pyrrhotite occurs only above 1000°C.

$$3Fe_3O_4 + FeS = 10FeO + SO_{2(g)}$$

The solubility of magnetite in sulphide melts has been investigated due to its importance in non-ferrous smelting (Stofko and others, 1974), (Kaiura and Toguri, 1974) (Elliott,
Figure 3.3 Fe/Wustite/Magnetite/Hematite/H$_2$/H$_2$O stability fields

1988). Kauru suspended magnetite spheres into FeS-Fe$_2$O$_4$ melts at 1200°C and measured the weight loss of the magnetite and weight gain of the melt separately. The evolution of SO$_2$ was inferred from changes in the sum of the two weights. It was found that magnetite dissolved readily in the melt without evolving SO$_2$ until the melt was magnetite saturated. SO$_2$ was not evolved even when the melt was close to magnetite saturation. It would appear paradoxical that SO$_2$ was evolved at the lower temperatures of 1000°C from magnetite/pyrite powders but not from magnetite fully wetted by molten FeS at 1200°C. This can be explained by considering that for a bubble of SO$_2$ to form beneath the surface of the melt, the partial pressure of SO$_2$ must exceed atmospheric pressure; no bubble is required from mixed powders, therefore SO$_2$ can be evolved at partial pressures...
Figure 3.4 Activities of the liquid Fe-S-O system at 1200° C, according to Stofko et al.

below 1 atm. Figure 3.4 shows the extent of oxygen solubility in Fe-S-O systems.
3.1.5 Sulphide Reduction

Pure hydrogen and carbon monoxide can directly reduce sulphides to the metal, for example the free energy of reaction for pyrrhotite is given by (energies from HSC ver.3.0):

\[ FeS_{(s)} + H_{2(g)} = Fe_{(s)} + H_2S_{(g)} \quad \Delta G^\circ = 15775 - 2.095T(K) \quad [\text{J/mol}] \quad (3.4) \]

and

\[ FeS_{(s)} + CO_{(g)} = Fe_{(s)} + COS_{(g)} \quad \Delta G^\circ = 24941 - 4.477T(K) \quad [\text{J/mol}] \quad (3.5) \]

The equilibrium constants for the reduction of pyrrhotite is several orders of magnitude lower than for the reduction of wustite. From (3.4) and (3.5), H₂S can be shown to be more stable than COS:

\[ H_2S_{(g)} + CO_{(g)} = H_2(g) + COS_{(g)} \quad \Delta G^\circ = +9166 - 2.375T(K) \quad [\text{J/mol}] \quad (3.6) \]

The equilibrium concentration of H₂S and COS above other metal sulphides is documented in Table III.2

Metal sulphates are readily reduced by H₂ or CO mixtures. Copper sulphate has been shown to proceed directly to the metal (Sohn and Kim, 1985).

3.2 Kinetics of Gas-Solid Reactions

Reduction of iron oxides has been the most extensively researched metallurgical solid/gas reaction due to its industrial importance to blast furnace operations and the production of direct reduced iron. Numerous studies have concentrated on the reaction rates of pellet sized lump ore. Of the studies which deal with fine particulate (<500µm), several different mechanisms have been reported, including uniform internal reduction (Turkdogan and Vinters, 1971a), shrinking un-reacted core (Monsen and others, 1995) and nucleation and growth (Sohn, 1978) (Matyas and Bradshaw, 1974). This chapter summarizes the mechanisms behind these kinetics. The application of these mechanisms to experimental
Table III.2 Equilibrium H$_2$S/H$_2$ and COS/CO over base metal sulphides as a function of temperature

<table>
<thead>
<tr>
<th></th>
<th>[H$_2$S]/[H$_2$]</th>
<th></th>
<th>[COS]/[CO]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500° C</td>
<td>600° C</td>
<td>700° C</td>
</tr>
<tr>
<td>FeS$_2$</td>
<td>15.7</td>
<td>40.0</td>
<td>83.4</td>
</tr>
<tr>
<td>FeS</td>
<td>1.0x10$^{-4}$</td>
<td>3.3x10$^{-4}$</td>
<td>8.2x10$^{-4}$</td>
</tr>
<tr>
<td>Cu$_2$S</td>
<td>2.5x10$^{-4}$</td>
<td>5.2x10$^{-4}$</td>
<td>9.0x10$^{-4}$</td>
</tr>
<tr>
<td>Ni$_3$S$_2$</td>
<td>3.9x10$^{-4}$</td>
<td>1.3x10$^{-3}$</td>
<td>2.7x10$^{-3}$</td>
</tr>
</tbody>
</table>

* FeS$_2$/FeS equilibrium

data will be presented in Chapter 4.

3.2.1 Shrinking Un-reacted Core Model

A full analysis of gas/solid reactions considers several possibilities: the solid reactant may be initially porous or non-porous; the reaction may or may not leave behind a solid product; the product may be more or less dense than the reactant, causing the particle to shrink or swell respectively; the exothermicity of the reaction may or may not generate a temperature profile in the solid. The shrinking un-reacted core model describes the transformation of a non-porous reactant into a porous product. The rate constant and gas diffusivities are assumed to be constant, implying that the particle is at a constant and uniform temperature. Reducing metal oxides are usually assumed to yield products with the same density (Szekely and others, 1976), thus the particle size is unchanged. Since the reactant is non-porous, reactions occur only at the product/reactant interface. This study involves predominantly spheroidal shaped particles, therefore the development will focus on a single spherical particle.

Figure 3.5 shows a general gas concentration profile in the particle during the course of the reaction. Consider the general reduction reaction:
In CO and H₂, each mol of reductant consumed generates one mol of gaseous product, therefore there is no net flow of gas in or out of the particle. The flow of gaseous reductant R across the laminar boundary layer is given by (Geiger and Poirier, 1994):

$$N_R = -N_{RO} = k A_p \left( C_R^2 - C_Z^2 \right)$$

$$= 4 \pi l_p^2 k (C_R^2 - C_Z^2) \text{ for a spherical particle}$$

**Figure 3.5** Concentration profiles forming in a spherical particle reacting with a fluid
where \( N_R \) is the molar flow-rate of \( R \) [mol/s], \( h \) is the mass transfer coefficient [m/s], \( A_p \) is the outside surface area of the particle [m\(^2\)], \( (C_R^p - C_R^a) \) is the concentration difference across the boundary layer [mol/m\(^3\)] and \( r_p \) is the original radius of the particle [m]. It is assumed that the particle does not change shape or dimension during reduction.

Empirical equations relate the mass transfer coefficient to gas properties and the particle’s shape and dimension, e.g. for spherical particles the Ranz-Marshall correlation applies at Reynolds numbers less than 100 (Ranz and Marshall, 1952):

\[
Sh = 2.0 + 0.6Re^{1/2} Sc^{1/3}
\]

where

\[
Sh = \frac{h d_p}{D_RRO} \quad Re = \left( \frac{d_p \nu \rho_R}{\eta} \right) \quad Sc = \left( \frac{\eta}{\rho \theta RRO} \right)
\]

\( D_RRO \) is the mutual diffusivity of \( R \) in \( RO \) [m\(^2\)/s], \( \eta \) is the gas viscosity [kg/ms], \( \rho \) is the gas density [kg/m\(^3\)] and \( \nu \) is the relative velocity between the bulk gas and the solid [m/s].

The mass transfer coefficient in a nearly stagnant gas reaches a limit given by:

\[
\lim_{Re\to0} h = \frac{D_RRO}{r_p}
\]

The diffusivity of a gas can be estimated from the theoretically derived Chapman-Enskog equation or, more accurately, from a semi-empirical relation due to Fuller (Geiger and Poirier, 1994):

\[
D_{RRO} = \frac{10^{-3} T^{1.75}}{P \left( v_R^{1/3} + v_R^{1/2} \right)^2} \left[ \frac{1}{M_{RO}} + \frac{1}{M_R} \right]^{1/2}
\]

where \( v_R \), \( v_R^{1/3} \) are tabulated diffusion volumes, \( M_R \), \( M_{RO} \) are the molecular weights of \( R \) and RO and \( P \) is the system pressure in atmospheres.

3-12
The flow-rate of R through the porous product is given by Fick's law of diffusion:

\[ N_R = -N_{RD} = -D_{ef} A \nabla C_R \]
\[ = -D_{ef} A \pi r^2 \frac{dC_R}{dr} \text{ for spherical particles in radial direction} \]  

(3.12)

where \( D_{ef} \) is the effective diffusion coefficient of R through the porous product. If the pores are much larger than the mean free path of the R atoms, then \( D_{ef} \) is related to \( D_{RRO} \) according to the void fraction \( \varepsilon \) and tortuosity \( \tau \) (Szekely and others, 1976):

\[ D_{ef} = D_{RRO} \left( \frac{\varepsilon}{\tau} \right) \]  

(3.13)

When the pore diameters approach the mean free path (i.e. gas atoms are more likely to collide with solid walls than with other gas atoms), Knudsen diffusion predominates:

\[ D_K = 9700 \ r_{pore} \left( \frac{T}{M} \right)^{1/2} \]  

(3.14)

which can be corrected for tortuosity and voidage with (3.13).

The rate at which R is consumed at the reaction interface (assuming the reaction proceeds to equilibrium and is first order with respect to R and RO) is written:

\[ N_R = -N_{RD} = k_{c} A \left[ C_R - \frac{C_{R0}}{K_{R0}} \right] \]
\[ = 4 \pi r_c^2 k \left[ C_R - \frac{C_{R0}}{K_{R0}} \right] \text{ for spherical particles} \]  

(3.15)

where \( k \) is the intrinsic reaction rate constant [m/s]. The Arrhenius relationship between \( k \) and temperature is often cited for activated processes (Bodsworth and Bell, 1972):

\[ k = k_o e^{-E_a/RT} \]  

(3.16)

where \( k_o \) is the frequency factor [m/s] and \( E_a \) is the activation energy [J/mol] and R is the gas constant [8.314 J/mol.K].

3-13
The consumption of R is related to the consumption of the oxide through the reaction stoichiometry (b in (3.7)) and the oxide molar density (ρ). The rate at which the interface moves is given by (Szekely and others, 1976):

\[
\frac{dr}{dt} = -\frac{b}{\rho_s} \cdot \frac{N_A}{A_c} \quad \text{For spherical particles}
\]

At pseudo-steady state, the flow of R across the boundary layer, the flow of R through the product layer and the consumption of R at the interface are identical. Equations (3.8), (3.12), (3.15) can then be solved with (3.17) to derive conversion/time relationships. Note that, since \( D_{R,RO} \), h and k are all positive values,

\[
C^*_{R} > C^p_{R} > C^c_{R} > C^{**}_{R}
\]

For example \( C^*_{R} \) is strictly greater than \( C^p_{R} \) since, if they were equal, diffusion across the boundary layer would stop (Lu, 1963). The two concentrations can however approach each other asymptotically. By analyzing the following asymptotic concentration profiles:

I \quad C_{RO} > C_{RP} = C_{RC} = C^{**}_{R} \quad \text{Mass transfer control}

II \quad C_{RO} = C_{RP} > C_{RC} = C^{**}_{R} \quad \text{Diffusion Control}

III \quad C_{RO} = C_{RP} = C_{RC} > C^{**}_{R} \quad \text{Chemical Control}

Szekely derived the following conversion/time relations: for mass transfer control:
\[ \frac{t}{\tau^m} = X \]

where

\[ \tau^m = \frac{\rho_s r_p^2}{3 b_h} \left[ C_{R_c} - C_{R}^m \right]^{-1} \]  \hspace{1cm} (3.20)

\( \tau^m \) is the time taken to consume the particle in this regime. If the particle is suspended in a nearly stagnant gas \((\text{Re} = 0)\), inclusion of the Ranz-Marshall equation gives:

\[ \tau^m = \frac{\rho_s r_p^2}{3 b D_{\text{eff}}} \left[ C_{R_c} - C_{R}^m \right]^{-1} \]  \hspace{1cm} (3.21)

For diffusion control, the following relationship was derived:

\[ \frac{t}{\tau^d} = 3 - 2X - 3(1 - X)^{2a} \]

where

\[ \tau^d = \frac{\rho_s r_p^2}{6 b D_{\text{eff}}} \left[ C_{R_c} - C_{R}^m \right] \]  \hspace{1cm} (3.22)

\( \tau^d \) is the time taken to consume the particle in this regime. Finally for chemical reaction control:

\[ \frac{t}{\tau^c} = 1 - (1 - X)^{1/a} \]

where

\[ \tau^c = \frac{r_p \rho_c}{b k} \left[ C_{R_c} - C_{R}^m \right]^{-1} \]  \hspace{1cm} (3.23)

\( \tau^c \) is the time taken to consume the particle under chemical control. Moreover it was shown that under a general concentration profile (Equation (3.18)), the time to reach a conversion \( X \) is exactly the sum of the times to reach that conversion under the above

---

\(^2\) The relationships developed in (Szekely, 1976) are in terms of dimensionless times. I have chosen to change the nomenclature to emphasize the time required to completely consume a particle under various controlling regimes.
asymptotic conditions, i.e.

$$\kappa(X) = \tau^a X + \tau^d (3 - 2X - 3(1 - X)^{1/3}) + \tau^p (1 - (1 - X)^{1/3}) \quad (3.24)$$

This "law of additive times" is exactly true if the reaction is first order with respect to the gas phase, and holds approximately for other rate expressions (Sohn, 1978). The time taken to consume a spherical particle is proportional to the particle diameter if the process is chemically controlled, and proportional to diameter squared for processes under stagnant mass transfer or diffusion control.

### 3.2.2 Reaction Modulus

From (3.20) (3.22) and (3.23) the three time constants $\tau^a$, $\tau^d$ and $\tau^p$ are defined by measurable physical properties of the particle and system. The mass transfer resistance may be significant but it can never control the complete consumption of a particle. This is because the diffusional resistance through the product layer must always be greater than diffusional resistance through the boundary layer. Therefore $\tau^a$ is usually less than either $\tau^d$ or $\tau^p$. Szekely and others (1976) defined the reaction modulus $\sigma_i^2$ as:

$$\sigma_i^2 = \frac{\tau^d}{\tau^p} = \frac{r_p k \beta}{6D_{e}} (1 + 1/K_{sp}) \quad (3.25)$$

It was shown that for $\sigma_i^2 < 0.1$, the overall process could be considered to be controlled entirely by the chemical reaction, while $\sigma_i^2 > 10$ implies that the overall process is controlled by diffusion through the product layer. The process otherwise proceeds under mixed control.

In their development, the rate controlling step was inherently defined to be the step which most determines the complete consumption of the particle. The instantaneous rate determining step, however, can change during the course of the reaction. To see this, consider a process that is overall controlled by diffusion through the product layer, i.e. $\sigma_i^2 > 10$: obviously, before a product layer forms, diffusion cannot be said to control the reaction rate and therefore the initial reaction rate must be controlled by either the surface
reaction or external mass transfer. It is possible to hypothesize a situation where the rate is controlled by mass transfer, chemical reaction and diffusion at different stages of the reaction.

3.2.3 Effect of incomplete reaction on controlling regimes

The development from Szekely and others (1976) assumed that the particle was fully reacted. If the reaction is incomplete, the following analysis is proposed. Let X represent the final conversion of the particle, and \( \tau^a \), \( \tau^d \) and \( \tau^c \) represent the time to completely react the particle under mass transfer, diffusion and chemical control respectively. The hypothetical times to achieve conversion X are \( t^a(X) \), \( t^d(X) \) and \( t^c(X) \) under mass transfer, diffusion and chemical control respectively. The "Law of Additive times" gives the actual reaction time to be:

\[
t(X) = t^a(X) + t^d(X) + t^c(X) \tag{3.26}
\]

The time to achieve a conversion X<1 under a specific control regime is related to the time to achieve complete conversion by equations (3.20) (3.22) and (3.23). The following reaction moduli are proposed:

\[
\sigma^2_a(X) = \frac{\tau^a X + \tau^d (1 - (1 - X)^{1/3})}{\tau^c (3 - 2X - 3(1 - X)^{2/3})} \tag{3.27}
\]

\[
\sigma^2_d(X) = \frac{\tau^d (1 - (1 - X)^{1/3}) + \tau^c (3 - 2X - 3(1 - X)^{2/3})}{\tau^d X} \tag{3.28}
\]

\[
\sigma^2_c(X) = \frac{\tau^c (3 - 2X - 3(1 - X)^{2/3})}{\tau^c (1 - (1 - X)^{1/3})} \tag{3.29}
\]

The controlling regimes for an incompletely reacted particle are then defined by:
This development shows that a process which does not proceed to completion can be controlled by the mass transfer, especially at low conversions. Partial roasting of sulphides may be better described by this model.

3.2.4 **Effect of an Inert Core on the Shrinking Un-reacted Core Model**

The particles in the current study consist of an oxide rim surrounding a sulphide core. At the temperatures of interest the sulphide core is (relatively) inert. The effect of this topology on the above equations is derived as follows: equation (3.24) can be expressed in terms of particle and interface radii as:

\[
\tau(r_c) = \tau(1 - \zeta^3) + \tau(1 - 3\zeta^2 + 2\zeta^3) + \tau(1 - \zeta)
\]

where

\[
\zeta = \frac{r_c}{r_p}
\]

(3.31)

Where \(r_p\) is the outside radius of the particle; \(r_c\) is the radius of the reaction interface and \(r_i\) is the radius of the inert core, i.e. \(r_i < r_c < r_p\). When the particle contains an inert core, conversion is complete when the radius of the reacting core equals the radius of the inert core, i.e.

\[
X = \frac{r_p^3 - r_c^3}{r_p^3 - r_i^3}
\]

(3.32)

Dividing by \(r_p^3\) and defining \(\alpha\) to be \(1-(r/r_p)^3\) (\(\alpha\) is constant for the particle), gives:

\[
X = \frac{1 - \zeta}{1 - \zeta^3} = \frac{1 - \zeta^3}{\alpha_i}
\]

(3.33)
Thus:

$$\zeta = (1 - \alpha x)^{1/3} \quad (3.34)$$

Substituting this into (3.31) gives:

$$\kappa(x) = \tau^a \alpha x + \tau^d \left( 3 - 3(1 - \alpha x)^{2/3} + 2\alpha x \right) + \tau \left[ 1 - (1 - \alpha x)^{1/3} \right] \quad (3.35)$$

3.2.5 Porosity and the Grain Model

The shrinking un-reacted core model assumes that the solid reactant is non-porous. The study of pellets necessitated the incorporation of reactant porosity to the model. One approach (Szekely and others, 1976) regarded a pellet as an assemblage of grains pressed together. Each grain is assumed to be non-porous and to obey the shrinking un-reacted core model. As was derived previously, the consumption time of a process controlled by diffusion through the solid layer is proportional to the diameter squared, while if the process is chemically controlled the consumption time is proportional to the particle diameter. Because $\sigma^2$ is proportional to $r_p$, the diffusional resistance becomes less significant as the grain size decreases. Diffusion of the reactant gas between grains nevertheless causes a concentration gradient to develop through the pellet. The gas/solid reaction occurs in a diffuse zone and, in the limit, at a non-uniform rate throughout the pellet. The rate of conversion depends on pellet and grain properties. The resulting equations must usually be solved numerically. The following approximate solution was developed (Szekely and others, 1976):

$$\kappa(x) = \tau^a \left( 1 - (1 - x)^{1/3} \right) + \tau^d \left( 3 - 2x - 3(1 - x)^{2/3} \right)$$

where

$$\tau^a = \frac{\rho_s}{b k C_s} \left( \frac{F \rho_s}{V_s} \right)$$

$$\tau^d = \left( \frac{V_p}{F \rho_s} \right) \left( \frac{V_p}{V_s A_p} \right) \frac{(1-\epsilon) \rho_s}{2 b D_{ps} C_s} \quad (3.36)$$

where $A$ and $V$ refer to the surface area and volume of the particle (p) or grain (g). This relation is another example of reaction kinetics which obeys the law of additive times.
In the above development all grains are assumed to be the same size and shape. If a grain size distribution is known a priori, a numerical solution is again required. This will be investigated below.

3.2.6 Effect of Grain Size Distribution on Conversion/Time Relationships
Thermogravimetric analysis is usually performed on fine powders for which a particle size distribution is known. The recorded weight loss translates into a size averaged conversion, which is generally not the same as the conversion of the average sized particle. To illustrate this, a pellet consisting of grains was modelled. Two particle size distributions were considered: i) normally distributed about a mean of 4μm with a standard deviation of 1μm (N(4,1)) and ii) uniformly distributed. For this example, the rate of the process was chosen to be controlled by the chemical reaction, hence the conversion/time relationship was independent of the pellet dimensions and shape. The particle size distribution was divided into intervals and the conversion of each interval calculated as a function of time using Equation (4.5). The weighted average conversion was then calculated for the whole pellet and the results plotted in Figure 3.6. It will be shown in the next section that a uniform internal reduction model gives a linear response when log(1-X) is plotted versus time. Figure 3.6 shows that initially (t/t < 0.5) all models give an approximately linear response on these axes. The response of a single sized grain pellet deviates at higher conversions, while the linear response of the models which assume a grain size distribution continues to higher conversions. This may explain the general success in fitting first order models to experimental data.

3.2.7 Uniform Internal Reduction
Experimentally, it has been determined that the conversion-time relationships for several gas-solid reactions are independent of the particle size. It has been proposed that in this instance, no concentration gradient forms in the particle and the reaction proceeds uniformly throughout the particle. This model is termed first order with respect to the solid, or uniform internal reaction, and is described by the following equation:
Figure 3.6  Effect of particle size distribution on conversion profile for N(4,1) grains undergoing a chemically controlled process

\[ \frac{dN_s}{dt} = -k_s N_s \left( C_s^o - C_s^{m} \right) \quad (3.37) \]

Integrating this differential equation with the initial condition that at t=0 N_s=N_{s0} gives:

\[ \log_a \left( \frac{N_s}{N_{s0}} \right) = -k_s \left( C_s^o - C_s^{m} \right) t \quad (3.38) \]

Therefore a plot of the left hand side versus time gives a straight line, whose slope is proportional to the rate constant.

3.2.8  \textbf{Higher Order Reaction Kinetics}

The following expression can be derived if the reaction rate is nth order with respect to the solid:

3-21
\[(1 - X)^{1-n} - 1 = (n - 1) \ k_r \ (C_e^0 - C_e^n) \ t \quad (3.39)\]

A plot of the left hand side versus \(t\) gives a straight line with slope proportional to the rate constant.

### 3.2.9 Nucleation and Growth Kinetics

Nucleation and growth refers to kinetics wherein the product phase develops in discrete locations and grows to cover the surface. Growth proceeds quicker than nucleation. The conversion/time profile, illustrated by Figure 3.7, obeys the following expression:

\[g(X) = \left[-\ln(1 - X)\right]^{1/n} \quad (3.40)\]

The sigmoidal shape at low conversions is reminiscent of auto-catalytic processes. Sigmoidal shapes have been observed in the reduction of hematite to magnetite in hydrogen (Matyas and Bradshaw, 1974) and the reduction of wustite in hydrogen (Sohn, 1978).

### 3.3 Classifying the Rate Controlling Step by the Activation Energy

Gas solid processes typically involve 7 steps (Smith): i) transport of reactants from the bulk fluid to the fluid-solid interface (external surface of particle) ii) intra-particle transport of reactants into the particle iii) adsorption of reactants onto pore walls iv) chemical reaction, generating an adsorbed product v) desorption of adsorbed products vi) transport of products from the interior of the particle to the surface and vii) transport of the gaseous product from the fluid-solid interface to the bulk fluid. Steps iii) iv) and v) are activated processes, while the rest are controlled by the counter-diffusivity of the gaseous species. The magnitude of the (apparent) activation energy derived from an Arrhenius plot is commonly used to identify the rate controlling step. The Chapman-Enskog theory predicts that the inter-diffusivity between two ideal gases is proportional to \(T^{3/2}\) (Geiger and Poirier, 1994). A relationship of \(T^{1.75}\) has been derived from a statistical analysis of several diffusing gases (Fuller and others, 1966). The reaction rate for diffusion controlled processes is also proportional to the concentration gradient, which is inversely proportional to the temperature, thus the net temperature dependencies are \(T^{-0.5}\)

3-22
Figure 3.7  Nucleation and growth conversion profile

and $T^{0.75}$ respectively. When plotted on Arrhenius axes, the apparent activation energy of a gaseous diffusion controlled process is $= 12\text{kJ/mol}$ between 500°C and 700°C. Activation energies for chemical reactions are typically above 200 kJ/mol, although some chemical reactions have activation energies as low as 60 kJ/mol. It is generally concluded that high activation energies imply an activated process, and low activation energies imply a diffusion or mass transport controlled process; intermediate activation energies are termed mixed control processes. From the above statements it is not possible to distinguish mixed control from chemically controlled processes by the activation energy alone. The mechanism can be conclusively determined only by observing how diffuse the reaction zone is microscopically.

Another factor which affects the reported value of the activation energy is how the rate equation is written. Some researchers write the equation as:
\[ \frac{dX}{dt} = k, (1-X) \left( p^\circ_R - p_R^{\infty} \right) \]  

\[ \frac{dX}{dt} = k, (1-X) \left( C^\circ_R - C_R^{\infty} \right) \]

(3.41)  

(3.42)

The first expression effectively lumps the temperature dependence of concentration in with the activation energy, which would underestimate the activation energy by 6-9 kJ/mol.
4.0 EXPERIMENTAL METHOD

4.1 Calcine Samples

Two calcine samples were donated by Falconbridge Ltd., Sudbury operations. The samples were assayed by the Metallurgical Technology Centre in Sudbury, and the results reported in Table IV.1 below.

Table IV.1 Mineralogy of the Sample Calcines

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>Fe</th>
<th>S</th>
<th>Fe₂O₃</th>
<th>Fe₃O₄</th>
<th>SiO₂⁺</th>
<th>SO₄⁺</th>
<th>Reducible Al₂O₃</th>
<th>Bal. Oxygen</th>
<th>Bal. Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>C97 Calcine</td>
<td>10.2</td>
<td>3.75</td>
<td>0.28</td>
<td>37.3</td>
<td>7.59</td>
<td>23.2</td>
<td>25.4</td>
<td>18.7</td>
<td>0.57</td>
<td>14.5</td>
<td>7.49</td>
<td></td>
</tr>
<tr>
<td>C92 Calcine</td>
<td>8.4</td>
<td>5.65</td>
<td>0.26</td>
<td>39.1</td>
<td>5.8</td>
<td>5.5</td>
<td>42.9</td>
<td>15.7</td>
<td>1.67</td>
<td>15.6</td>
<td>8.9</td>
<td></td>
</tr>
</tbody>
</table>

1 Oxygen content of magnetite, hematite and sulphate only.
2 Calculated from assay.

The C97 calcine was roasted from a high pentlandite rich concentrate hence the higher Ni/Cu ratio. The C92 calcine had a much higher hematite/magnetite ratio and assayed higher in sulphates. Iron not associated with oxides (i.e. Fe - [Fe as magnetite] - [Fe as hematite]) was assumed to be tied up as pyrrhotite, and calculated to be approximately 2.8% and 5.2% for the C97 and C92 calcines respectively.

4.2 Reducing Gas Compositions

The composition and designations of the gases used during this study are summarized in Table IV.2. 40% H₂ was used because of safety concerns.
Table IV.2 Gas Compositions used during thermogravimetric analysis

<table>
<thead>
<tr>
<th>Gas</th>
<th>Nominal Composition</th>
<th>Designation</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>100%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>99.998% (&lt;3\text{ppm} \text{O}_2)</td>
</tr>
<tr>
<td>CO</td>
<td>100%</td>
<td>CP</td>
<td>min 99.5% CO</td>
</tr>
<tr>
<td></td>
<td>40%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>± 2% rel</td>
</tr>
<tr>
<td></td>
<td>20%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>± 2% rel</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>40%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>± 2% rel</td>
</tr>
<tr>
<td></td>
<td>20%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>± 2% rel</td>
</tr>
<tr>
<td></td>
<td>15%, Bal. N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Analyzed</td>
<td>± 2% rel</td>
</tr>
<tr>
<td>Air</td>
<td>21% O&lt;sub&gt;2&lt;/sub&gt;, Bal N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Extra dry</td>
<td>&lt;10 ppm H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
</tbody>
</table>

4.3 Thermogravimetric Balance

A variety of methods are available for following the progress of gas/solid reactions, including mass-loss data (Szekley and others, 1976), (Turkdogan and Vinters, 1971a), off-gas analysis (Bickling, 1950), wet chemical analysis (Monsen and others, 1994) and microscopy (Zamalloa, 1995). Mass change methods are frequently used for measuring macroscopic conversion while microscopy is invaluable in determining the mechanism. Mass loss data is typically collected in two ways: isothermal procedures and non-isothermal procedures.

Thermogravimetric analyses were performed on the calcine using a SETARAM TGA-92 system, shown schematically in Figure 4.1. The apparatus consisted of four units:

- **Furnace/Balance.** Alumina crucibles containing samples of calcine were suspended from a measuring beam balance into a vertical alumina tube. The alumina tube was surrounded by a graphite heating element. The crucible hung adjacent to a type K
furnace thermocouple. The type B thermocouple supplied with the equipment, was exchanged since the K type is more accurate at temperatures below 1000°C (Powell and others, 1975).

As the sample loses mass, the crucible tends to rise: the motion is detected and corrected by controlling the current through four induction coils. The current through the coils is proportional to the mass change. This mechanism has reported a detection limit of 10μg.

The furnace is equipped with three gas inlet ports: high purity argon flowed across the furnace element to prevent the oxidation of graphite; a separate flow of high purity argon was used as the carrier gas, which conveyed vapours evolved from the sample away from the delicate balance mechanism; the sample gas (H₂, CO, Ar) was introduced through the auxiliary gas inlet. A rotameter on the gas discharge measured the combined exit gas flow-rate. A 5-way valve (Whitey SS-43ZFS2) allowed up to four gases to be selected as the auxiliary gas. The dead time in the auxiliary gas selection was measured by heating a calcine sample to +600°C in argon and switching the auxiliary gas to dry air. The time delay between the selection and a change in the sample mass was 40s. This arrangement allowed the sample gas to be switched during an experiment, eg. to go from a reducing gas to an inert gas in a very short time. All gas streams were exhausted to a fume hood.

A cooling water circuit (nom. 2 litres/min) was connected to cool the outer working area of the furnace. As a safety precaution, the furnace automatically shut down if the cooling water flow was interrupted.

Signals from the balance corresponding to the sample mass and furnace temperatures were transmitted via the regulating computer to the interfacing computer.

> The Regulating Computer controlled the operation of the furnace. Power to the graphite element was controlled through a PID algorithm which compared the furnace thermocouple reading to the temperature set-point. Safety interlocks were implemented on this computer, eg. if the flow of cooling water to the furnace fell below 2l/h the
Figure 4.1 Setaram TGA 92 Thermogravimetric Analyzer
furnace power was shut off and an error message reported on the screen. The furnace was also disabled by high temperature readings. Sample mass change data (mg) and furnace temperature readings (°C) were digitally transmitted to the interfacing computer.

- The interfacing computer was an IBM compatible personal computer running proprietary software. The software allowed the experimenter to program a desired experimental profile, follow the progress of the experiment, and store the results on the hard-disk. Auxiliary programs were written to convert the resulting data to a format suitable for importing into a spreadsheet (Quattro Pro v 5.0).

- Off-gas Mass Spectrometer
Experiments were performed by SETARAM in which the above apparatus was coupled to a Balzers mass spectrometer set to detect the gaseous species SO₂, CO₂, H₂O, H₂S and COS. This allowed mass loss data to be matched to the gas species evolved. According to the manufacturer, the signal from the mass spectrometer cannot be calibrated to give quantitative concentrations. Qualitative conclusions can, however, be drawn from coincident mass losses and mass spectrograph peaks.

4.4 Experimental Procedure
The thermobalance could be programmed to perform isothermal or non-isothermal thermogravimetric analysis. In isothermal analysis, reduction was performed at pre-set temperatures. In non-isothermal analysis, samples were heated in reducing environments at pre-set heating rates. The full experimental procedure is described below.

4.4.1 Non-isothermal Experiments
The cooling water supply to the thermobalance was turned on. A pre-weighed sample of calcine was placed in an alumina crucible and the sample suspended from platinum hangers. The length of the hangers ensured that the crucible rested adjacent to the measuring thermocouple tip. The balance was sealed and evacuated through a vacuum pump. When a pressure of below 0.05 atm was reached, argon was admitted through the auxiliary gas port until the pressure reached 1 atm. The auxiliary argon was then shut off, and the apparatus evacuated again. Flushing and evacuation were repeated four times to
ensure that minimal oxygen remained in the apparatus.

A flow-rate of 0.8l/h of argon was used as the carrier gas. The reacting gas was selected using the 5-way valve and admitted to the auxiliary port. The total gas flow-rate was controlled to 5 l/h as measured by a rotameter on the discharge. A non-isothermal heating profile was selected from Table IV.3 and the experiment started. The sample mass was recorded as the reactions occurred.

4.4.2 Isothermal Experiments
For isothermal experiments, samples were weighed, suspended in the balance and the balance evacuated and flushed as described in 4.4.1. A carrier gas flow-rate (0.8l/h Ar) was established. The 5-way valve was turned to select argon, and the auxiliary gas flow-rate adjusted to give a total flow of 5l/h. A reaction temperature was selected from Table IV.3 and the experiment started. The sample was heated in an inert atmosphere to the reaction temperature at the programmed heating rate (typ. 10° C/min). When the reaction temperature was reached, the system was allowed to equilibrate (typ. 5 min). The 5-way valve was turned to substitute the reacting gas mixture (Table IV.2) for the auxiliary argon. The mass change suffered during the heating and reaction stages was recorded.

4-6
Table IV.3 Pre-programmed Temperature For the Thermogravimetric Analyzer

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Iso 3° C/min</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>60</td>
<td>3</td>
<td>180</td>
</tr>
<tr>
<td>Non-Iso 10° C/min</td>
<td>3</td>
<td>10</td>
<td>3</td>
<td>60</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Non-Iso 20° C/min</td>
<td>3</td>
<td>20</td>
<td>3</td>
<td>60</td>
<td>180</td>
<td>60</td>
</tr>
<tr>
<td>Clean Furnace</td>
<td>0</td>
<td>60</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>Iso 500° C</td>
<td>0</td>
<td>20</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>84</td>
</tr>
<tr>
<td>Iso 540° C</td>
<td>0</td>
<td>20</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>86</td>
</tr>
<tr>
<td>etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.5 Standardization of sample size

In thermal analysis, small sample sizes minimize diffusional resistances and their low thermal inertias allow the reaction temperature to be accurately controlled. On the other hand, larger samples yield higher mass loss signals and hence greater signal to noise ratios. The following experiments were performed to set the sample size.

100mg, 50mg and 25mg samples of 1997 calcine (Table IV.1) were heated in strongly reducing atmospheres (40% H₂ or 100% CO) at a heating rate of 10° C/min. Three gas flow-rates were used (See Table IV.4.)

The results from this investigation are plotted in Figure 4.2. The mass loss profiles for calcine heated in H₂ show that the reaction rate of the 100mg sample was significantly slower than that of the 50mg or 25mg samples. It was concluded that diffusion through the thicker bed of calcine had allowed a significant concentration gradient of H₂ to develop through the bed, therefore the reaction rate varied through the bed. The 25mg and 50mg samples reacted at the similar rates, implying that no significant concentration
gradient had developed through these thinner beds. In addition, the mass loss profiles from two different gas flow-rates (med. flow = 5\,\text{lit/min}; fast flow = 15\,\text{lit/min}) were virtually identical, implying that the rates were not significantly affected by external mass transfer.

25mg and 50mg samples reduced in 5 \,\text{lit/min} of 100\% CO were identical within measurement error, and deviated only slightly from the 100mg sample. When the flow-rate was increased to 15 \,\text{lit/min} the reaction rate showed an unexpected decrease. Upon closer examination, this mass loss profile showed a nearly constant bias of 1\%, or 0.5 mg. The high flow-rate was well above the equipment's recommended design flow-rate. This, combined with the higher specific gravity of the CO mixture, are judged to have caused this bias.

If it is assumed that the sample mass change was due to oxygen removal by hydrogen, the resulting change in gas concentration can be calculated. Figure 4.3 plots the change
Figure 4.2 Effect of sample size on weight loss profile: top C97 in 40% H₂; bottom C97 in 100% CO
Effect of reaction on the reducing gas strength: C92, 40% H₂ at 10K/min.

in gas concentration as a 50mg sample of C92 calcine is reduced in 40% H₂. The gas strength is only slightly decreased (from 40% to 37% H₂), i.e. the gas flow is in sufficient excess to prevent starvation.

External diffusion does not control the reduction rate, as can be seen from the following calculation. The highest rate of mass change recorded in Figure 4.3 was approximately 1%/min at 700° C. For a 50mg sample, this corresponds to a H₂ consumption of 520x10⁹ mol/s. The dimensions of the crucible were 0.6 cm high x 0.5cm diameter, therefore the flux of H₂ into the crucible is 2.65 mol/cm² s. The counter-current diffusivity of H₂-H₂O at 700° C is 6 cm²/s (Geiger and Poirier, 1994). Fick's law can be used to approximate the difference between the gas concentration at the top of the crucible and at particle layer as follows:
\[ \dot{N}_{H_2} = D_{H_2} \frac{\Delta C_{H_2}}{\Delta y} \]

\[
2.6 \times 10^{-6} \text{ [mol/cm}^2\text{s]} = 6 \text{ [cm}^2/\text{g}] \times \frac{\Delta C_{H_2}}{0.6 \text{ cm}}
\]

\[ \therefore \Delta C_{H_2} = 264 \times 10^{-9} \text{ [mol/cm}^3] \]

The bulk hydrogen concentration in a 40% gas mixture at 700°C is $5 \times 10^{-4}$ mol/cm$^3$. Therefore, counter-current diffusion of H$_2$ in a stagnant environment would ensure that the concentration of reductant at the gas/solid interface is at most 6% lower than the bulk gas concentration. Note that the presence of turbulence around the crucible means that the actual concentration difference would be lower.

Since the two calcines are mineralogically similar, it was judged reasonable to extend the results of this investigation to the C92 calcine. Subsequent thermogravimetric experiments were standardized by using a sample size of 50 ± 3 mg and gas flow-rates of 5 l/min.

4.6 Procedure for Analyzing Gravimetric Data

The data from the interfacing computer was stored on the hard disk, and converted to a form which could be imported to a spreadsheet. The methods used to analyze conversion versus time data are described in this section.

4.6.1 Isothermal Methods

As was discussed in Chapter 3, reduction of iron oxide follows a UIR model at low temperatures and small particle sizes, while large pellets obey the shrinking un-reacted core model at high temperatures. Specifically, -350μm iron oxide particles reduced in hydrogen obeyed the UIR model at temperatures less than 800°C (Turkdogan and Vinters, 1971a). In the present study, 80% of the calcine is -50μm. Moreover, the iron oxides form a shell around the sulphide core, so the diffusion path for the gases is of the order of 20μm. UIR was therefore expected to apply for reduction in hydrogen. The diffusivity of CO/CO$_2$ is a factor of four lower than H$_2$/H$_2$O, however reduction in CO was likewise expected to be first order since the intrinsic reaction rate is known to be
orders of magnitude lower than in hydrogen.

Gravimetric measurements conducted at constant temperature allow the rate constant at that temperature to be calculated. A first order reaction can be written as:

\[
\frac{dN_s}{dt} = -k_r N_s \left(C_s^0 - C_s^m\right)
\]  

(4.2)

where \(N_s\) is the number of moles of solid reactant, \(k_r\) is the reaction rate constant, and \((C_s^0 - C_s^m)\) is the thermodynamic driving force for the reaction to proceed. This can be written as a function of solid conversion \(X\):

\[
\frac{dX}{dt} = k_r (1 - X) \left(C_s^0 - C_s^m\right)
\]  

(4.3)

Rearranging:

\[
\frac{dX}{(1 - X)} = k_r \left(C_s^0 - C_s^m\right) dt
\]  

(4.4)

Integrating, noting that at \(t=0\) \(X=0\) and \(t=t\) \(X=X\) gives:

\[-\ln(1 - X) = k_r \left(C_s^0 - C_s^m\right) t\]

(4.5)

Thus, for a reaction obeying the UIR model, a plot of \(\ln(1-X)\) versus \(t\) is linear, with slope proportional to \(k_r\). Repeated experiments at different temperatures generate a family of curves with different reaction rates coefficients. If an Arrhenius form of the rate constant is proposed,

\[
k_r = A e^{-\frac{E_r}{RT}}
\]

\[
\therefore \ln(k_r) = \ln(A) - \left(\frac{E_r}{R}\right) \frac{1}{T}
\]  

(4.6)

a plot of \(\ln(k_r)\) versus the inverse of the absolute temperature gives a straight line with
slope \(-E_a/R\) and an intercept of \(\ln(A)\).

Isothermal reaction rate constants can also be measured from the initial slope of conversion versus time (substitute \(X=0\) into equation (4.4)). This approach has been used to calculate the activation energy for the hydrogen reduction of various metal oxides (Busnes and others, 1997).

### 4.6.2 Non-isothermal Methods

Rearranging (4.3) directly gives an expression for the rate constant \(k_r\):

\[
k_r = \frac{\frac{dX}{dt}}{(1 - X) \left(C_a^i - C_a^o\right)}
\]  

(4.7)

This formulation is used in the differential method for analysis of non-isothermal gravimetric data. The reaction rate and extent are recorded and used to derive the reaction rate constant as a function of temperature. The reaction rate constant should be independent of the heating rate and the sample's thermal history.

Non-isothermal gravimetric data has also been analyzed using an integrating method (Sohn and Kim, 1985). By substituting in an Arrhenius form for the rate constant, integration of the differential equation was shown to simplify to:

\[
\ln \left[-\ln (1 - X)T^2\right] = \ln \left\{ A \left(\frac{\hat{f}(p_{fr})}{R} \frac{R}{aE_a} \left[1 - \frac{2RT}{E_a}\right]\right) \right\} - \frac{E}{RT}
\]

(4.8)

Where \(a\) is the heating rate \(\left(^\circ C/s\right)\), \(\hat{f}(p_{fr})\) is the thermodynamic driving force, and \(T\) bar is the temperature at 50\% conversion. This method was used to calculate the activation energy for the hydrogen reduction of pure copper sulphate crystals.

The accuracy of these two methods on systems undergoing multiple reactions was compared by considering the gaseous reduction of hypothetical mixture of sulphates (see Table IV.5). The rate constants for \(\text{BSO}_4\) and \(\text{CSO}_4\) were fixed to react at lower
temperatures than ASO₄. Euler's method was used to generate the hypothetical mass loss profile corresponding to a 10⁰ C/min heating rate. An "apparent" conversion (defined as the mass loss divided by the ultimate mass loss) was calculated and the results plotted according to the differential method and the integral method in Figure 4.4 (top). The slope of the top graphs are proportional to the activation energy.

In the top graph, the graphs are linear after the low temperature reactions are complete. The linear section of the differential method extends over a wider temperature/conversion range than the integral method. In the lower graph, the activation energies (derived from the slopes of the top graphs) are plotted against inverse temperature (Note the change in temperature scale). The differential method quickly converged to the correct value of (7000 R). The integral approach, however, converges slowly to this value, and had not reached the actual value by the end of the "experiment". The differential approach was found to be more robust than the integral equation for this hypothetical system when the activation energies, pre-exponential constants and mass fractions were varied over wide ranges. These results show that the integral method is adversely affected by multiple reactions, whereas the differential method is more robust. In this study, the differential approach was therefore used.

4.6.3 Thermodynamic Driving Force

Calculating the rate constant requires that the thermodynamic driving force be known as
Figure 4.4 Comparison of integral and differential analysis for determining the kinetics of multiple reactions: top rate constants; bottom activation energies.
a function of temperature. Following an approach used to determine the reduction kinetics of zinc ferrites in CO/CO₂ mixtures (Weenink and Themelis, 1991), the equilibrium gas concentration was assumed to correspond to the equilibrium between iron and its nearest oxide, i.e. iron/magnetite/R/R'O below 570°C and iron/wustite/R/R'O above 570°C. Considering the reduction of wustite in CO:

\[ Fe_{0.97}O + CO = 0.947Fe + CO_2 \]  \hspace{1cm} (4.9)

The equilibrium constant is simply:

\[ K_e(T) = \frac{p_{CO}}{p_{CO}} \]  \hspace{1cm} (4.10)

From the stoichiometry of the reaction:

\[ (p_{CO} + p_{CO})^* = (p_{CO} + p_{CO})^{\text{init}} = p^{\text{init}} \]  \hspace{1cm} (4.11)

Combining these equations gives:

\[ p_{CO}^* = \frac{p^{\text{init}}}{1 + K_e} \]  \hspace{1cm} (4.12)

The corresponding gas concentration \([\text{mol/l}]\) is obtained from the ideal gas law:

\[ \frac{n}{V} = C = \frac{p}{RT} \]  \hspace{1cm} (4.13)

where \(R\) is 0.08205 [\text{atm/mol K}] and \(p\) is the partial pressure. The thermodynamic driving force is defined as:

\[ F(\theta) = (C_{CO}^{\text{init}} - C_{CO}^*) \]  \hspace{1cm} (4.14)

The rate of reaction is assumed proportional to this driving force.

Table IV.6 summarizes the calculation of the thermodynamic driving force for the
Table IV.6  Calculation of $(C_A - C_A^{eq})$ for CO/CO$_2$/Fe/Fe$_3$O$_4$ and CO/CO$_2$/Fe/Fe$_{3sc}$O$_4$ systems

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_{eq}^A$</th>
<th>$(P_{CO}^{eq})^B$ [atm.]</th>
<th>$(C_{CO}^{init} - C_{CO}^{eq})^C$ [mol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4 Fe$_3$O$_4$ + CO = 3/4 Fe + CO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>540</td>
<td>1.034</td>
<td>0.492</td>
<td>0.007621</td>
</tr>
<tr>
<td>550</td>
<td>1.016</td>
<td>0.496</td>
<td>0.007463</td>
</tr>
<tr>
<td>560</td>
<td>0.999</td>
<td>0.500</td>
<td>0.007312</td>
</tr>
<tr>
<td>570</td>
<td>0.982</td>
<td>0.505</td>
<td>0.007163</td>
</tr>
<tr>
<td>Fe$_{3sc}$O$_4$ + CO = 0.947Fe + CO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>570</td>
<td>0.973</td>
<td>0.507</td>
<td>0.00713</td>
</tr>
<tr>
<td>580</td>
<td>0.939</td>
<td>0.516</td>
<td>0.006919</td>
</tr>
<tr>
<td>590</td>
<td>0.907</td>
<td>0.524</td>
<td>0.006716</td>
</tr>
<tr>
<td>600</td>
<td>0.877</td>
<td>0.533</td>
<td>0.006521</td>
</tr>
</tbody>
</table>

$^A$ From HSC, ver 3.0
$^B$ From Equation 4.11
Initial gas composition: 100% CO at 1 atm.
$p^{init} = 1.0$ atm.
$p_{CO}^{init} = 1.0$ atm.
$^C$ Equation 4.12, 4.13

CO/CO$_2$ system. This data and corresponding results for the H$_2$/H$_2$O system are plotted in Figure 4.5. As expected, the reducing strength of hydrogen increases with temperature, while that for CO decreases with temperature.

4.6.4  Comparison of Isothermal and Non-isothermal Analysis

The goals of non-isothermal and isothermal TGA are to determine an equation for the rate constant, usually expressed as a function of the activation energy and a pre-exponential constant. It has been noted that non-isothermal analysis is more efficient at achieving this because both parameters can be determined from a single run (Sohn and Kim, 1985). By comparison, at least two isothermal runs are required to obtain the same information, with six runs typical for error estimation. This statement is misleading in two ways: it does not reflect the experimental reality, and it does not fully take into account the statistical analysis required to estimate errors.
Figure 4.5 Thermodynamic Driving Force for CO/CO\textsubscript{2} and H\textsubscript{2}/H\textsubscript{2}O in Fe-FeO systems

Experimentally, it would not be acceptable to draw quantitative conclusions from a single non-isothermal run as neither error estimation nor reproducibility could be evaluated. Only by performing experiments at different heating rates could the effects of pore structure and reaction exothermicity be conclusively eliminated. Therefore, this author would conclude that isothermal and non-isothermal procedures require a similar number of runs. In this study, preparation of the sample and apparatus were rate determining, therefore isothermal and non-isothermal techniques were found to be equally time consuming.

To clarify the statistical characteristics of each method, the following analysis of results is considered. Both procedures first transform the rate constant data to give linear relationships when plotted appropriately (i.e. \( \log([k]\text{ vs. } 1/T) \)). Linear regression is then performed on the transformed variables yielding the slope and intercept of the line which best fits the data. As was shown earlier, the slope is proportional to the activation energy while the pre-exponential can be derived from the intercept. For the results of linear
regression to be valid, the following must be true of the data (Gutman and others, 1982):
i) the independent data (x values) must be known precisely ii) the dependant data (y data) must be mutually independent iii) the variance of the y data must be independent of the x data. Because a non-linear function is applied to the raw data (i.e. \( k \) is transformed to \( \ln(k) \)), both isothermal and non-isothermal data violate the third requirement. Researchers typically overlook this subtlety. The non-isothermal method violates ii) explicitly. To see this, consider that an error has occurred in measuring the conversion at time t (temperature T). This would result in a statistically acceptable error at time t; however this error would propagate into the next time/temperature intervals t+1, t+2... since the rate is calculated as \((X_{c,t+1} - X_{c,t})/\Delta t\). Thus the data at temperature T+1 is a function of the data at temperature T - violating iii). By contrast, isothermal experiments are statistically independent, therefore statistical conclusions and confidence limits can be calculated for the isothermal method.

4.7 Cyclone Reactor

Isothermal experiments were performed in a cyclone reactor similar to one used to investigate the reduction properties of iron ore fines (Monsen, 1992). Samples of calcine were reacted in batches of 200 mg for up to 1 minute at various temperatures and gas atmospheres. Repeated batches allowed sufficient quantities of pre-reduced calcine to be analyzed.

The unit was built from three pieces of 4" 316 stainless steel bar, each 1" thick. As illustrated in Figure 4.6, a cylindrical reaction chamber was machined in the central plate. A groove was cut from the edge of the plate to enter the chamber tangentially. This plate was then sandwiched between two outer plates. A hole was drilled and tapped into one of the outside plates to accommodate a 1/4" NPT fitting (the central port), while a transition piece connected the groove to a 1/4" NPT fitting (the tangential port). All pieces were originally designed to be screwed together to permit easy disassembly, however excessive gas leakage required that all joints be welded.

The operating principle behind the cyclone reactor is described below. If solids are present in the reaction chamber, a gas flow entering through the tangential port spins the
solids around the outer edge of the reaction chamber (similar to an industrial cyclone) while the gas escapes through the central port. When the gas flow is reversed (i.e. the gas enters the central port and exits from the tangential port) the solids are entrained with the gas flow and discharged from the reactor. This reactor is ideally suited for providing good gas contact with fine particulate (= 50μm) without high solids losses. Because the particulate is rapidly discharged, the residence time can be accurately controlled. The thermal inertia of the reactor compared to the sample calcine ensures that reactions occur isothermally.

The flow-sheet incorporating the cyclone reactor is shown in Figure 4.7. The key items
are: the cyclone reactor and gas pre-heating coil housed in a temperature controlled
furnace; a pneumatic feeder; a brass collection filter holder; four solenoid valves; and two
gas cylinders, one inert and one reducing. The units were inter-connected with 1/4" stainless steel tubing.

A thermocouple (type K) located on the outer skin of the reactor was connected to a
temperature controller, which compared the measured temperature to the desired set-point
and regulated the power input to the furnace heating elements. A thermocouple placed
in the exiting gas stream verified the reaction temperature.

Calcine (nom. 0.5 kg) was charged into a pneumatic feeder, which conveyed samples of
calcine to the reactor’s tangential port in a pulse of nitrogen. The cyclonic action
separated the calcine from the conveying gas, with the latter vented. The sample size was
reliably controlled by varying the duration of the pulse.

During the reaction cycles, reducing gas flowed through the stainless steel pre-heating coil
to the reactor’s tangential port. The partially reacted gas exited the reactor through the
central port and was flared. A fraction of the solids was entrained.

After the required reaction time, reacted calcine was removed from the reactor by
supplying an inert gas (N₂) to the central port. The particulate in the reactor was swept
out in the nitrogen stream, through the tangential port to a brass filter which collected the
solids and vented the gas. The three cycles (charging, reacting and purging) were
controlled by switching four computer controlled solenoid valves.

The cyclone reactor was successively used to characterize the reduction kinetics of
hematite fines (Monsen and others, 1995). It was originally intended that isothermal
reduction rates be measured using the cyclone reactor. Several obstacles prevented its
application in this study. Calcine is not a homogenous mineral, and the cyclone
segregated the material by size. Small, highly oxidized particles were preferentially
eclutriated while coarse silica was preferentially retained. Quantitative detection of iron,
Fe²⁺, Fe³⁺ while distinguishing between sulphide and oxide compounds was also not

4-21
Charging Reactor

Gaseous Reduction

Purging Reactor

Figure 4.7 Flow-sheet incorporating cyclone reactor.
practical.

The microscopic examination of typical particle crossections yields useful qualitative data, such as whether the reaction proceeded topochemically or by a uniform internal reduction. Such qualitative results are valid, notwithstanding the heterogenous nature of the material, because it is possible to visually differentiate between minerals. It is possible to view a large particle which has been sectioned across the equator and label the partial reduction observed "representative" because the reaction time and temperature are precisely known. The cyclone reactor was therefore only used to generate pre-reduced calcine samples for qualitative microscopic analysis and not for quantitative analysis.
5.0 RESULTS - THERMOGRAVIMETRIC ANALYSIS

5.1 General Behaviour of Calcines

Non-isothermal experiments were performed on each calcine in various reducing and inert atmospheres and at different heating rates using the SETARAM thermogravimetric analyzer (TGA) described in Chapter 4. The experimental procedure was described in Chapter 4. Six runs were performed by the vendor of the TGA apparatus in which the off-gases were additionally analyzed using mass spectrometer. These experiments generated qualitative information about the reaction rates of the calcines. The data were also used to yield quantitative information about the reaction rates and activation energies for the reduction of calcines in H₂ and CO atmospheres (Chapter 7 - Kinetics).

Table V.1 and Table V.2, Table VI.31 summarizes the schedule of experiments performed. Selected results are reproduced here, with others appended in Appendix A.
Table V.1 Non-isothermal TGA Experiments - C97 Calcines. Performed by author except as noted.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Calcine</th>
<th>Gas</th>
<th>Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>C97</td>
<td>10% CO</td>
<td>5</td>
</tr>
<tr>
<td>A2</td>
<td>C97</td>
<td>10% CO</td>
<td>10</td>
</tr>
<tr>
<td>A3</td>
<td>C97</td>
<td>10% CO</td>
<td>20</td>
</tr>
<tr>
<td>A4</td>
<td>C97</td>
<td>40% CO</td>
<td>5</td>
</tr>
<tr>
<td>A5</td>
<td>C97</td>
<td>40% CO</td>
<td>10</td>
</tr>
<tr>
<td>A6</td>
<td>C97</td>
<td>40% CO</td>
<td>20</td>
</tr>
<tr>
<td>A7</td>
<td>C97</td>
<td>100% CO</td>
<td>5</td>
</tr>
<tr>
<td>A8</td>
<td>C97</td>
<td>100% CO</td>
<td>10</td>
</tr>
<tr>
<td>A9</td>
<td>C97</td>
<td>100% CO</td>
<td>20</td>
</tr>
<tr>
<td>A10</td>
<td>C97</td>
<td>15% H2</td>
<td>5</td>
</tr>
<tr>
<td>A11</td>
<td>C97</td>
<td>15% H2</td>
<td>10</td>
</tr>
<tr>
<td>A12</td>
<td>C97</td>
<td>15% H2</td>
<td>20</td>
</tr>
<tr>
<td>A13</td>
<td>C97</td>
<td>20% H2</td>
<td>5</td>
</tr>
<tr>
<td>A14</td>
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<td>A19</td>
<td>C97</td>
<td>Ar</td>
<td>5</td>
</tr>
<tr>
<td>A20</td>
<td>C97</td>
<td>Ar</td>
<td>10</td>
</tr>
<tr>
<td>A21</td>
<td>C97</td>
<td>Ar</td>
<td>20</td>
</tr>
</tbody>
</table>

| MS97Ar | C97     | Ar      | 10 | Experiments performed by Setaram, incorporating off-gas analysis by mass spectrometer. |
| MS97H2 | C97     | 100% H2 | 10 |
| MS97CO | C97     | 100% CO | 10 |
Table V.2 Non-isothermal TGA experiments - C92 Calcine. Performed by author, except as noted.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Calcine</th>
<th>Gas</th>
<th>Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bal. N₂</td>
<td>° C/min</td>
</tr>
<tr>
<td>A22</td>
<td>C92</td>
<td>10% CO</td>
<td>5</td>
</tr>
<tr>
<td>A23</td>
<td>C92</td>
<td>10% CO</td>
<td>10</td>
</tr>
<tr>
<td>A24</td>
<td>C92</td>
<td>10% CO</td>
<td>20</td>
</tr>
<tr>
<td>A25</td>
<td>C92</td>
<td>40% CO</td>
<td>5</td>
</tr>
<tr>
<td>A26</td>
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<td>20</td>
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<td>A28</td>
<td>C92</td>
<td>100% CO</td>
<td>5</td>
</tr>
<tr>
<td>A29</td>
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<td>100% CO</td>
<td>10</td>
</tr>
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<td>A30</td>
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<td>15% H₂</td>
<td>5</td>
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<td>A37</td>
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<td>40% H₂</td>
<td>5</td>
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<td>A38</td>
<td>C92</td>
<td>40% H₂</td>
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<tr>
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<td>40% H₂</td>
<td>20</td>
</tr>
<tr>
<td>A40</td>
<td>C92</td>
<td>Ar</td>
<td>5</td>
</tr>
<tr>
<td>A41</td>
<td>C92</td>
<td>Ar</td>
<td>10</td>
</tr>
<tr>
<td>A42</td>
<td>C92</td>
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<td>20</td>
</tr>
<tr>
<td>MS92Ar</td>
<td>C92</td>
<td>Ar</td>
<td>10'</td>
</tr>
<tr>
<td>MS92H₂</td>
<td>C92</td>
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<td>10'</td>
</tr>
<tr>
<td>MS92CO</td>
<td>C92</td>
<td>100% CO</td>
<td>10'</td>
</tr>
</tbody>
</table>

Experiments performed by Setaram, incorporating off-gas analysis by mass spectrometer.

5-3
Figure 5.1 shows that both calcines lost mass when heated in argon. This has been observed by others (Celmer and others, 1987; Zamalloa, 1995) and attributed to gases evolved from: i) decomposition of sulphates, ii) solid state reaction between pyrrhotite and iron oxides, especially hematite and iii) decomposition of complex sulphides, yielding sulphur vapour which reacts with iron oxides to evolve SO₂.

The mass loss for C97 calcine accelerated above 600° C. The mass change was dependant on the heating rate, with the C97 calcine losing 2.2% of its mass when heated to 850° C at 10° C/min and 1.7% when heated at 20° C/min. The C92 started losing mass at a lower temperature (450° C). The mass change curve was characterized by inflections at 550° C and 700° C. This indicated that multiple reactions were responsible for the sample mass loss. The ultimate mass loss was a function of the heating rate, with the calcine losing 4% of its mass when heated to 850° C at 20° C/min and 4.2% when heated at 10° C/min.

To determine which reactions were occurring, calcines were subjected to TGA with the off-gas analyzed by a mass spectrometer. The instrument was tuned to detect SO₂, O₂ and H₂O. The results of this analysis are shown in Figure 5.2. Both calcines show that the mass loss below 500° C involved the evolution of SO₂ only. Mass losses above 600° C showed matching peaks of both SO₂ and O₂, indicative of sulphate decomposition. The C92 sample exhibited two such peaks: a low temperature peak at 540° C and a high temperature peak at 740° C, suggesting that two sulphate species were decomposing. The low temperature peak was absent in the C97 calcine.
Figure 5.1  Mass change when calcines are heated to 850° C in argon: top C92, bottom C97
Figure 5.2: Analysis of gases evolved when calcines heated in Ar: top C92, bottom C97
Dramatic mass changes were observed when the calcines were heated in reducing environments. C97 mass was reduced by 15% when heated in hydrogen at 10° C/min and approximately 14% when heated in CO, although it appeared that reduction had not completed in the latter case. The corresponding mass losses for the C92 calcine were 18% and 17% respectively.

According to Figure 5.3, the mass change curves for hydrogen reduction of C97 calcine was smooth, with significant mass loss occurring above 350° C. Mass loss of the C92 calcine similarly started above 350° C, however the mass loss curve exhibited an inflexion when the mass loss reached 3%. The mass changes for both calcines depended on the heating rate, such that a given mass loss was achieved at higher temperatures when heated at 20° C/min than when heated at 5° C/min.

The evolved gases from reducing calcines in H₂ were analyzed using combined TGA/MS, and the results plotted in Figure 5.4. Both calcines show small peaks in SO₂ at 300° C. The bulk of the mass loss occurred between 400° C and 500° C, coincident with the H₂O peak. At 550° C, the mass loss continued, but at a markedly slower rate. Above this temperature, the mass spectrometer showed that H₂S was evolved. The line marked S²⁺/O₂ indicates that a species having a molecular mass of 32 g/mol was released. In a hydrogen atmosphere the presence of oxygen molecules are unlikely. The ionizing energy of a mass spectrometer is able to split sulphur (denoted S²⁺, molecular mass = 32g/mol) from H₂S molecules. Given that this signal parallels that of the H₂S, it was concluded that elemental sulphur or sulphur radicals were being detected.
Figure 5.3 Mass change when calcines were heated in 40% H₂ at different heating rates: top C92, bottom C97
Figure 5.4 Analysis of gases evolved when calcines heated in 100% H₂: top C92, bottom C97
The mass change when calcines were heated in 100% CO at different heating rates are summarized in Figure 5.5. Significant mass loss in the C97 calcine started at approximately 400° C, and accelerating sharply at 570° C. Similarly, the C92 calcine started to lose mass when the temperature reached 400° C. However in contrast to the C97 calcine, the subsequent mass loss was not smooth, but rather a discontinuity at 3% mass loss. The reduction rate accelerated above 540° C.

Evolved gases from reducing both calcines in 100% CO were analyzed by combined TGA/M.S. and the results plotted in Figure 5.6. Both samples exhibited low temperature releases of SO_{2(0)} and COS_{2(0)} with little attendant mass loss. The major mass losses for both calcines coincided with strong CO_{2(0)} readings. Reduction started at a higher temperature for the C97 (560° C) than the C92 calcine (410° C).

The dependence of the reduction rate on the gas concentrations is summarized in Figure 5.7 and Figure 5.8 (calcines heated to 850° C at 10° C/min). As expected, the reduction rate is directly related to the concentration of the gaseous reductant. The nature of this dependence will be discussed in Chapter 7.
Figure 5.5 Mass change when calcines were heated in 100% CO at different heating rates: top C92, bottom C97
Figure 5.6 Analysis of evolved gases from heating calcines in 100% CO: top C92, bottom C97
Figure 5.7  Mass change when calcines heated at 10° C/min at different H₂ concentrations: top C92, bottom C97
Figure 5.8  Mass change when calcines heated at 10° C/min at different CO concentrations: top C92, bottom C97
5.2 Isothermal Reduction and Re-oxidation

Isothermal reduction and oxidation experiments were performed on the TGA apparatus using the procedure described in Chapter 4 with the following refinements. Figure 5.9 illustrates the experimental procedure. The calcine was heated to the reaction temperature at 10°C/min. When the reaction temperature was reached, the temperature was allowed to equilibrate for typically 5 min. When steady state was reached, auxiliary gas was changed to a reducing gas by turning the 5-way valve.

![Diagram of gas switching in isothermal reduction/re-oxidation experiments](image)

Figure 5.9 Gas switching in isothermal reduction/re-oxidation experiments

When the mass loss in the reducing environment was ostensibly complete, the 5-way valve was switched again and the apparatus flushed with argon. Subsequently, the valve was switched to admit ultra-dry air and the mass gain was recorded. When the oxidation reaction was complete, the valve was switched to argon. By modulating the valve between reducing gas, argon and air the sample was reduced and oxidized again.
These experiments were repeated at different temperatures (See Table V.3 and Table V.4) to provide isothermal reduction and re-oxidation data for the two calcines.
<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Calcine</th>
<th>Gas</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>C97</td>
<td>H2</td>
<td>450</td>
</tr>
<tr>
<td>C3</td>
<td>C97</td>
<td>H2</td>
<td>500</td>
</tr>
<tr>
<td>C4</td>
<td>C97</td>
<td>H2</td>
<td>550</td>
</tr>
<tr>
<td>C5</td>
<td>C97</td>
<td>H2</td>
<td>600</td>
</tr>
<tr>
<td>C6</td>
<td>C97</td>
<td>H2</td>
<td>650</td>
</tr>
<tr>
<td>C7</td>
<td>C97</td>
<td>H2</td>
<td>700</td>
</tr>
<tr>
<td>C8</td>
<td>C97</td>
<td>H2</td>
<td>750</td>
</tr>
<tr>
<td>C9</td>
<td>C97</td>
<td>H2</td>
<td>800</td>
</tr>
<tr>
<td>C12</td>
<td>C97</td>
<td>CO</td>
<td>500</td>
</tr>
<tr>
<td>C13</td>
<td>C97</td>
<td>CO</td>
<td>550</td>
</tr>
<tr>
<td>C14</td>
<td>C97</td>
<td>CO</td>
<td>600</td>
</tr>
<tr>
<td>C15</td>
<td>C97</td>
<td>CO</td>
<td>650</td>
</tr>
<tr>
<td>C16</td>
<td>C97</td>
<td>CO</td>
<td>700</td>
</tr>
<tr>
<td>C17</td>
<td>C97</td>
<td>CO</td>
<td>750</td>
</tr>
<tr>
<td>C18</td>
<td>C97</td>
<td>CO</td>
<td>800</td>
</tr>
<tr>
<td>Exp. #</td>
<td>Calcine</td>
<td>Gas</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>-----</td>
<td>----------------</td>
</tr>
<tr>
<td>C21</td>
<td>C92</td>
<td>H2</td>
<td>500</td>
</tr>
<tr>
<td>C22</td>
<td>C92</td>
<td>H2</td>
<td>550</td>
</tr>
<tr>
<td>C23</td>
<td>C92</td>
<td>H2</td>
<td>600</td>
</tr>
<tr>
<td>C24</td>
<td>C92</td>
<td>H2</td>
<td>650</td>
</tr>
<tr>
<td>C25</td>
<td>C92</td>
<td>H2</td>
<td>700</td>
</tr>
<tr>
<td>C26</td>
<td>C92</td>
<td>H2</td>
<td>750</td>
</tr>
<tr>
<td>C27</td>
<td>C92</td>
<td>H2</td>
<td>800</td>
</tr>
<tr>
<td>C30</td>
<td>C92</td>
<td>CO</td>
<td>500</td>
</tr>
<tr>
<td>C31</td>
<td>C92</td>
<td>CO</td>
<td>550</td>
</tr>
<tr>
<td>C32</td>
<td>C92</td>
<td>CO</td>
<td>600</td>
</tr>
<tr>
<td>C33</td>
<td>C92</td>
<td>CO</td>
<td>650</td>
</tr>
<tr>
<td>C34</td>
<td>C92</td>
<td>CO</td>
<td>700</td>
</tr>
<tr>
<td>C35</td>
<td>C92</td>
<td>CO</td>
<td>750</td>
</tr>
<tr>
<td>C36</td>
<td>C92</td>
<td>CO</td>
<td>800</td>
</tr>
</tbody>
</table>
The mass changes obtained for the isothermal reduction and re-oxidation of calcines in 40% H₂ and 100% CO are plotted in Figure 5.10 and Figure 5.11. The C97 calcine showed little mass loss when heated in argon to 600°C, while the C92 calcine exhibited an approximately 1.8% to 2.0% mass loss. This agrees with the results obtained in 5.1. The reaction rate is the slope of the mass change with time. By comparing the reduction sections of Figure 5.10 and Figure 5.11, it can be seen that at 600°C the reduction of calcines in 40% H₂ proceeded at a higher rate than reduction in 100% CO. It is also apparent that re-oxidation in dry air at 600°C proceeded faster than reduction.

The isothermal mass change profiles are plotted in Figure 5.12 and Figure 5.13. Reduction of both calcines in CO and H₂ was found to accelerate with increased temperature. Reduction in hydrogen was found to be faster than reduction in CO at all temperatures tested between 450°C and 800°C. Reduction of C92 in CO proceeded in two stages: an initial high rate process was followed by a slower process. This was particularly apparent at lower temperatures. This profile typically signifies multiple reactions occurring whether in parallel or in series. The fact that this behaviour was absent from the reduction of C97 indicates that this discontinuity was not caused by the gaseous environment.

The mass change profiles resulting from re-oxidizing the calcines at various temperatures are reproduced in Figure 5.14. The rate at which the calcines gained mass was measured at 7% wt./min. This rate was found to be essentially independent of the calcine, the pre-reducing atmosphere and the oxidation temperature. The rate fell off when the mass change (relative to the un-reduced calcine) was approximately zero, i.e. when the calcine was re-oxidized to approximately its original state. It was supposed that at this stage the oxygen was able to access the sulphide core, resulting in the evolution of SO₂. Thus mass gain from iron oxidation and mass loss from sulphide oxidation were occurring simultaneously.

5-19
Figure 5.10 Isothermal (H\textsuperscript{2}) Reduction and oxidation of calcium at 600°C top C92

- Mass Change [%]

- Temperature

- Mass Change [%]

- Temperature
Figure 5.11 Isothermal reduction (CO) and re-oxidation of calcines at 600° C: top C92, bottom C97
Figure 5.12  Isothermal reduction of calcines in CO-H₂: top C92, bottom C97
Figure 5.13 Isothermal reduction of calcines in 40% H₂: top C92, bottom C97
Figure 5.14 Isothermal re-oxidation of calcines pre-reduced in 40% H₂: top C92, bottom C97
5.2.1 Generation of samples for microscopic study

Since it is unwise to conclude the reaction mechanism based solely upon how the data fit a proposed model's profile (Szekely and others, 1976), polished sections of pre-reduced calcines were prepared. The objective was to identify different iron oxide and iron phases in reduced calcine samples. Optical microscopy was judged to be the best method for this application.

The TGA apparatus was used in the isothermal mode to prepare 50% reduced samples. The isothermal procedure described in Chapter 4 was followed, except that the mass was monitored during the isothermal reduction. When the calcine had lost 7% of its starting mass (representing removal of approximately 50% of the reducible oxygen), the reducing gas was replaced with argon and the sample cooled to room temperature. The reduced powder was epoxy mounted onto glass slides and polished sections prepared.

The cyclone reactor described in Chapter 4 better approximates the conditions in an industrial reactor such as a fluid bed. Calcine introduced into the cyclone reactor are heated to temperature in less than 1 second (cf. 40 minutes in the TGA), react for approximately 1 minute and are cooled to room temperature in less than five seconds (cf. 40 min in TGA). Polished sections of calcines reduced in the cyclone reactor were prepared. Table V.5 summarizes the schedule of microscopy performed.

Figure 5.15 shows the topochemical structure which characterized most of the observed calcines. The shell in the C92 calcine was observed to be uniform in thickness and less porous than the C97 calcine. Figure 5.16 shows that more porous structures result from the oxidation of pyrrhotite particles. The particle in the top micrograph is not as oxidized and retains a sulphide core.

Figure 5.17 is an example of calcine reduced 50% in 40% H₂. The topochemical structure from oxidation remains, i.e. sulphide core surrounded by an oxide shell. The oxide shells themselves are not banded. Micrographs from reducing calcines in CO are reproduced in Figure 5.18 for comparison. Some deposition of carbon on the sample is visible. As with reduction in H₂, the oxide rim does not show a banded structure, indicating that the
Table V.5 Calcines samples prepared for microscopic examination.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Calcine</th>
<th>Gas</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C92</td>
<td>C92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C97</td>
<td>C97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D6</td>
<td>C97</td>
<td>CO</td>
<td>600</td>
</tr>
<tr>
<td>D9</td>
<td>C97</td>
<td>H2</td>
<td>550</td>
</tr>
<tr>
<td>D10</td>
<td>C97</td>
<td>H2</td>
<td>600</td>
</tr>
<tr>
<td>D12</td>
<td>C97</td>
<td>H2</td>
<td>700</td>
</tr>
<tr>
<td>D18</td>
<td>C92</td>
<td>CO</td>
<td>600</td>
</tr>
<tr>
<td>D21</td>
<td>C92</td>
<td>H2</td>
<td>550</td>
</tr>
<tr>
<td>D22</td>
<td>C92</td>
<td>H2</td>
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<td>C92</td>
<td>H2</td>
<td>700</td>
</tr>
<tr>
<td>NH52</td>
<td>C97</td>
<td>CO</td>
<td>500, 20s</td>
</tr>
<tr>
<td>NH62</td>
<td>C97</td>
<td>CO</td>
<td>600, 20s</td>
</tr>
<tr>
<td>NH64</td>
<td>C97</td>
<td>CO</td>
<td>600, 40s</td>
</tr>
<tr>
<td>X29</td>
<td>C92</td>
<td>CO</td>
<td>600, 60</td>
</tr>
</tbody>
</table>
reduction occurred uniformly through the oxide.

Micrographs from the reduction of calcines in the cyclone reactor at 600°C in 100% CO are shown in Figure 5.19. In contrast with Figure 5.18, carbon deposition was not found, probably because the reaction time was much shorter than when the samples were pre-reduced in the cyclone. The oxide shells are prominent, and show no banded structure themselves.
Figure 5.16 Oxidized pyrrhotite particles, top C92, bottom C97. Field of view = 71\mu m x 47.5\mu m
Figure 5.17 Calcines reduced 50% in the TGA at 600°C in 40% H₂:10% CO₂, bottom.

Field of view = 71μm x 47.5 μm

C970.
Figure 5.18 Calcines reduced 50% in the TGA at 600°C in 100% CO: top C92, bottom C97. Field of view = 71μm x 47.5μm.
Figure 5.19 Calcines reduced in the cyclone reactor: 600° C, 60s. Field of view = 71µm x 47.5 µm
5.2.2 \textit{Behaviour of Pre-reduced Calcines in Inert Atmospheres}

To quantify the effect of pre-reduction on furnace emissions (i.e. emissions from reactions between hematite/magnetite and sulphides) the following experiments were undertaken (See Figure 5.20). The TGA apparatus was operated in the non-isothermal mode described in Chapter 4. Calcine samples were heated in a reducing environment until a pre-set temperature was reached (See Table V.6). At this point, argon was substituted for the reducing gas without interrupting the heating rate. The mass change after argon was introduced was assumed to be caused by SO$_2$ evolution from sulphate decomposition or oxide/pyrrhotite reactions described earlier, and approximates the behaviour of the pre-reduced calcines in the calcine banks.

The results are plotted in Figure 5.21 and Figure 5.22.

![Figure 5.20](image-url)
Table V.6  Schedule of experiments to determine effect of pre-reduction on SO$_2$ evolution.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Calcine</th>
<th>Gas</th>
<th>Temperature ° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>C97</td>
<td>CO</td>
<td>525</td>
</tr>
<tr>
<td>E2</td>
<td>C97</td>
<td>CO</td>
<td>560</td>
</tr>
<tr>
<td>E3</td>
<td>C97</td>
<td>CO</td>
<td>600</td>
</tr>
<tr>
<td>E4</td>
<td>C97</td>
<td>CO</td>
<td>640</td>
</tr>
<tr>
<td>E5</td>
<td>C97</td>
<td>H2</td>
<td>400</td>
</tr>
<tr>
<td>E6</td>
<td>C97</td>
<td>H2</td>
<td>430</td>
</tr>
<tr>
<td>E7</td>
<td>C97</td>
<td>H2</td>
<td>460</td>
</tr>
<tr>
<td>E8</td>
<td>C97</td>
<td>H2</td>
<td>490</td>
</tr>
<tr>
<td>E9</td>
<td>C92</td>
<td>CO</td>
<td>460</td>
</tr>
<tr>
<td>E10</td>
<td>C92</td>
<td>CO</td>
<td>500</td>
</tr>
<tr>
<td>E11</td>
<td>C92</td>
<td>CO</td>
<td>540</td>
</tr>
<tr>
<td>E12</td>
<td>C92</td>
<td>CO</td>
<td>580</td>
</tr>
<tr>
<td>E13</td>
<td>C92</td>
<td>H2</td>
<td>400</td>
</tr>
<tr>
<td>E14</td>
<td>C92</td>
<td>H2</td>
<td>430</td>
</tr>
<tr>
<td>E15</td>
<td>C92</td>
<td>H2</td>
<td>460</td>
</tr>
<tr>
<td>E16</td>
<td>C92</td>
<td>H2</td>
<td>490</td>
</tr>
</tbody>
</table>
Figure 5.21  Effect of pre-reduction in H₂ on smelting furnace SO₂ emissions: top C92, bottom C97.
Figure 5.22  Effect of Pre-reduction in CO on smelting furnace SO\(_2\) emission: top C92, bottom C97
5.2.3 Sources of Error

Three sources of error were associated with the thermogravimetric equipment: thermocouple reading; mass reading; reducing gas composition. In the mathematical treatment, the sample mass was used to determine both the conversion and the reaction rate during the course of the experiment. The sensitivity of the model parameters on signal modelling errors has been determined.

Temperature Error

The sample temperature was inferred from a type 'K' thermocouple positioned adjacent to the sample in the furnace. Reducing environments are corrosive to all types of thermocouples and may cause drifting in the signal or brittle fracture (Powell and others, 1975). The calibration of the furnace thermocouple was periodically checked by repeating a standard experiment (C97 in Ar at 10° C/min) and comparing the mass loss profile to

Figure 5.23 Effect of temperature error on rate constant determination: based on non-isothermal TGA - C97, 10° C/min, 40% H₂
previous runs. On one occasion the mass loss profile was shifted by three degrees after which the thermocouple was replaced. On two occasions the thermocouple fractured. When the thermocouple was replaced, the last completed experiment was repeated. On these occasions the results showed that the thermocouple had not drifted significantly prior to fracturing.

The effect of temperature measurement errors (+−5° C) when analyzing the hydrogen reduction of C97 was estimated, and is plotted in Figure 5.23. The activation energy is not affected, however the log of the pre-exponential constant would change by approximately 0.1 ° C. Thus a 5° C measurement contributes to a 10% error in the determination of the rate constant.
Conversion Error

![Graph showing the effect of weight bias on rate constant determination based on non-isothermal TGA, C97, 10°C/min, 40% H2.](image)

Figure 5.24 Effect of weight bias on rate constant determination: based on non-isothermal TGA, C97, 10°C/min, 40% H2

The conversion was calculated based on the initial sample mass, the recorded mass loss and the ultimate mass loss. The weighing mechanism on the TGA had a reported detection limit of 10μg, i.e. it could detect a fractional change of 2 \times 10^{-3}%. Repeated experiments under identical conditions revealed a reproducibility of the author’s experimental procedure of 0.5%. The effect of an 0.5% bias in the reported mass on the analysis the reduction of C97 in Figure 5.24. Underestimating the conversion causes an error of 10% in the reported activation energy. The effect on the pre-exponential constant was more dramatic, however this observation is somewhat artificial. The pre-exponential constant is the value of the rate constant at an infinite temperature, i.e. above industrial conditions. More usefully, an 0.5% bias in the measured mass leads to an error of 18% at temperatures between 300°C and 800°C.
Rate of Conversion Error

The reaction rate (\(dx/dt\) in Equation 4.6) was calculated numerically from the conversion data. A one way bias in conversion does not propagate through to its first derivative. The effect of introducing an alternating bias to the mass readings (i.e. the \(i\)th reading is \([w_i + b]\); the next reading is \([w_{i+1} - b]\) where \(w\) is the recorded mass and \(b\) is a bias) is shown in Figure 5.25. The alternating bias was estimated by analyzing the fluctuations in the reported mass of a sample placed in the TGA under standard conditions (50mg sample, 5\(\text{ml/h}\) gas flow-rate argon). The data at 50\(^\circ\)C and 850\(^\circ\)C revealed that the maximum fluctuation in mass was 0.02%. Higher fluctuations would be expected in the event that the sample were actually undergoing a mass loss reaction, therefore the effect of an 0.2% fluctuating bias was calculated. Experimentally, this scenario is most unlikely to occur - that is the bias is more likely to be randomly distributed. Therefore the expected error is estimated to be 5%.

Figure 5.25 Effect of alternating bias on rate constant determination based on non-isothermal TGA, C97, 10\(^\circ\)C/min, 40% H\(_2\)

5-40
Reducing gas mixtures with a certified analyzed reducing gas content of 2% relative were received from a reputable supplier (Cannox). A 40% H₂ mixture was certified to contain between 39.2% vol. and 40.8% vol. hydrogen. Applying the more pessimistic relative error of 5% to the analysis gave the results plotted in Figure 5.26. The error in rate constant is less than 2%.

Figure 5.26 Effect of error in reducing gas strength on non-isothermal thermogravimetric analysis.
6.0 GENERAL BEHAVIOUR OF CALCINES

6.1 Heating Calcines in Inert Atmospheres

The mass loss profiles for calcines heated to 850° C at 10° C/min in Ar are re-plotted in Figure 6.1. The C97 calcine sample lost a negligible amount of mass until heated above 600° C. By the end of the experiment, the sample had lost 2.2% of its starting mass. By contrast, the C92 sample started losing mass when the temperature reached 100° C. The mass loss accelerated sharply at about 400° C, and again at 700° C. Ultimately, the sample lost 4.2% of its mass when heated in an inert atmosphere.

![Figure 6.1 Weight loss profiles of calcine heated to 850° C at 10° C/min in argon](image)

Figure 6.2 shows the data re-plotted as the differential thermogravimetric trace versus temperature (dw/dt vs T where w is the percent mass change). The results from the off-gas analysis are included on the figure. In the C97 calcine, a valley in the DTG trace coincides with a peak in the SO₂ trace between 300° C and 550° C. The major DTG valley and SO₂ peak starts at 550° C and continues to 850° C at which point the
Figure 6.2 Rate of mass loss and evolution of SO$_2$ when calcines heated in Ar: top C92, bottom C97
experiment was terminated. A peak in the O₂ reading was observed between 650° C and also continued until 850° C.

The corresponding curve for the C92 calcine is more complex, with peaks/valleys starting at 250° C, 360° C, 490° C and 560° C. Oxygen evolution accompanied the 490° C and 560° C peaks. This signifies that four reactions were occurring when the C92 calcine was heated in an inert environment.

Table VI.1 Equilibrium data for calcine reactions evolving a gas (From HSC)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pₑ [atm.]</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>FeS + 10Fe₂O₃ = 7Fe₃O₄ + SO₄</td>
<td>382</td>
</tr>
<tr>
<td>½Ni₃S₂ + 10 ½Fe₂O₃ = 1 ½NiO + 7Fe₃O₄ + SO₄</td>
<td>518</td>
</tr>
<tr>
<td>Cu₂S + 9Fe₂O₃ = Cu₄O + 6Fe₃O₄ + SO₂</td>
<td>767</td>
</tr>
<tr>
<td>FeS + 3Fe₃O₄ = 10FeO + SO₂</td>
<td>1 036</td>
</tr>
<tr>
<td>1/3 Fe₅(SO₄)₃ = 1/3 Fe₄O₃ + 1 SO₂ + 0.5 O₂ ∗</td>
<td>636</td>
</tr>
<tr>
<td>2CuSO₄ = CuO.CuSO₄ + SO₂ + 0.5 O₂ ∗</td>
<td>702</td>
</tr>
<tr>
<td>NiSO₄ = NiO + SO₂ + 0.5 O₂ ∗</td>
<td>865</td>
</tr>
</tbody>
</table>

* In equilibrium with SO₂ + ½ O₂ = SO₃

Mass losses exhibited in an inert environment are due to reactions releasing gaseous products. Table VI.1 summarizes the temperatures at which some reactions involving calcine generate a pressure of 0.1 and 1.0 atm in an otherwise inert atmosphere. (These pressures were chosen since they approximate the conditions which would respectively lead to measurable and significant reaction rates). The different mass loss profiles
displayed by C92 and C97, especially below 600° C, may be explained by observing that
the C92 calcine contained more hematite than the C97 calcine. From Table VI.1 it can
be concluded that hematite and pyrrhotite combine to evolve SO₂ at quite low
temperatures. The corresponding reaction between magnetite and pyrrhotite is
thermodynamically favourable above 1000° C. Studies which compared the evolution of
SO₂ from hematite/pyrrhotite and magnetite/pyrrhotite mixtures showed that the hematite
mixture exhibited a sharp evolution profile at 450° C, while the magnetite mixture showed
a more gradual mass loss profile (Clemer and others, 1987). In that study, 1:1 mass ratios
were used which did not account for the reaction stoichiometries in Table VI.1. (a 10:1
mol ratio of Fe₂O₃:FeS is equivalent to an 18:1 mass ratio).

The equilibrium gas pressure P₃O₈ + SO₂ + O₂ for the decomposition of iron sulphate reaches
0.1 atm. at 636° C and 1 atm. at 730° C. It is concluded that the significant mass changes
exhibited by both calcines at about 600° C were attributed to the decomposition of
sulphates. The twin peaks shown by the C92 calcine indicate that two sulphate species
were present.

From the evidence gathered when the calcines were heated in an inert environment at
10° C/min, it is proposed that the reactions summarized in Figure 6.3 occur.
Figure 6.3 Reactions of calcine in inert atmospheres

6.2 Heating Calcines in Hydrogen

When the calcines were heated in a 40%H\textsubscript{2}, Bal. N\textsubscript{2} atmosphere, the mass loss profiles in Figure 6.4 were observed. The profile from heating the C97 calcine in argon is included for reference. The graph shows that both calcines exhibited dramatic mass losses starting at relatively low temperatures, 400° C for C97 and 300° C for C92. The ultimate mass losses exhibited by C92 and C97 were 18% and 15% respectively. The knee in the mass loss profile for the C92 calcine was attributed to the reduction of hematite, which was substantially higher in the C92 calcine than the C97. This is consistent with previous researchers who have found that the reduction of hematite proceeds rapidly at these temperatures (Turkdogan and Vinters, 1971a). The reduction rate fell off at 600° C. It was concluded that this represents the point at which the reducible oxygen had been removed and that further mass losses are due to the reduction of metal sulphides to the metal.

Differential thermogravimetric data and off-gas concentrations are plotted together in
Figure 6.4 Weight loss profiles of calcine heated to 850° C at 10° C/min in 40% H₂

Figure 6.5. Both calcines exhibit a major valley in the DTG trace between 300° C and 600° C which coincides with the peak in the H₂O analysis. This was concluded to be a result of the reduction of iron oxides. Both calcines evolved SO₂ between 250° C and 300° C. This reaction was less significant in the C97 calcine and there was little attendant mass loss. Both calcines evolved significant levels of H₂S starting at 500° C and increasing with temperature.

Metal sulphates are known to evolve SO₂ when reduced eg. (Sohn and Kim, 1985). The standard Gibbs energies for the reduction of iron, nickel and copper sulphates (Table VI.2) show that the reduction of iron, nickel and copper sulphate yielding SO₂ are highly favoured at 300° C. Kinetically, hydrogen reduction of copper sulphate is known to proceed rapidly between 250° C and 450° C (Sohn and Kim, 1985), (Jacinto and others, 1983). Experiments were performed to further quantify the rates at which pure copper sulphate (99%), nickel sulphate (99.99%) and iron (II) sulphate (99%) were reduced in hydrogen. The TGA apparatus was used to first dry 50mg samples in argon at 200° C
Figure 6.5  Rate of mass loss and evolution of H₂O when calcines heated in H₂
Table VI.2 Standard Gibbs energies for the reduction of sulphates in H₂ and CO at 300°C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^° ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{3} \text{Fe}_2(\text{SO}_4)_3 + 2\text{R} = 2\text{RO} + \text{SO}_2 + \frac{2}{3} \text{Fe} )</td>
<td>( \text{R=CO} )</td>
</tr>
<tr>
<td>FeSO₄ + 2R = 2RO + SO₂ + Fe</td>
<td>-112</td>
</tr>
<tr>
<td>NiSO₄ + 2R = 2RO + SO₂ + Ni</td>
<td>-100</td>
</tr>
<tr>
<td>CuSO₄ + 2R = 2RO + SO₂ + Cu</td>
<td>-208</td>
</tr>
</tbody>
</table>

until no further mass loss was observed. After cooling to room temperature, 40% hydrogen was introduced through the auxiliary gas inlet and the mass loss recorded at a constant heating rate of 10°C/min.

As shown in Figure 6.6, the sample masses of all tested sulphates dropped precipitously at relatively low temperatures. Copper sulphate was reduced suddenly at 330°C; nickel sulphate lost mass slowly between 340°C and 430°C (perhaps losing water of hydration) at which point the reduction rate accelerated; similarly, iron (II) sulphate lost mass between 250°C and 300°C, and accelerated sharply at 460°C. The experiments were halted before reduction was complete and the partially reduced product cooled under argon. To determine if the sulphates were reduced via the sulphide, the partially reduced product was added to 50ml of 1M solution HCl and the evolution of hydrogen sulphide tested. Only in the case of NiSO₄ was H₂S detected. It was therefore concluded that the SO₂ peaks at 300°C in Figure 6.5 were due to the reduction of metal sulphates to the metal, possibly with some nickel sulphide formed.

A pure hydrogen+inert atmosphere can thermodynamically reduce any metal oxide or sulphide to the metal, however thermal analysis of various metal sulphides in hydrogen revealed that the reduction of simple metal sulphides (eg. Fe₄S, PbS, ZnS) did not appreciably occur below 900°C (Gallabah and others, 1994). Reduction of pyrite to
Figure 6.6 Reduction of CuSO₄, NiSO₄, and FeSO₄ in H₂

Pyrrhotite started at about 600° C. Chalcopyrite was reportedly reduced to elemental copper via cubanite according to:

\[ 2CuFeS₂ + H_2(g) = CuFeS₃ + Cu + H_2S(g) \]  \hspace{1cm} (6.1)

and:

\[ CuFeS₃ + 3H_2 = 2Fe + Cu + 3H_2S \]  \hspace{1cm} (6.2)

The first reaction proceeded gradually at about 500° C, however meaningful evolution of H₂S did not occur until 900° C (Gaballah and others, 1994).

The calcine samples in the current research had been produced by fluid bed roasting concentrate at Falconbridge (Zamalloa, 1995). Complex sulphides were first thermally decomposed, for example pentlandite was roasted according to:
\[ \begin{align*}
N_{0.5}Fe_{0.5}S_8 + \frac{2x}{3}O_{2(g)} &= Fe_{(0.5-x)}Ni_{0.5}S_8 + \left( \frac{x}{3} \right)Fe_3O_4 \quad (6.3) \\
Fe_{(0.5-x)}Ni_{0.5}S_8 + \left( \frac{79.5-4x}{6} \right)O_{2(g)} &= 4.5NiO + \left( \frac{4.5-x}{3} \right)Fe_3O_4 + SO_{2(g)} \quad (6.4)
\end{align*} \]

A fluidized bed is an example of a well mixed reactor. For a theoretical well-mixed reactor, the residence time distribution is given by (Levenspiel, 1972):

\[ E = \frac{1}{\tau_{\text{resid}}} e^{-\frac{t}{\tau_{\text{resid}}}} \quad (6.5) \]

where \( \tau_{\text{resid}} \) is the mean residence time in the reactor. The fraction of the product exiting such a reactor before time \( t \) is given by the following integration:

\[ F(t) = \int_0^t \frac{1}{\tau_{\text{resid}}} e^{-\frac{t}{\tau_{\text{resid}}}} \, dt \quad (6.6) \]

If the mean residence time of solids in the roaster is 5 minutes, then equation (6.6) predicts that approximately 10% of the feed exits the reactor in the first thirty seconds, i.e. the calcine inevitably contains some under-roasted concentrate. Analysis of the Falconbridge roaster is complicated by the fact that there are two product streams: fine material elutriated with the off-gas, and coarse material exiting through the bed discharge. Nevertheless this type of analysis has been used to explain the presence of un-decomposed pyrrhotite, pentlandite and chalcopyrite in the calcine (Zamalloa, 1995).

Heating complex sulphides in hydrogen likely results in the evolution of hydrogen sulphide below 900 °C. It is concluded that the increased evolution of \( \text{H}_2\text{S} \) above 500 °C was due to the direct reduction of under-roasted concentrate necessarily present in the calcine.

Figure 6.7 is proposed to summarize the reactions which the calcines undergo when they
are heated in a 40% hydrogen environment at 10°C/min.

Figure 6.7 Summary of reactions when calcine is heated to 850°C in H₂

6.3 Heating Calcines in Carbon Monoxide

The mass loss profiles of calcines reduced in CO are re-plotted in Figure 6.8. When the temperature of the C92 calcine reached 500°C (corresponding to a mass loss of ±2.5%) the graph flattens out before continuing downward. This behaviour had also been observed in the hydrogen reduction and was attributed to the higher hematite content of C92 calcine which is easily reduced.

When the temperatures reached 600°C reduction became vigorous. At the end of the experiment C92 and C97 had lost 16.5% and 14% of their respective initial masses. It was obvious that reduction would have continued had the experiment not been terminated at 850°C. Comparing this with the profiles in H₂, it was concluded that reduction had
not proceeded as far, and that the reduction of metal sulphides to metal and COS, had probably not occurred to a significant extent.

The rate of mass change and the concentration of CO₂, COS and SO₂ are plotted versus temperature for calcines heated at 10° C/min in 100% CO in Figure 6.9. Gas analysis reported that COS was evolved between 200° C and 500° C, although there was little attendant mass change in this region. As with reduction in hydrogen, SO₂ was evolved at low temperatures. This peak was less dramatic in the C97 calcine than the C92 calcine. The major valley in the DTG trace occurred at 500° C and was coincident with a rise in measured CO₂. The C97 calcine showed a minor valley at 350° C followed by a more substantial valley at 500° C. The valley in the C92 calcine at 350° C was more pronounced than in the C97 calcine. It is known that the reduction of hematite to iron proceeds via magnetite (Monsen and others, 1996). It was therefore concluded that the valley at 350° C was due to the reduction of hematite to magnetite and the valleys at 500° C represented the subsequent reduction of magnetite to iron.
Figure 6.9 Analysis of evolved gases from heating calcines in 100% CO.
Table VI.2 showed that the CO reduction of sulphates is also thermodynamically favoured at 300° C. It is therefore concluded that the SO₂ release at 300° C-350° C resulted from the reduction of sulphates in the calcine and that the smaller peak in the C97 calcine was due to that calcine's lower sulphate assay.

It was concluded that the direct reduction of sulphides by CO to COS was responsible for the COS peaks at low temperatures. It was also noted that the ultimate mass change when calcines were heated in CO was less than when heated in H₂. This could result from either incomplete iron oxide reduction in CO or to increased sulphide reduction in H₂. COS is a highly toxic gas, and sulphur removal in this form is not industrially desirable.

**Figure 6.10** Reactions undergone by calcine when heated to 850° C in CO

From the evidence above, the diagram in Figure 6.10 is proposed to summarize the
reactions occurring when the calcines were heated in CO at 10° C/min.

Figure 6.11 illustrates the degree to which SO₂ evolution in the furnace can be controlled by gaseous pre-reduction. This is accomplished primarily by reducing the hematite and magnetite content of the calcine before they react with sulphide minerals.
Figure 6.11 Comparison of SO$_2$ evolution from calcines heated in Ar, H$_2$ and CO: top C92, bottom C97
7.0 **KINETIC STUDY OF GASEOUS REDUCTION OF CALCINES**

7.1 **Suitability of Uniform Internal Reduction Model**

It was shown in Chapter 3 that a plot of the amount of solid unconverted against time on a logarithmic scale would be linear for a first order uniform internal reduction process. Further it was shown that the slope of the line is proportional to the reaction rate constant and to the gaseous thermodynamic driving force, i.e.

\[-\ln(1 - \chi) = k \left( C^* - C^{\infty} \right) t \]  \hspace{1cm} (7.1)

![Graph showing isothermal reduction of C97 in H2 at 500°C, 550°C, 600°C, and 650°C](image)

**Figure 7.1** Isothermal reduction of C97 in H2 at 500°C, 550°C, 600°C, and 650°C

The data for the isothermal reduction of C97 in H2 (derived from the isothermal reduction-reoxidation experiments described earlier and plotted in Figure 7.1) show that the family of curves are straight lines. The lines get steeper with increased temperature, signifying that, as expected, the reaction rate increased with temperature. It was expected that the lines would pass through the origin, however this was not the case at higher
temperatures. Heating the calcine in argon causes some weight loss (i.e. oxygen removal). Therefore the calcine was already partially reduced before hydrogen was introduced into the TGA apparatus. The slopes of the lines allow the rate constants to be calculated, which will be performed in Section 7.3.1. Similar results were obtained using the C92 calcine. Deviation from linearity at high conversions may be due either to experimental error or to a change in the reaction mechanism, e.g. where weight loss was dominated by reduction of complex sulphides.

It is generally unwise to conclude the reaction mechanism based solely on how the data fit a proposed model's profile (Szekely and others, 1976). Polished sections of partially reduced calcines generated in the TGA apparatus and by the cyclone reactor were studied microscopically (Chapter 5). All samples showed sulphide cores surrounded by iron oxide rims. The oxide rims were essentially homogenous, i.e. absent of any banded or topochemical structure. Fleures of iron were dispersed randomly through the oxide rim. These observations are characteristic of a uniform internal reduction process.

It was therefore deemed reasonable to treat the reduction of calcine in H₂ as a uniform internal reduction. This agrees with previous studies into the reduction of iron oxide dusts eg. (Turkdogan and Vinters, 1971a), (Monsen and others, 1995).

7.2 Non-isothermal Thermogravimetric Reduction of Calcines

It was shown in Chapter 3 that a first order model with an Arrhenius form of rate constant can be tested by plotting the reaction rate constant, calculated from:

\[ k = \frac{dX/dt}{(1-X)(C_{A}^o - C_{A}^{eq})} \]  \hspace{1cm} (7.2)

on a log scale against the inverse of the absolute temperature. In this equation A is the gaseous reductant and \((C_{A}^o - C_{A}^{eq})\) is the concentration difference between the bulk concentration and the equilibrium concentration. The dependence of the concentration difference with temperature was developed in Chapter 4.0. A linear result confirms that a first order model with an Arrhenius form of rate constant describes the data. Calcine
samples were heated in 40%, 20% and 15% H₂ (Bal. N₂) at 5, 10 and 20º C/min (Chapter 5.0). Typical mass change profiles were plotted and discussed in section 5.1.

To convert mass loss to a percent conversion, it was necessary to estimate the ultimate mass lost when the calcines were fully reduced. Values of 18.5% and 16% were obtained when C92 and C97 calcines were heated in 40% H₂ at 5º C/min.

7.2.1 Hydrogen

Rate constants were derived from the mass change data using equation (7.2) and Figure 4.4. The results for calcines reduced in 40% H₂ at different heating rates are plotted as ln(kₜ) versus 1/T in Figure 7.3.

Each experiment yielded an approximately linear relationship up to a conversion of 60%, after which the reaction rate constant was less than the predicted value. Possible reasons for this behaviour were: i) a shrinking core mechanism had replaced UIR as the controlling mechanism, and diffusion through the product layer was rate controlling; ii) a mixed control mechanism had replaced UIR, and diffusion through the porous reactant was a significant resistance; iii) the solid reactant had been consumed. The first two reasons may be eliminated since the apparent activation energies for these mechanisms are positive (= 18 kJ/mol for (i), Eᵣ/2 for (ii) where Eᵣ is the activation energy of the intrinsic reaction) and hence would still have a negative gradient on the graph. In addition, the rate constant maxima for all experiments coincided with conversions between 60% and 70%. It was therefore concluded that at higher conversions the oxides had been reduced and that continuing mass loss was due to the reduction of another species. Reduction of complex sulphides has already been mentioned in this respect.

As can be seen on both Figure 7.2 (top) and Figure 7.3 (top), the linear sections of the curves overlap. This implies that the rate constant is independent of the heating rate in this region. The shifting of the linear sections with heating rate shows that, as expected, more oxides were reduced at low temperatures when lower heating rates were used.

The activation energies for reduction of both calcines, determined from the slopes of the
Figure 7.2  C92 reduced in H₂ at different heating rates: top Arrhenius plot; bottom conversion
Figure 7.3  C97 reduced in H₂ at different heating rates: top Arrhenius plot; bottom conversion
Arrhenius plots, were similar. The Arrhenius plot for the C97 calcine was linear at low
temperatures, while the C92 calcine deviated significantly at low temperatures and
conversions. The deviation was more dramatic at a heating rate of 20°C/min. In Chapter
3.0 it was shown that substances undergoing parallel reactions display this behaviour
when analyzed using the differential method. The chemical assays of the calcines
reported in Chapter 4 revealed that the hematite/magnetite weight ratios were
approximately 8:1 and 1:1 for the C92 and C97 calcines respectively, and that the C92
sample contained more sulphate. Reduction of hematite and sulphates were earlier shown
to proceed at low temperatures. It was concluded that the low temperature deviation of
the C92 calcine was due to secondary reactions such as the reduction of hematite.

To determine the order of the reaction with respect to hydrogen concentration, calcines
were heated at 10°C/min in 15%, 20% and 40% H₂. A first order relationship with
respect to the gas phase was proposed and tested by plotting the weight loss profiles on
Arrhenius diagrams (Figure 7.4). The overlapping nature of the rate constant at different
gas concentrations confirms the hypothesis. This was especially apparent for the C97
calcine, although the slopes for the C92 calcine appeared to vary with the gas
concentration. Possible reasons for the discrepancy in the C92 calcine are: i)
contamination of the results by secondary reactions ii) different behaviour of magnetite
when reduced from hematite.

Extensive non-isothermal analysis on each calcine was performed (See Table V.1 and
Table V.2, Table VI.31). The linear portions of the Arrhenius plots were collected and
plotted together in Figure 7.5. Linear regression was used to fit the following lines
through the linear portions of all data:

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

subject to

\[ 300°C < T < 700°C \]

\[ 0.1 < X < 0.7 \]

Where X is the fraction converted. For the C97 calcine, \( A=9380\text{mol}^{-1}\text{s}^{-1} \), \( E_r=63600 \)]
Figure 7.4 Non-Isothermal Arrhenius plot of calcines in 15%, 20%, 40% H₂. Top C92; bottom C97.
Figure 7.5 Linear portions of Arrhenius plots on a single graph: top C92, Bottom C97
J/mol and for the C92 calcine, $A=36000$ J/mol-s, $E_a=55400$ J/mol, and $R=8.314$ J/mol-K. The complete rate equations were therefore established:

$$\frac{dX/dt}{(1-X)} = \left( A e^{-E_a/RT} \left( C_{H_2}^* - C_{H_2}^{eq} \right) \right) \quad (7.4)$$

with the above values and the constraints according to (7.3).

There would appear to be little agreement between the activation energies and pre-exponential constants for the two calcines. However, when both equations are plotted on a single graph between 400° C and 700° C, the two relationships are, in fact, in close agreement. The largest discrepancy between the two relationships occurs at low temperatures, while at 700° C the agreement is very close ($k=3.9$ versus 4.5 ℓ/s·mol).

It has been calculated that the apparent activation energy for a gaseous diffusion controlled process at these temperatures lies between 18 and 23 kJ/mol. The observed activation energies are a factor of three higher, from which it is concluded that the reduction of calcine in the thermogravimetric analyzer was not controlled by a diffusion process (gaseous mass transfer or diffusion of gases through the product). A wide range of activation energies for the reduction of iron oxides has been reported in the literature, of which Table VII.1 is a sample. The values determined in this research are well within the reported range.

For final verification of the accuracy of these rate constant expressions, the weight loss profiles expected from heating calcines in $H_2$ at two heating rates and two gas concentrations was calculated and compared to the experimentally measured profiles in Figure 7.6. The graphs show that the calculated profiles are in excellent agreement up to a temperature of 600° C and a conversion of 60%. Better agreement was observed at higher heating rates.
Table VII.1  Activation energies for the hydrogen reduction of metal oxides

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>$E_a$ (kJ/mol)</th>
<th>Ref.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>17.6</td>
<td>Themelis, 1963</td>
<td>Literature Survey</td>
</tr>
<tr>
<td>FeO</td>
<td>19.9-41.8</td>
<td>El-Geassy, 1994</td>
<td>TGA</td>
</tr>
<tr>
<td>FeO</td>
<td>42.7</td>
<td>Bustnes, 1997</td>
<td>TGA</td>
</tr>
<tr>
<td>C92 Calcine</td>
<td>53.1</td>
<td>This Work</td>
<td>Iso TGA</td>
</tr>
<tr>
<td>C92 Calcine</td>
<td>55.4</td>
<td>Non-iso TGA</td>
<td></td>
</tr>
<tr>
<td>C97 Calcine</td>
<td>56.8</td>
<td>Iso TGA</td>
<td></td>
</tr>
<tr>
<td>C97 Calcine</td>
<td>63.6</td>
<td>Non-iso TGA</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>60.6</td>
<td>Towhid &amp; Szekely, 1981</td>
<td>TGA</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>60.7</td>
<td>Moinpour, 1988</td>
<td>TGA</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>74.4</td>
<td>Et Tabirou, 1988</td>
<td>SEM</td>
</tr>
<tr>
<td>FeO</td>
<td>80.3</td>
<td>Calc. from Turkdogan, 1972</td>
<td>TGA</td>
</tr>
<tr>
<td>FeO</td>
<td>159</td>
<td>Landler, 1966</td>
<td></td>
</tr>
</tbody>
</table>

7.2.2  Carbon Monoxide

It has been shown that the reduction of calcines in CO proceeds at a slower rate than in H$_2$. Reduction of iron oxides by CO is also known to be much slower than reduction by H$_2$, although no clear explanation has been given (Bodsworth and Hall, 1972). Given that uniform internal reduction was observed in hydrogen, uniform internal reduction was likewise expected for the reaction in CO.

Non-isothermal analysis of calcines were performed in CO+inert reductants following the procedure described in 7.2.1. The rate constant was calculated from the weight loss data (described above) and plotted in an Arrhenius form in Figure 7.7 and Figure 7.8. As expected, the value of the rate constant was orders of magnitude lower than for reduction.
Figure 7.6  Comparison between actual and calculated weight loss profiles: top C92; bottom C97
Figure 7.7  C92 reduced in CO at different heating rates: top Arrhenius plot; bottom conversion
Figure 7.8  C97 reduced in CO at different heating rates: top Arrhenius plot; bottom conversion.
in hydrogen (cf. 1.3 \( \text{mol-s} \) vs. 25 \( \times 10^{-3} \text{mol-s} \) at 560° C). In contrast to hydrogen, reduction in CO at different heating rates did not produce families of overlapping curves. Each reduction curve consisted of two approximately linear segments - a low temperature regime from 500° C to 600° C; and a high temperature regime above 600° C. The "knees" in the curves were especially pronounced at lower heating rates. The rate constant was found to be a function of the heating rate, which would not be predicted by the uniform internal reduction model.

The sharp decline in the rate constant for oxygen removal from the calcines may be caused by three factors: i) reduction is not first order with respect to the CO concentration ii) wustite becomes a stable phase above 570° C and/or iii) carbon was deposited on the pore surfaces according to the Naumann reversion reaction. While i) may or may not be the case, this would not explain the deviations arising from the reduction in 100% CO at different heating rates. Microscopic examination of polished sections of partially reduced calcines showed graphite deposition on the pore surfaces.

Experiments were performed with all permutations of heating rate (5° C/min, 10° C/min and 20° C/min) and gas strength (100% CO, 40% CO, 10% CO). All runs are graphed on the same Arrhenius plots (Figure 7.9). The data are very scattered and clearly do not fall upon a common curve. The knees in the reaction rates at approximately 600° C are clearly displayed. One profile indicates that the reaction rate was almost invariant with temperature above 600° C, i.e. the reduction reaction has a very small activation energy.

Reduction in a CO + inert atmosphere can result in a mass gain due to the carbon deposition reaction favoured at low temperatures:

\[
2CO_{(g)} = C_{(s)} + CO_{2(g)}
\]  

(7.5)

Alumina crucibles become noticeably discoloured after several trials in CO. To measure the effect of carbon deposition of the results, a 50mg sample of calcined alumina was heated in 100% CO to 850° C in the TGA apparatus and the mass gain profile recorded. The results showed that the amount of carbon deposited in a single trial could not be detected by the balance. Since elemental iron and nickel are known to catalyse the
Figure 7.9  Arrhenius plots of CO reduced calcines: top C92; bottom C97
sooting reaction (Bogdandy and von Engell, 1972) and since carbon is soluble in iron, metal filings were heated in 20% CO at 10° C/min on the TGA apparatus. Again no discernible mass gain was recorded, however examination of the product filings showed that some sintering had occurred. Carbon could cause sintering by locally dissolving and lowering the metal's melting point. It was concluded that the mass loss profiles for experiments in 100% CO did not require a correction to account for the mass of carbon sooted out, however the fact that some carbon deposition had occurred may contaminate the results of the kinetic analysis.

It was concluded that reduction of calcines in CO does not follow a first order uniform internal reduction model. The deviation was attributed to i) significant reduction occurred at temperatures at which wustite is stable and ii) deposition of carbon on the pore walls interfered with the adsorption of CO.

7.3 Isothermal Studies

A first order model in hydrogen had already been confirmed by plotting the weight loss data in the form of ln(1-X) versus time and observing a family of straight lines (See 7.2.1). According to Equation 4.4, the slope of each line is the product of the rate constant \( k_r \) and the thermodynamic driving force \( (C_A^\circ - C_A^\text{eq}) \). The variation of the thermodynamic driving force with temperature was established in Chapter 4.

7.3.1 Isothermal Study in \( H_2 \)

Linear regression was performed to determine the best fit lines through the linear portions of the data.

Table VII.2 illustrates the calculation of rate constants for the hydrogen reduction of C97 (40% \( \text{H}_2 \)). Arrhenius relationships were obtained by plotting ln(\( k_r \)) versus 1/T. Least squares regression on the transformed variables gave the following equation for the reduction rate constant:

\[
k_r = A \ e^{-E/RT}
\]

(7.6)
Table VII.2  Calculation of rate constant from isothermal kinetic data: C97 in 40% H₂

<table>
<thead>
<tr>
<th>Temperature [° C]</th>
<th>Slope from Regression</th>
<th>(C_A^* - C_A^{eq}) Ch. 4</th>
<th>(k_r) (l/mol s)</th>
<th>(\ln(k_r))</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>2.39E-4</td>
<td>9.1E-4</td>
<td>0.263</td>
<td>-1.337</td>
</tr>
<tr>
<td>500</td>
<td>6.56E-4(^A)</td>
<td>1.11E-3</td>
<td>0.593</td>
<td>-0.522</td>
</tr>
<tr>
<td>550</td>
<td>1.20E-3</td>
<td>1.30E-3</td>
<td>0.921</td>
<td>-0.082</td>
</tr>
<tr>
<td>600</td>
<td>1.86E-3</td>
<td>1.38E-3</td>
<td>1.346</td>
<td>0.2969</td>
</tr>
<tr>
<td>650</td>
<td>2.59E-3</td>
<td>1.41E-3</td>
<td>1.839</td>
<td>0.609</td>
</tr>
<tr>
<td>700</td>
<td>4.79E-3</td>
<td>1.44E-3</td>
<td>3.330</td>
<td>1.203</td>
</tr>
<tr>
<td>750</td>
<td>7.09E-3</td>
<td>1.47E-3</td>
<td>4.831</td>
<td>1.575</td>
</tr>
</tbody>
</table>

\(^A\) See Figure 7.1

where for C97 \(A=3570\) mol/l-s, \(E_a=56800\) J/mol; for C92 \(A=3221\) mol/l-s and \(E_a=53100\) J/mol.

The correlation coefficients were both nearly unity (0.99), indicating that the relationship between \(1/T\) and \(\ln(k_r)\) is well approximated by a straight line.

Isothermal experiments fulfill the requirements for statistical analysis mentioned in Chapter 4, namely i) \(x\) values (\(1/T\)) are precisely known ii) \(y\) values (\(\ln(k_r)\)) are mutually independent and iii) variance of the \(y\) is independent of the \(x\). Confidence intervals can therefore be derived and plotted with the data. The 100(1-\(\gamma\))% confidence intervals for the data can be determined respectively from (Guttman and others, 1982):

\[
y = \hat{y} \pm t_{n-2,\gamma/2} \left( \frac{1}{n} + \frac{(x - \bar{x})^2}{S(X^2)} \right)^{1/2}
\]
where \( y \) is the experimentally determined value of \( \log_e(k) \), \( \hat{y} \) is the value of \( \log_e(k) \) at temperature \( T \) estimated from the regression equations, \( x \) is \( 1/T \), \( x \) bar is the average of the experimental \( (1/T)s \), \( t_{n-2\pi} \) is the student \( t \) variable with \( n-2 \) degrees of freedom where \( n \) is the number of independent experiments, and \( s_{\hat{y}}^2 \) is an unbiased estimate of the variance, given by:

\[
s_{\hat{y}}^2 = \frac{\sum (y_i - \hat{y})^2}{n-2}
\]

and \( S(X^2) \) is the corrected sum squares of \( x \), given by:

\[
S(X^2) = \sum x_i^2 - n\bar{x}^2
\]

Table VII.3 shows the analysis of variance constructed for hydrogen reduction of C97 calcine. The regression equation is the linear relationship which fits the experimental data with minimum variance. Other equations may be drawn through the data, although with necessarily higher variance. Such a line falling outside the 95% confidence bands may be rejected as representing the true relationship between \( \log_e(k) \) and \( 1/T \) with a confidence of 95%. Comparing the graphs for C92 and C97 calcines (Figure 7.10) reveals that their respective 95% confidence regions do not overlap. It must therefore be concluded that there is no single linear relationship which describes the hydrogen reduction of both calcines to within a 95% confidence limit, i.e. the behaviour of the two calcines in hydrogen are statistically distinct.

Although the data from the two calcines were statistically distinct, both expressions show similar slopes and activation energies. Confidence intervals for the value of the slope can be calculated from:

\[
\beta = b \pm t_{n-2\pi} \sqrt{\frac{s_{\hat{y}}^2}{S(X^2)}}
\]

where \( \beta \) is the real slope, \( b \) is slope estimated from regression analysis. Substituting the
Table VII.3  Analysis of variance for the isothermal reduction of C97 in 40% H₂

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>y</th>
<th>y-y</th>
<th>Source</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000/T</td>
<td>log₆(Kₐ)</td>
<td></td>
<td></td>
<td>Crude Sum of Squares Σy²</td>
<td>6.453</td>
</tr>
<tr>
<td>13.8</td>
<td>-1.337</td>
<td>-1.27</td>
<td>-0.077</td>
<td>Due to mean ny²</td>
<td>0.434</td>
</tr>
<tr>
<td>12.9</td>
<td>-0.522</td>
<td>-0.66</td>
<td>0.117</td>
<td>Due to slope Bxy</td>
<td>5.944</td>
</tr>
<tr>
<td>12.2</td>
<td>-0.0817</td>
<td>-0.12</td>
<td>0.074</td>
<td>Residual Sum Squares</td>
<td>0.074</td>
</tr>
<tr>
<td>11.5</td>
<td>0.2969</td>
<td>0.35</td>
<td>-0.031</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.8</td>
<td>0.6094</td>
<td>0.78</td>
<td>-0.202</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.3</td>
<td>1.2026</td>
<td>1.16</td>
<td>0.046</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.8</td>
<td>1.575</td>
<td>1.50</td>
<td>0.073</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ s_\varepsilon^2 = 0.074 + 5 = 0.0148 \]
\[ S(X^2) = 12.47 \]
\[ S(Y^2) = 6.02 \]
\[ S(XY) = 8.61 \]
\[ R^2 = (S(XY))^2 / (S(X^2)S(Y^2)) = 0.99 \]

values into this equation gives activation energies for the C92 and C97 calcine as 53100±4000 J/mol and 57000±4000 J/mol. Since these confidence limits overlap, the hypothesis that the two activations are the same cannot be rejected. It is reasonable to conclude that the two activation energies may be the same and that the intercept (pre-exponential constant) is responsible for the distinction between the two regression equations. One explanation for this is that in determining the rate constant from the isothermal data, it was necessary to assign a weight loss to correspond to 100% conversion. The ultimate weight losses were extrapolated from the non-isothermal tests. Errors in the ultimate weight losses would propagate more to the intercept on the Arrhenius plot than to the slope.

7.3.2  Isothermal Study in CO

The isothermal experimental procedure described above was repeated for both calcines in
100% CO. When the data is plotted as \( \log_a(1-X) \) vs \( t \) (Figure 7.11), both calcines deviated from linearity at low conversions. The deviation is particularly pronounced for the C92 calcine, which can be explained by its higher hematite and sulphate assays. It was therefore concluded that the CO reduction of both calcines did not proceed according to first order kinetics. The same conclusion had been drawn earlier from the non-isothermal thermogravimetric analysis. Attempts to fit a power-law kinetic relationship to the data were unsuccessful, as it was found that the power law exponents varied with temperature. In conclusion, no mechanism for the CO reduction of calcines could be determined from isothermal experiments.
Figure 7.11  Isothermal reduction of Calcines in 100% CO: top C92, bottom C97.
7.4 Summary of Thermogravimetric Kinetic Study

7.4.1 Calcine Reduction in Hydrogen

Microscopic analysis of partially reduced Ni/Cu calcines determined that reduction followed a uniform internal reduction model. Non-isothermal TGA was used to derive expressions for rate constants as a function of temperature. The observed rates were first order with respect to both the hydrogen concentration and to the solid. The expressions for hydrogen reduction of both calcines were accurate between 300° C and 700° C and up to a solid conversion of 60%. It was not possible to determine whether the expressions for the different calcines could be statistically replaced with a single expression.

Isothermal experiments determined that the rate constant expressions for the two calcines were statistically distinct, however their activation energies were the same to within a 95% confidence limit. The activation energy derived from the rate data was similar in magnitude to energies for the hydrogen reduction of other transition metal oxides. The discrepancy in their pre-exponential constants was thought to be due to the difficulty in measuring the percent conversion in a complex mineral.

The four relations for the rate constant for the isothermal and non-isothermal hydrogen reduction of nickel/copper calcines are plotted together in Figure 7.12. To put this graph into a process design perspective, if a reaction rate constant of 1 l/mol·s were needed to achieve a required process throughput (e.g. conversion given a fixed residence time) then the expressions would recommend an operating temperature between 514° C - 560° C. This temperature range would be sufficiently narrow to proceed with designing a reactor from a heat balance and material of construction point of view.

An analysis of procedural errors gave an expected error of about 20% using the Arrhenius expressions to predict the rate constant at a given temperature.

7.4.2 Calcine Reduction in CO

Microscopic examination of calcines partially reduced in CO confirmed that reduction had
Figure 7.12 Rate Constants for H₂ reduction of Ni/Cu calcines: "NI" from non-isothermal TGA, "I" from isothermal TGA.

proceeded uniformly. However non-isothermal and isothermal analysis failed to confirm either a first order or power law relationship for reduction in CO. Carbon deposition was observed in calcines pre-reduced in the TGA apparatus, however they were absent in samples pre-reduced in the cyclone reactor. The rate was noticeably retarded above the wustite eutectoid. It was concluded that the stabilization of wustite or the deposition of carbon on pore walls, catalyzed by iron and nickel, had interfered with the reduction process. The fact that wustite stabilization did not affect the reduction rate when hydrogen was used favours carbon deposition as the mechanism by which reduction rates were retarded.

In the absence of an empirical expression, the following qualitative conclusions can be drawn:

- The rate constant for reduction in CO was approximately 20 times lower than reduction in H₂ between 500° C and 800° C; this agrees with other researcher's
results (Turkdogan and Vinters, 1971a);

- reduction was very slow below 500°C;
- significant reduction rates were observed above 600°C;

7.5 Industrial Significance

Reducing gas mixtures are industrially made from (Stocchi, 1990) i) steam reformed natural gas:

\[ CH_4(g) + H_2O(g) = CO(g) + 3H_2(g) \] \hspace{1cm} (7.11)

and ii) autothermal reforming of natural gas:

\[ CH_4(g) + \frac{1}{2} O_2(g) = CO(g) + 2H_2(g) \] \hspace{1cm} (7.12)

Autothermal reforming processes have lower capital costs and are less subject to wear and tear. Steam reforming produces more hydrogen per tonne natural gas, but is an endothermic process and sulphur readily poisons the catalysts.

It has been shown to be a slower reductant than pure H₂, however CO performs other useful functions in iron oxide reductions. In H₂/CO mixtures, CO can react with water vapour according to the water shift reaction. Oxide reduction then proceeds according to:

\[ MO + H_2(g) = M + H_2O(g) \] \hspace{1cm} (7.13)

\[ CO(g) + H_2O(g) = CO_2(g) + H_2(g) \] \hspace{1cm} (7.14)

The water shift reaction is catalyzed by iron oxides and transition metals. Water vapour can also react with previously deposited carbon:

\[ C(g) + H_2O(g) = H_2(g) + CO(g) \] \hspace{1cm} (7.15)
The significant fuel value in carbon monoxide may be exploited in several ways. It can help overcome the endothermic heat of H₂ reduction or steam reforming. Excess may be used to raise steam for plant use or for power generation.
8.0 BEHAVIOUR OF PRE-REDUCED CALCINES

This research has demonstrated that calcine reduction can be performed at low temperatures outside the smelting furnace. The behaviour of pre-reduced calcine in the furnace is predicted in this chapter.

The rate at which pre-reduced calcines re-oxidize affects the industrial applicability of reduction outside the smelting vessel and has implications on equipment selection. At Falconbridge, air is brought into the freeboard to combust the CO evolved from the coke. Subjecting pre-reduced calcine to a hot oxidizing environment would undo many of the benefits of pre-reduction. The relationship between oxidation rate and temperature is important in determining the industrial feasibility of pre-reduction.

The furnace off-gas is a major contributor to the smelter SO₂ emission. As has been shown in earlier chapters, SO₂ is released when sulphates decompose and from solid state reactions between iron oxides and pyrrhotite. This source is too dilute and of too high a volume to economically treat in an acid plant. Lime scrubbing high volumes of off-gas volume is an expensive option. Evidence has been presented in this thesis which suggests that smelting a pre-reduced calcine would emit less SO₂.

Pre-reduced calcines were exposed to oxidizing and inert atmospheres in the TGA apparatus. The results are discussed below.

8.1 Re-oxidation of Pre-reduced Calcines

It was established in Chapter 5 that oxidation of calcines in air proceeded faster than reduction in 40% H₂ at all temperatures. Figure 8.1 illustrates the isothermal reduction of C97 at 600° C in a 40% H₂ environment followed by re-oxidation in air. It is instructive to look at a partially reduced calcine e.g. one that has been pre-reduced to remove 7% of its starting mass. This represents a calcine in which approximately 50% of the reducible oxygen is removed. The reduction rate of this calcine by a 40% H₂ mixture is 1%/min; the oxidation rate of this calcine in air is, by comparison, approximately 8%/min.
Figure 8.1  Reduction of C97 calcine in 40% H₂ at 600°C followed by re-oxidation in air.

To determine the temperature at which the rate of re-oxidation of pre-reduced calcine becomes significant, additional TGA experiments were performed. Samples of C97 calcine were deeply pre-reduced in the TGA apparatus by heating them (10°C/min to 850°C) in reducing atmospheres (40% H₂; 100% CO). The samples were quenched in argon to room temperature. The apparatus was tared and the pre-reduced samples were reheated in dry air at 10°C/min to 850°C. The mass change profiles during the re-oxidation stage are plotted in Figure 8.2.

Both samples started to gain mass immediately (i.e. above 100°C). At 400°C the rate of re-oxidation was approximately 0.3%/min. The pre-reduced calcines accumulated a mass gain of 11% when the temperature reached 500°C. This mass gain was attributed to the oxidation of iron. Starting at 660°C, both samples started to loose mass and continued to do so until the end of the experiment. This was concluded to be caused by SO₂ evolved from the oxidation of the sulphide core. The behaviour of both calcines was
Figure 8.2 Re-oxidation of calcines deeply reduced in H\textsubscript{2} and CO: 10\textdegree\ C/min in air

identical up to a temperature of about 550\textdegree\ C. Above this temperature the hydrogen pre-reduced calcine gained approximately 2\% more mass than the calcine reduced in CO. It has been concluded earlier that deep calcine reduction in H\textsubscript{2} reduced some metal sulphides to the metal, while CO reduction tended not to. Calcine from which sulphur had been removed during reduction would be expected to sustain a higher relative mass gain during subsequent oxidation.

Mass change profiles for calcines heated in air were obtained from isothermal reduction/reoxidation experiments (Chapter 5). Figure 8.3, shows the mass change profile for resulting from isothermal re-oxidation of pre-reduced calcines. Above 500\textdegree\ C, calcines gained oxygen at approximately 7\%/min (8 mg oxygen per 100mg calcine/min). When the weights of the calcines had been re-oxidized to their original values (i.e. a net mass change of zero), the oxidation rate fell dramatically.

Figure 8.4 shows a plot of the maximum re-oxidation rate as a function of temperature
Figure 8.3 Isothermal re-oxidation of pre-reduced calcines: top C92, bottom C97
Figure 8.4 Arrhenius diagram for the re-oxidation of pre-reduced calcines

on Arrhenius axes. It is concluded that the maximum rate of oxidation weakly increases with increasing temperature. An apparent activation energy of 12 kJ/mol was measured, which implies that re-oxidation was controlled by gaseous diffusion. Other researchers concluded that oxidation of Ni/Cu concentrate followed shrinking un-reacted core kinetics controlled by diffusion of oxygen through the iron oxide product (Zamalloa, 1995). Diffusion control was also reported in the oxidation of magnetite fines (Monsen and others, 1996).

Calcines pre-reduced in hydrogen re-oxidized approximately 20% faster than when pre-reduced in CO. Others have observed that the pore structure of the iron product is finer for hydrogen reduced hematite than CO reduced hematite, especially below 500° C (Turkdogan and Vinters, 1972). This finer pore structure contributes to the pyrophoric nature of reduced iron, and may explain the different oxidation rates in pre-reduced calcines.
It is therefore concluded that pre-reduced calcines are readily re-oxidized at temperatures as low as 300°C. Above 550°C oxidation was a shrinking core process controlled by the diffusion of oxygen through the iron oxide product. Re-oxidation of H₂ reduced calcines proceeded at approximately 8%/min (i.e. calcine gained 8mg of oxygen per 100mg pre-reduced calcine per minute) at 600°C and was weakly dependant on temperature. Re-oxidation of CO reduced calcines was approximately 20% slower.

Since re-oxidation was a shrinking core process, oxygen did not have access to the sulphide core until the iron shell was fully oxidized. Only then was the sulphide core oxidized, SO₂ released and a mass loss observed.

Re-oxidation rates are sufficiently high to affect the design of storage bins and conveying systems to the furnace. The terminal settling velocity of a 20μm calcine particle in the furnace freeboard (700°C air) may be calculated from Stoke's law (Denn, 1980).

\[
v_p = g_c \frac{D_p^2 (\rho_g - \rho_p)}{18 \eta} \tag{8.1}
\]

for \( Re < 1 \)

where \( g_c \) is 9.81 m/s², \( D_p \) is the particle diameter (20μm), \( \rho_g \) and \( \rho_p \) are the gas and calcine densities (0.36 kg/m³ and 4000 kg/m³ respectively), and \( \eta \) is the gas viscosity (= 42x10⁻⁶ Pa·s). This gives a terminal velocity of approximately 2cm/s. Since the freeboard height of the Falconbridge furnace is greater than 1 m, fine calcine particles may be completely re-oxidized if allowed to settle in the freeboard.

8.2 Heating Pre-reduced Calcines in Inert Atmospheres

Experiments were performed in which calcines were in reducing atmospheres and subsequently heated in argon (Chapter 5). The purpose was to simulate the behaviour of pre-reduced calcines in the smelting furnace, particularly with respect to the evolution of SO₂.
Figure 8.5 Effect of pre-reduction on subsequent weight loss - all data

The results from Chapter 5 have been re-plotted in Figure 8.5 to show the mass loss after pre-reduction as a function of the degree of pre-reduction. The graph shows that pre-reduction sharply diminished the subsequent evolution of SO2, and that the agent of pre-reduction and the temperature at which pre-reduction took place were secondary to the reduction mass loss. In other words the evolution of SO2 from the pre-reduced calcine was a function of the degree of pre-reduction only; whether the calcine was pre-reduced in CO or H2 was largely irrelevant.

The graph indicates that modest levels of pre-reduction could sharply suppress SO2 generation in the furnace. Furnace emissions could be practically eliminated if the C92 calcine were pre-reduced by 3.7% or the C97 calcine were pre-reduced by 1.7%.
9.0 CONCLUSIONS

The kinetics of gas/solid reactions were discussed. The behaviour of shrinking un-reacted core processes was compared to that of uniform internal reduction processes. Expressions relating conversion to reaction time were modified to account for a geometry in which an inert core is surrounded by a reactive shell. It was found by analysis that the rate of mass transfer across the boundary layer can control the overall conversion. Complete reduction of an homogenous spherical particle, in contrast, is rarely mass transfer controlled.

The expressions for shrinking un-reacted core process were then extended to consider the partial conversions of solids. The resulting equations show that external mass transfer can control such processes.

The reaction modulus of a mixed control process \(\sigma_{c}^{2}\), defined as the ratio of the times taken for complete conversion under chemical control and under diffusion control, is used to defining controlling regimes for solid gas reactions. If \(\sigma_{c}^{2} < 0.1\), the reaction is considered chemically controlled; if \(\sigma_{c}^{2} > 10\), the process is considered diffusion controlled. This concept has been extended to include the possibility of mass transfer control. Three reaction moduli \(\sigma_{c}^{2}(X), \sigma_{d}^{2}(X), \sigma_{m}^{2}(X)\) were introduced. All are functions of the extent of reaction \(X\). If \(\sigma_{c}^{2}(X) < 0.1\), then partial conversion to 100X% is a chemically controlled process; similarly, if \(\sigma_{d}^{2}(X) < 0.1\), the partial conversion is controlled by diffusion through the product layer; and if \(\sigma_{m}^{2}(X) < 0.1\), then partial conversion is mass transfer controlled.

By definition, uniform internal reduction gives a straight line when \(\log(1-X)\) is plotted against time. It was shown that the conversion of an assemblage of grains with a normal particle size distribution and which reacts as shrinking un-reacted cores under chemical control also gives an approximately linear response on the same axes, particularly at low conversions. The relationship became more linear as the particle size distribution was made flatter. It is suggested that the mechanism for uniform internal reduction may be the reduction of in-homogenously sized constituent grains and particles according to the shrinking un-reacted core model.

Critical analysis of non-isothermal techniques for measuring reaction rates was carried out. It was
shown that either an integral or a differential analysis of non-isothermal conversion data could extract the activation energy and pre-exponential constant for systems undergoing a single reaction. However the integral method is not as robust and should not be used on systems containing significant amounts of substances undergoing multiple reactions. The differential method is more robust under these conditions.

Non-isothermal methods were compared to isothermal methods with respect to their ability to extract Arrhenius parameters from conversion-time data. It was argued that both methods are equally efficient in determining activation energies. It was also argued that a sequence of isothermal experiments is more statistically robust than a sequence of non-isothermal experiments.

The mass change exhibited by two calcine samples in hydrogen, carbon-monoxide and argon atmospheres was investigated using non-isothermal coupled with mass spectrometer analysis of the off-gas. In argon atmospheres, it was concluded that solid state reactions between pyrrhotite and metal oxides evolved SO₂ above 400° C; sulphate decomposition was increasingly responsible for mass changes above 600° C. The C92 calcine contained more sulphate and hematite, and therefore lost more mass than the C97 sample.

In hydrogen atmospheres, sulphates were reduced between 200° C and 300° C, evolving SO₂ and yielding elemental metals. The highest rate of mass change was recorded at 400° C, coincident with H₂O evolution. This was concluded to represent the reduction of iron oxides. Above 510° C, H₂S was evolved, indicative of direct reduction of sulphides.

In carbon-monoxide atmospheres, sulphates were reduced at low temperatures (300° C). Reduction of metal oxides started at 500° C. Low temperature releases of COS were recorded, however with little attendant mass change. Above 500° C, COS was evolved, indicating that direct sulphide reduction was occurring.

Microscopic analysis of partially reduced samples revealed that the oxide rim of partially reduced calcines did not exhibit a banded structure. Reduction in H₂ was found to obey a uniform internal reduction model (first order with respect to the solid) and proportional to \((C_A^o - C_A)\). The activation energies and pre-exponential constants measured by non-isothermal and isothermal experiments are
Table IX.1 Rate Constant Parameters for Isothermal Reduction of Calcines in H₂

<table>
<thead>
<tr>
<th></th>
<th>A [10⁸ mol⁻¹ s⁻¹]</th>
<th>Eₐ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isothermal</td>
<td>3221</td>
<td>53.1</td>
</tr>
<tr>
<td>Non-isothermal</td>
<td>3600</td>
<td>55.4</td>
</tr>
<tr>
<td>C97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isothermal</td>
<td>3570</td>
<td>56.8</td>
</tr>
<tr>
<td>Non-isothermal</td>
<td>9380</td>
<td>63.6</td>
</tr>
</tbody>
</table>

summarized in Table IX.1. The 95% confidence intervals for the isothermal activation energies are ± 5kJ/mol therefore it can be concluded that the activation energy for H₂ reduction of both calcines is the same.

A plot of rate constant versus temperature reproduced in Figure 9.1 shows that, despite the discrepancy in pre-exponential constant, the relations in Table IX.1 give similar values for the rate constant.

No consistent relationship for the CO reduction of calcines could be derived from non-isothermal and isothermal experiments. It was concluded that reduction was retarded by the deposition of graphite onto the pore surfaces according to the Naumann reversion reaction:

\[ 2CO_{\omega} = C_{\omega} + CO_{2\omega} \]  \hspace{1cm} (9.1)

It was confirmed that the reduction rate of iron oxides was slower in CO than in H₂.

The isothermal re-oxidation rate of deeply reduced calcines was measured. Re-oxidation was shown to proceed above 200° C. Above 500° C, re-oxidation was not strongly dependant on the reaction temperature (an activation energy of 12 kJ/mol was measured). It was concluded that oxidation was a shrinking un-reacted core process controlled by diffusion through the iron oxide product, in agreement with other observers. Re-oxidation was 20% faster in hydrogen reduced calcine than in CO reduced calcine. The implications of re-oxidation on the feasibility of pre-reduction were
Figure 9.1 Rate constants for the hydrogen reduction of nickel calcines

The behaviour of pre-reduced calcine banks in the smelting furnace was simulated by heating pre-reduced calcines in Ar. Pre-reduced samples lost less mass on heating in argon than the original calcine. It was concluded that limited pre-reduction evolved less SO$_2$ than untreated calcines. The proposed mechanism which brought this about was i) sulphates were decomposed during reduction, and ii) iron oxides were reduced, preventing their solid state reaction with pyrrhotite. SO$_2$ was practically eliminated by reducing the calcine samples by 3% (C92) and 1.7% (C97).
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Toronto: Wiley.


Roskill, Internet Search


R-4


<table>
<thead>
<tr>
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<th>Mass change profiles</th>
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</thead>
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<td>1</td>
<td>Calcines heated in 20% $H_2$</td>
</tr>
<tr>
<td>2</td>
<td>Calcines heated in 15% $H_2$</td>
</tr>
<tr>
<td>3</td>
<td>Calcines heated in 40% CO</td>
</tr>
<tr>
<td>4</td>
<td>Calcines heated in 10% CO</td>
</tr>
</tbody>
</table>
Figure 1.1 Mass change profiles for calcines heated in 20% H$_2$: top C92, bottom C97
Figure 1.2 Mass change profiles for calcines heated in 15% H₂: top C92, bottom C97
Figure 1.3  Mass change profiles for calcines heated in 40% CO: top C92, bottom C97
Figure 1.4 Mass change profiles for calcines heated in 10% CO: top C92, bottom C97
APPENDIX B    REPORT FROM SETARAM

B.1    Description of Apparatus
B.2    Results in Ar
B.3    Results in 100% H₂
B.4    Results in 100% CO

B-1
Mr CROWE  
UNIVERSITY OF TORONTO  
Dpt of Metallurgy and Material Science  
184 College Street  
M5S 1A4 TORONTO  
CANADA  

September 26, 1997

Dear Mr CROWE,

You will find enclosed the report of the test carried out for you with our TG-MS.

Should you have any comment or question do not hesitate to contact us.

Yours sincerely,

L. BENOIST  
Applications Manager
TG-MS of minerals

I - Type of instrument

A) TG 92

The experiments have been carried out with the TG 92 thermoanalyzer which consists of:

- the microbalance B 92
- all atmospheres furnace, up to 1750°C (graphite heating element)
- the CS 32 controller with the following functions:
  . regulation and programming of the temperature furnace
  . T, TG, DTG and DTA signals monitoring and digitalization
  . transfer of signals to micro-computer
- the compatible PC Pentium® 120 MHz with a RAM of 16 Mbytes, a 1.44 Mbyte floppy disk (3"5) drive, a 1 Gbytes hard disk and SVGA colour monitor
- a multicolour printer/plotter for the redrawing of the recorded curves.

The TG 92 has been used with the following options:

- TG only with platinum suspensions and alumina crucibles
- carrier gas sweeping
- primary vacuum (purge)
- forced primary vacuum device
- automatic gas switching system by electrovalves.

B) Mass spectrometer

The instrument used is the Balzers Thermostat with the following caracteristics:

  Mass scale : 1 to 300 amu
  Capillary : 1 m long in quartz
  Capillary heater up to 200°C
  Inlet at the atmospheric pressure in continuous
  We used also an optimal software enabling the superimposition of MS and TG data.
Gas Analysis

Your thermobalance and our ThermoStar® - the optimal TA-MS team

Fast and continuous analysis
Reactive/condensible gases
Lowest concentrations
TA/MS data on one screen
ThermoStar –
The compact gas analysis for your thermobalance

Simple interface to commercial thermobalances
Continuous and rapid analysis of the gases evolving from thermal processes
Detection of trace concentrations of reactive and condensable gases
No chemical reactions in the gas inlet due to the use of only inert materials
No condensation effects in the gas inlet, heated from the point of sampling to the ion source

Analysis software
Büel & GuadstarTM
Qualitative analysis of all gases evolving during thermal analysis
Quantitative analysis with on-line calculation of concentrations
Simultaneous data acquisition from a thermal analyser via Analog Input Module

(e.g. temperature, sample weight and differential weight loss)
Presentation of mass spectrometric data as a function of the thermobalance temperature
Convenient data evaluation supported by a spectrum library, statistical and magnifying functions, and cursors

Xenon in air
The spectrum shows the excellent detection limit. Integrated over 14 scans at 10 s/amu, under optimal conditions, laboratory air.

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TOTAL PAGE(S) 02
ThermoStar - The compact gas analysis for your thermobalance

Sample introduction to commercial thermobalance
Continuously and rapidly analysis of gases evolving from thermal processes
Detection of even the smallest gas contaminations
No need to heat the furnace to the use or only little heating

Analysis equipment

- Raman Gas Spectrometer

- Quantitative analysis of gases evolving during thermal analysis

- Continuous gas analysis and detection of small gas contaminations

- No need to heat the furnace to the use or only little heating
II - **Experimental conditions**

Samples are analyzed in an alumina crucible with an argon flow (1 l/h) as a carrier gas and three conditions of active gas (flow : 6 l/h) : Argon, Hydrogen and carbon monoxide.

A purge and a primary vacuum controlled by the MS is carried out before.

The procedure is:

- 3 minutes isothermal at 50°C
- 50°C up to 850°C at 10 K/min
- 3 minutes isothermal at 850°C
- 850°C down to 20°C at 60 K/min.

III - **Results**

Two figures are given by analysis:

First one : presents the signals TG (%), Temperature (°C) and amu (A) : 18, 32, 34 and 44 versus time.

Second one : presents the signals TG (%), DTG (%/min), Temperature (°C) and amu (A) : 60 and 64 versus time.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Sample</th>
<th>Active gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-92</td>
<td>Argon</td>
</tr>
<tr>
<td>2</td>
<td>C-92</td>
<td>Argon</td>
</tr>
<tr>
<td>3</td>
<td>C-97</td>
<td>Argon</td>
</tr>
<tr>
<td>4</td>
<td>C-97</td>
<td>Argon</td>
</tr>
<tr>
<td>5</td>
<td>C-92</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>6</td>
<td>C-92</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>7</td>
<td>C-97</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>8</td>
<td>C-97</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>9</td>
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<tr>
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<td>C-92</td>
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<td>C-97</td>
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</tr>
<tr>
<td>12</td>
<td>C-97</td>
<td>CO</td>
</tr>
</tbody>
</table>

H. LEFEVBRE
Fig. 1: Experiment: C-92 UNDER ARGON
Atm.: Ar
Crucible: Al2O3

Procedure:
50°C 3min -> 850°C 10K/min 3min -> RT 60K/min (Seq 1 - 4)

Mass (mg): 54.29
Fig. 5: Experiment: C-92 UNDER HYDROGEN
Atm.: H2
Crucible: Al2O3

Procedure: 50°C 3min -> 850°C 10K/min 3min -> RT 60K/min (Seq 1 - 4)

Mass (mg): 53.5
Fig.: 8  Experiment: C-97 UNDER HYDROGEN  Atm.: H2  Crucible: Al2O3
09-11-97  Procedure: 50°C 3min -> 850°C 10K/min 3min -> RT 60K/min (Seq 1 - 4)
Mass (mg): 53,55

TG/ %

DTG/ %/min

DG

TG

10  60

-0.10

-0.20

-0.30

-0.40

-0.50

-0.60

10  20  30  40  50  60  70  80  90  Time/ min

64.00/ A

60.00/ A

Temperature/ °C

850

2.6E-012

2.8E-012

1.4E-012

2.4E-012
Fig: 10  Experiment: C-92 UNDER CO  Atm.: CO  Crucible: Al2O3

Procedure: 50°C 3min -> 850°C 10K/min 3min -> RT 60K/min (Seq 1 - 4)

Mass (mg): 52.62