The Ignition Properties of Pyrite, Pyrrhotite
Pentlandite and Violarite

Lisa Catherine Mackey

This thesis is presented in fulfilment of the requirements for the award of
Doctor of Philosophy

Curtin University of Technology
To Mum and Dad

With Love
ABSTRACT

The oxidation and ignition behaviour of the four major sulfide minerals present in the nickel concentrates smelted at the Kalgoorlie Nickel Smelter (KNS) has been established. These minerals are pyrite (FeS$_2$), pyrrhotite (Fe$_{1-n}$S, where n = 0 to 0.125), pentlandite ((FeNi)$_{9}$S$_8$) and violarite (Ni$_2$FeS$_4$).

The characteristic behaviour of these sulfides has been examined using Thermogravimetry-Differential Thermal Analysis (TG-DTA) under normal oxidation conditions (10°C/min, air atmosphere). By increasing the heating rate to 40°C/min and using an oxygen atmosphere, the tendency of the sulfides to ignite was established. Ignition was characterised by a highly exothermic reaction which occurred in association with a rapid mass loss over a short time span. Significant overheating of the samples beyond the temperature of the surroundings was observed. Pyrite, pyrrhotite and violarite all exhibited ignition behaviour while pentlandite did not.

Using Isothermal Thermogravimetry (TG) the sulfides were subjected to shock heating conditions (heating rate = 3000-5000°C/min, oxygen atmosphere) analogous to those which exist in an industrial flash smelter. The order of reactivity of the sulfides agreed with that observed during TG-DTA ignition trials. Even under these more
(ii)

intensely oxidising conditions pentlandite did not ignite. The effect of particle size on the ignition temperature was determined, larger particles igniting at a higher temperature. The magnitude of this effect varied according to the characteristics of the minerals.

Products collected during Isothermal TG were examined by optical microscopy, Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EPMA). Using these techniques it was possible to establish the morphology of the products and hence, to propose mechanisms for the reaction of the four sulfide minerals under ignition conditions.

In order to simulate the thermal environment which exists in the KNS, a pilot scale model of the reaction shaft was used. Nickel sulfide concentrates of varying mineralogy and particle size distribution were smelted under various conditions. The effect of larger particle size and increasing oxygen partial pressure on the reactivity of these concentrates was established.

The products were quenched at the base of the shaft and collected for examination by optical microscopy, SEM and EPMA. Products ranged from unreacted to completely oxidised particles. The morphology and composition of these species were identified. Approximately 30 particles in each of 26 samples were examined with a view to establishing the frequency of occurrence of the
particular product types in concentrates of differing mineralogy and particle size. This allowed proposals to be made regarding the fate of the individual sulfide minerals during ignition in the pilot scale flash reactor.
ACKNOWLEDGEMENTS

I would like to express my appreciation to my supervisor, Associate Professor J.G. Dunn. He has been an infinite source of support both academically and personally throughout all of my postgraduate studies. I am very grateful for his faith in my abilities and his positive outlook on life. The assistance of my associate supervisor, Professor T.N. Smith, with the interpretation of the results of the pilot scale studies and the writing of my thesis has been invaluable. Mr I. Stevenson acted as a research assistant on the pilot scale reactor. Since then he has maintained a continued interest in my studies while working for the Kalgoorlie Nickel Smelter. His support is much appreciated.

This work would not have been possible without the generosity of the staff at the CSIRO Division of Exploration Geoscience, Floreat Park. I would like to thank Dr J. Graham for his constructive criticism of certain aspects of the work. Dr R. Hill provided both inspiration and the ore samples. Dr E. Nickel trained me in the techniques of mineral characterisation using optical microscopy. All three of these people were a great source of encouragement. I am most appreciative for the use of CSIRO facilities, namely the sample preparation equipment and the electron probe microanalyser. Mr A. Bowyer and Mr B. Robinson kindly
donated their time to instruct me in these two areas respectively. The assistance I received from these people at CSIRO was instrumental in allowing me to complete my research.

The staff of the School of Applied Chemistry have aided me in various ways, ranging from encouragement to technical and academic assistance. Particular thanks are extended to Mr I. Sills, of the Thermal Characterisation Laboratory. His advice, technical expertise and efforts in maintaining the equipment are sincerely appreciated.

I am grateful to the staff of the School of Applied Geology for the use of their facilities. I would particularly like to mention Mr J. Pudney and Mr P. Glover who helped me with the preparation of polished sections. Associate Professor R. Pidgeon provided valuable advice regarding the operation of the Frantz Separator.

Mr J. Lauridsen of the Department of Chemical Engineering is acknowledged for his assistance in the running of the Etec Autoprobe. Thanks are extended to Mr A. Van Riessen and Mrs E. Miller of the Scanning Electron Microscopy Laboratory in the Department of Applied Physics for providing advice regarding the use of the SEM, and to Ms J. Steer of the X-Ray Laboratory in this same Department for analysing my samples.
I would also like to acknowledge Western Mining Corporation's Kalgoorlie Nickel Smelter for their interest in the work and for funding the pilot scale reactor research. The staff of both the smelter and the Kambalda Nickel Operations provided concentrate samples and performed chemical and mineralogical analyses on many samples.

I am grateful to my fellow PhD students; Patrick Fernandez and Tony Chamberlain, for their support, many fruitful discussions and assistance with proofreading my thesis.

Very special thanks are extended to my parents. Throughout my years of undergraduate and postgraduate study they have been an unfailing source of encouragement and strength. Without their constant interest in my studies and their faith in me none of this would have eventuated.

Finally, I should like to thank Peter Weissenborn for his love and understanding. Despite being busy with his own PhD research he has spent many hours patiently listening to my theories and proofreading my thesis.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter/Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(vii)</td>
<td></td>
</tr>
<tr>
<td><strong>TABLE OF CONTENTS</strong></td>
<td>(vii)</td>
</tr>
<tr>
<td><strong>ACKNOWLEDGEMENTS</strong></td>
<td>(iv)</td>
</tr>
<tr>
<td><strong>LIST OF FIGURES</strong></td>
<td>(xi)</td>
</tr>
<tr>
<td><strong>LIST OF TABLES</strong></td>
<td>(xvii)</td>
</tr>
<tr>
<td><strong>CHAPTER 1</strong> INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Flash Smelting</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Outokumpu Flash Smelting as Practised at Kalgoorlie, Western Australia</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Ignition Reactions and the Smelting of Sulfides</td>
<td>8</td>
</tr>
<tr>
<td>1.4 Variables Affecting Ignition in the Flash Smelter</td>
<td>9</td>
</tr>
<tr>
<td>1.4.1 Mineralogical Composition of the Feed</td>
<td>10</td>
</tr>
<tr>
<td>1.4.2 Particle Size Distribution of the Feed</td>
<td>12</td>
</tr>
<tr>
<td>1.4.3 Preheat Temperature of the Process Gas</td>
<td>14</td>
</tr>
<tr>
<td>1.4.4 Oxygen Concentration in the Process Gas</td>
<td>15</td>
</tr>
<tr>
<td>1.5 Techniques Utilised in the Study of Flash Smelting</td>
<td>16</td>
</tr>
<tr>
<td>1.5.1 Isothermal Thermogravimetry</td>
<td>17</td>
</tr>
<tr>
<td>1.5.2 Laminar Flow Furnace</td>
<td>19</td>
</tr>
<tr>
<td>1.5.3 Other Experimental Simulations</td>
<td>21</td>
</tr>
<tr>
<td>1.5.4 Mathematical Modelling</td>
<td>23</td>
</tr>
<tr>
<td>1.6 Mechanistic Studies of Ignition Reactions</td>
<td>24</td>
</tr>
<tr>
<td>1.6.1 Coal</td>
<td>25</td>
</tr>
<tr>
<td>1.6.2 Metals</td>
<td>27</td>
</tr>
</tbody>
</table>
(viii)

1.6.3 Sulfides
   (i) Chalcopyrite 31
   (ii) Pyrite 39
   (iii) Other Sulfide Minerals 43

1.7 Proposed Research 45

CHAPTER 2 EXPERIMENTAL METHODS 48

2.1 Laboratory Scale Studies 48
   2.1.1 Samples 48
   2.1.2 Sample Upgrading using Magnetic Separation 48
   2.1.3 Characterisation Techniques
      (i) Chemical Analysis 50
      (ii) Particle Size Analysis 51
      (iii) Surface Area Measurement 53
      (iv) X-Ray Diffraction (XRD) 53
      (v) Optical Microscopy 53
      (vi) Scanning Electron Microscopy (SEM) 55
      (vii) Electron Probe Microanalysis (EPMA) 55
   2.1.4 Thermal Analysis Techniques
      (i) Simultaneous Thermogravimetry-Differential Thermal Analysis (TG-DTA) 56
      (ii) Isothermal Thermogravimetry 57

2.2 Pilot Scale Studies 59
   2.2.1 Samples 59
   2.2.2 Characterisation Techniques
      (i) Chemical Analysis 59
      (ii) Particle Size Analysis 60
      (iii) X-Ray Diffraction 61
      (iv) Optical and Electron Microscopy 61
   2.2.3 Pilot Scale Reactor 62
CHAPTER 3 UPGRAADING AND CHARACTERISATION OF MINERALS AND CONCENTRATES 66

3.1 Upgrading Minerals 66
   3.1.1 Characterisation of Starting Materials 68
   3.1.2 Magnetic Separation 71

3.2 Characterisation of Upgraded Minerals 75
   3.2.1 Wet Chemical Analysis 75
   3.2.2 EPMA 77
   3.2.3 SEM 79

3.3 Characterisation of Mixed Sulfide Concentrates 81
   3.3.1 XRD Analysis 82
   3.3.2 XRF and Chemical Analysis 84
   3.3.3 Particle Size Analysis 86
   3.3.4 SEM and EPMA 87

CHAPTER 4 THERMAL ANALYSIS STUDIES OF PYRITE, PYRRHOTITE, PENTLANDITE AND VIOLARITE 91

4.1 Secondary Pyrite 91
4.2 Primary Pyrite 96
4.3 Pyrrhotite 101
4.4 Pentlandite 106
4.5 Violarite-Pyrite 112
4.6 Summary 116

CHAPTER 5 THERMAL ANALYSIS STUDIES OF PYRITE, PYRRHOTITE, PENTLANDITE AND VIOLARITE UNDER IGNITION CONDITIONS 118

5.1 TG-DTA 119
   5.1.1 Secondary Pyrite 122
   5.1.2 Primary Pyrite 126
   5.1.3 Pyrrhotite 126
   5.1.4 Pentlandite 127
5.1.5 Violarite-Pyrite

5.2 Isothermal TG
5.2.1 Ignition Temperatures
5.2.2 Extent of Reaction Plots
5.2.3 Particle Size Effects

5.3 SEM/EPMA Evidence Regarding the Mechanism of Sulfide Ignition
5.3.1 Secondary Pyrite
5.3.2 Primary Pyrite
5.3.3 Pyrrhotite
5.3.4 Pentlandite
5.3.5 Violarite-Pyrite

5.4 Summary

CHAPTER 6 PILOT SCALE STUDIES OF NICKEL SULFIDE CONCENTRATES UNDER IGNITION CONDITIONS

6.1 Pilot Scale Reactor
6.1.1 Extents of Reaction
6.1.2 Particle Size Effects

6.2 SEM/EPMA and Optical Microscopic Evidence Collected on the Ignited Products
6.2.1 General Product Morphology
6.2.2 Particle Size Distribution of Smelted Concentrates
6.2.3 Classification of the Product Types
6.2.4 Product Distribution in the Smelted Concentrates

6.3 Summary

CHAPTER 7 CONCLUSIONS

REFERENCES
LIST OF FIGURES

1.1 The general arrangement of the Kalgoorlie Nickel Smelter.

2.1 Schematic of the pilot scale reactor.

2.2 A general view of the pilot scale reactor.

2.3 A view of the reaction shaft and exit duct showing the propane burner, quench holes and the thermocouples.

3.1 An optical micrograph of a polished section of the primary ore showing pentlandite and pyrrhotite as the major sulfide phases. Frame width = 2200μm. Pn = pentlandite, Po = pyrrhotite.

3.2 An optical micrograph of a polished section of the secondary ore showing violarite and pyrite as the major sulfide phases. Frame width =1130μm. Py = pyrite, V_{pn} = violarite (from pentlandite), V_{po} = violarite (from pyrrhotite).

3.3 Backscattered electron micrographs of the 45-75μm fractions of the unreacted sulfides:
   (a) Leinster pyrite
   (b) pyrite (ex BGS)
   (c) Kambalda pyrrhotite
   (d) Renison Bell pyrrhotite
   (e) pentlandite
   (f) violarite-pyrite mixture
   (g) violarite-pyrite mixture (optical micrograph, frame width = 2200μm.)

3.4 Backscattered electron micrographs of the unreacted nickel sulfide concentrates:
   (a) KNO
   (b) AMC
4.1 TG-DTA records of the $45-75\mu m$ fractions of the sulfide samples (heating rate = $10^\circ C/min$, air atmosphere):
(a) secondary pyrite
(b) primary pyrite
(c) Kambalda pyrrhotite
(d) Renison Bell pyrrhotite
(e) pentlandite
(f) violarite-pyrite mixture

5.1 TG-DTA records of the $45-75\mu m$ fractions of the sulfide samples (heating rate = $40^\circ C/min$, oxygen atmosphere):
(a) secondary pyrite
(b) primary pyrite
(c) Kambalda pyrrhotite
(d) Renison Bell pyrrhotite
(e) pentlandite
(f) violarite-pyrite mixture

5.2 Extent of reaction versus temperature for the $45-75\mu m$ fraction of the sulfide samples as measured using Isothermal TG:
(a) secondary pyrite and the violarite-pyrite mixture
(b) Kambalda pyrrhotite and pentlandite.

5.3 Ignition temperature versus particle size for the sulfide samples as measured using Isothermal TG.

5.4 Hematite product of secondary pyrite collected at the ignition temperature. Note the existence of radial porosity ($45-75\mu m$ fraction, BSE image).

5.5 TG-DTA record of the $45-75\mu m$ fraction of secondary pyrite (heating rate = $400^\circ C/min$, nitrogen atmosphere).

5.6 Porous pyrrhotite particles generated by pyrolytic decomposition of pyrite (TG-DTA sample collected at $700^\circ C$, heating rate = $400^\circ C/min$, nitrogen atmosphere, $45-75\mu m$ fraction, BSE image).
5.7 (a) Primary pyrite particles collected just prior to the ignition temperature showing an initial product layer of oxide (45-75μm fraction, BSE image).

(b) Hematite product from primary pyrite collected at the ignition temperature. Radial porosity is evident (45-75μm fraction, BSE image).

(c) An ignited primary pyrite particle which has fractured. The initial oxide layer is still apparent (45-75μm fraction, BSE image).

5.8 (a) Hematite ignition product of Kambalda pyrrhotite. Oxidation has occurred along the twinning planes. Some particles still contain areas of unreacted sulfide (45-75μm fraction, BSE image).

(b) Hematite ignition product of Renison Bell pyrrhotite. The particle morphology is essentially equivalent to that for Kambalda pyrrhotite (45-75μm fraction, BSE image).

5.9 TG-DTA record of the 45-75μm fraction of Kambalda pyrrhotite (heating rate = 400°C/min, nitrogen atmosphere).

5.10 (a) Pentlandite particles collected at 685-690°C. A dense oxide layer has formed surrounding the sulfide core and substantial voids are present (45-75μm fraction, BSE image).

(b) An optical micrograph showing pentlandite particles collected at 720-725°C. Two oxide layers are evident, the outer layer displaying red internal reflections (45-75μm fraction, frame width = 220μm).

(c) Pentlandite particles collected at 750-755°C. The sulfide core has reduced in size while the voids have enlarged (45-75μm fraction, BSE image).

5.11 TG-DTA record of the 45-75μm fraction of pentlandite (heating rate = 400°C/min, nitrogen atmosphere).
5.12  (a) Violarite particles collected at the ignition temperature. A porous oxide layer is evident around the sulfide core (45-75μm fraction, BSE image).

(b) Violarite ignition products (45-75μm fraction, BSE image).

(c) The pyrolytic decomposition product of violarite. Particles have a coarsely porous structure. Note the pyrrhotite particle in the top left corner (TG-DTA sample collected at 700°C, heating rate = 40°C/min, nitrogen atmosphere, 45-75μm fraction, BSE image).

6.1  (a) The predominantly molten products which were collected following smelting of the KNO concentrate in the pilot scale reactor (BSE image).

(b) 45-75μm fraction of smelted KNO products (BSE image).

6.2  Secondary electron micrographs showing hollow particles:
(a) a relatively smooth surfaced sphere.
(b) a sphere having an irregular texture.

6.3  (a) Secondary electron micrograph of a sphere which possesses a very crystalline surface.

(b) Backscattered electron micrograph of three spheres having varying degrees of crystallinity.

6.4  (a) Backscattered electron micrograph of a 45-75μm size fraction of smelted KNO products.

(b) X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.4(a).

6.5  (a) Backscattered electron micrograph of a >106μm size fraction of KNO smelted products.
(b) X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.5(a).

6.6
(a) Optical micrograph of a rounded, unignited particle showing the onset of oxidation at the particle edges (frame width = 220µm).

(b) Optical micrograph of an unignited particle which exhibits a substantial degree of oxidation around the edges and the development of porosity (frame width = 220µm).

6.7
Smelted KNO concentrate, extent of reaction = 48.9%
Magnification = X 170
(a) Secondary electron image
(b) Iron distribution
(c) Nickel distribution
(d) Sulfur distribution

6.8
Smelted UCC concentrate, extent of reaction = 49.9%
Magnification = X 160
(a) Secondary electron image
(b) Iron distribution
(c) Nickel distribution
(d) Sulfur distribution

6.9
(a) A partially oxidised nickel-iron sulfide particle which contains a mixture of oxide (grey) and sulfide (yellow) phases (optical micrograph, frame width = 220µm).

(b) Two partially oxidised nickel-iron sulfides showing specks of oxide throughout the sulfide spheres and around the particle edges (optical micrograph, frame width = 220µm).

6.10
(a) Two partially oxidised iron sulfide particles which comprise oxide dispersed throughout the sulfide phase (optical micrograph, frame width = 220µm).
(b) A partially oxidised iron sulfide particle showing skeletal crystals of oxide (optical micrograph, frame width = 220µm).

6.11 (a) Oxide particles and an oxide/nickel sulfide particle. An angular hematite particle possessing red internal reflections is evident. Some of the oxides comprise two phases (optical micrograph, frame width = 220µm).

(b) An oxide/nickel sulfide particle which contains two types of oxide (optical micrograph, frame width = 220µm).

(c) Two oxide/nickel sulfide particles and a partially oxidised nickel-iron sulfide. All particles exhibit a mixture of oxide phases (optical micrograph, frame width = 220µm).

6.12 (a) Backscattered electron micrograph of smelted AMC products.

(b) X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.12(a).

6.13 An oxide/nickel sulfide sphere showing specks of sulfide dispersed throughout the two oxide phases (optical micrograph, frame width = 220µm).
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Analytical data for the upgraded mineral samples.</td>
<td>76</td>
</tr>
<tr>
<td>3.2</td>
<td>Stoichiometries of the sulfide minerals (45-75μm fractions) as determined by EPMA.</td>
<td>76</td>
</tr>
<tr>
<td>3.3</td>
<td>Phase composition of the sulfide concentrates as determined using quantitative XRD.</td>
<td>83</td>
</tr>
<tr>
<td>3.4</td>
<td>Chemical composition of the sulfide concentrates as determined using XRF and chemical analysis.</td>
<td>85</td>
</tr>
<tr>
<td>3.5</td>
<td>Particle size distribution of the sulfide concentrates determined using dry sieving.</td>
<td>85</td>
</tr>
<tr>
<td>3.6</td>
<td>(a) Stoichiometries of the minerals present in the unreacted KNO concentrate as determined by EPMA.</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>(b) Stoichiometries of the minerals present in the unreacted AMC concentrate as determined by EPMA.</td>
<td>88</td>
</tr>
<tr>
<td>5.1</td>
<td>Comparison of the extrapolated onset and offset temperatures and the peak temperature ranges for the major exothermic activity of the iron and nickel sulfides under normal oxidation conditions (100°C/min, air) versus ignition conditions (400°C/min, oxygen) using TG-DTA.</td>
<td>120</td>
</tr>
<tr>
<td>5.2</td>
<td>Ignition temperatures of the 45-75μm fractions of the sulfide samples as measured using Isothermal TG.</td>
<td>132</td>
</tr>
<tr>
<td>5.3</td>
<td>Ignition temperatures (°C) of various size fractions of the sulfide samples as measured using Isothermal TG.</td>
<td>140</td>
</tr>
</tbody>
</table>
6.1 Extents of reaction measured for the concentrates during pilot scale flash smelting.

6.2 (a) Extent of reaction in size fractions of four samples of UCC concentrate which had been smelted in the pilot scale reactor using an air atmosphere.
(b) Particle size distribution of the smelted UCC samples presented in Table 6.2(a).

6.3 (a) Extent of reaction in size fractions of two samples of AMC concentrate which had been smelted in the pilot scale reactor.
(b) Particle size distribution of the smelted AMC samples presented in Table 6.3(a).

6.4 (a) Extent of reaction in size fractions of four samples of KNO concentrate which had been smelted in the pilot scale reactor.
(b) Particle size distribution of the smelted KNO samples presented in Table 6.4(a).

6.5 Number of unreacted/unignited particles of the four sulfide minerals remaining in the products collected after smelting AMC, KNO, MAG and UCC concentrates using the pilot scale reactor.

6.6 EPMA data on smelted KNO samples showing the frequency of occurrence (%) for the five classifications of product.

6.7 EPMA data on smelted UCC samples showing the frequency of occurrence (%) for the five classifications of product.
6.8 EPMA data on smelted AMC samples showing the frequency of occurrence (%) for the five classifications of product.

6.9 EPMA data on smelted MAG samples showing the frequency of occurrence (%) for the five classifications of product.
CHAPTER 1  INTRODUCTION

The oxidation of metal sulfides is a commercially important process. Several metals of significant economic value, including nickel, copper, lead and zinc, occur as sulfide ores (Szekely, Evans and Sohn 1976, p347). These ores commonly contain iron sulfide minerals. In order to recover the metals the iron sulfide component of the ores must be oxidised. This is primarily achieved using pyrometallurgical methods.

The conventional pyrometallurgical process for metal winning from sulfide ores involves three stages, these being roasting, smelting and converting. During roasting the sulfides are partially oxidised in air or oxygen enriched air to remove the iron sulfides, iron oxide and sulfur dioxide being produced. The oxidation of iron sulfides is very exothermic and occurs preferentially to oxidation of copper and nickel sulfides.

Roasting is performed in either a multiple hearth roaster or a fluidised bed roaster. The heat released by the oxidation reaction is usually sufficient to raise the temperature of the system to a point where roasting becomes autogenous. This means that the reaction energy alone is sufficient to heat and oxidise the incoming feed. However, in some instances, the burning of fossil fuel may be required to supplement the heating. This
occurs, for example, when the feed material is excessively moist (Biswas and Davenport 1976, p61).

Smelting is performed in a reverberatory furnace. Pulverised coal, fuel oil or natural gas are burnt at one end of the furnace to generate hot gases which provide heat to melt the charge in the presence of a siliceous flux. The charge is actually calcine fed directly from the roasters. The energy requirements for smelting hot roaster calcines are considerably less than those for smelting cold wet flotation concentrates (Biswas and Davenport 1976, p5).

The function of the smelting stage is essentially to produce two immiscible layers. The oxidised species combine with the flux to form a liquid silicate or slag layer which is discarded. The molten sulfides are collected in the matte layer.

During the conversion process air is blown into the liquid matte to oxidise any remaining iron sulfide. Silicate flux is added to remove the resulting iron oxide as slag. Nickel and copper, together with their associated sulfur, remain in the matte phase. When processing nickel ores the product is collected at this stage and typically comprises 70% nickel and 20% sulfur. When processing copper ores, however, more air is blown into the converters to oxidise the sulfur associated with the copper. The end product is crude (99%) copper which
contains only 0.02-0.1% sulfur (Biswas and Davenport 1976, p180).

Hence, three units are required for conventional sulfide processing. The use of separate roasting and smelting stages is inefficient in terms of energy usage as the fuel value of the sulfides is not fully utilised. The reverberatory furnace has a substantial energy requirement. Another drawback of this furnace is that it generates large volumes of combustion gases which are dilute in sulfur dioxide. Consequently, procedures for the fixation and disposal of sulfur dioxide are very uneconomical (Bryk et al. 1958). Today the roasting and smelting stages are often combined into a one step process known as "flash smelting".

1.1 Flash Smelting

Flash smelting was independently developed in the 1940s by two companies: Outokumpu Oy in Finland and the International Nickel Company of Canada (INCO). The two processes are fundamentally different in both their furnace design and their method of introduction of the concentrate. The INCO process uses a small hearth-type furnace into which concentrate, flux and industrial oxygen (~95 mass % oxygen) are blown horizontally from both ends (Biswas and Davenport 1976, p160; Davenport and Partelpoeg 1987, p38). The heat released by the
oxidation of the iron sulfides present in the concentrate is sufficient to melt the particles and to form matte and slag layers in the base of the furnace. No additional heat is required, the process being completely autogenous.

The Outokumpu process uses a vertical reaction shaft. The concentrate, flux and air enter at the top of this shaft, the molten particles falling into a matte/slag bath, known as a settler, situated below. Unlike the INCO process which uses oxygen at ambient temperatures, the Outokumpu process uses preheated air, sometimes incorporating oxygen enrichment. The latter process is not autogenous and the combustion of some fossil fuel, either oil or pulverised coal, is necessary to supplement the heat balance in the furnace (Davenport and Partelpoeg 1987, pp10-11; Terry 1987, p16).

Flash smelting is commonly referred to as "suspension smelting" (Asteljoki, Sulanto and Talonen 1984). This implies that a fine grained sulfide concentrate is fed into a reaction shaft with air or oxygen to form a suspension. It is important that the concentrate is well dispersed in the gas stream to allow rapid heating of the individual particles. Under these conditions the reaction is extremely fast and is complete in less than a second.

Hence, the flash smelting process has a significant
economic advantage over the conventional roasting and smelting processes. The short reaction time involved permits a very high throughput of concentrate. A typical feed rate for an Outokumpu flash furnace is in excess of 1000 tonnes per day (Biswas and Davenport 1976, p164). Another advantage of flash smelting is the minimal requirement for external heat input after initiation of reaction in the shaft. The iron sulfide content of the feed concentrate actually provides the majority of the energy requirement for the process.

The high sulfur dioxide content of the combustion gas stream makes flash smelting very attractive from an environmental viewpoint. This gas stream can be economically processed to produce sulfuric acid. Over recent years the pyrometallurgical industry has become increasingly aware of the need to conserve energy and to reduce the level of environmental pollution caused by their operations. Hence, flash smelting is used today in preference to the conventional roasting and smelting techniques. Of particular significance to the mineral industry in Western Australia is the treatment of nickel sulfide concentrates by the Outokumpu process.

1.2 Outokumpu Flash Smelting as Practised at Kalgoorlie, Western Australia

The Western Mining Corporation (WMC) Kalgoorlie Nickel
Smelter (KNS) was commissioned in 1972 and rebuilt in 1978 to its current design which has a smelting capacity of approximately 520 000 tonnes of concentrate per annum. The general arrangement of this smelter is shown in Figure 1.1.

Sulfide ore is mined from various locations within WA and then concentrated by flotation to give a feed stock containing about 12% nickel. The associated levels of iron and sulfur are typically 33% and 26% respectively. The size specification on the feed material is that 80% must pass a 75μm sieve. This material is blended with silicate flux, coal and recycled dust from the process, then introduced to the reaction shaft through four burners. Here it contacts process air which has been preheated to approximately 480°C and which is at times enriched to a maximum level of 27% oxygen. Dispersion heads are employed to ensure that the solid particles form an even distribution right across the reaction shaft. The staff of the KNS estimate that 80-85% of the furnace energy requirements are provided by the sulfide oxidation reaction.

The reaction shaft has a diameter of 7m and a vertical height of 6m. Situated below this is a settler which measures 35m in length, 7m in width and 1m in height. The molten reacted particles fall into this settler. Here the silicate fluxing material combines with the iron oxide species to form a fayalite slag. This slag
Figure 1.1: The general arrangement of the Kalgoorlie Nickel Smelter.
typically comprises 41% iron, 35% silica, 0.3% nickel and 0.6% sulfur. The unoxidised iron and nickel sulfide species comprise the more dense matte layer. This phase contains approximately 45% nickel, 23% iron and 24% sulfur (Grimsey 1980; Hastie et al. 1984; Williams 1981). The predominant mineral species present in the matte are pentlandite \((\text{FeNi})_9\text{S}_6\), awaruite (an iron-nickel alloy) and heazlewoodite, \((\text{Ni}_3\text{S}_2)\) (Jorgensen, Kametani and Kobayashi 1986; Segnit 1977). The whole furnace is maintained at a temperature of 1300-1350°C by the combustion of fuel oil. This is introduced through oil burners at the top of the reaction shaft and in the sidewalls of the settler.

The matte layer is tapped off at regular intervals and transported by ladle to the converters. Here it is mixed with silica and air (or oxygen enriched air) is blown through the molten mixture to oxidise the remaining iron sulfides. The final nickel content in the matte is 72% while the iron content is reduced to less than 1%. This material is then granulated, dried and either sold to overseas markets as a final product or railed to WMC's Kwinana Nickel Refinery, south of Perth, for refining.

The slag flows to the far end of the furnace which is heated by two sets of three Soderberg electrodes. Coke is added to ensure strongly reducing conditions. This facilitates the reduction of any nickel-bearing oxides back to nickel metal. This metal then enters the matte
layer. The cleaned slag is continuously tapped, granulated and sent to waste (Page 1982).

The combustion gases pass out of the furnace through the uptake shaft to the waste heat boiler. Here the gases are cooled and steam is produced for power generation to serve the plant.

1.3 Ignition Reactions and the Smelting of Sulfides

It is generally accepted that the reaction of sulfide minerals in a flash smelter occurs via an ignition mechanism. Ignition is defined as corresponding to the establishment of self-sustaining combustion after the termination of heat supply from an external stimulus (Vilyunov and Zarko 1989, p320). Consider, for example, a particle being heated in a furnace. A point is reached at which the rate of heat generation from the chemical reaction of this particle exceeds the rate of heat loss. Providing this heat is used to raise the temperature of the particle rather than that of its surroundings, a further rise in reaction rate will be observed. The end result is a rapid escalation in particle temperature followed by a self-accelerating reaction with the release of large quantities of heat. This may occur in the condensed or gas phase (Vilyunov and Zarko 1989, p320) and will proceed completely independently of the external environment providing sufficient quantities of oxidant
are available (Dunn, Jayaweera and Davies 1985).

In order to ensure that the optimum performance is obtained from an industrial flash smelter it is necessary to investigate the ignition process. Two parameters of fundamental importance to this process have been identified (Dunn, Jayaweera and Davies 1985):

(1) The ignition temperature- this is defined as the minimum temperature required to cause ignition of the concentrate. This can be related to the preheat temperature of the process gas fed to the smelter.

(2) The extent of reaction (oxidation) of the concentrate at different temperatures of preheated process gas.

The ignition temperature is not a fixed value. Experimental determinations using different types of apparatus have resulted in large differences between the published values (Medard 1989, p258). In order to obtain comparable results all experimental variables must be strictly controlled.

1.4 Variables Affecting Ignition in the Flash Smelter

Several variables have been identified as having an affect on the ignition process in the flash smelter.
These include the mineralogical composition and particle size distribution of the feed, the preheat temperature of the process gas and the level of oxygen enrichment. Several laboratory and pilot scale studies have been conducted to examine the effects of these variables on the flash smelting process.

1.4.1 Mineralogical Composition of the Feed

There are four main sulfide minerals present in the feed material to the Kalgoorlie Nickel Smelter: pentlandite \(((\text{FeNi})_9 \text{S}_8)\), violarite \((\text{Ni}_2\text{FeS}_4)\), pyrite \((\text{FeS}_2)\) and pyrrhotite \((\text{Fe}_{1-n} \text{S})\), where \(n = 0\) to \(0.125\). These are the theoretical stoichiometries and significant variations may be seen in the naturally occurring minerals. Pentlandite and violarite are the two major nickel-bearing sulfides, while pyrite and pyrrhotite may each contain up to a few percent of nickel in solid solution (Nickel, Ross and Thornber 1974; Henley et al. 1973). The relative concentrations of the individual minerals in the feed vary according to the origin of the ore.

Ore is mined at three main locations in Western Australia for processing by the KNS, these being Kambalda, Leinster and Windarra (Williams 1981). The geology of the Kambalda ores has been documented by Nickel, Ross and Thornber (1974). These deposits comprise massive pentlandite-pyrrhotite assemblages which have been
subjected to supergene alteration and weathering. The orebodies are divided into four zones: primary, transition, supergene and oxide. Primary ore is predominantly pyrrhotite and pentlandite, with small quantities of pyrite (labelled "primary pyrite" to distinguish it from the supergene alteration form), chalcopyrite and spinel phases (magnetite and chromite).

Alteration commences in the transition zone with the appearance of specks of violarite throughout the pentlandite grains. Hence, violarite is known as a "supergene alteration product" of pentlandite. During this process nickel is released and it is available to react with pyrrhotite to generate an iron-rich type of violarite. The quantity of this phase formed is not as large as the quantity of pentlandite-derived violarite due to the limited amount of nickel present. When pentlandite conversion is complete and no more nickel is available, the remaining pyrrhotite is dissolved and reprecipitated as secondary pyrite and marcasite. The resulting violarite-secondary pyrite/marcasite assemblage constitutes the supergene zone. In the oxide zone violarite is converted to nickel carbonate and goethite, while pyrite and marcasite are converted to goethite.

Laboratory studies (Dunn and Smith 1984) have established that pyrite and violarite are far more reactive than pentlandite and pyrrhotite. This statement was based upon the measurement of the furnace preheat temperatures
required to initiate ignition of each sulfide mineral in a thermogravimetric analyser.

The results of an independent study conducted using a laboratory laminar flow furnace were in agreement with the above stated order of reactivity (Jorgensen 1978). Pyrite was the most readily ignited mineral followed by violarite and pentlandite. Pyrrhotite was the least reactive mineral. This order was determined by oxidising 37-53μm nickel concentrate samples at different temperatures. The products were examined by X-Ray Diffraction (XRD). The temperature at which each species disappeared from the XRD trace was used to establish the order of mineral reactivity.

1.4.2 Particle Size Distribution of the Feed

Particle size is a very important variable in the flash smelting process. A reduction in the particle size distribution of a concentrate will increase the available surface area and has been found to increase the rate of reaction of a nickel concentrate (Jorgensen 1978).

A significant link has been identified between the particle size of sulfide minerals and their ignition temperatures (Dunn and Smith 1984). The furnace preheat temperature required to ignite pentlandite in a thermal analyser varied from 425-430°C for the <45μm
fraction up to 560-565°C for the >90μm fraction, this being an increase of 135°C. The corresponding temperatures for the same size fractions of pyrrhotite were 470-475°C and 540-545°C respectively, representing an increase of 70°C. The relative order of reactivity of these two minerals has changed with increasing particle size. Below 75μm pentlandite displayed a lower ignition temperature than pyrrhotite. Values for the 75-90μm fractions of both minerals were equal while the >90μm fraction of pyrrhotite ignited at a temperature 20°C lower than pentlandite.

A 50°C increment was observed between the ignition temperatures of the <45μm and the >90μm fractions of violarite, the values being 380-385°C and 430-435°C respectively. Pyrite ignition was virtually independent of particle sizing. The <45μm fraction ignited at 380-385°C, a 15°C increment being required to ignite the >90μm fraction. Pyrite was obviously the most reactive mineral regardless of particle size. While violarite did exhibit a particle size effect comparable with that of pyrrhotite, it was far more readily ignited than either pyrrhotite or pentlandite.

The effect of particle size on the extent of reaction experienced by a typical nickel sulfide concentrate at increasing furnace preheat temperatures has been investigated (Dunn 1983). It was found that the extent of reaction of a Kambalda concentrate at 510°C in a
thermal analyser increased from ~55% for the 90-125μm fraction to ~85% for the <45μm fraction. With increasing furnace preheat temperature the difference between the extents of reaction for the two size fractions decreased. As a result of this work particle size specifications were introduced for the feed supplied to the KNS. It is now necessary that 80% of feed material is finer than 75μm (Hastie et al. 1984). This modification has resulted in an improved and more consistent smelter matte grade. Consequently there has been a substantial saving in annual energy costs for the smelter. Hence it is apparent that in order to make sensible statements regarding reactivity based upon mineralogical variations particle sizing must be considered.

1.4.3 Preheat Temperature of the Process Gas

Laboratory scale research has indicated that the predominant mechanism of heat transfer to small particles (<100μm) prior to ignition in a flash smelter is by conduction from the surrounding gas rather than radiation from the furnace walls (Jorgensen 1979). At a gas preheat temperature of 380°C ignition of a nickel sulfide concentrate did not occur despite the furnace preheat temperature being increased from 380°C to 1100°C. However, once the gas temperature was raised to 600°C ignition occurred when the furnace temperature
was only 380°C. Raising the latter to 1100°C had a relatively minor effect on the extent of reaction observed. Hence in order to achieve ignition it is essential that the process gas introduced into a flash smelter is at a temperature sufficiently high to provide the necessary heating effect in particles.

A mathematical model developed for the Outokumpu flash smelting of copper concentrates has indicated that increasing the preheat air temperature above that required to initiate ignition has a relatively small effect on the rate of reaction (Themelis, Makinen and Munroe 1985).

1.4.4 Oxygen Concentration in the Process Gas

Studies on the ignition of nickel sulfide concentrates under simulated flash smelting conditions have shown that increasing the oxygen content of the process gas from 21 to 100% caused an increase in the observed reaction rate but had a negligible effect on the temperature at which ignition occurred (Condina et al. 1982; Jørgensen 1978).

This observation was supported by Munroe (1987) who smelted copper concentrates using a laboratory reactor. He reported that the overall degree of sulfur removal was not significantly affected by oxygen enrichment although the rate of reaction was noticeably enhanced. It was
found that at a level of 50% oxygen enrichment, 75% of sulfur removal occurred within 0.8m from the entry point of the concentrate. At 21% oxygen the same level of sulfur removal was not achieved until a point 2m from the entry point was reached.

These findings were consistent with by evidence obtained from mathematical modelling studies of the flash smelting process (Chaubal 1986; Hahn and Sohn 1990; Kim 1987; Themelis, Makinen and Munroe 1985).

1.5 Techniques Utilised in the Study of Flash Smelting

Although flash smelting entered the industrial scene more than 40 years ago, the complexity of this process has prevented researchers from obtaining an unambiguous view of the reaction mechanisms involved. Several different techniques have been employed in an attempt to elucidate the processes occurring in the reaction shaft. Sampling from the industrial system is problematical as the products fall into a molten matte/slag bath. Hence laboratory equipment has been designed such that the product is quenched and collected immediately it exits the shaft.

It is necessary to exercise extreme care when making proposals regarding industrial flash smelting on the
basis of laboratory test work. Sample heating rates must be sufficiently high to simulate ignition conditions otherwise a stepwise oxidation process will occur (Dunn and Jayaweera 1985). A survey of the work performed using different experimental techniques indicates some variation and conflict in the published results. In order to obtain comparable data the experimental conditions governing the heat flow balance must be strictly controlled to ensure that the material is exposed to a similar thermal environment in each apparatus (Jorgensen 1978; Jorgensen, Moyle and Wadsley 1988).

In the following sections several of the main research techniques used in laboratory, pilot scale and mathematical modelling studies will be discussed. The limitations associated with some of them regarding their capacity to simulate true suspension smelting conditions will be highlighted. The majority of flash smelting research has been performed using chalcopyrite. Two techniques have been employed to investigate nickel sulfide systems, these being Isothermal Thermogravimetry and the Laminar flow furnace.

1.5.1 Isothermal Thermogravimetry

This laboratory scale technique was developed to simulate the conditions of shock heating which occur in a flash
smelter (Dunn, Jayaweera and Davies 1985). Samples are weighed into a platinum crucible which is suspended above the furnace of a thermogravimetric analyser. The latter is preheated to an appropriate temperature, usually in the range 400-900°C, and then raised on a cam shaft around the sample. A flowing oxygen atmosphere is employed but the gas is not preheated. The sample heating rate is estimated to be approximately 4500°C/min.

This method is used to measure the temperature at which ignition of a material occurs. This is indicated by a sharp mass loss in the case of nickel sulfide samples (Dunn, Jayaweera and Davies 1985). Overheating of the sample thermocouple due to the highly exothermic nature of the ignition reaction is evident from the temperature trace. The extent of reaction of the material with increase in temperature can be calculated based upon the observed mass loss at each temperature. It is assumed that the mass loss at 900°C corresponds to 100% reaction.

When using this technique to simulate flash smelting conditions two points must be considered. Firstly, there are no facilities for preheating the process gas prior to its entry into the furnace. The second consideration is the form taken by the sample. During flash smelting the particles react in a gas-solid suspension. A characteristic of thermal analytical techniques, however,
is that the sample reacts in a packed bed. Thus the particles are in contact with each other and with the crucible. Heat transfer effects will differ greatly from those which exist in the industrial smelter. For this reason it is preferable to use as small a mass of sample as possible (Jorgensen 1978) in order to minimise particle interactions. Sample sizes from 1 to 13mg were investigated (Dunn, Jayaweera and Davies 1985). It was found that below 3mg ignition frequently did not occur. Above 8mg the sample was often ejected from the pan due to the force of the reaction. A sample size of 5mg was chosen.

1.5.2 Laminar Flow Furnace

This laboratory scale apparatus was originally employed in the study of the decomposition behaviour of pulverised fuel particles (Sainsbury et al. 1966) but has since been applied to sulfides (Jorgensen and Segnit 1977). The laminar flow furnace is essentially a vertical tube surrounded by a heating element. Feed material, together with a small flow of cold carrier gas, enters the top of the furnace via a water-cooled feeder tube. Here it mixes with a preheated gas stream and both the solids and carrier gas rapidly reach the furnace temperature. The temperature of the furnace can be varied up to 1100°C as can the gas preheat temperature. Both are normally maintained at the same level. The reacted particles and
gas are aspirated into a water-cooled collector probe. Separation of the particles from the gas is then achieved by a cyclone. The transit time of the sample through the furnace is monitored by adjusting the distance of the collector from the feeder tube and is usually of the order of 0.1s.

One criticism of this method is that flow through the furnace is laminar as opposed to the turbulent flow conditions which exist in an industrial flash smelter. It was argued, however, that the minimum scale of microturbulence in the industrial system would be of the order of the particle separation distance (Jorgensen 1978). Thus the gas within this distance would be non-turbulent relative to the particle.

A second criticism of this method in its application to sulfide smelting is the low particle densities in the preheated gas stream. Feeding rates of the order of 0.25g/min were used resulting in very dilute suspensions (Jorgensen 1978; Jorgensen 1986). Consequently the overall gas composition would be relatively unchanged as a result of particle combustion. This is not the case in the industrial system where the stoichiometric requirement of gas for complete combustion of the feed is calculated. Consequently an increase in sulfur dioxide concentration and a decrease in oxygen concentration is observed down the reaction shaft (Themelis and Kellogg 1983).
Conditions in the laminar flow furnace will be more oxidising than those in the industrial smelter due to the excess oxygen available. Thus, the reaction products will proceed to the highest oxidation state. It has also been suggested that the particle temperatures recorded will be somewhat higher than those expected in the industrial system (Hahn and Sohn 1987). This system is considered to be a model for the combustion behaviour of single particles (Otsuka and Soma 1980).

1.5.3 Other Experimental Simulations

Most other laboratory simulations have been performed using a vertical furnace tube with facilities for gas preheating and for quenching of the sample as it leaves the tube. These invariably resembled the laminar flow furnace in general design (Asaki et al. 1985; Chau Bailey 1986; Huffman et al. 1989; Jorgensen 1986 & 1987; Munroe 1987; Otsuka and Soma 1980). However, furnace dimensions, feeding rates of the concentrate, gas and furnace temperatures and the composition of the combustion gas varied considerably.

A different experimental approach involved the use of a laboratory scale dispersed particle jet reaction system (Kang, Steinhauser and Wuth 1983; Kang and Pyun 1988; Wuth 1984). This essentially comprised a feeding system and a concentrate burner. The latter contained a special
accelerator nozzle through which the gas-concentrate mixture passed. Immediately upon exiting the nozzle, the particles were heated to their ignition temperature by the pilot burner. The product was quenched in a water-filled basin. The approximate temperature of the jet was 1550°C, particle residence time being 29ms.

Studies have also been performed on a pilot scale. A model of a flash smelter, including the matte/slag bath, has been employed (Kimura et al. 1986; Kemori, Ojima and Kondo 1988). A concentrate feeding rate of one ton per hour was used, preheated oxygen enriched air, flux and supplementary fuel also being fed to the top of the reaction shaft. Several sampling ports were located down the shaft to collect the product prior to entry into the molten bath. A water-filled sampler was used.

While the majority of research on ignition has focused on flash smelting simulation, some work has been performed using a cyclone smelting pilot plant (Barin and Sauert 1980; Barin, Modigell and Sauert 1983). Cyclone smelting is another process based upon the suspension smelting concept. Sulfide concentrate is fed into the top of the cyclone while oxygen enters tangentially. The reaction rate is very rapid and the resulting molten products fall into a matte/slag bath. The retention time of particles smaller than 1000μm in the cyclone chamber is approximately 80ms and temperatures of up to 1830°C have been measured. The average temperature in the cyclone is
assumed to be 1630°C.

1.5.4 Mathematical Modelling

Elucidation of the flash smelting process has also been attempted from a theoretical aspect using mathematical modelling. Models for the thermodynamic and rate phenomena existing in the shaft have been developed and the results obtained from them have been compared with experimental observations (Chaubal 1986; Hahn and Sohn 1987 & 1990; Kim 1987; Themelis and Kellogg 1983; Themelis, Makinen and Munroe 1985; Themelis, Wu and Jiao 1988). There are two basic types of models: a uni-dimensional one and a two-dimensional one. The uni-dimensional model assumes that motion of particles occurs only in the axial direction of gas flow. Radial particle dispersion is neglected. At a certain distance from the entry point of the concentrate velocity, temperature and particle density are considered to be uniform. The two-dimensional model, however, considers both axial and radial distributions. This model will provide a better description of the smelting process, particularly in the entry region of the reactor (Themelis, Wu and Jiao 1988).

These models have been utilised to predict the effects of many variables on flash smelting, including oxygen concentration of the process gas, particle size of the
concentrate and preheat temperature of the gas. Predictions have also been made regarding the particle temperature profiles in the shaft, degree of desulfurisation of the particles with distance travelled and the change in the size distribution of the particles during oxidation. These data have led to several findings of importance to the operators of the industrial flash smelters. For example, models have indicated that sulfide reaction is essentially complete within one metre of the concentrate burner (Themelis, Wu and Jiao 1988). This is significant as a reduction in shaft height would reduce the heating requirements of the smelter.

1.6 Mechanistic Studies of Ignition Reactions

Although the ignition reactions of sulfide minerals have been the subject of several studies, a reaction mechanism has not been conclusively established. In the past an oxygen diffusion concept has been assumed when considering the reaction of a gas at the surface of a solid (Wen and Wang 1970). This is commonly referred to as the "shrinking-unreacted core" model and a good explanation of this model has been presented in the literature discussing coal combustion (Mohan, Mckinley and Douglas 1979).

The shrinking-core mechanism is a surface oxidation process controlled by the rates of both chemical reaction
and mass transport. Reaction is initiated at the particle surface resulting in the formation of a product layer. To allow further reaction oxygen must diffuse through this layer to access the unreacted material. The gaseous oxidation products then diffuse back out into the gas stream. With time the reaction surface progresses into the particle forming an ever thickening product layer surrounding the characteristic unreacted shrinking-core of reactant (Mohan, McKinley and Douglas 1979). However, the relevance of this theory to ignition reactions involving particle melting is questionable.

Ignition reactions occur in coal and metal particles and hence a survey of the associated literature regarding the reaction mechanism is relevant.

1.6.1 Coal

When pulverised coal particles are injected into a hot furnace they experience extremely rapid heating rates, followed by ignition. Two factors are critical to the determination of the reaction characteristics of such a system (Annamalai and Durbetaki 1977; Howard and Essenhigh 1966; Merrill 1973):

1. The volatile content of the coal
2. The particle size distribution of the coal
It is generally agreed that coals with a high content of volatile matter are more susceptible to ignition than those with a low volatile content (Juntgen 1977; Nettleton and Stirling 1967). Experimental studies have indicated that the temperature at which ignition of particles of a certain coal occurs is closely related to the point at which the rate of volatile loss from these particles becomes appreciable (Nettleton and Stirling 1967). This theory was supported by microscopic evidence which showed that the reacted coal particles exhibited a honeycomb structure typical of a volatilised char.

The mechanism for ignition of a coal particle involves two reaction types: homogeneous combustion of the volatiles in the gas phase and heterogeneous combustion of the char at the particle surface (Shadman and Cavendish 1980; Wall et al. 1986). The relative importance of each reaction seems to be largely dictated by the size of the coal particles together with the sample heating rate and the volatile content of the coal (Juntgen 1977). It appears that small particles are dominated by surface oxidation. For larger particles the volatile matter released on heating burns in an envelope surrounding the individual coal particles (Shadman and Cavendish 1980). The char, or devolatilised coal particle, is shielded from oxygen at this point by the volatile flame (Timothy, Sarofim and Beer 1982). The mechanism then changes as the rate of volatile release diminishes. The flame zone gradually moves towards the
particle surface where the devolatilised coal particle is combusted (Annamalai and Durbetaki 1977; Shadman and Cavendish 1980; Smith and Smoot 1980; Timothy, Sarofim and Beer 1982).

The variation in mechanism with particle size of the coal has been attributed to the flux of pyrolysis products produced at the particle surface during heating (Howard and Essenhigh 1966). Pyrolysis is a volumetric reaction and larger particles are capable of generating a higher surface flux of volatiles than are smaller ones. Consequently, the reaction zone for a larger particle will stabilise at a distance from the particle surface, preventing heterogeneous combustion. A critical particle size requirement of 65μm has been suggested for this mechanism (Howard and Essenhigh 1966). For smaller particles reaction will stabilise on the particle surface and both gas-phase and heterogeneous oxidation will occur. However, the rate of the latter process is small unless the particle size is below 15μm.

1.6.2 Metals

When a metal particle is heated in an oxidising atmosphere surface reaction causes the formation of an outer oxide layer which separates the oxidising agent from the metal. The reaction rate is then determined by the speed of reagent transfer through the product layer
(Merzhanov 1975). For ignition to occur the oxidant must penetrate this layer and access the metal surface at a sufficiently rapid rate to cause temperature escalation. In a study of boron ignition the complete removal of the oxide has been specified as a necessary condition for ignition (King 1974; Meese and Skifstad 1974).

Another factor of great importance is particle melting (Meese and Skifstad 1974; Merzhanov 1975). The kinetics of the gas-solid reaction are possibly too slow and hence it seems that the metal and/or its oxide must melt in order to trigger ignition. This has been reported in a study of aluminium (Macek 1966). Ignition was found to occur when the particle temperature exceeded 2000°C. This corresponds to the melting point of alumina.

Several studies have indicated that gas-phase reaction is of fundamental importance to the ignition mechanism of metal particles (Law 1976; Macek 1966; Yuasa and Takeno 1982). Beryllium provides a good example of this (Macek 1966). Ignition actually occurs at the boiling point of the metal (2480°C) rather than the melting point of the oxide (2530°C). The beryllium vapour is able to force its way through to the surface, igniting upon contact with the gas stream. It appears that beryllium oxide is relatively permeable to gases at this temperature. Hence, the ignition characteristics of a particular metal obviously depend upon the physical properties of the associated oxide.
A gas-phase mechanism appears to govern the behaviour of particles of a magnesium-aluminium alloy (Yuasa and Takeno 1982). A protective oxide film is initially formed over the molten metal particle. However, as the temperature becomes sufficiently high (750-930°C) magnesium vapour is able to break through the film causing ignition to occur. A very rapid heating rate has been observed to cause the particles to fragment.

Boron is far more difficult to ignite than the previously mentioned metals. Boric oxide boils (1860°C) at a significantly lower temperature than boron melts (2030°C). Consequently it seems that the initial combustion process is a surface reaction. Oxygen diffuses in through a molten oxide layer to access the unreacted metal, rather than the metal vapour diffusing out. The resulting oxidation process generates heat which causes the oxide to evaporate. If this rate of evaporation exceeds the rate of oxide formation the surface layer will eventually boil off, allowing particle melting and ignition (King 1974; Meese and Skifstad 1975).

The temperature history of an individual particle is fundamental to the determination of its ignition behaviour. In the same way that a metal powder has a distribution of sizes, so a gas stream is characterised by velocity, temperature and oxidant concentration distributions. Consequently the individual particles
within a system can experience varying degrees of heating. This effect will be further enhanced by particle size variations. Hence it is not surprising that microscopic examination of metal ignition products has provided evidence of three different reaction types (Yuasa and Takeno 1982):

(1) Non-ignition: Heating effects were insufficient to cause particle melting or significant surface reaction. Such particles were virtually identical in composition and appearance to the unreacted material, but the corners were rounded.

(2) Partial reaction: Surface oxidation resulted in the formation of a protective oxide coating which prohibited the particles from igniting. The particle shape resembled that of the unreacted material, but the surface morphology was very different, being far more complicated.

(3) Ignition: Heating effects were sufficiently vigorous to prevent significant surface oxidation. Gas-phase ignition occurred once particles had melted. The product particles were smooth and spherical in shape.

An interesting particle type was formed when aluminium particles were ignited in the presence of hydrogen (Macek 1966). Spectacular fragmentation was observed during reaction and hollow bubbles of alumina were present in
the products. One explanation for the formation of bubbles is that inflation of molten alumina occurs due to the boiling of aluminium. Alternatively, bubble formation has been attributed to the evolution of dissolved permanent gases, that is, hydrogen. The latter theory is preferred, however, considering that bubbles occur almost exclusively in media containing hydrogen.

Violent fragmentation was also observed in an ignition study of zirconium (Nelson 1966). This occurred when nitrogen was present either in the oxidising gases or when it was alloyed with the metal. Fragmentation was not observed in a pure oxygen atmosphere. It was proposed that in the early stages of combustion both oxygen and nitrogen were rapidly absorbed by the metal droplet. However, zirconium dioxide is the thermodynamically favoured product and consequently nitrogen was released as the reaction progressed. When the vapour pressure of this gas was sufficient it caused the droplet to fragment.

1.6.3 Sulfides

(i) Chalcopyrite

The flash smelting technique was originally developed to process copper sulfide ores and hence, mechanistic studies of the ignition of chalcopyrite, the dominant
copper-bearing sulfide, are by far the most abundant. It is thought that the flash reaction of chalcopyrite involves three different stages (Kim 1987):

1. Thermal decomposition of chalcopyrite and dissociation of labile sulfur

2. Gas-phase oxidation of the sulfur

3. Oxidation of the resulting decomposed sulfides by gas-solid and/or gas-liquid reaction.

Five distinct regions have been identified in the sulfur removal pattern (Kim and Themelis 1986; Kim 1987). Initially there is an induction stage during which the particles are heated by convection and radiation, the sulfur loss being minimal. The point at which the particles suddenly display a rapid rise in temperature is defined as the ignition temperature and this identifies the second stage. In this stage the sulfide particles decompose, the rate of sulfur removal achieving its maximum value. The evolved sulfur vapour burns in the bulk gas stream and at the boundary layer of the particles. This process is extremely fast and oxidation at the particle surface is prevented. It is estimated that dissociation of sulfur vapour from particles smaller than 25µm is complete at this stage, however, an overall analysis indicated that only 5% of the original sulfur from all particles had been removed (Kim 1987).
In the next stage sulfide decomposition occurs simultaneously with oxidation at the particle surface. The sulfur removal rate decreases despite the fact that the particle temperature has increased. This is because the oxidation process now includes a gas-solid reaction, oxygen diffusing through the boundary and the reacted layer to reach the unreacted core.

Reaction then proceeds to a gas-liquid mode. Sulfides melt at a lower temperature than oxides and hence a molten sulfide core is formed, being enclosed in a highly porous, solid iron oxide crust (Kim 1987; Munroe 1987). This is an extremely unstable phase due to the vigorous dissociation and oxidation reactions which are occurring. The particle temperature increases rapidly and gas evolution occurs within the core. The crust and the core are separated along their boundary and ultimately particle fragmentation may occur. Sulfide is ejected as molten droplets, all of which are fairly uniform in size, irrespective of the initial particle size of the sulfide. The crust appears spherical indicating that fragmentation occurs near the oxide melting point. The thickness of the crust is largely determined by the rate of particle heating. A very thin, dense crust will result when heating is rapid. Conditions of slow heating, however, will produce a thicker and more porous crust.

The final stage of reaction comprises the oxidation of
the droplets which formed during fragmentation. Fragmentation will not always occur, depending upon the size of the particle and the extent of gas formation within the core. Large particles are more likely to fragment due to the relatively large volume of the molten core and the increased amount of entrapped labile sulfur. Smaller particles, however, contain less sulfur vapour and the predominant reaction product is a molten core surrounded by an oxide crust which is full of holes (Munroe 1987).

One experimental study reported that particles larger than 70μm fragment and that 50% of the resulting droplets have an average diameter of 30μm (Munroe 1987). The degree of fragmentation observed increased as the oxygen content of the process gas increased. Oxygen enrichment would enhance reaction rates by promoting gas evolution within the particle and therefore increasing the likelihood of fragmentation.

The proposal of fragmentation has been a source of major controversy in the literature. A completely opposite observation, that is, particle agglomeration, has been reported (Kemori, Ojima and Kondo 1988; Kimura et al. 1986). Although some researchers believe that the particle population in the shaft is too low to allow a significant incidence of particle collision (Themelis and Kellogg 1983), agglomeration theory disputes this. Studies have shown that the measured particle size of
material reacted in a pilot scale flash furnace increased rapidly when the temperature exceeded \(1150^\circ\text{C}\) (Kimura et al. 1986). This was said to be due to contact between molten particles. A second study using the same furnace found that the original concentrate grew from an average size of 50\(\mu\text{m}\) to one of over 250\(\mu\text{m}\) (Kemori, Ojima and Kondo 1988). Despite the fact that smaller particles are well known to be more reactive, the coarser material displayed a higher degree of desulfurisation. It has been proposed that agglomeration results from the collision of reacted particles with one another and with less oxidised solid particles (Kemori, Ojima and Kondo 1988; Kimura et al. 1986). Hence, these larger particles show an increased fraction of sulfur loss.

In order to reconcile these two opposing views, that is, agglomeration versus fragmentation, a two stage process has been proposed (Themelis, Wu and Jiao 1988). In the upper level of the reaction shaft the sulfur content in the particles is high, as is the oxygen content in the process gas. These conditions favour particle fragmentation, this probably occurring close to the oxide melting point. Once particles have completely melted fragmentation was said to cease and agglomeration to commence. This particularly occurs when conditions in the shaft are such that the flow is highly turbulent and the density of the particle suspension is sufficient to allow frequent collisions.
Extensive characterisation of products from experimental and industrial copper flash smelting furnaces has been performed using the techniques of light and electron microscopy (Hagni and Vierrether 1988; Hagni, Vierrether and Sohn 1988; Pignolet-Brandom, Hagni and Munroe 1986). Consistent with the observations for metal particles, the sulfide products were found to be very diverse in morphology, representing varying degrees of reaction. It is well known that all particles do not experience the necessary conditions to achieve complete reaction in the flash furnace shaft. The distribution of particle sizes of the feed, together with variations in the local temperature and gas composition, result in individual particles experiencing vastly differing thermal histories. While some may react to completion, others may remain virtually unaltered.

Two types of reaction were found to be occurring during copper smelting: 1) gas-liquid reaction and 2) gas-solid reaction (Hagni and Vierrether 1988; Hagni, Vierrether and Sohn 1988). Products of the former type predominated, these being spheres, hollow spheres known as "cenospheres" and fragmented particles. Particles which had reacted via a gas-solid process were angular, never having achieved a temperature sufficiently high to cause melting. These species were far less prolific than the molten products.

Further classification of the products was made based
upon the appearance of the particle cross-section (Hagni and Vierrether 1988). Alteration and exsolution textures were identified, the characteristics of each being as follows:

(1) Alteration textures: These are largely a result of gas-solid reactions but they may also be generated by reaction between liquid and gaseous phases. Alteration textures normally comprise an unreacted core of sulfide which is surrounded by a rim of oxidised material.

(2) Exsolution textures: These are characteristic of gas-liquid reactions. Four variations of this texture have been identified, the predominant type comprising irregular patches of one phase uniformly distributed throughout a second phase. This type is thought to result when the product cools at a slow rate. A more rapid cooling rate results in the exsolution of lamellae of one phase from another. The formation of either skeletal crystals or rounded blebs within a second phase accounts for the two remaining exsolution textures. Some particles may comprise oxide and sulfide phases which have completely separated as a result of liquid immiscibility. Particles dominated by exsolution texture may also exhibit a rim of alteration product. This indicates that they have experienced continued reaction after resolidification.

The phases identified in smelted chalcopyrite products
(Hagni and Vierrether 1988) exhibit a wide variation in copper, iron and sulfur contents and they include: unreacted chalcopyrite; intermediate solid solution (i.e. mookhoekite (Cu$\text{Fe}_9\text{S}_{16}$)); bornite (Cu$_5$FeS$_4$); digenite (Cu$_{2-x}$S); pyrrhotite (Fe$_{1-x}$S); chalcocite (Cu$_2$S); covellite (CuS); magnetite (Fe$_3$O$_4$); hematite (Fe$_2$O$_3$); cuprospinel (CuFe$_2$O$_4$) and delafossite (CuFeO$_2$). Small amounts of cuprite (Cu$_2$O) and metallic copper have also been identified.

The reaction of chalcopyrite normally incorporates particle melting. Reaction commences with the formation of intermediate solid solution and the release of a small amount of sulfur. Further reaction produces bornite solid solution. Intermediate solid solution and bornite are the most common phases evident in exsolution textures. The production of bornite causes the release of iron which reacts to form hematite and magnetite. Cuprospinel and delafossite are also formed. Bornite and chalcopyrite may continue reacting to generate digenite, chalcocite and covellite. The most intense degree of oxidation will produce pyrrhotite, metallic copper and cuprite.

Magnetite and hematite appear as rims or shells surrounding the molten sulfide and as small spheres within the sulfide. These spheres form due to the high surface tension of the oxide. Some oxide may also be present as skeletal crystals which have exsolved from the
Cu-Fe-S-O melt on cooling. Many iron oxide particles are actually free of sulfide. These are usually spheres, cenospheres and fragmented cenospheres which have formed as a result of the disintegration of larger particles (Hagni and Vierrether 1988; Hagni, Vierrether and Sohn 1988).

The sequence of phases formed by the less frequent mode of gas-solid reaction is similar to that detailed above. Angular chalcopyrite particles may exhibit bornite alteration rims, or they may completely alter to bornite. Further reaction produces digenite and chalcocite. The products include bornite with digenite rims, digenite with chalcocite rims or particles which have altered to either digenite or chalcocite. Rims of hematite, magnetite and cuprospinel also form surrounding the sulfide particles.

(ii) Pyrite

Of the four sulfides which are important in nickel smelting only pyrite has been studied extensively. Mineralogical examination of chalcopyrite concentrates containing pyrite has led to the identification of pyrite flash furnace products (Hagni and Vierrether 1988; Hagni, Vierrether and Sohn 1988). The results are analogous to those for chalcopyrite, there being a wide range of product types. Both gas-liquid and gas-solid reactions
occurred. It was found that pyrite initially reacts to form pyrrhotite with the release of sulfur vapour. This pyrrhotite appears as thin fibrous grains radiating out from the pyrite core. The products vary from particles of pyrite with a thin pyrrhotite rim to particles showing complete replacement of all pyrite with pyrrhotite. Reaction of the pyrrhotite particles may continue in the solid phase with the formation of rims of magnetite and hematite. Complete oxidation to hematite commonly occurs. Hematite particles retain the radial, fibrous appearance of the pyrrhotite. It was noted that oxidation of pyrrhotite rarely occurred until complete conversion of the pyrite had been achieved.

Alternatively, pyrite may decompose to pyrrhotite and melt, resulting in a gas-liquid reaction. Melting does not occur until the conversion to pyrrhotite has been completed and hence, no pyrite remains in these products. All stages of oxidation are observed in the spherical particles, ranging from thin magnetite rims surrounding pyrrhotite to completely oxidised spheres. Skeletal magnetite was also observed to crystallise out in the pyrrhotite phase. Hematite was far less abundant than magnetite in these molten products.

The ignition characteristics of pyrite have been studied using the laminar flow furnace and the following mechanism has been proposed (Jorgensen 1981a):
(1) Heating of the pyrite particles to ignition temperature ($500-600^\circ$C). Particle morphology was unaltered.

(2) Decomposition of pyrite to pyrrhotite ($700^\circ$C) and burning of the evolved sulfur at or near the particle surface.

(3) Further oxidation of pyrrhotite resulting in the formation of oxide-sulfide intergrowths.

(4) Formation of an Fe-S-O melt ($\sim 900^\circ$C) and rapid escalation of particle temperature.

It was proposed that the trigger for pyrite ignition was the structural change associated with pyrrhotite formation (Jorgensen, Moyle and Wadsley 1988). Pyrrhotite has a very porous structure when formed from pyrite, a 20% volume reduction being associated with this decomposition process.

The average maximum temperature reached by a 37-53$\mu$m stream of pyrite particles burning in an air atmosphere preheated to 700$^\circ$C was approximately 1480$^\circ$C (Jorgensen 1981b; Jorgensen and Zuiderwyk 1984). Individual particle temperatures of the order of 1850$^\circ$C were measured. Reaction times were very rapid, the 37-53$\mu$m screen size fraction, for example, achieved complete combustion in approximately 60ms. Shorter
reaction times were recorded when the oxygen concentration of the atmosphere was increased.

The examination of pyrite concentrate which had been smelted in a laminar flow furnace identified several product types including angular particles, spheres and cenospheres (Jorgensen 1980a). The surfaces of the spheres often exhibited a skeletal oxide structure which had developed during particle cooling and resolidification. Cenospheres were thought to form as a result of gas evolution from molten particles. When intact cenospheres were broken they were invariably found to contain some solid material. This was largely magnetite, only a small amount of sulfur being detected. When cenospheres were formed access of oxygen to the interior of the particle would be limited. Hence, the contained material would probably undergo no further reaction following the moment of cenosphere formation. As most of this material analysed as magnetite it appears that cenosphere formation occurred when the molten droplets had virtually completely reacted.

Studies on pyrite support the fragmentation theory, an overall size reduction of the particles during ignition being reported (Jorgensen 1981a). Besides fragmentation, collapse of the cenospheres was suggested as another contributing factor. Some size degradation did occur due to the thermal shock experienced by particles on heating to reaction temperature. A 50μm pyrite particle was
estimated to experience an average heating rate of 18 000°C/s when injected into the laminar flow furnace, the latter being preheated to approximately 700°C. The resulting thermal stress would cause particles to break apart. Particles also ruptured during decomposition of pyrite to pyrrhotite.

It was noted that the formation of cenospheres actually caused a particle size increase (Jorgensen 1980a). For example, the 74-105μm size fraction of pyrite concentrate produced cenospheres up to 270μm in diameter. For the 37-53μm and 53-74μm fractions the largest cenospheres formed were 165μm and 205μm respectively. However, the net effect of ignition was that of size reduction.

(iii) Other Sulfide Minerals

The combustion behaviour of two other sulfide minerals, galena (PbS) and sphalerite (ZnS), has been investigated using the laminar flow furnace (Jorgensen 1980b). The rate of reaction of these minerals was slow at air temperatures up to 700°C for galena and 1200°C for sphalerite. Reaction times were of the order of seconds and the resulting particle morphology was in accordance with the shrinking core theory. An unreacted core of sulfide remained, this being surrounded by a shell of oxidation product. The probable rate controlling factor was diffusion through the oxide layer. However, a
dramatic increase in reaction rate was observed when the air temperature exceeded 700°C and 1200°C for galena and sphalerite respectively. This was attributed to the volatilisation of the sulfides and subsequent gas-phase oxidation. Molten spheres were evident in the products at this stage and reaction times approached those measured for pyrite.

A comprehensive study of the cyclone smelting of zinc sulfide has indicated that the oxidation of this mineral can also be explained by a gas-phase concept (Barin and Sauert 1980; Barin, Modigell and Sauert 1983). The fast velocity of the gas-solid flow in the upper part of the cyclone causes a high degree of turbulence and consequently the rates of mass and heat transfer are elevated. As a result reaction rates are very fast and high temperatures have been measured (~1830°C). Under these conditions zinc sulfide is observed to vaporise and dissociate according to the following reaction:

$$\text{ZnS}_{(s)} \rightarrow \text{Zn}_{(g)} + 0.5\text{S}_2_{(g)}$$

This will then trigger very rapid combustion in the gas phase:

$$\text{Zn}_{(g)} + 0.5\text{S}_2_{(g)} + \text{O}_2 \rightarrow \text{ZnO}_{(g)} + \text{SO}_2_{(g)}$$

$$\text{Zn}_{(g)} + 0.5\text{S}_2_{(g)} + 1.5\text{O}_2 \rightarrow \text{ZnO}_{(g)} + \text{SO}_3_{(g)}$$

It has been calculated that the sulfide particles will
vaporise within 20ms. Complete reaction occurs within the residence time of the particles in the cyclone (80ms). The diffusion of oxidant through a porous oxide layer has been shown to be far too slow to account for the rapid reaction of zinc sulfide which is observed in cyclone smelting. Calculated residence times for this gas-solid reaction are of the order of 29s. Hence, these results are in keeping with the general trend in the literature on ignition reactions which seems to favour a concept of gas-phase reaction rather than surface oxidation.

1.7 Proposed Research

Previous research on iron sulfides and iron-nickel sulfides has primarily been performed using nickel concentrates which contain a mixture of minerals. A comprehensive study has not been carried out to determine the ignition properties of the individual sulfides which comprise the feed material to the KNS. Research on pyrite and pyrrhotite has used either synthetic materials or minerals of a different geological origin. No work has been located on the ignition behaviour of pentlandite or violarite.

The purpose of this study is essentially two fold. It is first intended to establish the ignition properties of samples of pyrite, pyrrhotite, pentlandite and
violarite. These samples will be isolated from ores which are typically smelted by the KNS and they will then be extensively characterised. The behaviour of these samples will be examined in the laboratory using three different techniques:

1. TG-DTA: Using a heating rate of $10^0\text{C}/\text{min}$ and an air atmosphere the relative order of reactivity of the sulfides will be established, together with their characteristic oxidation reactions.

2. TG-DTA: Using a heating rate of $40^0\text{C}/\text{min}$ and an oxygen atmosphere the tendency of the minerals to ignite will be ascertained.

3. Isothermal TG: This method will be used to subject the sulfides to shock heating conditions analogous to those existing in the flash smelter. Ignition temperatures will be measured, together with the extent of reaction for each sulfide at increasing furnace preheat temperatures. The effect of varying the particle size from $<45\mu\text{m}$ to $90-125\mu\text{m}$ on the ignition temperature of each sulfide will be examined.

The second part of this study aims to establish the behaviour of some nickel sulfide concentrates using a pilot scale flash reactor. Four concentrates provided by the KNS will be smelted and the relative reactivities of these materials ascertained. These results will be
rationalised by reference to the behaviour of the individual minerals during Isothermal TG.

A detailed examination of the laboratory and pilot scale ignition products will be performed using optical and electron microscopy with a view to establishing the mechanism for ignition of pyrite, pyrrhotite, pentlandite and violarite.
CHAPTER 2  EXPERIMENTAL METHODS

2.1  Laboratory Scale Studies

2.1.1  Samples

The following samples were used for the laboratory scale studies:

(1) Supergene ore- from the Rocky's Reward open pit operation at Leinster, WA.

(2) Primary ore- from the Kambalda region, WA.

(3) Pyrite- supplied by the British Geological Survey (BGS). The geographical origin of this sample was not known.

(4) Pyrrhotite- supplied by the Department of Mineralogy and Petrology at the Museum of Victoria. This sample had been collected from the Renison Bell (RB) mine in Tasmania.

2.1.2  Sample Upgrading using Magnetic Separation

The primary and supergene ore samples were reduced in size using a hand pulverizer followed by an alumina disc
grinder. The plate separation in the grinder was set at 1mm. Further grinding was performed by hand in a mortar and pestle. The resulting material was sieved in Brass Endecotts Laboratory Sieves on a Rotaps Sieve Shaker to collect the 45-125μm fraction.

It was necessary to employ magnetic separation to obtain samples of pyrite, violarite, pyrrhotite and pentlandite from the ore samples. Due to the ferrimagnetic nature of the pyrrhotite sample, this mineral was separated from the primary ore using a hand magnet. A Frantz Magnetic Separator was utilised for further upgrading. The 45-125μm samples were wet sieved at 45μm in ethanol to remove any adhering fines and then dried. This step was necessary to generate a sample which would flow freely down the vibrating chute of the separator.

The Frantz separator was operated at a constant forward slope of 25° on the vibrating chute. The current through the magnet and the side slope on the chute were varied. The samples were first processed at a low current setting and a side slope of 30° to ensure complete removal of all pyrrhotite and other ferrimagnetic material. The chute was then dismantled and any adhering material was cleaned off.

The primary ore sample was processed at a current setting of 0.4 A and a slope of 10°. The material responding in the magnetic fraction at this setting comprised the
pentlandite sample. The supergene ore sample was processed at 0.6 A and 5°. The non-magnetic fraction was then run at 0.8A and 5°, the magnetic fraction at this second setting being collected as the violarite sample. The non-magnetic material was further processed at 1.5A, 10°, the non-magnetics at this setting being collected as pyrite.

The pyrite sample from the British Geological Survey and the Renison Bell pyrrhotite sample were reduced in size using a hammer and a small percussion mortar and pestle. They were then ground by hand in a mortar and pestle to pass a 125µm sieve. The pyrite required no further upgrading. The pyrrhotite sample was ferrimagnetic and so it could be upgraded using a hand magnet, the non-magnetic material being discarded.

Hence six sulfide samples were collected for use in the laboratory scale studies. A representative subsample of each was separated out using a Quantachrome Rotary Microriffler for chemical analysis.

2.1.3 Characterisation Techniques

(i) Chemical Analysis

The sulfides were analysed for iron, nickel and sulfur according to classical wet chemical techniques. Three
separate analyses on each sample were performed as follows:

(1) Sulfur: This was determined gravimetrically as barium sulfate. Samples were decomposed using bromine, followed by aqua regia. A cation exchange resin was employed to remove the iron prior to addition of barium chloride.

(2) Iron: Potassium dichromate titration was used to determine the iron content. Bromine was required for the digestion of pentlandite, this being followed by aqua regia. The remaining samples required aqua regia digestion only. Iron hydroxide was precipitated, filtered off and redissolved prior to dichromate titration. This prevented interference occurring due to the presence of nickel.

(3) Nickel: Sample digestion proceeded as for iron analysis. Tartaric acid was used to complex the iron in solution prior to precipitation of nickel with dimethylglyoxime for gravimetric analysis.

(ii) Particle Size Analysis

All of the samples were dry sieved to collect the following fractions: 45-75μm, 75-90μm and 90-125μm. Sieving was normally performed for a period of 15min
using a Rotaps Sieve Shaker. After this time the collecting pan was emptied and sieving was continued for a further 5 min. The collecting pan was again emptied, this cycle being repeated until a negligible quantity of material was observed in the collector.

The 45-75 μm pyrite (ex BGS) sample was wet sieved at 45 μm to remove any adhering fines. The pyrite, violarite and pentlandite samples which had been separated from the primary and supergene ores were treated in this manner prior to magnetic separation. Wet sieving was performed using a Nytrel-TI screen fabric stretched over a teflon ring. The sample was mixed with ethanol in a beaker and the suspended fines were poured through the screen. This process was continued until the supernatant was essentially clear after mixing. The solid was then loaded onto the sieve and washed to remove any remaining fines. The two pyrrhotite samples could not be wet sieved as the ferrimagnetic nature of this mineral prevented its dispersion in a solvent.

Some of each of the 90-125 μm fractions of the sulfides was ground to pass a 45 μm sieve. This material was then wet sieved in ethanol at 20 μm, a 20-45 μm fraction being collected and dried. As wet sieving was not possible for the two pyrrhotite samples it was necessary to use a sub-45 μm fraction. All samples were stored in a desiccator under vacuum to prevent oxidation.
(iii) Surface Area Measurement

Surface area measurements were performed by the Particle Analysis Facility at Curtin University of Technology using a Quantachrome Autosorb I. This is an automated nitrogen sorption analyser.

(iv) X-Ray Diffraction (XRD)

XRD analyses were performed by the X-Ray Laboratory at Curtin University of Technology using a Siemens D500 X-Ray Diffractometer. Due to the small quantity of sample available, material was sprinkled onto double sided tape which had been mounted on an amorphous silica sample holder. Traces were recorded using Cu kα radiation, the X-ray tube being operated at 40kV and 30mA. A two-theta angle range of 10-80° was scanned at 0.04°/s. The resulting data was matched to the corresponding JCPDS files using a computer matching programme.

(v) Optical Microscopy

Samples were prepared as polished sections for examination by optical microscopy using an epoxy mounting resin. When milligram quantities of material were handled these were mounted using 1cm inside diameter, 1cm
long perspex tubes. The tube was fixed to a smooth surface with double sided tape and the sample was sprinkled in, followed by the resin. The tape served a dual purpose in that it prevented the sample being washed aside by the resin and it contained the resin within the tube. Once the resin had cured it was relatively simple to break the sample mount away from the tape and surface. Larger quantities of samples were mounted in the standard manner using 2.5cm Leco plastic moulds, employing vaseline as a release agent.

An alternative means of mounting small quantities of samples was used. A 2.5cm diameter resin button was prepared and the required number of holes of approximately 1mm depth and appropriate diameter were drilled into the surface. These were filled with sample, a drop of resin being placed on top. Once hardened, this resin was ground down until the face of the button was smooth and a cross-sectioned surface of the particles was exposed.

Grinding and polishing of the sections was achieved using P600 and P1200 silicon carbide papers mounted on glass plates, followed by 3-6µm and 1-3µm diamond impregnated polishing wheels.

Optical examination of the polished sections was performed under reflected light using a Zeiss Microscope in the CSIRO Division of Exploration Geoscience, Floreat
Park. Micrographs were recorded using 35mm daylight film.

(vi) Scanning Electron Microscopy (SEM)

SEM work was performed using a Jeol JSM-35C Scanning Electron Microscope. This was equipped with a Robinson Backscattered Electron (BSE) Detector and an X-ray Energy Dispersive detector. Prior to examination polished sections were coated with a thin layer of carbon to render them electrically conducting. Samples to be examined without sectioning were mounted on a metal butt using double sided tape and then coated with gold. The majority of photographic work was performed in the backscattered mode at an accelerating voltage of 25kV. Photographs were recorded using Ilford FP4 120 black and white roll film. Ilford chemicals and paper were used for developing and printing.

(vii) Electron Probe Microanalysis (EPMA)

EPMA was performed on carbon coated, 2.5cm diameter polished sections using a Cameca SX-50 Electron Probe at the CSIRO Division of Exploration Geoscience. Data was processed by ANU/CSIRO WANU-SX Software V7.03. Analyses were conducted at an accelerating voltage of 25kV and a beam current of 30nA. Iron and nickel were measured
using a count time of 20s on the LiF detector. Sulfur was analysed for 40s on the PET detector. Pyrite and nickel metal standards were employed. In the product particles oxygen was determined by difference. On average 30 particles in each sample were analysed. Several points across each particle were examined when inhomogeneity was evident.

2.1.4 Thermal Analysis Techniques

(i) Simultaneous Thermogravimetry-Differential Thermal Analysis (TG-DTA)

TG-DTA was used to examine the oxidation behaviour of the six sulfide materials. Data was collected using a Stanton Redcroft Model 781 Simultaneous Thermal Analyser-Differential Thermal Analyser interfaced to an IBM compatible personal computer. A sample mass of approximately 3mg was weighed out using a Perkin Elmer AD-2 Autobalance. Alumina crucibles were used. These measured 3.5mm in depth and 4mm in internal diameter. An empty crucible was used as the reference pan. Oxidation runs were performed by heating the sample at a rate of 10°C/min to a maximum temperature of 1000°C in a flowing air atmosphere (30mL/min). A silica gel drying tube was incorporated into the gas line.

To achieve ignition conditions using the TG-DTA 5mg
samples were heated at 400°C/min to 1000°C in an oxygen atmosphere. Pyrolytic decomposition trials were performed by heating a 5mg sample at 40°C/min in a nitrogen atmosphere. To ensure a non-oxidising atmosphere in the latter instance an oxygen scrubber was incorporated into the gas line. This consisted of finely divided copper mixed with a catalyst and impregnated onto an inert support material. The purpose of the catalyst was to promote the formation of copper(II) oxide at room temperature. All TG-DTA traces were plotted using a Roland DG X-Y plotter, Model DXY-980A.

(ii) Isothermal Thermogravimetry

In order to simulate the more rapid heating rates involved in flash smelting a Stanton Redcroft TG-750 Thermobalance was used in an isothermal manner. This technique has been labelled "Isothermal Thermogravimetry" (Isothermal TG) and it was developed by Dunn, Jayaweera and Davies (1985).

A 5mg sample was weighed into a platinum crucible suspended above a water cooled furnace. The crucible measured 2.5mm in depth, the diameter across the base being 4mm, while the internal diameter across the top was 5mm. A lip occurred approximately 1.5mm down from the top of the crucible. This allowed the crucible to be suspended in a stirrup above the furnace. A flowing
oxygen atmosphere (30mL/min) was necessary to cause ignition. The furnace was preheated to a specified temperature at which stage the sample was shielded from any heating effects by an asbestos mat. This mat was then removed and the furnace was raised around the sample. The resulting heating rate experienced by the particles was estimated to be of the order of 3000-5000°C/min. The furnace reached a maximum temperature of approximately 900°C.

Isothermal TG was used to identify the furnace preheat temperature necessary to ignite the sample. This value was recorded as the ignition temperature and it was usually readily identified by a marked overheating in the temperature trace. A sharp mass loss invariably accompanied ignition. The magnitude of this mass loss at any given temperature was directly proportional to the extent of reaction of the sample at that temperature. A value was calculated for this term, that is, extent of reaction, based upon the mass loss measured at a given furnace preheat temperature compared with that measured at 900°C. Data was collected at 50°C or 100°C intervals as appropriate.
2.2 Pilot Scale Studies

2.2.1 Samples

Pilot scale studies were performed using nickel sulfide concentrates. The Kalgoorlie Nickel Smelter supplied a sample of the ground sulfide concentrate which is typically fed to the flash furnace. This material was mined and upgraded at the Kambalda Nickel Operations (KNO), being referred to as KNO Concentrate. Two other concentrates were supplied, MAG and UCC. These materials had been isolated at different points in the KNO feed preparation circuit. The former was collected after the concentrate had passed through a magnetic separator. Hence this was enriched in the magnetic sulfide pyrrhotite. The UCC concentrate was collected from the Unit Cell Cleaners. A fourth sample was studied, this having originated from the Agnew Mining Company (AMC). All of these samples were used as received.

2.2.2 Characterisation Techniques

(i) Chemical Analysis

A complete chemical analysis of each of the nickel concentrates used in pilot scale studies was provided by the KNO, this information being obtained using X-Ray Fluorescence (XRF). Iron and nickel analyses were
determined by the staff at the KNS using an acid digestion followed by Atomic Absorption Spectrometry (AAS). Combustion in a Leco furnace was used to measure the sulfur content.

Samples collected after processing in the pilot scale reactor were sent to the KNS for iron and sulfur analyses. These results were utilised to provide an indication of the extent of reaction experienced by a sample. If extensive oxidation had occurred significant sulfur depletion was evident. Consequently the iron and nickel levels in the products increased relative to those in the unreacted material. The calculation employed in this study was defined as follows:

\[
\% \text{ Extent of Reaction} = 100 \left[ 1 - \frac{\%S_{\text{product}}}{\%S_{\text{reactant}}} \times \frac{\%Fe}{\%Fe} \right]
\]

Obviously this value was greatest in those samples which had been most oxidised. The iron factor corrected for the replacement of sulfur by the lower molecular weight element oxygen. This calculation has previously been implemented by Jorgensen (1978). Using this value the relative reactivity of each concentrate to the flash smelting process could be assessed.

(ii) Particle Size Analysis

The particle size distribution of the nickel concentrates was determined in duplicate by standard dry sieve
analysis. For each trial approximately 50g of material was separated from the bulk sample using the coning and quartering technique. This material was then loaded onto a stack of sieves of the following sizes: 45, 75, 106 and 212µm. The sieve stack was shaken for a period of 15 minutes before checking the collector as described in Section 2.1.3(ii).

(iii) X-Ray Diffraction

The four nickel sulfide concentrates were characterised by the Geological laboratory at the KNO using a direct calculation method of quantitative XRD. This method yielded a mineralogical analysis of each sample.

(iv) Optical and Electron Microscopy

These techniques have been described in Sections 2.1.3(v) - 2.1.3(vii). The Cameca Probe was used to measure the stoichiometries of some of the pilot scale reactor products. However, this instrument only became available for a limited period of time at the end of the project. Consequently most of the work on these products was performed using an Etec Autoprobe. Operation conditions were similar to those stated for the Cameca Probe, however, a 10s count time was used. Data was processed using the Magic IV correction program.
The Etec Autoprobe was also used to generate x-ray maps showing the distribution of iron, nickel and sulfur in a group of particles. The chosen particles were first photographed using the secondary electron detector. The same field of view was then scanned again with the x-ray detector (a Wavelength Dispersive Spectrometer) set to record the appropriate element. All photography was performed using polaroid positive/negative 4x5 land film, type 55.

2.2.3 Pilot Scale Reactor

The pilot scale flash reactor was constructed by the staff of the Chemical and Mechanical Engineering Departments at Curtin University of Technology. It was intended to model only the reactions occurring in the shaft, isolating these from the subsequent reactions which occur in the matte/slag bath. The linear scale of the reactor to that of the KNS shaft was 1:10. To ensure that the residence time of the feed in the reactor was comparable with the industrial system the scale of velocities was also fixed at 1:10. Consequently, the throughput ratio between the model and a burner in the KNS smelter was 1:1000. As the model represented only one of the four burners in the actual plant the ratio of overall throughput was 1:4000. A schematic of the reactor is shown in Figure 2.1 and two photographs are seen in Figures 2.2 and 2.3.
FIGURE 2.1: Schematic of the pilot scale reactor.
Figure 2.2: A general view of the pilot scale reactor.
Figure 2.3: A view of the reaction shaft and exit duct showing the propane burner, quench holes and the thermocouples.
The reactor essentially comprised a turbulent jet contained within a cylindrical shaft. This shaft measured 500mm in length and 300mm in diameter. It was insulated by a 100mm thickness of Triton Kaowool Wetfelt. A propane burner was employed to heat and maintain the walls at approximately 900°C. The burner was fired through a tangential port 100mm down from the top of the reactor so that the gases passed in a helical path down the reactor walls.

The sulfide concentrate was stored in a hopper and continuously stirred whilst being fed to the reactor via a screw feeding system. The rate of solids delivery was controlled by adjustment of the revolution frequency of the screw feeder and was normally set at 170g/min. The concentrate fell through a 15mm diameter tube into the top of the reactor. A conical dispersion head located at the base of this tube served to disperse the solids out into the reaction shaft. Dispersion was enhanced by a small flow of air entering at the screw feeder and passing down the tube with the solids.

During a typical trial the reactor was maintained under a slight vacuum (pressure = 756mm Hg) which was controlled by several valves and suction from a centrifugal fan. This served to draw in the air required for combustion and sample quenching, and the gases from the propane warm up burner. The required volume of air for reaction stoichiometry was approximated by assuming the reactant
and product materials to be FeS and Fe$_3$O$_4$ respectively. Air and oxygen were drawn into the reactor through an intake horn to allow metering of the flow. This gas was preheated to approximately 450-500°C by a series of four electrical heating elements. It then passed into a 44mm tube surrounding the feed tube and thus contacted the concentrate at the top of the reaction shaft where a suspension was formed.

It was necessary to quench the reacting materials at the base of the shaft to ensure the collection of individual particles rather than a fused mass. Four rows of 18 holes were drilled around the wall of the conical exit duct and air or high purity nitrogen was drawn in by the reactor vacuum. The number of holes was adjusted to give a satisfactory velocity of the quench jets which would provide rapid quenching without interfering with the reacting jet above the designated quench level.

The solid and gas mixture were separated in a cyclone. The final product was collected in a cylindrical vessel which incorporated four sliding trays. This made it possible to collect several samples during each trial. Any fine dust which escaped collection in the cyclone was removed by a filter before the combustion gas was diluted with air and released to the atmosphere.

During a trial the reactor and exit duct temperatures were monitored using a series of Nicrosil-Nisil (type N)
thermocouples which were located as follows:

T1 preheated combustion air
T2 reactor wall, 100mm down
T3 reactor wall, 200mm down
T4 reactor wall, 300mm down
T5 exit duct

It was not possible to monitor reactor jet temperatures continuously due to accretion of solid onto the thermocouples.

The oxygen content of the exhaust gas stream was monitored using a Teledyne Model 320 oxygen analyser. The degree of leakage of air into the reactor was estimated periodically by passing a metered flow of nitrogen through the reactor while at normal operating vacuum and measuring the oxygen level. Allowance for this leakage was then made when calculating the required volume of combustion air.

A typical smelter trial comprised two main stages. An initial period was allowed for system stabilisation. During this time an air quench was employed. This was followed by approximately 5min of stable smelting during which the product was quenched in nitrogen. Air quenching was originally used during the stable smelting stage but there were indications that this caused further oxidation of the sample. Hence, only the nitrogen quenched samples were retained for examination.
CHAPTER 3 UPGRADING AND CHARACTERISATION OF MINERALS
AND CONCENTRATES

The concentrates typically smelted in the KNS contain four major sulfide minerals: pyrite; pyrrhotite; pentlandite and violarite. In Chapters 4 and 5 the oxidation and ignition behaviour of these individual minerals will be established. It was essential to ensure that the properties of the mineral samples used were as close as possible to the properties of those minerals present in the KNS concentrates. As pure samples of an appropriate origin were not available it was necessary to develop methods for isolation of the minerals from suitable orebodies.

3.1 Upgrading Minerals

The only viable method for upgrading ore samples to obtain their constituent minerals was to use the Frantz Isodynamic Separator. This instrument separates minerals based upon variations in their response within an applied magnetic field. By changing both the current through the electromagnet and the cross slope of the sample chute, minerals of varying degrees of paramagnetism and diamagnetism can be separated.

The degree of success of this technique was greatly
dependent upon the chosen starting material. It was necessary to ensure that the particle grains were relatively homogeneous. This was a problem with pyrite and violarite as they are prone to oxidise both within the orebody and after mining when they come into contact with the atmosphere. Sulfate, oxide and carbonate species form around the grain edges and hinder magnetic separation.

Efficient separation of pentlandite from violarite was not possible using the Frantz Separator due to the similar magnetic behaviour of these two iron-nickel minerals. They are both classified as "Pauli paramagnetic" (Townsend et al. 1972; Townsend et al. 1977). Vaughan and Craig (1978, p85) state that this type of paramagnetism is found in metallic materials where the outermost electrons are extensively delocalised. Application of an external field causes an imbalance between spin-up and spin-down electrons in a partly filled band, so causing a net magnetic moment. The magnetic susceptibility values are very small. Experimentally, it was found that the difference between the susceptibilities of pentlandite and violarite was insufficient to allow satisfactory separation.

The most suitable starting materials were found to be a primary and a supergene ore sample. A typical nickel orebody supplying feed to the KNS is divided into four zones: primary, transition, supergene and oxide (Nickel,
Ross and Thornber 1974). Collection of a sample from the primary and the supergene zones ensured that pentlandite and violarite did not occur together. Samples were obtained from a Kambalda primary zone and a Leinster supergene zone. These ores are typically fed to the KNS. Thorough characterisation of the samples prior to grinding was performed to verify the constituent minerals and to ensure that significant oxidation had not occurred. It was then possible to proceed with Frantz Separation.

3.1.1 Characterisation of Starting Materials

Figure 3.1 shows an optical micrograph of a polished section of the primary ore sample. This ore was predominantly comprised of pentlandite (Pn) and pyrrhotite (Po). Some chalcopyrite, primary pyrite and a small amount of spinel were also present. No violarite was observed. These findings are typical for a primary ore sample from Kambalda (Nickel, Ross and Thornber 1974). Under reflected light pentlandite is easily distinguished from pyrrhotite by its yellow-gold colour, compared with the more pink hue of pyrrhotite. Another distinguishing feature is the octahedral cleavage exhibited by pentlandite. This characteristic allows pentlandite to be differentiated from primary pyrite which is similar in colour.
Figure 3.1: An optical micrograph of a polished section of the primary ore showing pentlandite and pyrrhotite as the major sulfide phases. Frame width = 2200μm. Pn = pentlandite, Po = pyrrhotite.

Figure 3.2: An optical micrograph of a polished section of the secondary ore showing violarite and pyrite as the major sulfide phases. Frame width = 1130μm. Py = pyrite, Vpn = violarite (from pentlandite), Vpo = violarite (from pyrrhotite).
An optical micrograph of the supergene ore appears in Figure 3.2. The major phases present in this sample were violarite ($V_{pn}$ and $V_{po}$) and secondary pyrite (Py). Violarite is a violet-grey colour under reflected light compared with the yellow colour of secondary pyrite. Both of these minerals exhibit significant porosity compared with pentlandite and pyrrhotite.

Violarite primarily occurred in the blocky formation shown on the left side of Figure 3.2 ($V_{pn}$). This mineral has formed during the supergene alteration process by the reaction of pentlandite. The characteristic octahedral cleavage of the latter mineral has been preserved during alteration and is inherited by violarite. An equation for this process has been presented by Nickel, Ross and Thornber (1974):

$$\text{Fe}_{\text{4.1}}\text{Ni}_{\text{4.9}}\text{S}_{\text{8.0}} \rightarrow \text{Fe}_{\text{2.6}}\text{Ni}_{\text{1.8}}\text{S}_{\text{8.0}} + 1.1\text{Ni}^{2+} + 1.5\text{Fe}^{2+} + 5.2e^-$$

(pentlandite) (violarite)

The nickel released in this process will react with pyrrhotite to form a second type of violarite which is iron rich compared with the blocky form. Nickel, Ross and Thornber (1974) presented the following equation:

$$0.33\text{Fe}_7\text{S}_8 + 1.1\text{Ni}^{2+} \rightarrow 0.33\text{Fe}_{\text{3.0}}\text{Ni}_{\text{3.3}}\text{S}_{\text{8.0}} + 1.32\text{Fe}^{2+} + 0.44e^-$$

(pyrrhotite) (violarite)

Pyrrhotite-derived violarite ($V_{po}$) is shown in Figure 3.2. This phase has a "fringed" or "saw-tooth-like"
appearance, having inherited this from the twin lamellar structure of pyrrhotite (Nickel, Ross and Thornber 1974). \( V_{po} \) occurs around the boundaries of the secondary pyrite grains and along fractures. It is less abundant than \( V_{pn} \) due to the limited quantity of nickel available.

In generating the above equations Nickel, Ross and Thornber (1974) assumed that the number of sulfur atoms per unit volume in pentlandite and pyrrhotite was maintained in the newly formed violarite. The loss of iron and nickel was calculated to cause volume reductions of 15% and 8% during the formation of \( V_{pn} \) and \( V_{po} \) respectively. This accounts for the observed porosity of the violarite in Figure 3.2.

Some of the iron released during the supergene alteration process precipitates as a carbonate. Hence it is likely that the grey phase in Figure 3.2 is siderite.

When all of the pentlandite has been consumed nickel is no longer generated and consequently pyrrhotite conversion to violarite ceases. Secondary pyrite then forms. This is a result of the dissolution of pyrrhotite and its reprecipitation as pyrite. The associated loss of iron causes the pyrite to be porous. Nickel, Ross and Thornber (1974) presented the following equation:

\[
\text{Fe}_7\text{S}_8 \rightarrow 4\text{FeS}_2 + 3\text{Fe}^{2+} + 6\text{e}^-
\]

(pyrrhotite) (pyrite)
Deposition of layers of pyrite from solution results in the colloform structure evident in the top of Figure 3.2 (to the right of the blocky violarite). Thus, morphological characteristics together with colour differences were utilised to differentiate between violarite and secondary pyrite in a polished section.

A small quantity of primary pyrite was also identified in the secondary ore sample. This is not an alteration product, but rather occurs with the primary ore. It is readily distinguished from the secondary mineral by its lack of porosity.

3.1.2 Magnetic Separation

Magnetic separation of the constituents of the primary ore was uncomplicated. Pyrrhotite in Kambalda ore is typically monoclinic and shows ferrimagnetic behaviour. Such material is too strongly magnetic to be processed by the Frantz separator and it was removed using a hand magnet. While some material may have been physically entrained with the pyrrhotite, XRD analysis did not detect significant quantities of any other phases.

The remaining material was processed on the Frantz Separator and a relatively pure pentlandite sample was recovered. This was confirmed by XRD. The discarded non-magnetic fraction was examined using the X-ray
detector on the SEM. This sample contained chalcopyrite, primary pyrite and some remaining pentlandite. Hence magnetic separation was very successful for the primary ore which is consistent with the known magnetic character of the constituents. The literature classifies pentlandite as Pauli paramagnetic and pyrite as diamagnetic (Townsend et al. 1972; Vaughan and Craig 1978, p93). Hence, pentlandite will move towards an applied field while pyrite will move away. This explains the ease with which the separation of these two minerals was achieved using the Frantz separator. Chalcopyrite is antiferromagnetic (Vaughan and Craig 1978, p92), this being a weak form of paramagnetism. The magnetic susceptibility of this mineral was obviously lower than that for the Pauli paramagnetic pentlandite as it was possible to collect most of the pentlandite before chalcopyrite started to respond.

Magnetic separation of the secondary pyrite-violarite sample presented some difficulties. As violarite has a similar magnetic character to pentlandite, being Pauli paramagnetic, it was expected that separation of the supergene ore would proceed in a straightforward manner. However, this was not the case. The secondary pyrite responded over a wide range of settings. While a pure sample of this mineral was readily obtained, it was not possible to isolate violarite.

Extensive trials were conducted on the Frantz Separator
in order to identify the setting which yielded the maximum content of violarite. A sample of each trial fraction was prepared as a polished section for examination using the X-ray detector on the SEM. An estimate of the composition of each fraction was achieved by scanning approximately 20 particles to check for sulfur, nickel and/or iron. These results indicated that it was not possible to upgrade violarite beyond a 40-50% mixture with pyrite. XRD analysis confirmed the presence of violarite and pyrite in the fraction chosen, together with some silica.

The pyrite sample showed trace amounts of violarite by XRD analysis and some silica was detected. Marcasite was also found to be present in both the violarite-pyrite mixture and the pyrite sample. Marcasite is known to occur in violarite-pyrite assemblages (Nickel, Ross and Thornber 1974), being porous and frequently colloform as is secondary pyrite. It is thought to have similar magnetic properties to pyrite (Vaughan and Craig 1978, p95).

It is apparent that the secondary pyrite in the supergene ore responds differently to magnetic separation than does the pyrite present in the primary ore. The former has a higher magnetic susceptibility, being comparable with that of pentlandite and violarite. Gaudin and Spedden (1943) reported on the magnetic separation of sulfide minerals and they encountered an analogous problem. They
found sphalerite to display non-uniform magnetic behaviour and they attributed this to the presence of iron in solid solution. Secondary pyrite is likely to contain nickel which could be a source of the problem. However, possibly the main cause of complication was the presence of particles which contained both pyrite and violarite. As evident from Figure 3.2, the majority of the pyrrhotite-derived violarite inclusions are less than 45μm at their widest point. Consequently, this phase would not have been liberated by grinding to 45-125μm sized particles. Grinding to a finer size was not desirable due to the need for a freely flowing sample during Frantz separation.

Thus magnetic separation was found to be a satisfactory technique for separating pyrrhotite, pentlandite and pyrite, while violarite could only be upgraded to a 40-50% mixture with pyrite.

Two samples of a different origin from those of the KNS feed concentrates were also examined. A pyrite sample from the British Geological Survey required no upgrading. XRD analysis did not detect the presence of any contaminating phases. A pyrrhotite sample from the Renison Bell mine in Tasmania contained a silicate species as shown by XRD analysis. Purification was simple because, like the pyrrhotite phase in the primary ore from Kambalda, Renison Bell pyrrhotite was found to be ferrimagnetic. Hence, a hand magnet was used. Minor
amounts of silicate were likely to be entrained with the pyrrhotite. These two samples were examined in order to compare their reactivities with those of the Kambalda and Leinster minerals. In this way any variations in the behaviour of pyrite and pyrrhotite samples from different origins could be identified.

3.2 Characterisation of Upgraded Minerals

3.2.1 Wet Chemical Analysis

The results of wet chemical analysis performed on the six sulfide samples are presented in Table 3.1. The first four samples listed represent those sourced from the Leinster supergene ore and the Kambalda primary ore samples. Of these, the pyrrhotite and pentlandite samples showed an analysis total of 96-98%, while the pyrite and violarite-pyrite samples only totalled 82-87%. The contaminating species comprising the deficit for each sample were silicates, oxides and carbonates as evident during optical microscopic and XRD examination. On the basis of the nickel content of the violarite-pyrite mixture, this sample was estimated to be 40-50% violarite. The British pyrite and the Renison Bell pyrrhotite samples showed analysis totals of 100%.
<table>
<thead>
<tr>
<th>Samples</th>
<th>%Fe</th>
<th>%Ni</th>
<th>%S</th>
<th>Total%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>37.5</td>
<td>-</td>
<td>44.8</td>
<td>82.3</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>57.4</td>
<td>-</td>
<td>39.1</td>
<td>96.5</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>29.6</td>
<td>35.0</td>
<td>33.2</td>
<td>97.8</td>
</tr>
<tr>
<td>Violarite-Pyrite</td>
<td>27.6</td>
<td>17.2</td>
<td>42.0</td>
<td>86.8</td>
</tr>
<tr>
<td>Pyrite (ex BGS)</td>
<td>47.6</td>
<td>-</td>
<td>52.8</td>
<td>100.4</td>
</tr>
<tr>
<td>Pyrrhotite (ex RB)</td>
<td>61.2</td>
<td>-</td>
<td>39.3</td>
<td>100.5</td>
</tr>
</tbody>
</table>

Table 3.1: Analytical data for the upgraded mineral samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Fe$_{0.98}$S$_2$</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe$_{0.85}$S</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>Ni$<em>{4.90}$Fe$</em>{4.45}$S$_8$</td>
</tr>
<tr>
<td>Violarite</td>
<td>Ni$<em>{2.00}$Fe$</em>{1.05}$S$_4$</td>
</tr>
<tr>
<td>Pyrite (ex BGS)</td>
<td>Fe$_{0.99}$S$_2$</td>
</tr>
<tr>
<td>Pyrrhotite (ex RB)</td>
<td>Fe$_{0.86}$S</td>
</tr>
</tbody>
</table>

Table 3.2: Stoichiometries of the sulfide minerals (45-75μm fractions) as determined by EPMA.
3.2.2 EPMA

The average stoichiometry of each mineral was calculated based upon EPMA data collected on approximately 20 particles in the 45-75μm size fractions (Table 3.2). Care must be exercised when discussing these values and making comparisons with those reported in the literature. It has been found that the stoichiometry of these minerals will vary significantly according to the associated level of iron and nickel sulfide minerals present in the original orebody (Harris and Nickel 1972). Pentlandite, for example, may contain between 18 and 34 at% nickel, the higher nickel content being characteristic of pentlandite in a nickel sulfide assemblage, the lower one indicating an iron sulfide assemblage (Misra and Fleet 1973). Deviation also occurs from the stoichiometric metal:sulfur ratio of 9:8, most natural pentlandites being slightly sulfur-deficient. Table 3.2 shows that the pentlandite sample has a metal:sulfur ratio of 9.35:8 indicating a sulfur deficiency. 28.2 at% nickel was present. This is within the range of nickel contents expected for an assemblage comprising pentlandite and monoclinic pyrrhotite (Harris and Nickel 1972).

Similar observations have been made regarding violarite, a sulfur deficiency relative to the ideal stoichiometry \((\text{FeNi})_3\text{S}_4\) normally being observed (Misra and Fleet 1974; Desborough and Czamanske 1973). The metal:sulfur
ratio of 3.05:4 shown in Table 3.2 is consistent with this statement. While violarite is nominally assigned the formula $\text{Ni}_2\text{FeS}_4$, it can vary widely over the range from $\text{Ni}_3\text{S}_8$ to $\text{Fe}_3\text{S}_4$ (Vaughan and Craig 1985). Being a supergene alteration product, the violarite stoichiometry will be determined by the composition of its precursor. Nickel (1973) has reported that the iron:nickel ratio in violarites occurring in the supergene profiles over nickel sulfide ores can vary from nearly zero to 1:1. The stoichiometry given in Table 3.2 was measured on the blocky, pentlandite-derived violarite, the iron:nickel ratio being 1.02:2.00. Pyrrhotite-derived violarite was not analysed in the current work. It was a less abundant phase and was often not liberated from the pyrite particles. Consequently further discussion of violarite implies the phase derived from pentlandite.

The stoichiometry measured for Kambalda pyrrhotite was $\text{Fe}_{0.85}\text{S}$. 0.4-0.8 wt% nickel was also detected. The iron content was calculated at 45.8 at%. These results agree with the values of 45.6-46.3 at% iron and 0.5-0.9 wt% nickel reported by Nickel, Ross and Thornber (1974) for monoclinic pyrrhotite present in a Kambalda ore.

Renison Bell pyrrhotite showed a virtually identical stoichiometry to the Kambalda mineral, although the associated nickel content was negligible. It has been shown that a positive correlation exists between the nickel content of monoclinic pyrrhotite and that of the
coexisting pentlandite (Harris and Nickel 1972). A
report published on the geology of the Renison Bell mine
(Newnham 1973) states that the massive sulfide deposits
present are primarily comprised of pyrrhotite, pyrite,
arsenopyrite and chalcopyrite. No nickel sulfides are
mentioned, which would account for the lack of nickel
present in the pyrrhotite grains.

The stoichiometries for the pyrite samples from Leinster
and the British Geological Survey were Fe$_{0.98}$S$_2$ and Fe$_{0.99}$S$_2$
respectively. These are close to the ideal iron:sulfur
ratio of 1:2. On average 1-3 wt% nickel was measured in
the Leinster sample, negligible quantities of nickel
being detected in the British sample. The former has
been identified as a secondary mineral. Nickel, Ross and
Thornber (1974) found a comparable level of nickel in a
secondary pyrite sample. This observation was attributed
to nickel enrichment of the solution from which secondary
pyrite was precipitated.

3.2.3 SEM

Electron micrographs of polished sections of the
45-75μm fractions of the sulfide samples are shown in
Figures 3.3(a)-(f). All particles exhibited an angular,
block-like shape. The Leinster pyrite particles (Figure
3.3(a)) were porous and some showed the colloform
structure. In contrast with these observations, the
Figure 3.3: Backscattered electron micrographs of the 45-75μm fractions of the unreacted sulfides:
(a) Leinster pyrite

Figure 3.3(b): pyrite (ex BGS)
Figure 3.3(c): Kambalda pyrrhotite

Figure 3.3(d): Renison Bell pyrrhotite
Figure 3.3(e): pentlandite

Figure 3.3(f): violarite-pyrite mixture
Figure 3.3(g): violarite-pyrite mixture (optical micrograph, frame width = 2200µm.)
British pyrite particles in Figure 3.3(b) possessed very smooth cross-sections. This is consistent with the expected appearance of primary pyrite and explains the absence of nickel in these grains. Nickel, Ross and Thornber (1974) found less than 0.7 wt% nickel in primary pyrite samples. Hence, the Leinster and the British pyrite samples are fundamentally different in that they are secondary and primary minerals respectively. In the following pages they will simply be referred to as secondary and primary pyrite.

Both the Kambalda and the Renison Bell pyrrhotite samples (Figures 3.3(c&d)) were non-porous and showed evidence of sub-45μm material as a result of dry sieving. Fines were most predominant in the Renison Bell sample. Elimination of this material via wet sieving was not possible. Hence, the reactivity of the pyrrhotite samples may be increased compared with the other sulfides.

The pentlandite particles shown in Figure 3.3(e) were also non-porous. Significant fracturing of the particles was observed, usually around the grain edges. This must have occurred during the grinding process and was probably a result of the characteristic octahedral cleavage of pentlandite. The reactivity of this mineral may be enhanced by the associated increase in surface area.
Figure 3.3(f) shows the violarite-pyrite sample. The pyrrhotite-derived violarite is readily identified by its characteristic fringed appearance. It is difficult to differentiate between the blocky violarite and secondary pyrite in this micrograph. The use of optical microscopy overcame this problem as shown by Figure 3.3(g). The yellow pyrite grains can be distinguished from the lighter violarite grains. The poor level of purity of this sample is apparent.

Hence, characterisation procedures revealed that all samples, except the violarite-pyrite mixture and the secondary pyrite sample, appear to be better than 95% pure. The pyrite and the violarite-pyrite samples comprise 82-87% of sulfide minerals. They also contain silicate and carbonate species. The effect of these contaminants will primarily be to absorb heat. They should not significantly interfere with the reactivity of the secondary pyrite sample. Elucidation of the behaviour of violarite in the mixture, however, will be complicated by the presence of pyrite.

3.3 Characterisation of Mixed Sulfide Concentrates

Four nickel sulfide concentrates were provided by the KNS for examination in the pilot scale studies. Two of these concentrates comprised typical feed materials for the smelter, these being KNO and AMC. While the latter is no
longer fed to the smelter it has been replaced by a concentrate of very similar mineralogy. Two further materials were examined: UCC and MAG. These were collected from the Unit Cell Cleaners and the magnetic separators in the KNO feed preparation circuit respectively. The behaviour of these concentrates in the pilot scale reactor will be compared with that exhibited by the upgraded mineral samples in the laboratory. Hence, it was necessary to thoroughly characterise the concentrates.

3.3.1 XRD Analysis

Quantitative XRD analyses of the four sulfide concentrates were performed by the staff of the Geological laboratory at the Kambalda Nickel Operations. The results have been presented in Table 3.3. This data was utilised to provide a general indication of the sulfide phases present in each concentrate and the relative abundance of these phases. Some variation was found between duplicate analyses, particularly for the KNO and the AMC samples. Discrepancies of up to 10-15% were observed in the quantity of a given phase. Hence these results must be considered approximate.

AMC primarily comprised pyrite and violarite, with minor amounts of pentlandite and pyrrhotite being present. The MAG concentrate was collected from a magnetic separator
<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Sulfide Phases Detected via XRD (%)</th>
<th>Total Sulfide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pn</td>
<td>Po</td>
</tr>
<tr>
<td>KNO</td>
<td>42</td>
<td>32</td>
</tr>
<tr>
<td>AMC</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>MAG</td>
<td>8</td>
<td>72</td>
</tr>
<tr>
<td>UCC</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.3: Phase composition of the sulfide concentrates as determined using quantitative XRD.

NOTE: Pn = Pentlandite, Po = Pyrrhotite, Py = Pyrite, Vi = Violarite
and hence it contained a high level of ferrimagnetic pyrrhotite, together with minor quantities of pyrite, pentlandite and violarite. The KNO and UCC concentrates were both predominantly composed of pentlandite and pyrrhotite, UCC being more concentrated in the latter mineral. Pyrite and violarite were present in small amounts. Notice that the analysis totals for the sulfide contents of all concentrates were low, being in the range 82-90%. These deficits were accounted for by the presence of talc, chlorite, quartz, siderite, magnesite and magnetite.

3.3.2 XRF and Chemical Analysis

The majority of data regarding the chemical composition of the concentrates was determined by the KNS using XRF. These results appear in Table 3.4. The iron and sulfur contents, however, were determined using acid digest/AAS and Leco combustion respectively. The purpose of this was to maintain a consistent experimental technique between the collection of these results and those collected on the smelted concentrates. There was no need for complete XRF analysis of the latter as they were characterised by comparing the iron and sulfur contents with those in the unreacted concentrates.

The analysis total for each of the four concentrates was in the range 89-96%. Small quantities of copper (<1%),
<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Fe (%)</th>
<th>S (%)</th>
<th>Ni (%)</th>
<th>MgO (%)</th>
<th>SiO₂ (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO</td>
<td>39.1</td>
<td>33.2</td>
<td>11.8</td>
<td>3.0</td>
<td>5.4</td>
<td>92</td>
</tr>
<tr>
<td>AMC</td>
<td>33.2</td>
<td>31.0</td>
<td>11.4</td>
<td>5.2</td>
<td>8.6</td>
<td>89</td>
</tr>
<tr>
<td>MAG</td>
<td>49.9</td>
<td>31.6</td>
<td>4.9</td>
<td>2.9</td>
<td>3.8</td>
<td>93</td>
</tr>
<tr>
<td>UCC</td>
<td>44.9</td>
<td>34.7</td>
<td>11.0</td>
<td>2.0</td>
<td>3.6</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 3.4: Chemical composition of the sulfide concentrates as determined using XRF and chemical analysis.

<table>
<thead>
<tr>
<th>Size Fraction (μm)</th>
<th>KNO (%)</th>
<th>AMC (%)</th>
<th>MAG (%)</th>
<th>UCC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 45</td>
<td>50.2</td>
<td>57.2</td>
<td>45.1</td>
<td>25.2</td>
</tr>
<tr>
<td>45 - 75</td>
<td>23.9</td>
<td>26.7</td>
<td>29.2</td>
<td>20.4</td>
</tr>
<tr>
<td>75 - 106</td>
<td>17.0</td>
<td>9.6</td>
<td>11.4</td>
<td>19.2</td>
</tr>
<tr>
<td>106 - 212</td>
<td>8.7</td>
<td>4.8</td>
<td>7.0</td>
<td>28.9</td>
</tr>
<tr>
<td>&gt; 212</td>
<td>0.2</td>
<td>1.7</td>
<td>7.3</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 3.5: Particle size distribution of the sulfide concentrates determined using dry sieving.
cobalt (<0.5%), aluminium oxide (<1%) and calcium oxide (<1.0%) were also detected.

Calculation of the expected iron, nickel and sulfur contents of the concentrates according to the XRD data in Table 3.3 revealed some discrepancies between these results and those measured via XRF (Table 3.4). These can be attributed to the experimental errors incurred in the representative sampling of a large quantity of material and the errors inherent in the quantitative XRD determination.

3.3.3 Particle Size Analysis

The results of particle size analysis using dry sieving for each of the four concentrates are shown in Table 3.5. KNO concentrate comprised 74% of material finer than 75μm and 9% more coarse than 106μm. The sizing of the AMC concentrate was similar, the corresponding figures being 84% and 6.5% respectively. The MAG concentrate was of a slightly more coarse distribution, with 74% of material <75μm and 14% >106μm. UCC was the most coarse concentrate with only 46% <75μm and 35% >106μm. The size specification for feed material to the KNS is that 80% must pass a <75μm sieve. UCC was the only concentrate which deviated significantly from this specification.
3.3.4 SEM and EPMA

Polished sections of the KNO and AMC concentrates were examined using SEM and EPMA. The MAG and UCC concentrates were not examined as they were sampled from the same feed circuit as the KNO concentrate and hence comprised the same minerals, differing mainly in percentage composition and particle sizing. Figures 3.4(a&b) show backscattered electron images of typical groups of particles in the unreacted KNO and AMC concentrates. The grains were angular and randomly shaped. Notice the presence of dark, non-sulfide phases in these micrographs, particularly in the top right of Figure 3.4(b).

Approximately 30 particles of each of the KNO and AMC concentrates were examined via EPMA and the measured stoichiometries are shown in Tables 3.6(a&b). Pyrite particles in both concentrates exhibited a stoichiometry consistent with the results shown for the two pyrite samples in Table 3.2. KNO pyrite contained less nickel on average (0.1-1.0%) than did the AMC pyrite (0.2-4.0%). This trend in nickel contents is analogous to that shown by the British pyrite and the Leinster pyrite samples. Recall that these are primary and secondary minerals respectively. AMC is mined from a supergene deposit and so most of the pyrite present is likely to be of secondary formation. Hence the precipitation of this mineral from a nickel enriched
Figure 3.4: Backscattered electron micrographs of the unreacted nickel sulfide concentrates:
(a) KNO

Figure 3.4(b): AMC
<table>
<thead>
<tr>
<th>Average Stoichiometry</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{0.98}$S$_2$</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Fe$_{0.85}$S</td>
<td>Pyrrhotite</td>
</tr>
<tr>
<td>Ni$<em>{4.90}$Fe$</em>{4.43}$S$_8$</td>
<td>Pentlandite</td>
</tr>
</tbody>
</table>

Table 3.6(a): Stoichiometries of the minerals present in the unreacted KNO concentrate as determined by EPMA.

<table>
<thead>
<tr>
<th>Average Stoichiometry</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{0.99}$S$_2$</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Fe$_{0.85}$S</td>
<td>Pyrrhotite</td>
</tr>
<tr>
<td>Ni$<em>{1.70}$Fe$</em>{1.47}$S$_4$</td>
<td>Violarite</td>
</tr>
<tr>
<td>Ni$<em>{5.03}$Fe$</em>{4.40}$S$_8$</td>
<td>Pentlandite</td>
</tr>
</tbody>
</table>

Table 3.6(b): Stoichiometries of the minerals present in the unreacted AMC concentrate as determined by EPMA.
solution would explain the enhanced nickel level observed. The large particle in the centre of Figure 3.4(b) has a similar porous appearance to the pyrite-violarite minerals from the Leinster supergene ore (Figure 3.3(f)). This contrasts with the smooth appearance of the KNO particles, this concentrate being mined from a primary deposit. Hence, a lower level of nickel is expected in the KNO pyrite as was observed with the British pyrite.

Pyrrhotite in both the KNO and AMC concentrates exhibited a stoichiometry consistent with the Kambalda and Renison Bell samples (Table 3.2). The average associated nickel contents (0.2-1.0%) were also similar to that of the Kambalda sample. The stoichiometry for KNO pentlandite agreed with that shown in Table 3.2. No violarite was analysed in this concentrate. AMC violarite was more metal rich than the Leinster sample. An average nickel:iron:sulfur ratio of 1.70:1.47:4 for the former was measured, compared with 2:1.05:4 for Leinster violarite. However, there was a fair degree of variation in the stoichiometry of the AMC mineral. A small amount of pentlandite was also detected. Hence, it appears that this concentrate contains ore from the transition region where pentlandite conversion to violarite is still occurring. The presence of pyrrhotite in the AMC concentrate is also indicative of transition ore (Nickel, Ross and Thornber 1974).
Thus, in summary, it is apparent that MAG is primarily a pyrrhotite bearing concentrate. KNO and UCC comprise pyrrhotite and pentlandite, UCC being of a more coarse particle size distribution. AMC is composed mainly of pyrite and violarite. Hence, the properties of these concentrates are such that behavioural differences can be rationalised by reference to variations in mineralogy and particle size distribution. Smelting of the concentrates in the pilot scale reactor and examination of the products will provide an indication of the ignition behaviour of the individual minerals under flash smelting conditions for comparison with the results of the laboratory scale studies.
CHAPTER 4 THERMAL ANALYSIS STUDIES OF PYRITE,
PYRRHOTITE, PENTLANDITE AND VIOLARITE

The 45-75μm size fractions of the six sulfide samples were examined under oxidising conditions (heating rate = 10°C/min, air atmosphere) using TG-DTA. The reaction sequences in progress were investigated and the relative reactivity of the sulfides was established.

In the discussion of thermal analytical results the temperatures ranges quoted normally refer to the extrapolated onset and offset values for a particular event. Repeat trials showed a slight variation in the recorded temperatures and values are quoted to within ±5°C. Mass gains prior to approximately 300°C were caused by buoyancy effects. These were allowed for in the calculation of mass losses. The variation in the mass loss measured between duplicate trials was ±2-5%.

4.1 Secondary Pyrite

Figure 4.1(a) shows a typical TG-DTA trace for the secondary pyrite/marcasite sample. A small degree of exothermic activity was first evident in the DTA trace from approximately 400°C, while the major exotherm occurred in the temperature range 450-530°C. This exotherm comprised one main peak with a shoulder
Figure 4.1: TG-DTA records of the 45-75μm fractions of the sulfide samples (heating rate = 10°C/min, air atmosphere): (a) secondary pyrite

Figure 4.1(b): primary pyrite
resolving at 495°C. Associated with this activity was a sharp mass loss in the TG curve from 455°C to 520°C. 15.0% mass was lost by 485°C, at which temperature a point of inflection was observed in the TG curve. The rate of mass loss then decreased, a further 7.8% reduction in mass occurring until 520°C. This second mass loss corresponded with the appearance of the shoulder in the DTA curve. The sample mass then held relatively constant until 575°C when a 4.2% loss occurred, finishing at 625°C. This event was associated with a slight endothermic drift. The mass trace continued to slope gradually down, a total loss of 31.3% being registered by 1000°C. This is lower than the theoretical value of 33.4% expected for complete oxidation of all pyrite to hematite. This is most likely due to the presence of impurities. Silica for example, would not undergo any mass change. Reference to Table 3.1 shows that the iron and sulfur analysis total for this sample was only 82%.

The TG-DTA curve for secondary pyrite displayed marked similarity to the behaviour of a <45µm pyrite sample examined in a study by Dunn, De and O'Connor (1989a). These authors reported a major exotherm between 420°C and 490°C, a shoulder occurring from 470-490°C. Mass losses were observed in the ranges 440-480°C and 550-605°C, the latter being associated with a slight endotherm from 550-610°C. The general features of this TG-DTA record matched those of the secondary pyrite
sample except that the former possessed an additional effect near 400°C, several small sharp exotherms being present. The temperatures at which events occurred also differed. These variations were most likely due to the differences in the origins of the samples and in the particle size ranges examined.

Dunn, De and O'Connor (1989a) assigned the exothermic activity and the first mass loss to direct oxidation of pyrite to form hematite. They proposed that sulfate formation occurred simultaneously with the oxidation reaction. The mass loss and endothermic effect from 550°C-610°C were attributed to decomposition of iron(III) sulfate. The products collected at various temperatures were examined. It was reported that the particles consisted of concentric layers of oxidation products.

The observations made for secondary pyrite in the present study can be explained by analogy to the above findings. It appears that secondary pyrite oxidises to hematite with simultaneous iron sulfate formation during the period of exothermic activity to 530°C. The reason for the change in the slope of the TG curve at 485°C and the associated shoulder in the DTA curve is not readily apparent. It is possible that the rate of oxidation has altered, a reduction in the rate of mass loss perhaps reflecting a decreased rate of oxidation due to the inhibiting effect of layers of oxidation and sulfation.
products.

The mass loss and associated endotherm from 575-625°C in Figure 4.1(a) are explained by the decomposition of iron(III) sulfate to form hematite. In order to verify this reaction assignment samples of synthetic iron(II) sulfate and iron(III) sulfate were oxidised under the same conditions as those used for the sulfide samples. Iron(II) sulfate showed a broad endothermic effect in the range 425-555°C which is most likely due to the oxidation of iron(II) to iron(III). Beyond this temperature the TG-DTA curve for this sample matched that for iron(III) sulfate. The latter commenced gradual mass loss and endothermic behaviour at approximately 570°C, the extrapolated onset and offset temperatures for the major mass loss being 620°C and 665°C respectively. This mass loss was associated with an endothermic peak and is indicative of decomposition of iron(III) sulfate to form hematite. These observations are comparable with those reported by Pelovski et al (1990).

The extrapolated onset (575°C) and offset (625°C) temperatures for decomposition of the sulfate formed during oxidation of secondary pyrite are lower than the corresponding values for the synthetic sulfate. This may be a result of differences in the degree of crystallinity of these materials. Dunn, De and O'Connor (1989a & 1989b) could not detect sulfate during XRD examination of pyrite oxidation products even though it was present at
levels in excess of 20%. They suggested that this may have been due to a low degree of crystallinity. Thus, it is possible that the sulfate formed by secondary pyrite at a heating rate of 10°C/min is somewhat amorphous and may decompose at a lower temperature than the more crystalline synthetic material.

On the basis of the above discussion it is apparent that the reaction sequence for 45-75μm secondary pyrite heated at 10°C/min using an air atmosphere and an alumina crucible proceeds as follows.

(i) In the temperature ranges 400-495°C and 495-530°C simultaneous oxidation and sulfation reactions occur:

\[
\text{FeS}_2 + \frac{3}{2} O_2 \rightarrow 0.5\text{Fe}_3\text{O}_4 + 2\text{SO}_2
\]

\[
2\text{FeS}_2 + \frac{5}{2} O_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2
\]

(ii) From 575-625°C iron(III) sulfate decomposes:

\[
\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2 + 1.5\text{O}_2
\]

These reactions are formal representations of the phases reacted and produced. They do not indicate the mechanism of reaction. For example, Dunn, De and O'Connor (1989a) stated that iron(III) sulfate formation may occur by either oxidation of iron(II) sulfate or sulfation of hematite. The latter process involves oxidation of
sulfur dioxide to form sulfur trioxide which then reacts with hematite. This explanation is favoured as it accounts for the absence of a mass gain for sulfate formation prior to the onset of oxidation and mass loss.

Very little literature was located on thermal analysis studies of marcasite. It has been suggested that this polymorph of pyrite is relatively unstable compared with pyrite and will commence oxidation at a lower temperature when heated in air (Kopp and Kerr 1958). However, research on the ignition of sulfide aerosols (Chernyavskii, Filippov, and Bekchiu 1977) reported that both minerals ignite at the same temperature. In the current study pyrite and marcasite were not differentiated when discussing the secondary pyrite sample.

4.2 Primary Pyrite

Exothermic activity for the primary pyrite sample (Figure 4.1(b)) commenced at 455°C. Two shoulders were visible on the left side of the major exotherm, these being in the ranges 455-490°C and 490-535°C. The major exotherm was a very sharp and extremely energetic peak which occurred from 535°C to 545°C. This event caused an overheating of the sample temperature by 15°C above that of the programmed temperature as evident from the deviation of the temperature profile from a linear
response.

Primary pyrite displayed only one major mass loss, this being 31.3% in magnitude and occurring between 465°C and 545°C. Two inflection points were evident in this curve, the first at 515°C and the second at 535°C. At 515°C the rate of mass loss increased. The portion of the curve from 535-545°C showed the maximum rate of mass loss and it corresponded closely with the period of the major exotherm. The mass losses for the three portions of this curve were 9.9%, 7.6% and 13.8% respectively. In the region where sulfate decomposition was observed for secondary pyrite (575-625°C), there was a slight tailing off in the TG trace for primary pyrite amounting to a 1.8% drop in mass. Hence, it appears that sulfate formation was minimal for this sample or alternatively, that the majority of sulfate formed had decomposed prior to a furnace temperature of 575°C. The total mass loss to 1000°C was 34.8% which is consistent with complete oxidation of pyrite to hematite.

It seems likely that primary pyrite undergoes oxidation and sulfation prior to 535°C. An explanation for the behaviour of this mineral beyond this temperature can be proposed by analogy with a previous study of a 53-74μm fraction of pyrite (Jorgensen and Moyle 1982). The latter sample was examined by TG-DTA at a heating rate of 10°C/min. Exothermic activity was reported to commence at approximately 430°C. This was
followed by a major exotherm beginning somewhere between 530°C and 550°C and corresponding with the period of most rapid mass loss. This event caused a temperature overheating of 9-29°C, depending upon the experimental conditions. The TG curve showed a single stage mass loss of 32%.

Using electron microscopy Jorgensen and Moyle (1982) examined the products collected at various stages in the TG-DTA oxidation profile. They found that below 530°C pyrite oxidised to hematite, a dense oxide layer forming around an unreacted core of sulfide. Beyond this temperature any remaining pyrite decomposed to pyrrhotite and oxidised. This caused the reaction rate to increase, the associated exothermic activity being very energetic. The absence of a sulfate decomposition stage in the TG curve was attributed to the intensity of the oxidation reaction causing the sample temperature to rise above that at which sulfate is stable.

These observations are comparable with those for the primary pyrite sample examined in the current work. This mineral appears to be reacting via a two stage mechanism. Surface oxidation and sulfation first occur followed by pyrolytic decomposition of pyrite and oxidation of the resulting pyrrhotite and sulfur vapour. During the latter stage the sample temperature rose 15°C above the programmed temperature to reach a value of approximately 560°C. This is indicative of the very
exothermic manner in which the newly formed pyrrhotite and sulfur vapour oxidise. As evidence of sulfate decomposition beyond this event was minimal, it is likely that the degree of sample overheating was sufficient to remove the majority of sulfate formed. Thus the following reaction sequence describes the behaviour of 45-75μm primary pyrite during oxidation in an air atmosphere.

(i) In the temperature ranges 455-490°C and 490-535°C oxidation and sulfation occur:

\[
\begin{align*}
\text{FeS}_2 + \frac{3}{2} \text{O}_2 & \rightarrow \text{0.5Fe}_2\text{O}_3 + 2\text{SO}_2 \\
2\text{FeS}_2 + \frac{3}{2} \text{O}_2 & \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2
\end{align*}
\]

(ii) From 535-545°C any remaining pyrite decomposes to form pyrrhotite and sulfur vapour, both of which then oxidise:

\[
\begin{align*}
\text{FeS}_2 & \rightarrow \text{FeS} + \text{S}_{(g)} \\
\text{S}_{(g)} & \rightarrow^2 \text{SO}_2 \\
\text{FeS} & \rightarrow^2 0.5\text{Fe}_2\text{O}_3
\end{align*}
\]

This reaction sequence accounts for 13.8% of the total 34.8% mass loss. Hence, a substantial amount of primary pyrite has not reacted by 535°C.
Above 565°C any remaining iron(III) sulfate decomposes:

\[ \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{O}_2 \]

The reaction mechanisms for primary and secondary pyrite are thus significantly different. Pyrite may either oxidise directly to hematite or an intermediate step may occur where pyrrhotite is generated and then oxidised. The extent to which each mechanism contributes to the overall reaction sequence will depend on the sample and the experimental conditions. Dunn, De and O'Connor (1989b) reported that pyrrhotite was formed during oxidation of 90-125μm particles of pyrite but not during oxidation of <45μm particles. They proposed that the greater surface area of the finer material allowed complete oxidation of these particles prior to the decomposition temperature of pyrite. The larger particles, however, did not have sufficient time to oxidise through to the particle core. Consequently, the pyrite remaining at 515°C decomposed and pyrrhotite was formed.

The primary and the secondary pyrite samples examined in this study were both 45-75μm in size. However, as shown by the SEM micrographs in Figures 3.3(a&b), the secondary sample appeared to be far more porous. This was confirmed by surface area measurements which yielded a value of 0.6m²/g for the secondary sample compared with
0.1m²/g for the primary sample. The greater surface area of secondary pyrite would render it more reactive to sulfation and oxidation. Consequently complete reaction occurred prior to the temperature for pyrolytic decomposition of pyrite to pyrrhotite. This was not the case for the less porous primary pyrite.

4.3 Pyrrhotite

The general TG-DTA oxidation profiles for the 45-75μm Kambalda and Renison Bell pyrrhotite samples (Figures 4.1(c&d) respectively) were very similar. Both samples displayed a characteristic endotherm at approximately 325°C. This was caused by a transition in crystal structure from the monoclinic form of pyrrhotite to the hexagonal form (Deer, Howie and Zussman 1962, pp146-147). This endotherm is a valuable diagnostic for detecting the presence of pyrrhotite in a sulfide mixture.

Exothermic activity for Kambalda pyrrhotite commenced at 480°C, becoming more significant by 520°C and continuing until 655°C. The major exotherm was partially resolved into two peaks at 570°C. A single mass loss of 12.4% occurred from 530°C to 640°C, a gradual loss of 3.8% continuing to 1000°C. The total mass loss of 16.2% is higher than the value of 14.7% expected for complete oxidation of Fe₉S₈₅ to
Figure 4.1(c): Kambalda pyrrhotite

Figure 4.1(d): Renison Bell pyrrhotite
hematite.

Exothermic activity commenced at a lower temperature for the Renison Bell pyrrhotite, first being evident at 430°C. The major exotherm occurred from 500°C to 640°C, being split into two peaks at 570°C. The sample lost 12.4% mass up to 650°C, a change of slope appearing in the same temperature region as the peak splitting. A similar slope change was present in the TG trace for the Kambalda pyrrhotite sample, although it was not so marked. The TG curve for Renison Bell pyrrhotite displayed a gradual downward trend to 1000°C, the total mass loss being 15.0%. This is consistent with complete oxidation of Fe_{0.85}S to hematite. There was no obvious evidence of sulfate formation or decomposition for either pyrrhotite sample. The magnitude of the DTA response for oxidation of both samples was comparable.

Thermal analytical studies of pyrrhotite are scarce in the literature, particularly those of natural samples. A TG-DTA study of sub-125µm synthetic Fe_{0.97}S has been performed (Kennedy and Sturman 1975). Although this pyrrhotite is of a different stoichiometry from the Kambalda and Renison Bell samples and the experimental conditions of the work differed, that is, larger sample masses were used together with an oxygen atmosphere, general comparisons can be drawn between these results and those of the current study.
From 425°C to 520°C Kennedy and Sturman (1975) reported that synthetic pyrrhotite oxidised to form iron(II) sulfate, magnetite and hematite. A net mass gain of approximately 2% was recorded. Renison Bell pyrrhotite showed gradual exothermic activity from 430-500°C (Figure 4.1(d)) but there was no apparent change in mass. The Kambalda pyrrhotite sample showed similar behaviour in the temperature range 480-520°C. Assuming sulfation to be occurring in both samples, the expected mass gain must have been offset by the mass loss due to oxidation. It has been shown that the sulfation reaction is favoured by small particle size and increased oxygen concentration (Dunn, De and O'Connor 1989b). The synthetic pyrrhotite sample was oxidised in an oxygen atmosphere and hence, it is likely that a greater degree of sulfation occurred for this sample than for the two pyrrhotite samples examined in the current study.

The major exothermic activity for the synthetic pyrrhotite sample occurred between 520-570°C and was associated with a mass loss. Kennedy and Sturman (1975) attributed this to the direct oxidation of any remaining pyrrhotite to hematite. The observations for the Renison Bell and Kambalda pyrrhotite samples were in agreement with this, significant exothermic reaction and mass loss commencing at temperatures of 500°C and 520°C for the two samples respectively.

The behaviour of the Kambalda and Renison Bell pyrrhotite
samples above 570°C was in sharp contrast with that of the synthetic sample. In the temperature range 575-625°C Kennedy and Sturman (1975) found that magnetite and iron(II) sulfate were oxidised to hematite and an iron(III) sulfate/hematite species respectively. A small exothermic effect was associated with this, together with a 1.5% mass gain. Above 625°C a mass loss of 8.5% and an endothermic drift occurred as the iron(III) sulfate/hematite species decomposed. Reaction was complete by 725°C.

Kambalda and Renison Bell pyrrhotite continued to lose mass from 570°C and a second major exothermic peak was observed. All TG-DTA activity was complete by 650-655°C. It appears that sulfate decomposition occurred simultaneously with further oxidation of these two pyrrhotite samples. The increased rate of mass loss at 570°C suggests a more rapid rate of reaction. This temperature agrees with the value recorded for the onset of iron(III) sulfate decomposition when a synthetic sample of sulfate was oxidised using TG-DTA in the current study. When sulfate is formed it generates a product layer of increased volume compared with that of the original sulfide due to the addition of oxygen molecules. Hence, decomposition of this layer would be expected to allow more ready access of oxidant to the core of unreacted sulfide and so to increase the rate of reaction.
Thus, the following reaction sequence can be proposed for both the Kambalda and Renison Bell pyrrhotite samples. Temperatures have been quoted for DTA activity of the latter.

(i) At 325°C monoclinic pyrrhotite alters to the hexagonal structure.

(ii) In the temperature range 430-500°C oxidation and sulfation reactions occur:

$$2Fe_{0.86}S \rightarrow \frac{O}{2} 0.86Fe_2O_3 + 2SO_2$$

$$Fe_{0.86}S \rightarrow \frac{O}{2} 0.86FeSO_4 + 0.14SO_2$$

(iii) From 500-570°C pyrrhotite oxidises directly to hematite:

$$2Fe_{0.86}S \rightarrow \frac{O}{2} 0.86Fe_2O_3 + 2SO_2$$

(iv) Further oxidation of pyrrhotite occurs between 570-640°C together with sulfate decomposition. It is not clear whether the iron(II) sulfate will oxidise to iron(III) sulfate before decomposing, or whether it will decompose directly to hematite. Hence, decomposition equations for both species have been included:

$$2FeSO_4 \rightarrow Fe_2O_3 + 2SO_2 + 0.5O_2$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2 + 1.5O_2$$
The Kambalda pyrrhotite sample reacted at a higher temperature than the Renison Bell sample. Surface area measurements were performed on the 45-75\( \mu \text{m} \) fractions and values of 0.14 m\(^2\)/g and 0.21 m\(^2\)/g were obtained for the two samples respectively. Thus the lower reactivity of the Kambalda sample may be partially explained by its lower surface area. It was also noted in Section 3.2.3 that the quantity of fines present in the 45-75\( \mu \text{m} \) fraction of the Renison Bell sample was greater than that in the Kambalda sample. Smaller particles would trigger reaction at a lower temperature.

4.4 Pentlandite

The TG-DTA oxidation record for Kambalda pentlandite, shown in Figure 4.1(e), is more complicated than the records for the iron sulfide minerals. Little work has been reported on the oxidation of pentlandite and consequently, the reaction sequence is not clear. One study has been performed using TG-DTA-Mass Spectrometry (Dunn and Kelly 1980). However, the experimental conditions of this study varied significantly from those used in the current work. Dunn and Kelly (1980) collected TG and DTA data separately and used large sample masses (250mg for TG, 25mg for DTA). In the current work TG and DTA data were collected simultaneously using a 3mg sample. A large sample mass will cause problems as the temperature of the sample will
Figure 4.1(e): pentlandite

Figure 4.1(f): violarite-pyrite mixture
not be uniform due to slow heat transfer. Also, the gas exchange with the surrounding atmosphere will be reduced (Brown 1988, p15). Consequently, significant discrepancies were observed between the results of Dunn and Kelly's work and those of the current study, particularly in the temperatures at which events occurred. Despite this, it was possible to draw general analogies between the two studies.

The TG curve in Figure 4.1(e) displayed a relatively sharp mass gain of 3.0\% from 490-600°C. A slight exothermic trend commenced at 465°C. These effects are indicative of sulfate formation. Dunn and Kelly (1980) detected the presence of iron(II) sulfate and nickel sulfate in products collected above 460°C, iron(II) sulfate being generated at a faster rate than nickel sulfate.

The major exothermic event in Figure 4.1(e) was a very sharp peak from 600-620°C, a rapid mass loss of 3.1\% occurring in the temperature range 600-615°C. These observations suggest that oxidation is occurring. It has been reported (Kullerud 1962) that synthetic pentlandite will decompose at 610°C with the formation of (Fe,Ni)\(_{1-x}\)S and (Ni,Fe)\(_{3x}\)S\(_2\). These species contain low levels of nickel and iron respectively. The former was said to possess a hexagonal pyrrhotite structure and a metal:sulfur ratio of 9:10 or slightly higher. Assuming the formation of (Fe,Ni)\(_{1-x}\)S, oxidation of this phase
would account for the major exotherm evident at 600°C. This is consistent with thermodynamic considerations since the oxidation of iron sulfides is known to be a more exothermic process than the oxidation of nickel sulfides (Turnbull and Wadsley 1988). Thornhill and Pidgeon (1957) also reported that iron was preferentially oxidised during the roasting of pentlandite.

Further support for this reaction assignment was provided by examination of the TG-DTA behaviour for the two pyrrhotite samples (Figures 4.1(c&d)). The second half of the major exotherm in both of these traces peaked at a temperature near to 600°C, in close agreement with the peak value for the pentlandite exotherm. The magnitude of the DTA response for each of these three samples was also comparable. Hence, it appears that at approximately 600°C pentlandite decomposes to form pyrrhotite, the latter then oxidising.

Beyond 615°C the Kambalda pentlandite sample continued to lose mass in several stages. A gradual loss occurred from 615-690°C in association with an endothermic effect. This matched the temperature range recorded when synthetic samples of iron(II) sulfate and iron(III) sulfate were decomposed in the current study. Dunn and Kelly (1980) reported comparable observations. They found that the content of iron(II) sulfate present during pentlandite oxidation reached a maximum at 610°C and was substantially reduced by 700°C. Hence, the mass
loss and endotherm from 615°C can be attributed to the decomposition of iron sulfate.

From 690-715°C pentlandite experienced an increased rate of mass loss together with a small exothermic effect. These observations are consistent with an oxidation reaction. There was little evidence available on which to assign this reaction. Dunn and Kelly (1980) suggested that nickel containing sulfides would oxidise in this region. This was supported by the results of a study (Dunn and Kelly 1977) on the oxidation of synthetic millerite (NiS). A sharp mass loss and an exotherm were observed in the range 682-692°C for the millerite sample. Hence, it seems likely that the mass loss and exotherm evident from 690-715°C in Figure 4.1(e) are caused by the oxidation of a nickel sulfide species.

The slope of the TG curve in Figure 4.1(e) decreased between 715-790°C and the DTA trend was endothermic. These observations are indicative of sulfate decomposition. To confirm this a sample of nickel sulfate was oxidised using identical conditions to those employed for the sulfide samples. Decomposition of the sulfate was first apparent at 705°C when a gradual mass loss commenced in the TG curve. The extrapolated onset and offset temperatures for the sharp mass loss which followed were 740°C and 800°C respectively. An endothermic effect occurred from 710-805°C in the DTA curve. Hence the mass loss from 715-790°C for
pentlandite can be assigned to nickel sulfate decomposition. This is consistent with findings by Dunn and Kelly (1980). These authors reported that the level of nickel sulfate present during pentlandite oxidation reached a maximum by 700°C. Decomposition then commenced and continued until temperatures in excess of 800°C.

At 790°C in Figure 4.1(e) a sharp endotherm was evident, this being followed immediately by an exotherm. The latter corresponded with a rapid mass loss between 790°C and 845°C. Dunn and Kelly (1980) also observed a mass loss and endotherm in this region. They detected Ni$_3$S$_2$ in the XRD traces of samples quenched above 760°C and consequently, they assigned the TG-DTA behaviour near 800°C to oxidation of this phase. It is known that Ni$_3$S$_2$ has an incongruent melting point close to 800°C (Kullerud and Yund 1962). Hence, the endotherm at 790°C in Figure 4.1(e) and the following exotherm are accounted for by the melting of Ni$_3$S$_2$ and the rapid oxidation of the resulting liquid.

Beyond 845°C the mass trace continued to fall gradually, perhaps due to the decomposition of any remaining nickel sulfate. The total mass loss to 1000°C was approximately 12.1%.

Hence the following reaction sequence can be proposed for pentlandite.
(i) Iron(II) sulfate and nickel sulfate form in the
temperature ranges 490-615°C and 490-715°C
respectively.

(ii) At 600°C (NiFe),S₁₈ decomposes to form
an iron sulfide species (possibly pyrrhotite) and a
nickel sulfide species.

(iii) Between 600-615°C the newly formed iron sulfide
species oxidises to hematite.

(iv) From 615-690°C iron(III) sulfate decomposes:

\[ \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{O}_2 \]

(v) Oxidation of a nickel sulfide species occurs between
690-715°C.

(vi) From 715-790°C nickel sulfate decomposes:

\[ \text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_2 + 0.5\text{O}_2 \]

(vii) At 790°C \( \text{Ni}_{3+x} \text{S}_2 \) melts, then oxidises between
790-845°C:

\[ \text{Ni}_{3+x} \text{S}_2 \text{ (s)} \rightarrow \text{Ni}_{3+x} \text{S}_2 \text{ (l)} \]

\[ \text{Ni}_{3+x} \text{S}_2 \text{ (l)} - \frac{3}{2} \text{O}_2 \rightarrow (3+x)\text{NiO} + 2\text{SO}_2 \]
4.5 Violarite-Pyrite

The majority of exothermic activity for the violarite-secondary pyrite mixture (Figure 4.1(f)) occurred over the temperature range 400-510°C. The major exotherm was partially resolved into two peaks from 400-470°C and 470-510°C. Two shoulders were evident on the left side of the first peak, occurring in the temperature ranges 400-430°C and 430-450°C. The presence of at least 50% of pyrite in the mixture made it difficult to distinguish the reactions of violarite. No previous reports on violarite oxidation were located in the literature.

A sharp 10.6% mass loss was evident in the violarite-pyrite TG curve between 410-500°C. The rate of this loss increased at 455°C. The latter temperature agreed with that at which mass loss commenced for the secondary pyrite sample (Figure 4.1(a)). Hence, it seems that oxidation of violarite accounted for the TG-DTA activity prior to 450-455°C. Above this temperature the oxidation of secondary pyrite then contributed. The DTA activity for the violarite-pyrite mixture was less energetic than that for pyrite alone, indicating that violarite oxidises less exothermically than does pyrite.

Despite the lack of a significant mass gain in Figure 4.1(f), sulfation reactions obviously occurred since the
behaviour of the TG curve beyond 575°C was characteristic of sulfate decomposition. A gradual mass loss and a slight endothermic trend were apparent from 575-615°C. This agrees closely with the behaviour of the secondary pyrite sample, suggesting that iron(III) sulfate formed by the pyrite component of the violarite-pyrite mixture decomposed in this temperature range.

A further gradual mass loss and endotherm were evident from 615-675°C. Iron(III) sulfate formed by pentlandite (Figure 4.1(e)) was found to decompose in this temperature range. Hence, it appears that sulfation of the iron component of the two iron-nickel sulfides generates a more crystalline sulfate which decomposes at a higher temperature than sulfate formed from pyrite.

Beyond 675°C there were similarities between the DTA profiles of the violarite-pyrite mixture and the pentlandite sample. Hence the behaviour of violarite can be rationalised by reference to that of pentlandite.

From 675-735°C the rate of mass loss for violarite increased and a small exotherm was evident. This was indicative of the oxidation of a nickel sulfide species. From 735-770°C a continuing mass loss and slight endothermic effect were consistent with nickel sulfate decomposition. The endotherm at 790°C and the small exothermic effect which followed can be attributed to the
melting and oxidation of Ni\textsubscript{1-x}S\textsubscript{2}. However, the mass loss associated with this event was only slight, unlike the sharp mass loss evident for pentlandite. This suggests that minor quantities of this phase were present during violarite oxidation. Recognition of the Ni\textsubscript{1-x}S\textsubscript{2} melting point at 790°C was a good diagnostic for detecting the presence of violarite and pentlandite in a sulfide mixture.

The similarity between the DTA traces of the pentlandite and violarite samples beyond 675°C suggests that the iron content of violarite may oxidise preferentially to leave a nickel sulfide species as occurred for pentlandite. It has been reported (Craig 1971) that violarite will decompose at 461°C, in the presence of an equilibrium vapour, to form pyrite, vaesite and monosulfide solid solution. The pyrite and vaesite species may contain small quantities of nickel and iron respectively and consequently they are represented by the following formulae: pyrite, (Fe,Ni)S\textsubscript{2} and vaesite, (Ni,Fe)S\textsubscript{2}. Hence it is possible that the period of exothermic activity from 450-510°C in Figure 4.1(f) corresponds to the oxidation of newly formed pyrite together with the secondary pyrite present in the mixture.

Hence the following reaction sequence can be proposed for the oxidation of violarite.
(i) Above 400°C violarite undergoes oxidation and sulfation reactions, presumably to form hematite, iron(II) sulfate and nickel sulfate.

(ii) Above 450°C violarite decomposes to form an iron sulfide species (possibly pyrite) and a nickel sulfide species.

(iii) Between 450-510°C the newly formed iron sulfide species oxidises to hematite.

(iv) From 615-675°C iron(III) sulfate decomposes:

\[ \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 1.5\text{O}_2 \]

(v) A nickel sulfide species oxidises between 675-735°C.

(vi) From 735-770°C nickel sulfate decomposes:

\[ \text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_2 + 0.5\text{O}_2 \]

(vii) At 790°C \( \text{Ni}_{3\text{x}}\text{S}_2 \) melts, then oxidises:

\[ \text{Ni}_{3\text{x}}\text{S}_2 \text{ (s)} \rightarrow \text{Ni}_{3\text{x}}\text{S}_2 \text{ (l)} \]

\[ \text{Ni}_{3\text{x}}\text{S}_2 \text{ (l)} \rightarrow \frac{3}{2} (3+\text{x})\text{NiO} + 2\text{SO}_2 \]
4.6 Summary

The behaviour of pyrite, pyrrhotite, pentlandite and violarite has been established under oxidising conditions (heating rate = 10°C/min, air atmosphere, alumina crucibles) using a TG-DTA apparatus. Exothermic activity for the violarite, primary and secondary pyrite samples commenced between 400-455°C. The pyrrhotite samples, however, did not undergo significant oxidation until approximately 500°C, while the corresponding temperature for pentlandite was 600°C. Based on these observations the following order of decreasing reactivity of the sulfides to oxidation can be proposed:

pyrite, violarite > pyrrhotite > pentlandite

Of the two pyrite samples, secondary pyrite commenced oxidation at a lower temperature than primary pyrite. This was most likely due to the greater surface area of the former. Similarly, Renison Bell pyrrhotite was more reactive than the Kambalda mineral, the latter having a lower surface area.

The secondary pyrite and the two pyrrhotite samples appear to react by direct oxidation with the formation of hematite. Primary pyrite includes a pyrolytic decomposition step where pyrrhotite is generated and then oxidised. This step only occurs when pyrite remains unreacted at temperatures of 530-550°C, and hence, it
was not observed for the more reactive secondary pyrite.

Sulfation effects were most significant for pentlandite, this being the only mineral to display a substantial mass gain prior to oxidation. The overall TG-DTA activity for the two iron-nickel sulfides, pentlandite and violarite, continued until at least 800°C, while the pyrite and pyrrhotite samples had finished reacting by approximately 625°C and 655°C respectively.

The reaction sequence for violarite is similar to that for pentlandite. Decomposition to form an iron sulfide and a nickel sulfide species is apparently fundamental to the reaction mechanism of both minerals. This triggers the onset of the major exothermic activity, the iron sulfide species oxidising preferentially to the nickel sulfide species. Reaction of the latter occurs at a higher temperature and in a less exothermic manner.
CHAPTER 5  THERMAL ANALYSIS STUDIES OF PYRITE,
PYRRHOTITE, PENTLANDITE AND VIOLARITE
UNDER IGNITION CONDITIONS

In this Chapter the behaviour of pyrite, pyrrhotite, pentlandite and violarite was examined under ignition conditions using thermal analysis techniques. In Chapter 4 the oxidation behaviour of these samples was investigated using TG-DTA at a heating rate of $10^\circ\text{C/min}$ together with a 3mg sample mass and an air atmosphere. It has been shown (Dunn, Jayaweera and Davies 1985) that by increasing the intensity of the oxidising conditions, that is, by using a larger sample mass, a faster heating rate and an oxygen atmosphere, samples can be ignited. Thus, to generate ignition conditions in this study, 5mg samples of the sulfides were heated in the TG-DTA apparatus at $40^\circ\text{C/min}$ in a flowing oxygen atmosphere.

An alternative means of studying ignition reactions is to use Isothermal TG. This technique is a modification of conventional thermal analytical methods. The term "isothermal" refers to the fact that the sample is not subjected to a defined rate of heating as normally occurs during thermal analysis. The furnace is actually preheated to a specific temperature and then raised rapidly around the sample. This generates a heating rate estimated to be in the order of 3000-5000$^\circ\text{C/min}$. The purpose of this experimental technique is to simulate the
conditions of shock heating which occur during the flash smelting process.

Hence the behaviour of the six sulfide samples under ignition conditions using both TG-DTA and Isothermal TG will be examined.

5.1 TG-DTA

The TG-DTA profiles for the 45-75μm size fractions of the sulfide samples collected under ignition conditions are presented in Figures 5.1(a-f). Ignition reactions using TG-DTA are reportedly characterised by a single highly exothermic peak which occurs over a relatively short time span (Dunn, Jayaweera and Davies 1985). This is accompanied by a rapid, one stage mass loss and a sample temperature which rises significantly above the programmed furnace temperature. These criteria were used to assess the behaviour of the minerals.

The temperature range over which the major exothermic activity occurred for each sulfide sample under ignition conditions has been compared with the corresponding temperature range for exothermic activity under normal oxidation conditions (Table 5.1). In all cases the peak onset temperature has shifted to a higher value. This is at least partly an instrumental effect caused by the four fold increase in heating rate. Since a sample has a
Figure 5.1: TG-DTA records of the 45-75 μm fractions of the sulfide samples (heating rate = 40°C/min, oxygen atmosphere):
(a) secondary pyrite

Figure 5.1(b): primary pyrite
Figure 5.1(c): Kambalda pyrrhotite

Figure 5.1(d): Renison Bell pyrrhotite
Figure 5.1(e): pentlandite

Figure 5.1(f): violarite-pyrite mixture
<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Major Exotherm (10°C/min, air)</th>
<th>Major Exotherm (40°C/min, oxygen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Peak Range (°C)</td>
</tr>
<tr>
<td>Secondary Pyrite</td>
<td>450-530</td>
<td>80</td>
</tr>
<tr>
<td>Primary Pyrite</td>
<td>455-545</td>
<td>90</td>
</tr>
<tr>
<td>Kambalda Pyrrhotite</td>
<td>520-655</td>
<td>135</td>
</tr>
<tr>
<td>Renison Bell Pyrrhotite</td>
<td>500-640</td>
<td>140</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>600-620</td>
<td>20</td>
</tr>
<tr>
<td>Violarite-Pyrite</td>
<td>400-510</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of the extrapolated onset and offset temperatures and the peak temperature ranges for the major exothermic activity of the iron and nickel sulfides under normal oxidation conditions (10°C/min, air) versus ignition conditions (40°C/min, oxygen) using TG-DTA.
finite heat capacity there will always be a thermal lag between the true sample temperature and that recorded by the thermocouple (Wendlandt 1986, p41). This lag will increase with increase in heating rate and events will apparently occur at higher temperatures.

Table 5.1 shows that for all samples except pentlandite, the temperature range of the major exothermic peak has substantially reduced on increasing the heating rate. Therefore, the reaction has occurred in a shorter time span at a heating rate of 40°C/min relative to one of 10°C/min. This is indicative of an ignition reaction. Pentlandite, however, showed more than a three fold increase in peak temperature range with faster heating rate. This is an instrumental effect, the increased thermal lag causing events to be spread over a wider range.

The amplitude of the DTA peaks is expected to increase with faster heating rates due to an increase in the response of the instrument (Wendlandt 1986, pp228-232). The use of a larger sample mass will also enhance the DTA response. Consistent with these expectations, the DTA scale associated with the major exothermic activity for pentlandite has doubled (compare Figures 4.1(e) & 5.1(e)). However, the intensity of exothermic activity for the other sulfides was enhanced significantly beyond the level expected as a result of the change in heating rate and sample mass. A 10-20 fold increase was observed
for the secondary pyrite sample, both pyrrhotite samples, and the violarite-pyrite mixture. The peak intensity increase for the primary pyrite sample was only four fold as the oxidation reaction was also very exothermic. The DTA full scale ranges for all samples except pentlandite were comparable.

Examination of Figures 5.1(a-d) shows that the pyrite and the pyrrhotite samples all displayed a single stage mass loss. The temperature trace for each also showed evidence of significant sample overheating beyond the programmed furnace temperature. Hence, it appears that these four samples have ignited. Figure 5.1(e) shows that pentlandite possessed a multistage mass loss and negligible sample overheating. This mineral does not appear to ignite. The behaviour of the violarite-pyrite mixture (Figure 5.1(f)) was not clear. Sample overheating was apparent indicating ignition, although the mass loss was not complete in a single stage.

In the following discussion the behaviour of the six sulfides under ignition conditions in the TG-DTA will be examined individually.

5.1.1 Secondary Pyrite

Secondary pyrite (Figure 5.1(a)) ignited over the temperature range 475-530°C. The TG-DTA record shows
that the onset of both the rapid mass loss and the sharp exotherm corresponded closely with the point at which sample overheating commenced. At the peak of exothermic activity the temperature of the secondary pyrite sample was 550°C, this being 55°C higher than the programmed furnace value. Hence, once reaction began it seems that sufficient energy was generated to trigger sample overheating and ignition almost immediately. There was no indication of the occurrence of significant oxidation prior to this event. There was also no evidence of sulfate formation since the TG-DTA curve did not show an endothermic effect and mass loss following the main exotherm.

Dunn, De and O'Connor (1989a) reported similar observations when heating a <45μm sample of pyrite at 40°C/min in an oxygen atmosphere. This sample ignited in the range 475-500°C. They proposed that the trigger for this process was decomposition of pyrite to form pyrrhotite and sulfur vapour. A rapid gas phase reaction would then occur followed by reaction of the whole particle.

Thus, it seems that secondary pyrite has probably ignited as a result of pyrrhotite formation. Jorgensen and Moyle (1982) detected pyrrhotite above 530-550°C when oxidising pyrite at a heating rate of 10°C/min. An intense exotherm was evident from 535-545°C during oxidation of primary pyrite at the same heating rate in
the current study (Figure 4.1(b)). Hence 530-550°C can be considered the normal decomposition temperature for pyrite. Ignition of the secondary pyrite sample occurred below this temperature. This is due to self heating of the sample. When a heating rate of 10°C/min is used, the onset of oxidation does not release sufficient energy to heat the sample above the programmed furnace temperature to the decomposition temperature. Increasing the heating rate to 40°C/min and using an oxygen atmosphere creates a more intense thermal environment within the furnace. Consequently, the heat released by reaction is used to further heat the sample rather than being conducted away to the surroundings. Ignition will then occur before the furnace has reached the pyrite decomposition temperature.

The lack of evidence for sulfate formation in Figure 5.1(a) is supported by Dunn, De and O'Connor (1989a). They found that the mass loss due to sulfate decomposition during pyrite oxidation was reduced when the heating rate was increased from 2.5°C/min to 40°C/min using an air atmosphere and disappeared altogether when the atmosphere was changed to oxygen at the faster heating rate. In the latter instance, that is, using a heating rate of 40°C/min and an oxygen atmosphere, the sample was observed to glow red. This indicated significant escalation of the particle temperature above the temperature of the furnace. It was thought that the sample temperature during ignition
probably exceeded that at which sulfate was stable which explains the lack of a separate mass loss for sulfate decomposition.

The oxidation TG-DTA trace for secondary pyrite (Figure 4.1(a)) showed that when the furnace temperature reached 575°C iron(III) sulfate commenced decomposition. Hence, in order for complete decomposition of sulfate to occur during ignition the sample temperature must exceed this value. However, according to Figure 5.1(a), the overheating effect at the ignition temperature of secondary pyrite only raised the sample temperature to 550°C.

It is a function of thermal analytical techniques that the temperature measured by the sample thermocouple will lag behind the true sample temperature when the thermocouple is located below the sample pan (Wendlandt 1986, p41). This is a result of the heat capacity of the sample and crucible and the heat losses to the surrounding gas. These losses will be more significant during ignition when the sample is glowing indicating a further source of loss in the form of radiation from the sample. Consequently, while the measured temperature of the secondary pyrite during ignition was 550°C, it is likely that the true sample temperature was significantly higher than this and sufficient to cause decomposition of iron(III) sulfate.
5.1.2 Primary Pyrite

Ignition of primary pyrite (Figure 5.1(b)) occurred at 540°C. This temperature corresponds with that at which pyrite decomposes to form pyrrhotite under normal oxidation conditions. Some exothermic activity did commence at 505°C, together with a gradual mass loss. However, the energy released by this reaction was apparently insufficient to trigger particle overheating and ignition prior to the decomposition temperature. This is possibly explained by the low surface area of primary pyrite (0.1m²/g) which would result in a reduced heating effect per unit volume of the sample.

There was no evidence of sulfate decomposition for primary pyrite in agreement with the observations for the secondary mineral. The sample temperature rose 60°C above the programmed value during the period of overheating at ignition, reaching a value of 615°C. Hence, any sulfate formed would have decomposed.

5.1.3 Pyrrhotite

The Kambalda (Figure 5.1(c)) and Renison Bell (Figure 5.1(d)) pyrrhotite samples ignited at 585°C and 555°C respectively. The lower ignition temperature of the latter is possibly partially due to its higher surface area (0.21m²/g) compared with the Kambalda sample.
(0.14 m²/g). Each of these traces showed a similar sharp mass loss and a major exotherm, together with a 50-55°C overheating in the sample temperature profile.

Both pyrrhotite samples displayed evidence of some reaction before ignition was triggered. Exothermic activity commenced slowly at 465°C for the Renison Bell sample and increased at 520°C. At the latter temperature a gradual mass loss became apparent prior to the major loss at ignition. Activity of the less reactive Kambalda sample did not begin until 525°C, there being no change in mass until ignition occurred at 585°C. Hence, it appears that both pyrrhotites underwent an induction period during which reaction commenced without the heat released being sufficient to trigger ignition until a later stage.

This preliminary oxidation may have involved reaction of the sub-45µm material which had adhered to the 45-75µm particles during dry sieving. As the micrographs in Figures 3.3(c&d) showed there appeared to be a greater quantity of fine material present in the Renison Bell sample. This possibly contributed to the increased level of reactivity observed for this sample.

5.1.4 Pentlandite

Comparison of Figures 4.1(e) and 5.1(e) shows that the
general shape of the DTA profile for pentlandite has not significantly altered as the conditions during TG-DTA became more intensely oxidising. The broadening of the DTA peaks and the doubling of peak intensity are simply a reflection of the use of a faster heating rate and a larger sample mass. A significant change in reaction mechanism from oxidation to ignition does not appear to have occurred.

The mass loss attributed to iron(III) sulfate decomposition during normal oxidation of pentlandite (Figure 4.1(e)) occurred from 615-690°C. This was still apparent under more intensely oxidising conditions (Figure 5.1(e)), having shifted to a higher temperature range (670-720°C). Unlike the pyrite and pyrrhotite samples, when pentlandite was heated at 40°C/min in an oxygen atmosphere there was no significant deviation of the sample temperature above the programmed value during the period of exothermic activity. This supports the theory that sample overheating during ignition is responsible for the decomposition of sulfates during the oxidation of pyrite and pyrrhotite.

5.1.5 Violarite-Pyrite

The presence of a substantial quantity of secondary pyrite in the violarite sample complicated the interpretation of the behaviour of violarite under
ignition conditions (Figure 5.1(f)). However, this mixture ignited at a temperature of 460°C, this being 15°C lower than the ignition temperature of the secondary pyrite sample (475°C). This suggests that violarite is the more reactive of the two minerals.

As expected for an ignition reaction, there was only one major exothermic peak in the DTA trace for the violarite-pyrite sample. This peak was associated with a 45°C overheating of the sample temperature above the programmed value, a maximum temperature of 520°C being achieved. However, the behaviour of the violarite-pyrite mixture was not typical of ignition. Only 16.6% of the total mass loss of 28.3% occurred in association with the major exotherm. A slight mass gain was apparent from 475-610°C, followed by a very slight loss from 610-705°C. There was no discernable DTA activity in either temperature range. The rate of mass loss increased from 705-795°C and a small exothermic effect was observed. From 795-820°C the mass loss became quite sharp. A very minor endotherm was evident at 800°C, followed by an equally minor exotherm.

It appears that decomposition of violarite is instrumental to the ignition mechanism. Violarite ignited at 460°C which agrees with the temperature stated by Craig (1971) for decomposition of this mineral to form an iron sulfide and a nickel sulfide species. Hence, it is likely that the major exothermic activity in
Figure 5.1(e) was triggered by decomposition of violarite and ignition of the resulting iron sulfide species. The secondary pyrite present in the mixture will also ignite in this temperature range.

The nickel sulfide species formed when violarite decomposed did not appear to ignite, but rather oxidised beyond 700°C as indicated by the small exotherm and gradual mass loss in this temperature region. The melting point and exotherm near 800°C, together with a sharp mass loss, suggest melting and oxidation of \( \text{Ni}_{3-x} \text{S}_2 \).

The slight mass gain and subsequent loss which occurred between 475-610°C and 610-705°C respectively, were indicative of a small amount of sulfate formation followed by decomposition. These events were relatively insignificant as shown by the lack of DTA activity. It is possible that slight sulfation of the nickel sulfide species occurred from 475-610°C. The mass loss from 610-705°C suggests iron sulfate(III) decomposition. However, the quantity of this phase present was obviously minimal indicating that the degree of overheating which occurred during ignition was sufficient to decompose the majority of iron(III) sulfate which had formed. Nickel sulfate decomposes at a higher temperature than iron(III) sulfate and is probably still present at this point. The mass loss due to decomposition of this phase is likely to be occurring in the same temperature range as that for
the nickel sulfide oxidation reactions.

Hence, while the iron sulfide component of violarite showed behaviour indicative of ignition, reaction of the nickel sulfide component was analogous to that observed at a heating rate of 10°C/min in air (Figure 4.1(f)).

5.2 Isothermal TG

The sulfide samples were subjected to shock heating conditions using Isothermal TG (heating rate = 3000–5000°C/min, oxygen atmosphere). The mass change experienced by a sample after being introduced into the furnace at a specific preheat temperature was recorded. The preheat temperature was gradually increased until a sharp mass loss was first registered. This value was classified as the ignition temperature, being confirmed by a deviation in the sample temperature reading above the programmed furnace value.

5.2.1 Ignition Temperatures

The ignition temperatures for the 45–75μm fractions of the six sulfide samples have been presented in Table 5.2. These values were reproducible to within 5–10°C.

The ignition behaviour of the two pyrite samples was very
<table>
<thead>
<tr>
<th>Sulfide Sample</th>
<th>Ignition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary pyrite</td>
<td>450-455</td>
</tr>
<tr>
<td>Primary pyrite</td>
<td>490-495</td>
</tr>
<tr>
<td>Kambalda pyrrhotite</td>
<td>540-545</td>
</tr>
<tr>
<td>Renison Bell Pyrrhotite</td>
<td>490-495</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>720-725</td>
</tr>
<tr>
<td>Violarite-pyrite</td>
<td>430-435</td>
</tr>
</tbody>
</table>

Table 5.2: Ignition temperatures of the 45-75μm fractions of the sulfide samples as measured using Isothermal TG.
definite. Both samples showed an immediate rapid mass loss at the point of temperature overheating. Secondary pyrite ignited at 450-455°C. Primary pyrite ignited at a higher temperature (490-495°C) as would be expected due to its lower surface area.

Renison Bell pyrrhotite ignited at the same temperature as the primary pyrite, while Kambalda pyrrhotite did not ignite until 540-545°C. As for pyrite, the order of reactivity of the pyrrhotite samples can be attributed to the lower surface area of the Kambalda material. Both pyrrhotite samples showed evidence of a mass gain prior to a rapid loss. This is suggestive of slight sulfate formation. There was also a small induction period in the temperature trace prior to overheating. However, by temperatures of 550°C and 600°C for the Renison Bell and Kambalda samples respectively, these anomalies had disappeared, ignition occurring immediately and without any initial mass gain. It is likely that preliminary oxidation occurred at the particle surface during the induction period, the heat released by this process then triggering ignition after a slight delay.

The violarite-pyrite mixture ignited at 430-435°C. This value is 20°C below the ignition temperature for the secondary pyrite sample and suggests that violarite is more reactive to ignition by Isothermal TG than is secondary pyrite.
The behaviour of pentlandite was difficult to interpret. Signs of overheating first appeared in the temperature trace around $685^\circ\text{C}$. At this point the TG curve showed a gain in mass due to sulfation, followed by a gradual loss. It was not until $720^\circ\text{C}$ that a sharp mass loss was first evident although this was still preceded by sulfation. This value was recorded as the ignition temperature although it is doubtful whether ignition in the true sense was actually occurring.

Hence, the relative order of decreasing reactivity of the sulfides to ignition conditions using Isothermal TG was as presented below. Note that the primary pyrite and the Renison Bell pyrrhotite samples ignited at the same temperature.

$$\text{violarite} \rightarrow \text{pyrite} \rightarrow \text{pyrrhotite} \rightarrow \text{pentlandite}$$

This order of reactivity contradicts previous work which has reported that pyrite and violarite are more reactive than pentlandite, with pyrrhotite being the least reactive mineral (Dunn and Smith 1984). This work was performed using Isothermal TG and sulfide samples sourced from the Kambalda region. Hence, these results should be comparable with those obtained in the current study for the Leinster and Kambalda samples. The ignition temperatures of the 45-75$\mu$m fractions were reported as follows: pyrite, 390-395$^\circ\text{C}$; violarite, 395-400$^\circ\text{C}$; pentlandite, 475-480$^\circ\text{C}$; and pyrrhotite, 495-500$^\circ\text{C}$.
The values measured in the present study are thus 35-60°C higher than those reported for violarite, pyrite and pyrrhotite, but in the case of pentlandite the measured ignition temperature is 245°C higher. As the equipment used in both studies was identical, the source of these discrepancies must lie in the samples, their method of handling and the interpretation of results.

Since wet sieving was not performed in the study by Dunn and Smith (1984) a lower ignition temperature may be expected due to the presence of fines adhering to the larger particles. It is also possible that samples were contaminated with the more reactive sulfides or that the minerals may have been in a state of partial alteration. The discrepancy observed for pentlandite could be due to the interpretation of the results. It has been shown in the current work that the behaviour for pentlandite is not consistent with a typical ignition process. Sulfation and oxidation reactions are apparently occurring simultaneously, complicating the identification of the ignition temperature. A lower temperature would be obtained by recording the value at which overheating was first evident, particularly in the presence of a contaminating species.

5.2.2 Extent of Reaction Plots

Extent of reaction plots were constructed by comparing
the mass loss experienced by the sulfide at a given furnace preheat temperature with that at 900°C, the maximum furnace temperature. Triplicate measurements for the mass loss at each temperature agreed within ±2-5%. The purpose of these plots was to establish the manner in which the sulfides reacted with increasing temperature under shock heating conditions.

The extent of reaction plots for the sulfide samples are shown in Figures 5.2(a&b). Secondary pyrite (Figure 5.2(a)) underwent a 27.2% loss in mass at the ignition temperature. As the preheat furnace temperature was increased to 900°C a total loss of 28.8% occurred. Secondary pyrite thus reacted 94.4% to completion at the ignition temperature. The primary pyrite sample reacted completely at the ignition temperature, an average mass loss of 32.5% being measured over the whole temperature range to 900°C. The extent of reaction for this sample was independent of the furnace preheat temperature and it was not necessary to draw an extent of reaction curve.

Kambalda pyrrhotite (Figure 5.2(b)) lost 12.2% mass at the ignition temperature. This value increased to 13.8% by 900°C. Hence, the extent of reaction showed a slight dependence on the furnace preheat temperature, values increasing from 88% to 100%. The extent of reaction for the Renison Bell pyrrhotite sample was essentially independent of temperature. An average mass loss of 12.6% was measured at all temperatures. This
Figure 5.2: Extent of reaction versus temperature for the 45-75μm fraction of the sulfide samples as measured using Isothermal TG (a) secondary pyrite and the violarite-pyrite mixture.
Figure 5.2(b): Kambalda pyrrhotite and pentlandite.
data was not plotted.

Pyrite and pyrrhotite essentially reacted to completion once ignited using Isothermal TG. The slight temperature dependence of the extent of reaction shown for the secondary pyrite and Kambalda pyrrhotite samples may be due to the presence of impurities. For example, the secondary pyrite sample was purified from a pyrite-violarite ore. Residual violarite may be contributing to the observed behaviour.

In contrast with the trends observed for pyrite and pyrrhotite, the extent of reaction for the violarite-pyrite mixture exhibited a marked dependence on the furnace preheat temperature. Values increased from 73.9% at ignition to 100% at 900°C (Figure 5.2(a)). The corresponding mass losses were 19% and 25.7% respectively. It is probable that this trend would be more pronounced had there not been a considerable quantity of pyrite present. The latter would elevate the measured extent of reaction.

Interpretation of the behaviour of pentlandite was somewhat complex, particularly the calculation of the sample mass loss at temperatures above 800°C. Prior to this temperature the TG curve levelled out after the period of rapid mass loss as was the case for pyrite, pyrrhotite and violarite. A baseline value was usually reached within 30s from the time at which the furnace was
raised around the sample. However, at temperatures above 800°C, the mass trace for pentlandite showed an initial shorter period of rapid loss, this being followed by a less steep, continual loss. A baseline value was not reached and it was necessary to choose an arbitrary time interval (2 min) after which the mass was recorded for calculation. The extent of reaction plot (Figure 5.2(b)) showed the most significant temperature dependence of all of the sulfides. At the ignition temperature only 43.3% extent of reaction was measured. This corresponded to a mass loss of 4.2%, a total loss of 9.7% occurring by 900°C.

Hence, it is apparent that the behaviour of the iron sulfides differs markedly from that of the iron-nickel sulfides. The pyrite and pyrrhotite samples all reacted virtually to completion once ignited, the measured extent of reaction being essentially independent of furnace temperature. The violarite-pyrite mixture and the pentlandite sample, however, showed a significant dependence of the extent of reaction on the furnace temperature. The behaviour of pentlandite did not conform with typical ignition behaviour.

5.2.3 Particle Size Effects

The effect of variations in particle size on the measured ignition temperature via Isothermal TG was investigated
using four of the six sulfide samples: secondary pyrite; Kambalda pyrrhotite; pentlandite and violarite-pyrite. Four particle size ranges were examined, these being 20-45μm, 45-75μm, 75-90μm and 90-125μm. As wet sieving of pyrrhotite was not possible, a 20-45μm fraction could not be collected. Consequently a sub-45μm fraction was used. The ignition temperature for this fraction may be lower than would have been recorded for a 20-45μm fraction due to the presence of a substantial amount of sub-20μm material. The results are presented in Table 5.3 and a plot of ignition temperature versus particle size has been constructed in Figure 5.3.

Each mineral showed a definite trend to increasing ignition temperature with increasing particle size. The ignition temperatures for secondary pyrite and the violarite-pyrite mixture were within 20°C of each other for all size fractions. Note that the violarite-pyrite size fractions up to 75μm ignited at a lower temperature than those of pyrite, while the trend was reversed for the larger particles. This suggests that the ignition temperature of violarite was more influenced by particle size than was that of pyrite. An 80°C increase in ignition temperature was observed between the most fine and coarse fractions of the violarite-pyrite mixture compared with a 60°C increase for secondary pyrite. The corresponding values for the Kambalda pyrrhotite sample and the pentlandite sample were 105°C and 130°C respectively. The value for the violarite
<table>
<thead>
<tr>
<th>Sulfide sample</th>
<th>Size Fraction (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20-45</td>
</tr>
<tr>
<td>Secondary pyrite</td>
<td>420-425</td>
</tr>
<tr>
<td>Violarite-pyrite</td>
<td>410-415</td>
</tr>
<tr>
<td>Kambalda pyrrhotite</td>
<td>470-475</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>635-640</td>
</tr>
</tbody>
</table>

Table 5.3: Ignition temperatures (°C) of various size fractions of the sulfide samples as measured using Isothermal TG.
Figure 5.3: Ignition temperature versus particle size for the sulfide samples as measured using isothermal TG.
mixture would probably have been higher had there not been a substantial quantity of pyrite present, while the pyrrhotite value would have been lower had it been possible to examine a 20-45μm fraction.

The general order of decreasing effect of particle size on the ignition temperature of these samples was:

pentlandite > pyrrhotite > violarite > pyrite

The magnitude of the particle size effect measured for each sample and the relative trend was comparable with the results of a previous study (Dunn and Smith 1984).

5.3 SEM/EPMA Evidence Regarding the Mechanism of Sulfide Ignition

In order to establish the mechanism for ignition of the sulfide minerals the products generated during Isothermal TG trials were examined. Using this technique products could be rapidly quenched from several hundred degrees celsius to room temperature. Samples were collected both at the ignition temperature and 5-10°C below this value. These were prepared as polished sections for SEM and EPMA examination.
5.3.1 Secondary Pyrite

Prior to ignition there was no observable alteration in the secondary pyrite particles. At the ignition temperature, however, complete reaction had occurred to form a very porous product as seen from Figure 5.4. Notice that the general shape of the unreacted particles has been preserved as heating effects during Isothermal TG were not sufficient to cause melting. Ignited pyrite was red in colour and XRD evidence confirmed the presence of hematite.

Products having a similar porous appearance have been reported in thermal analysis and roasting studies (Dunn, De and O'Connor 1989a & 1989b; Jorgensen and Moyle 1982; Jorgensen and Moyle 1984; Nguyen 1990). Nguyen (1990) found that when the isothermal roasting temperature of pyrite was increased from 500°C to 550°C the morphology of the products underwent a dramatic change. At 500°C the particles consisted of concentric layers of iron oxide, while at 550°C a porous network had developed throughout the oxide particles. Partially oxidised particles collected at the latter temperature were examined and found to contain either pyrite with a porous pyrrhotite rim, pyrrhotite only, or pyrrhotite and iron oxide. There were no reported instances of pyrite, pyrrhotite and oxide phases occurring in the same particle. Hence, it was concluded that the reaction mechanism involved complete decomposition of pyrite to
Figure 5.4: Hematite product of secondary pyrite collected at the ignition temperature. Note the existence of radial porosity (45-75μm fraction, BSE image).
form pyrrhotite prior to the onset of oxidation. It was proposed that the newly formed pyrrhotite was shielded from oxidation while there was a positive pressure of sulfur emanating from the particle.

To confirm the potential for the formation of pyrrhotite during ignition of secondary pyrite a sample was pyrolytically decomposed by heating it at 40°C/min in a flowing nitrogen atmosphere using the TG-DTA instrument. It was necessary to use this technique rather than Isothermal TG as the latter was not amenable to the maintenance of a non-oxidising atmosphere. The resulting TG-DTA profile is presented in Figure 5.5.

Secondary pyrite displayed very definite decomposition behaviour with the appearance of a major endotherm in the temperature range 600-675°C. This was associated with a sharp 16.8% mass loss from 610-665°C. A gradual loss in mass also occurred from 415-610°C and continued from 665-1000°C. A total loss of 22.5% was recorded.

Jorgensen and Moyle (1982) reported that pyrrhotite was detected above 530-550°C when heating pyrite at 10°C/min in an air atmosphere. The higher temperature shown when using a nitrogen atmosphere in Figure 5.5 is partly due to the increased heating rate. Another contributing factor relates to the activation energy associated with the pyrite decomposition process. In a nitrogen atmosphere breakage of the iron and sulfur bonds
Figure 5.5: TG-DTA record of the 45-75μm fraction of secondary pyrite (heating rate = 40°C/min, nitrogen atmosphere).
must be achieved using thermal energy. In an air atmosphere oxygen is adsorbed onto the particle surface. This reduces the energy requirement for the bond breaking process and allows the reaction to proceed at a lower temperature.

To verify the morphology and composition of the pyrolytic decomposition product of secondary pyrite, samples were collected for examination. The heating programme was terminated at approximately 700°C and the product was allowed to cool slowly in nitrogen. A backscattered electron micrograph of some typical particles is shown in Figure 5.6. It is apparent that decomposed pyrite has a very porous structure. This caused complications during EPMA as the intensity of the reflected electron beam was reduced as a result of scattering from the rough surface. Consequently, the iron, nickel and sulfur counts registered by the detectors were low and the overall analysis totals were only 80-90%. An average stoichiometry of Fe_{0.88}S was calculated for the decomposed pyrite which is consistent with the presence of pyrrhotite. The mass loss expected for the generation of this species is 23% which is comparable with the observations in Figure 5.5.

The porous nature of the pyrite decomposition product is similar to that reported by Jorgensen and Moyle (1982). These authors calculated that the decomposition of pyrite to form pyrrhotite causes a volume reduction of
Figure 5.6: Porous pyrrhotite particles generated by pyrolytic decomposition of pyrite (TG-DTA sample collected at 700°C, heating rate = 40°C/min, nitrogen atmosphere, 45-75μm fraction, BSE image).
approximately 20%. In order to accommodate this, the newly formed pyrrhotite assumes a porous structure. They found that this structure was maintained during subsequent oxidation to hematite.

The observations of the current study are in agreement with this theory. Comparison of Figures 5.4 and 5.6 reveals a similarity in the morphology of the ignition and decomposition products of secondary pyrite. The type of pore network apparent in both products was similar to that described by Nguyen (1990) as "radial". This means that the pores radiate from the particle centre, reflecting the path taken by the sulfur vapour released from the pyrite core. Such porosity will allow ready access of oxygen to the sulfide particle and reaction will proceed to completion at a rapid rate once decomposition has occurred.

Hence, it appears that pyrrhotite formation is fundamental to the ignition mechanism for secondary pyrite. This is apparently true whether the sample is heated at 40°C/min using TG-DTA or 3000-5000°C/min using Isothermal TG. The data collected using both techniques were indicative of a rapid single stage reaction. The TG-DTA ignition profile in Figure 5.1(a) showed one short period of intense exothermic activity. In Figure 5.2(a) it was seen that the extent of reaction for secondary pyrite was essentially independent of furnace preheat temperature once ignition conditions had
been achieved using Isothermal TG.

The small effect particle size exerted on the ignition temperature of secondary pyrite (Figure 5.3) is indicative of the high level of reactivity of this mineral. Particle size would probably exert a major influence if the ignition process relied upon direct attack of the oxidant at the particle edge. This is not the case for pyrite. The evolution of sulfur vapour outwards causes a rapid gas phase reaction and also opens up the remaining sulfide structure, reducing opposition to oxidant access. However, some slight oxidation at the particle surface must presumably occur in order to trigger self heating and decomposition of the pyrite. This process will be favoured by a larger particle surface area. This explains the small increase in ignition temperature with larger particle size of pyrite.

The following reaction mechanism can be proposed for the ignition of secondary pyrite.

(i) Preliminary surface oxidation:

\[ \text{FeS}_2 + O^\Delta \rightarrow 0.5\text{Fe}_3\text{O}_3 + 2\text{SO}_2 \]

(ii) Self heating to the decomposition temperature of pyrite and subsequent formation of pyrrhotite:

\[ 0.88\text{FeS} \rightarrow \text{Fe}_{0.88}S + 0.76\text{S}_{(g)} \]
(iii) Oxidation of the released sulfur vapour creating further self heating of pyrite:

$$S_{(g)} + O_2 \rightarrow SO_2$$

(iv) Oxidation of the newly formed pyrrhotite:

$$Fe_{0.88}S \rightarrow 0.44Fe_2O_3 + SO_2$$

The temperatures at which these reactions occur will vary according to the heating rate and the experimental technique used.

5.3.2 Primary Pyrite

In contrast with the observations for secondary pyrite, the primary pyrite sample collected prior to the ignition temperature showed evidence of reaction. The particles pictured in Figure 5.7(a) have developed a slight rim of product <5μm in thickness. This rim was not continuous and appeared to be partially detached from the particle core.

Once ignition had occurred the observations for the two pyrite samples were fundamentally equivalent. Figure 5.7(b) shows that the ignition products of primary pyrite exhibited radial porosity, consistent with the presence of pyrrhotite as a reaction intermediate. The product
Figure 5.7(a): Primary pyrite particles collected just prior to the ignition temperature showing an initial product layer of oxide (45-75μm fraction, BSE image).

Figure 5.7(b): Hematite product from primary pyrite collected at the ignition temperature. Radial porosity is evident (45-75μm fraction, BSE image).
Figure 5.7(c): An ignited primary pyrite particle which has fractured. The initial oxide layer is still apparent (45-75μm fraction, BSE image).
was red in colour and analysed as hematite via XRD. Notice, however, that the initial layer observed around the particles prior to ignition was still evident in the ignited product. This is readily seen from the particle pictured in Figure 5.7(c).

The ability of primary pyrite to decompose to form pyrrhotite was confirmed by heating a sample at 40°C/min in a nitrogen atmosphere using TG-DTA. The recorded profile was very similar to that for secondary pyrite. A definite endotherm was apparent from 610-690°C in association with a sharp mass loss from 625-670°C. A total mass loss of 26.9% was observed at 1000°C.

Ignition products of pyrite having a similar product rim to the ignited primary pyrite particles shown in Figures 5.7(b & c) have been previously reported (Dunn, De and O'Connar 1989b; Jorgensen and Moyle 1982; Nguyen 1990). The initial oxide layer was thought to form due to the direct oxidation of pyrite without the pyrrhotite intermediate. This is a surface oxidation process and will result in the formation of a compact product layer as opposed to the porous network which results when sulfur vapour is lost and pyrrhotite forms. The expected volume reduction for the oxidation of pyrite to hematite can be calculated by assuming density values of 5g/cm³ and 5.3g/cm³ (Palache, Berman and Frondel 1944) for pyrite and hematite respectively. This yields a value of
approximately 37%. Jorgensen and Moyle (1981) stated that the cracking observed in the oxide rim was necessary to relieve the strain produced by crystallographic and volume mismatch between the pyrite and the oxide.

The absence of a product layer surrounding particles of secondary pyrite prior to ignition is probably a result of the increased surface area and consequently, greater reactivity of this mineral compared with that of the primary mineral. Decomposition of the secondary pyrite was apparently triggered before a significant oxide layer could form. These observations are supported by the TG-DTA ignition trials. Comparison of Figures 5.1(a&b) shows that while secondary pyrite virtually ignited as soon as exothermic activity commenced, primary pyrite underwent an induction period. Exothermic activity commenced at 505°C, however, the sample did not actually ignite until 540°C. The TG trace showed a gradual mass loss in this induction period and it seems likely that surface oxidation was occurring.

One other characteristic feature of pyrite oxidation is demonstrated by the particle of ignited primary pyrite shown in Figure 5.7(c). This particle has fractured as have several of the particles pictured in Figure 5.7(b). A previous study (Dunn, De and O'Connor 1989b) has proposed that the internal sulfur pressure during pyrite decomposition is sufficient to cause this fracturing.
Hence, it appears that decomposition to form pyrrhotite is fundamental to ignition of the primary pyrite. The reaction mechanism is thus equivalent to that presented for secondary pyrite, with the exception that surface oxidation is more significant for the primary sample.

5.3.3 Pyrrhotite

It was found that apart from differences in reaction temperatures, the ignition mechanisms for the Kambalda and the Renison Bell pyrrhotite samples were essentially equivalent. SEM examination revealed no significant evidence of reaction in the particles collected prior to ignition in either case. The ignited products of both samples were very porous, being identified as hematite using XRD. Typical ignition products of the Kambalda and Renison Bell pyrrhotite samples are shown in Figures 5.8(a&b).

The expected volume reduction associated with pyrrhotite oxidation and the formation of hematite is calculated to be 26%, assuming density values of 4.6g/cm$^3$ and 5.3g/cm$^3$ (Palache, Berman and Frondel 1944) for the two minerals respectively. This accounts for the observed porosity in the ignited products. Note that in contrast with the radial porosity of the pyrite-derived hematite, oxidation of both pyrrhotite samples generated pores which ran either along the length or across the
Figure 5.8(a): Hematite ignition product of Kambalda pyrrhotite. Oxidation has occurred along the twinning planes. Some particles still contain areas of unreacted sulfide (45-75μm fraction, BSE image).

Figure 5.8(b): Hematite ignition product of Renison Bell pyrrhotite. The particle morphology is essentially equivalent to that for Kambalda pyrrhotite (45-75μm fraction, BSE image).
width of the hematite particles. It appears that when hematite was formed it inherited the fine lamellar twinning characteristic of pyrrhotite in the same manner that violarite did during supergene alteration (Figure 3.2). This observation is supported by a study of sulfide roasting (Thornhill and Pidgeon 1957). These authors reported that pyrrhotite appeared to oxidise preferentially along certain crystallographic planes.

It is apparent from Figures 5.8(a&b) that some of the pyrrhotite grains contain areas of what appears to be unreacted sulfide. It seems that while the bulk of both samples completely oxidised, some particles did not experience the necessary heating effects. However, raising the preheat temperature approximately 50-100°C above the ignition point eliminated this effect and complete reaction occurred. This observation may contribute to the slight temperature dependence of the extent of reaction plot for Kambalda pyrrhotite (Figure 5.2(b)). The Renison Bell pyrrhotite sample, however, showed 100% extent of reaction as soon as ignition conditions were achieved. The net effect of the unreacted areas shown in Figure 5.8(b) was apparently not significant. The effect may have been more noticeable for the Kambalda pyrrhotite sample due to the lower surface area and reduced reactivity of this material.

To ascertain the capacity of pyrrhotite to decompose with the release of sulfur vapour, the Kambalda sample was
heated at 400°C/min in a flowing nitrogen atmosphere. The resulting TG-DTA profile is presented in Figure 5.9. The decomposition behaviour of pyrrhotite was not as definite as that for pyrite. A gradual mass loss commenced at 500°C but there was no detectable endothermic activity associated with this loss. The gradient of the TG curve altered at 580°C, becoming less steep. A similar TG-DTA profile was obtained for the Renison Bell sample. Both pyrrhotite samples were sulfur rich (Fe$_{0.86}$S) compared with the stoichiometric iron sulfide, troilite (FeS). Hence, they can potentially decompose with the release of a small amount of sulfur as shown by the following equation:

$$\text{Fe}_{0.86}\text{S} \rightarrow 0.86\text{FeS} + 0.14\text{S}_{(g)}$$

The total mass loss to 1000°C in Figure 5.9 was 4.2%. This is comparable with the value calculated for decomposition of pyrrhotite to form FeS.

The TG-DTA decomposition trial was terminated at 600°C and the products were collected for microscopic examination. Unlike the decomposed pyrite, significant porosity had not developed in the pyrrhotite particles at this stage. Hence, the ignition of pyrrhotite is not triggered by a definite and complete decomposition reaction as occurs for pyrite. It is possible, however, that the onset of gradual sulfur loss produces a gas phase reaction between sulfur and oxygen, this being
Figure 5.9: TG-DTA record of the 45-75μm fraction of Kambalda pyrrhotite (heating rate = 40°C/min, nitrogen atmosphere).
exothermic and causing particle heating. This would then cause increased sulfur loss. The heat released by this process may eventually trigger ignition of the whole particle. As Figure 5.3 showed, there was a significant increase in the ignition temperature of Kambalda pyrrhotite as the particle size increased. One reason for this would be the reduced heating effect per unit volume of the sample which would occur following gas phase reaction at the surface of the larger particles.

Support for this theory was provided by a study of synthetic pyrrhotite samples (Dunn and Chamberlain 1991). Sulfur vapour evolution was suggested to be the controlling factor in the ignition of pyrrhotite. Several samples of varying iron:sulfur ratio were prepared. It was found that as the pyrrhotite composition became increasingly sulfur rich the ignition temperature decreased.

Hence, the proposed ignition mechanism for both Kambalda and Renison Bell pyrrhotite is as follows. The measured stoichiometry for the latter sample has been presented.

(i) Pyrrhotite begins to decompose with the formation of stoichiometric iron sulfide and the release and subsequent oxidation of sulfur vapour:

\[ \text{Fe}_{0.86} \text{S} \rightarrow 0.86\text{FeS} + 0.14\text{S}_{(g)} \]
\[ S_{(x)} + O_2 \rightarrow SO_2 \]

(ii) The resulting heating effect causes further decomposition of pyrrhotite and sulfur vapour oxidation until ignition of the whole particle is triggered:

\[ 2FeS \rightarrow^{O} Fe_2O_3 + 2SO_2 \]

5.3.4 Pentlandite

The behaviour of pentlandite during Isothermal TG was somewhat complex. It was necessary to examine samples collected at several temperatures in order to elucidate the reaction sequence. Figure 5.10(a) shows the typical morphology of particles collected at 685-690°C. At this point a slight overheating was evident in the sample temperature and the mass curve showed a small gain followed by a gradual loss. However, there was no net reduction in the sample mass. A thin (<5μm) product layer of oxide has formed surrounding an apparently unaltered core and large voids are present around the grain edges. Comparison of this micrograph with Figure 3.3(e) suggests that these voids may be a result of reaction in the cracked regions formed in the unreacted pentlandite particles during initial grinding. This effect would be expected to enhance the reactivity of pentlandite due to the associated increase in surface area.
Figure 5.10(a): Pentlandite particles collected at 685-690°C. A dense oxide layer has formed surrounding the sulfide core and substantial voids are present (45-75μm fraction, BSE image).

Figure 5.10(b): An optical micrograph showing pentlandite particles collected at 720-725°C. Two oxide layers are evident, the outer layer displaying red internal reflections (45-75μm fraction, frame width = 220μm).
Figure 5.10(c): Pentlandite particles collected at 750–755°C. The sulfide core has reduced in size while the voids have enlarged (45–75μm fraction, BSE image).
The products collected at 720-725°C exhibited no apparent difference from those collected 30°C earlier even though a sharp mass loss was now evident. An optical micrograph of these products is shown in Figure 5.10(b). Two layers were apparent around the particle cores. This highlighted the benefit of combining optical and electron microscopy. The atomic number difference between these two phases was obviously insufficient to allow their differentiation via backscattered electron microscopy. However, they were readily identified optically. The lighter grey outer layer displays the red internal reflections which are characteristic of hematite. The presence of this phase was confirmed by XRD. Magnetite was also detected by XRD and so it seems likely that the inner darker grey layer is magnetite. Optical examination of the particles collected at 685-690°C also confirmed the presence of both magnetite and hematite.

The mass increase and subsequent decrease present in the TG traces at both of these temperatures indicate that sulfation and oxidation reactions are occurring. However, at 720°C, the extent of oxidation is sufficient to cause a net mass loss. These observations can be understood by examination of the TG-DTA ignition trace for pentlandite in Figure 5.1(e). It is apparent that sulfation first occurred as indicated by the initial mass gain. Oxidation of the iron sulfide component followed, but a net mass loss was not evident until
700-720°C when the iron sulfate present had decomposed. Beyond 720°C a sharp mass loss occurred, being attributed to the oxidation of a nickel sulfide species. It appears that reaction of pentlandite at a heating rate of 40°C/min was very similar to that at a rate of 3000-5000°C/min, sulfate being formed in both instances.

Particles collected at 750-755°C (Figure 5.10(c)) and 800-805°C were still of the same fundamental appearance as those collected at lower temperatures. With increasing temperature the size of the voids around the particle edges appears to have grown while the particle core has reduced in size. Products formed above 800°C were not examined as they were no longer discrete particles, having fused in the sample crucible. This correlates with the endotherm evident in the TG-DTA trace (Figure 5.1(e)) at 800°C, this feature being attributed to the melting of Ni$_{3x}$S$_2$. Judging by the continual mass loss in the TG curve at these temperatures, it is likely that the products would have shown increasing oxidation of the particle core. These observations explain the marked temperature dependence of the extent of reaction for pentlandite evident in Figure 5.2(b).

Hence, pentlandite does not possess an ignition temperature in the sense of pyrite and pyrrhotite in that there is not a 5-10°C interval over which the reaction mechanism dramatically changes with the formation of a
porous product. Pentlandite will not ignite and react to completion, but rather oxidises in a stepwise manner.

Approximately twenty particles of the sample collected at 800°C using Isothermal TG were analysed by EPMA. The thin product rim caused complications as it was difficult to ensure that the beam area was centred on the rim without including part of the core or the mounting material. Consequently the analysis totals were low, being 87-96% on average.

Iron was present in the product rim, there being little evidence of sulfur and only a small amount of nickel was detected (<5% when calculated as nickel oxide). This is consistent with the identification of hematite and magnetite by XRD analysis. The particle cores presented no analytical problems and they were found to comprise nickel and sulfur, with less than 3% iron being measured. The calculated average stoichiometry of the core was Ni₅S₃. Thus it appears that the iron content of pentlandite has migrated to the particle rim where it is preferentially oxidised, leaving behind a sulfide core enriched in nickel. This concept has been discussed in a report on sulfide roasting (Thornhill and Pidgeon 1957) where pentlandite was observed to form an iron oxide shell surrounding a core of Ni₅S₃ and Ni₇S₉. These products were examined after roasting at 685°C for 30min. The current study has shown that ion migration is in fact very fast, being essentially complete within 1-2min.
The pyrolytic decomposition behaviour of pentlandite was examined by heating a sample at 40°C/min in a flowing nitrogen atmosphere. The resulting TG-DTA profile is shown in Figure 5.11. A sharp endotherm was apparent at 610°C. This is indicative of a phase change, no significant mass loss being evident. Pentlandite has been reported (Kullerud 1962) to decompose at 610°C to form (Fe,Ni)_{1-x}S and (Ni,Fe)_{3x}S_2. Mass loss in the TG trace did not commence until a temperature of 805°C. In the range 805-905°C a gradual loss occurred, being followed by a more steep loss which continued until 1000°C. Both mass losses were associated with endothermic peaks, the onset temperatures being 845°C and 915°C respectively. The former was very sharp and typical of a melting reaction.

The oxidation profile for pentlandite (Figure 5.1(e)) showed an endotherm at 800°C, this being attributed to the melting of Ni_{3x}S_2. This is 45°C lower than the onset temperature for the melting peak in Figure 5.11. A previous study (Kullerud 1962) reported that when either synthetic or natural pentlandite samples were heated in an evacuated tube a sharp endotherm occurred at 862-864°C. They suggested that this apparently high melting point may have been due to the presence of iron in solid solution in the Ni_{3x}S_2 phase. This is supported by Kullerud, Yund and Moh (1969) who found that an iron rich (Ni,Fe)_{3x}S_2 phase was stable from 806-862°C, Ni_{3x}S_2 being stable below 806°C. Hence the temperature
Figure 5.11: TG-DTA record of the 45-75μm fraction of pentlandite (heating rate = 40°C/min, nitrogen atmosphere).
discrepancy between the melting peak in the oxidation and
decomposition TG-DTA profiles for Kambalda pentlandite
can be easily explained. During oxidation the iron
present in the (Ni,Fe)$_{3x}$S$_2$ phase will be preferentially
oxidised leaving a more nickel rich sulfide which will
melt at a lower temperature.

The TG-DTA profile in Figure 5.11 shows no tendency for
pyrolytic decomposition of pentlandite with the release
of sulfur vapour. The morphology of the oxidation
products is consistent with attack of oxygen at the
particle surface as occurs in the "shrinking-unreacted
core" model (Mohan, McKinley and Douglas 1979). This
model implies that as oxidation proceeds an ever
thickening product layer will form surrounding an ever
shrinking core. Oxidant must pass through this layer to
access the unreacted core. This process will be
significantly influenced by the surface area of the
sample. Consequently, reaction of larger particles
should be retarded due to their lower surface area. This
explains the particle size effect observed for
pentlandite in Figure 5.3.

It seems that the mechanism for pentlandite reaction is
determined by decomposition of this mineral at 610°C to
form an iron sulfide species and a nickel sulfide
species. Sulfur vapour loss does not occur in a
temperature range relevant to the oxidation process. Once
decomposition has occurred, iron will migrate to the rim
where it is preferentially oxidised. The nickel sulfide species will oxidise at a higher temperature. The products show layers of iron oxide surrounding an unoxidised core of nickel sulfide. Thus pentlandite does not ignite during laboratory scale ignition studies.

5.3.5 Violarite-Pyrite

The violarite-pyrite mixture did not undergo significant reaction prior to the ignition temperature. Once this material ignited, however, rims of highly porous product were observed surrounding the particle cores. Figure 5.12(a) shows a backscattered electron micrograph of a typical group of products. The darker colour of the rim of the reacted violarite particles compared with that of the core is indicative of the presence of a phase of lower average atomic number, this being consistent with the formation of oxide. A second product type can be seen in the top of Figure 5.12(b), slightly to the left of centre. This particle exhibited porosity around the rim, but there was no obvious difference between the average atomic number of the rim compared with that of the particle core. Another product of this type is present near the top left corner of this micrograph.

Approximately 20 particles of a sample ignited at 550°C were examined using EPMA. Complications arose due to the rim porosity causing scattering of the electron beam and
Figure 5.12(a): Violarite particles collected at the ignition temperature. A porous oxide layer is evident around the sulfide core (45-75μm fraction, BSE image).

Figure 5.12(b): Violarite ignition products (45-75μm fraction, BSE image).
Figure 5.12(c): The pyrolytic decomposition product of violarite. Particles have a coarsely porous structure. Note the pyrrhotite particle in the top left corner (TG-DTA sample collected at 700°C, heating rate = 40°C/min, nitrogen atmosphere, 45-75µm fraction, BSE image).
consequently analysis totals varied from 60-80%. It was found that the rims were primarily iron oxide, XRD analysis confirming the presence of hematite and perhaps magnetite. However, unlike the pentlandite rims, a fair proportion of nickel was evident (up to 20% when calculated as nickel oxide). The lighter rims still contained a significant quantity of sulfur (10-20%) and there was a higher content of nickel present than iron.

Analysis of the violarite cores yielded results which were far more variable than those for pentlandite. As shown by Figure 5.12(a) some of the cores appear to be porous and consequently analysis totals were slightly low (90-99%). An average stoichiometry of Ni$_{3.8}$S$_{3}$ was calculated, but results ranged from Ni$_{2.6}$S$_{3}$ to Ni$_{8.2}$S$_{3}$. This includes the stoichiometry of Ni$_{4.3}$S$_{3}$ which was measured for the pentlandite cores. The associated iron level in the violarite core was higher than for pentlandite, being up to 10%. A few particles showed an even higher value, these normally being associated with cores having lower levels of nickel.

The porosity of the violarite product rim resembles that of the pyrite-derived hematite and suggests that sulfur evolution is involved in the reaction mechanism. To verify this the decomposition behaviour of the violarite-pyrite mixture was established by heating a sample at 40°C/min in a nitrogen atmosphere. The resulting TG-DTA trace was dominated by the pyrite
component of the mixture. A sharp mass loss occurred in the temperature range 600-655°C, in association with an endotherm between 590-670°C. These match the values recorded during decomposition of the secondary pyrite sample (Figure 5.9(a)). There were only slight variations between the behaviour of these two samples. The violarite-pyrite mixture exhibited a 4.0% mass loss prior to 600°C, compared with a corresponding value of 3.3% for pyrite. There was also a small endothermic effect at 545°C in the former trace, suggesting that violarite may have commenced pyrolytic decomposition prior to pyrite.

Samples of the decomposition products of the violarite-pyrite mixture were collected at 700°C for microscopic examination. It was found that, like pyrite, violarite has the capacity to evolve sulfur with the formation of porous particles. This is shown by the electron micrograph presented in Figure 5.12(c). Note the presence of a pyrrhotite particle in the top left corner of this micrograph. The porosity of the decomposed violarite is not as fine grained as that of the decomposed pyrite and it has not penetrated uniformly through to the particle core.

To verify the stoichiometry of the decomposed violarite EPMA was utilised. Not surprisingly the analysis totals were low (85-100%) and some variation was observed in the results. The metal:sulfur ratio had increased with
respect to the value of 3:4 observed in the unreacted material, values ranging from 3.7:4 to 4.2:4. An average stoichiometry of \( \text{Ni}_{2.48} \text{Fe}_{1.36} \text{S}_{4} \) was calculated, corresponding to a metal:sulfur ratio of 3.84:4. The nickel:iron ratio in the unreacted violarite of 2:1 has approximately been preserved. Recalculation of the stoichiometry assuming no change in the nickel and iron levels from those in the unreacted sample yielded a value of \( \text{Ni}_{2.00} \text{Fe}_{1.10} \text{S}_{3.23} \).

Hence, it appears that violarite reaches a temperature at which pyrolytic decomposition occurs, the evolution of sulfur generating a porous product. This would then allow ready access of oxidant and so explains the high degree of reactivity observed for violarite.

During ignition of violarite iron migrates to the particle rim where it is preferentially oxidised leaving a nickel sulfide core. The latter will oxidise at a higher temperature, presumably by diffusion of oxygen through the porous oxide layer to access the unreacted sulfide. This accounts for the increase in the extent of reaction of the violarite-pyrite mixture as the furnace preheat temperature increases (Figure 5.2(a)).

While the pentlandite cores and rims contained minimal quantities of iron and nickel respectively, the segregation of these elements was not so definite for violarite. The cores still contained some iron, while
the rims contained nickel and sometimes sulfur. The faster rate of reaction for violarite possibly did not allow time for complete ion migration. The decomposition products also showed some variation in stoichiometry, and it is likely that those ignited particles which still contained sulfur in the rim had not had time to completely decompose and react.

Hence, the following mechanism can be proposed for the ignition of violarite.

(i) Decomposition of violarite at 460°C with the evolution of sulfur vapour, this vapour then oxidising to sulfur dioxide.

(ii) Diffusion of iron to the particle surface where it is preferentially oxidised to form hematite.

(iii) Oxidation of the nickel sulfide core to an increasing extent with increase in temperature.

Steps (i) and (ii) describe the ignition mechanism of violarite. Oxidation of the nickel sulfide core as described in step (iii) does not constitute an ignition process.
5.4 Summary

When the heating rate employed during TG-DTA was increased from 10°C/min to 40°C/min and an oxygen atmosphere was used rather than air, conditions in the furnace became less favourable to stepwise oxidation and more conducive to ignition. The intensity of the thermal environment increased and heat was less likely to be lost to the surroundings, being used instead to further heat the particles. A one step ignition mechanism was observed for the pyrite and pyrrhotite samples. However, the iron-nickel sulfides, pentlandite and violarite, still showed a multistage process.

Both pyrite samples ignited when a pyrrhotite intermediate was formed. The temperature at which this occurred varied according to the surface area of the sample, a higher surface area giving a lower ignition temperature. The surface area of secondary pyrite was greater than that of the primary mineral. The energy released during initial surface oxidation of the former was sufficient to heat the particles above the furnace temperature. The ignition peak thus appeared in the DTA trace at a temperature below the decomposition temperature of pyrite. This was not the case for the primary pyrite, the ignition peak for this mineral appearing at the decomposition temperature.

There was no evidence of iron(III) sulfate decomposition
for the pyrite or the pyrrhotite samples. This suggests that the overheating effect during ignition of these sulfides was sufficient to elevate the sample temperature beyond the point at which sulfate is stable.

Ignition of the violarite-pyrite mixture was apparently triggered by the decomposition of violarite to form an iron sulfide species and a nickel sulfide species. The former ignited and, together with ignition of the pyrite present of the mixture, comprised the major exothermic activity. The remaining nickel sulfide species did not show ignition behaviour, but rather oxidised in a stepwise manner above 700°C.

The change in experimental conditions did not alter the reaction mechanism for pentlandite. The differences between the TG-DTA traces recorded at 10°C/min and 40°C/min were attributed to the faster heating rate and the increased sample mass. Iron(III) sulfate and nickel sulfate decomposition reactions were still apparent.

According to the temperature of the onset of the major exotherm the general order of decreasing reactivity of the sulfide samples under ignition conditions (40°C/min, oxygen atmosphere) using TG-DTA is as follows:

violarite > pyrite > pyrrhotite > pentlandite
The secondary pyrite and Renison Bell pyrrhotite samples were more reactive than the primary pyrite and the Kambalda pyrrhotite samples respectively, the former minerals having a larger surface area.

The ignition behaviour of the sulfides under shock heating conditions using Isothermal TG (heating rate = 3000-5000°C/min, oxygen atmosphere) was very similar to that observed during TG-DTA, despite the 100 fold increase in heating rate. The relative order of decreasing reactivity of the sulfides to ignition conditions using both techniques was the same. Pentlandite did not display ignition behaviour in either situation.

The ignition temperatures recorded for the pyrite and pyrrhotite samples and the violarite-pyrite mixture using Isothermal TG were 25-65°C lower than those recorded during TG-DTA. The shock heating of particles during the former technique apparently created a more vigorous thermal environment. Less heat was conducted away to the surroundings and particles self heated to their ignition temperature at an earlier stage.

Examination of the sulfide ignition products collected during Isothermal TG confirmed that ignition of pyrite was triggered by decomposition to form pyrrhotite with the release of sulfur vapour. Similarly, pyrrhotite appears to ignite when sulfur is evolved. The extent of
reaction for both sulfides was essentially independent of the furnace preheat temperature, the heat released at the onset of reaction being sufficient to cause ignition and complete oxidation of the whole particle.

The reaction mechanism for both pentlandite and violarite involves diffusion of iron to the particle surface where it is preferentially oxidised, leaving a core enriched in nickel and sulfur. The thermodynamics of nickel sulfide oxidation are less favourable than those of iron sulfide oxidation and consequently, nickel sulfide species do not oxidise until a higher temperature. This accounts for the temperature dependence of the extents of reaction for these two minerals. As the furnace temperature is increased the extent of reaction will rise due to the progressive oxidation of the nickel sulfide core.

There is a fundamental difference between the reaction mechanisms for the two iron-nickel sulfides. While the pentlandite particles show an apparently dense oxide rim, violarite particles have a porous rim consistent with the release of sulfur vapour. Pyrolytic decomposition trials confirmed that violarite will release sulfur on heating to form porous particles. Consequently, the iron sulfide content of this mineral will react rapidly, presumably igniting due to the ready access provided for the oxidant. The iron sulfide component of pentlandite does not appear to ignite. Pyrolytic decomposition trials indicated that sulfur evolution is not involved in the
reaction of this mineral.

Despite an increase in the heating rate from 10°C/min to several thousand degrees celsius per minute, the reaction mechanism for pentlandite does not alter significantly. This mineral appears to react by a surface oxidation mechanism consistent with the "shrinking-unreacted core" model. Oxidation is triggered by decomposition of pentlandite to form an iron sulfide species and a nickel sulfide species. Iron sulfide first oxidises, followed by nickel sulfide, each reacting to an increasing degree as the furnace temperature is increased.
The ignition behaviour of the four major sulfide minerals which comprise the nickel sulfide concentrates fed to the KNS has been examined in Chapter 5. The purpose of Chapter 6 was to investigate the behaviour of the concentrates. Four samples of varying mineralogy and particle size distribution were examined, these being labelled KNO, AMC, MAG and UCC. Two of these, KNO and AMC, were of a mineralogy typically smelted by the KNS. KNO was predominantly a pentlandite-pyrrhotite containing concentrate as was the UCC. However, the pyrrhotite content of the latter was higher and the particle size distribution was more coarse (Table 3.5). AMC comprised mainly pyrite and violarite while MAG contained in excess of 70% pyrrhotite (Table 3.3).

Experimentation with the concentrates using the industrial system is problematical due to the difficulties associated with representatively sampling the product in the reaction shaft. At the base of the shaft the particles fall into a molten matte/slag bath and they can only be collected as a fused mass. Laboratory scale ignition methods have been criticised for their inability to simulate the heat and mass transfer conditions which exist in a flash smelter. Hence, in order to gain an insight into the ignition of
sulfide concentrates under conditions comparable with those existing in the industrial system a pilot scale reactor was used.

The pilot scale reactor was a model of the reaction shaft of the KNS. It essentially comprised a preheated shaft equipped with solids feeding and product collection devices. There were facilities for delivering preheated combustion gas to the reactor and a gas/solid suspension was formed in the shaft. The whole system was maintained under a slight vacuum. Unlike the industrial smelter the molten particles did not fall into a slag-matte bath, but rather they were quenched at the base of the shaft using nitrogen gas. This allowed the collection of a solid product for chemical analysis. It was thus possible to study the ignition processes in isolation from the subsequent slag-matte reactions. The effects of varying the concentrate mineralogy and particle size distribution on the measured extents of reaction were investigated, as was the effect of oxygen enrichment of the combustion gas.

6.1 Pilot Scale Reactor

The four nickel sulfide concentrates were smelted using either an air atmosphere or one enriched to a level of 35% oxygen. It was experimentally difficult to measure ignition temperatures using this reactor and consequently,
the relative reactivity of the concentrates was established based upon the extents of reaction observed under a given set of conditions. In order to calculate the extent of reaction, iron and sulfur analyses were performed on the products by the staff at the KNS. Using the corresponding data on the unreacted concentrates (Table 3.4) and the formula presented in Section 2.2.2(i), an extent of reaction was calculated for each trial.

6.1.1 Extents of Reaction

The extents of reaction for all valid trials under each set of conditions have been averaged and the results are summarised in Table 6.1. Each trial was performed at least four times and the average values are considered to have a relative variation of $\pm 5\%$. At times there were significant variations in the results of apparently equivalent trials. These were attributed to fluctuations in the operating conditions and were discarded.

The AMC and KNO concentrates exhibited similar extents of reaction when smelted in air, these being higher than the values for MAG and UCC. Using a 35\% oxygen atmosphere the reactivity of all concentrates was enhanced. The extent of reaction for the KNO and UCC concentrates increased by 14\% and 17\% respectively, while the corresponding increase for AMC was 20\%. The most
<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Average Extent of Reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>air</td>
</tr>
<tr>
<td>AMC</td>
<td>52</td>
</tr>
<tr>
<td>KNO</td>
<td>50</td>
</tr>
<tr>
<td>MAG</td>
<td>45</td>
</tr>
<tr>
<td>UCC</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 6.1: Extents of reaction measured for the concentrates during pilot scale flash smelting.
significant increase was observed for the MAG concentrate which showed a 29% rise in extent of reaction. Hence, the order of reactivity changed when a 35% oxygen atmosphere was used, AMC and MAG being the most reactive concentrates, followed by KNO, UCC being the least reactive material. It appears that once sufficiently intense smelting conditions are established, the MAG concentrate is extremely reactive. Thus, the order of decreasing reactivity of the concentrates to pilot scale flash smelting using a 35% oxygen atmosphere is as follows:

\[
\text{AMC} > \text{MAG} > \text{KNO} > \text{UCC}
\]

6.1.2 Particle Size Effects

To examine the effect of particle size on the reactivity of the concentrates the extents of reaction for UCC can be compared with those for the mineralogically similar, but significantly finer, KNO concentrate. As shown by Table 3.5, 54.5% of UCC is larger than 75\(\mu\)m compared with a corresponding figure of 25.9% for KNO. The extents of reaction for UCC under both sets of conditions in the pilot scale reactor (Table 6.1) are lower than those for KNO. Thus it seems that reaction is reduced in the coarse material.

To clarify the effect of particle size four samples of
UCC concentrate which had been smelted using an air atmosphere were sieved into six size fractions and the extent of reaction of each fraction was determined. The results are shown in Table 6.2(a). A definite trend to decrease in extent of reaction was evident as the particle size increased. 75-78% extent of reaction occurred in the sub-45µm material, compared with less than 50% once the particle size increased beyond 75µm, and 25-33% in the 106-150µm fraction.

To ensure that this was a real trend equivalent size fractions of the unreacted concentrate were analysed for iron and sulfur. This verified that the composition of each fraction was relatively uniform. The size distribution of the oxidised product was also measured. Comparison of Table 6.2(b) with the data for the unreacted concentrate in Table 3.5 shows that there was not a significant change in particle sizing following reaction. This verifies that the increased extent of reaction evident in the smaller particles was not a result of fragmentation of the larger particles during reaction.

Similar trials were performed using the AMC concentrate. Two samples were examined, one smelted in air, the other in 35% oxygen. The extent of reaction for each of four size fractions was determined and the results have been presented in Table 6.3(a). The trend for these samples was not as definite as that for the UCC material.
<table>
<thead>
<tr>
<th>Size Fraction (µm)</th>
<th>Extent of Reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 45</td>
<td>77.2</td>
</tr>
<tr>
<td>45 - 75</td>
<td>63.9</td>
</tr>
<tr>
<td>75 - 106</td>
<td>43.0</td>
</tr>
<tr>
<td>106 - 150</td>
<td>24.6</td>
</tr>
<tr>
<td>150 - 212</td>
<td>12.9</td>
</tr>
<tr>
<td>&gt; 212</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Table 6.2(a): Extent of reaction in size fractions of four samples of UCC concentrate which had been smelted in the pilot scale reactor using an air atmosphere.

<table>
<thead>
<tr>
<th>Size Fraction (µm)</th>
<th>Material Present (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 45</td>
<td>18.6 19.7 19.0 20.4</td>
</tr>
<tr>
<td>45 - 75</td>
<td>17.3 17.3 16.9 17.9</td>
</tr>
<tr>
<td>75 - 106</td>
<td>22.3 21.1 21.5 21.0</td>
</tr>
<tr>
<td>106 - 150</td>
<td>17.6 17.0 16.7 16.1</td>
</tr>
<tr>
<td>150 - 212</td>
<td>18.5 18.6 18.2 16.7</td>
</tr>
<tr>
<td>&gt; 212</td>
<td>5.7    6.3    7.8    7.9</td>
</tr>
</tbody>
</table>

Table 6.2(b): Particle size distribution of the smelted UCC samples presented in Table 6.2(a).
### Table 6.3(a):

<table>
<thead>
<tr>
<th>Size Fraction (μm)</th>
<th>Extent of Reaction (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>air</td>
<td>35% O₂</td>
<td></td>
</tr>
<tr>
<td>&lt; 45</td>
<td>49.6</td>
<td>86.7</td>
<td></td>
</tr>
<tr>
<td>45 - 75</td>
<td>54.8</td>
<td>88.2</td>
<td></td>
</tr>
<tr>
<td>75 - 106</td>
<td>47.4</td>
<td>83.3</td>
<td></td>
</tr>
<tr>
<td>&gt; 106</td>
<td>36.5</td>
<td>66.3</td>
<td></td>
</tr>
</tbody>
</table>

Extent of reaction in size fractions of two samples of AMC concentrate which had been smelted in the pilot scale reactor.

### Table 6.3(b):

<table>
<thead>
<tr>
<th>Size Fraction (μm)</th>
<th>Material Present (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>air</td>
<td>35% O₂</td>
<td></td>
</tr>
<tr>
<td>&lt; 45</td>
<td>38.9</td>
<td>25.7</td>
<td></td>
</tr>
<tr>
<td>45 - 106</td>
<td>49.6</td>
<td>40.2</td>
<td></td>
</tr>
<tr>
<td>&gt; 106</td>
<td>11.5</td>
<td>34.1</td>
<td></td>
</tr>
</tbody>
</table>

Particle size distribution of the smelted AMC samples presented in Table 6.3(a).
Consider the sample smelted in air. While particles larger than 75µm exhibited lower extents of reaction than the finer material, the 45-75µm fraction reacted to a larger extent than the <45µm fraction. The sample smelted using 35% oxygen enrichment showed a high extent of reaction in the three finer fractions compared with the >106µm fraction. Hence, the influence of particle size on the reactivity of the AMC concentrate appears to be less marked than that for the UCC concentrate.

It is necessary to exercise caution when interpreting the results for AMC. Particle size analysis of the smelted products revealed a trend to increased coarseness of the samples following smelting as indicated by comparison of Table 6.3(b) with the data for the unreacted concentrate (Table 3.5). Some of the small particles apparently increased in size during ignition which may explain why there is not a clear particle size trend.

KNO products were also examined and the extents of reaction for size fractions of four smelted samples are presented in Table 6.4(a). Like the UCC samples, there was a definite trend to decreasing extent of reaction as the particle size increased. However, Table 6.4(b) shows that the size distribution of the products has increased relative to that of the unreacted concentrate (Table 3.5) as occurred for the AMC samples.

As a general rule, larger particles showed a decreased
### Table 6.4(a): Extent of reaction in size fractions of four samples of KNO concentrate which had been smelted in the pilot scale reactor.

<table>
<thead>
<tr>
<th>Size Fraction (µm)</th>
<th>Extent of Reaction (%)</th>
<th>air</th>
<th>air</th>
<th>35% O₂</th>
<th>35% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 45</td>
<td></td>
<td>69.1</td>
<td>63.8</td>
<td>70.3</td>
<td>83.2</td>
</tr>
<tr>
<td>45 - 75</td>
<td></td>
<td>59.3</td>
<td>57.7</td>
<td>62.2</td>
<td>73.3</td>
</tr>
<tr>
<td>75 - 106</td>
<td></td>
<td>41.6</td>
<td>44.6</td>
<td>57.4</td>
<td>54.5</td>
</tr>
<tr>
<td>&gt; 106</td>
<td></td>
<td>23.3</td>
<td>26.2</td>
<td>48.6</td>
<td>31.6</td>
</tr>
</tbody>
</table>

### Table 6.4(b): Particle size distribution of the smelted KNO samples presented in Table 6.4(a).

<table>
<thead>
<tr>
<th>Size Fraction (µm)</th>
<th>Material Present (%)</th>
<th>air</th>
<th>air</th>
<th>35% O₂</th>
<th>35% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 45</td>
<td></td>
<td>26.7</td>
<td>22.9</td>
<td>37.8</td>
<td>33.3</td>
</tr>
<tr>
<td>45 - 75</td>
<td></td>
<td>22.9</td>
<td>20.8</td>
<td>14.8</td>
<td>21.3</td>
</tr>
<tr>
<td>75 - 106</td>
<td></td>
<td>26.4</td>
<td>24.9</td>
<td>13.4</td>
<td>21.3</td>
</tr>
<tr>
<td>&gt; 106</td>
<td></td>
<td>23.9</td>
<td>31.4</td>
<td>34.0</td>
<td>24.1</td>
</tr>
</tbody>
</table>
extent of reaction. This was particularly so for the KNO and the UCC concentrates, being less marked for the AMC concentrate.

6.2 SEM/EPMA and Optical Microscopic Evidence Collected on the Ignited Products

Products collected from the pilot scale reactor were prepared as unsectioned samples or as polished sections for examination by optical microscopy, SEM and EPMA. General observations regarding product morphology were made and several different product types were identified. It was possible to establish the change in product distribution with variations in the concentrate mineralogy, particle size and the intensity of the smelting conditions.

6.2.1 General Product Morphology

Heating effects were sufficiently intense in the pilot scale reactor to cause the sulfides to melt. Particles quenched from the molten state assumed a spherical shape due to surface tension effects. Figures 6.1(a&b) show backscattered electron micrographs of typical groups of products collected after flash smelting KNO concentrate. These products were simply mounted on a sample holder for examination without cross-sectioning. Particles ranged
Figure 6.1(a): The predominantly molten products which were collected following smelting of the KNO concentrate in the pilot scale reactor (BSE image).

Figure 6.1(b): 45-75μm fraction of smelted KNO products (BSE image).
from an angular morphology to a spherical one, with some of intermediate shape also being apparent. AMC, MAG and UCC products were of a similar appearance, a range of particle types being observed in all samples.

Enlarged views of some products are seen in Figures 6.2(a&b) and 6.3(a&b). These were taken using either the secondary electron detector or the backscattered electron detector. These particles were typically 50-100µm in diameter and they showed a wide variation in surface texture, many containing holes. The surface of the sphere in Figure 6.2(a) is smooth and consistent with the expected form of a frozen droplet. Figure 6.2(b) shows a distorted sphere, the surface being somewhat irregular. The particle in Figure 6.3(a) has a crater-like effect. The products in the top left and the right hand side of Figure 6.3(b) have frozen in a crystalline structure, while the other has a less regular texture. These textural variations possibly arise due to different rates of particle cooling. Variations in the composition of the molten particles may also be expected to produce different crystal formations during resolidification.

Similar species have been reported previously in the ignition products of pyrite and chalcopyrite (Hagni and Vierrether 1988; Jorgensen and Segnit 1977; Jorgensen 1980a). The holes in the spheres were attributed to the evolution of sulfur dioxide from the molten particles during smelting. Sulfur dioxide appeared to inflate the
Figure 6.2: Secondary electron micrographs showing hollow particles:
(a) a relatively smooth surfaced sphere.

Figure 6.2(b): a sphere having an irregular texture.
Figure 6.3(a): Secondary electron micrograph of a sphere which possesses a very crystalline surface.

Figure 6.3(b): Backscattered electron micrograph of three spheres having varying degrees of crystallinity.
particles and hollow spheres were formed. These were labelled "cenospheres" (Jorgensen 1980a) following the use of this term for similar reaction products of coal. The spheres shown in Figures 6.2(a)-6.3(b) are consistent with this explanation and products of this type will henceforth be referred to as "cenospheres". It should be noted that some of these particles have probably broken as a result of the sample collection and handling process rather than during reaction in the smelter.

6.2.2 Particle Size Distribution of Smelted Concentrates

The results of particle size analysis performed on several samples of smelted KNO concentrate have been reported in Section 6.1.2, Table 6.4(b). Comparison of this data with that in Table 3.5 shows that the products have increased in size, there being a substantial reduction in the quantity of sub-45μm material present. Unreacted KNO comprised 50% of material smaller than 45μm compared with 23-38% in the products. Similar results were found for the AMC concentrate, the particle size distribution of several smelted samples having been presented in Table 6.3(b). Unreacted AMC was 57% finer than 45μm while the products contained 26-39% of material in this size fraction. The results were not so definite for the more coarse UCC concentrate (Table 6.2(b)) where only a slight trend to larger particle size was apparent.
Jorgensen (1983) observed that unreacted chalcopyrite particles were approximately equiaxed in two dimensions while the third dimension was up to 1.8 times longer. He calculated that particles passing a 37-53μm sieve would melt to produce spheres having diameters in the range 57-81μm. Figures 3.4(a&b) show that many particles in the unreacted KNO and AMC concentrates possess an apparently oblong shape. Thus, while long particles may pass through a sieve according to their two smaller dimensions, the molten equivalent will not. This will create an apparent increase in the particle size distribution.

Inflation of molten particles by gaseous reaction products will further increase the particle size. Cenospheres as large as 165μm were produced during ignition of a 37-53μm size fraction of pyrite in a laminar flow furnace (Jorgensen 1980a). However, despite this, Jorgensen (1981a, 1983) reported a net degradation of particle size in pyrite and chalcopyrite products. This was attributed to several factors including particle rupture due to thermal and mechanical stress. However, it was thought more likely that the immiscible sulfide and oxide phases formed within a particle would separate or pinch off creating two smaller particles.

Another explanation proposed by Jorgensen (1981a) to explain product size reduction is that the build up of pressure within the cenospheres may cause fragmentation.
and ejection of the molten contents. The cenospheres shown in Figures 6.2(a&b) are consistent with this mechanism. The holes evident would allow the ejection of material, but these spheres have not completely fragmented. It is also possible that the build up of internal vapour pressure may be released without the necessity for fragmentation as is suggested by the cenosphere pictured in Figure 6.3(a). Gas appears to have bubbled out through the walls of this molten particle.

Kim and Themelis (1986) explained that the extent to which fragmentation occurred during ignition of chalcopyrite depended upon the amount of gas trapped within a molten particle. Larger particles usually contain more gaseous products and hence are more likely to fragment. During mathematical modelling they assumed that particles smaller than 50µm did not fragment. Experimental observations by Munroe (1987) supported this, it being reported that particles larger than 70µm invariably fragmented. Thus, the substantial quantity of sub-75µm material present in the nickel sulfide concentrates used in the current work may be another reason why a net size reduction was not observed. Although, even the more coarse UCC concentrate did not appear to undergo fragmentation.

One study (Kimura et al. 1986) has reported an increase in the size distribution of smelted chalcopyrite as a
result of particle agglomeration. However, sulfur elimination was reportedly higher in the larger particles due to coalescence of small molten particles having a high degree of oxidation. This was in direct conflict with the observations of the current study which showed sulfur elimination to decrease with increasing particle size.

Hence, the reason for the size increase of the KNO and AMC smelted products compared with the unreacted concentrates seems most likely to be sphere and cenosphere formation. The less reactive UCC concentrate apparently formed fewer of these species. There was little evidence of agglomeration in any of the products.

6.2.3 Classification of the Product Types

Figures 6.4(a) & 6.5(a) show backscattered electron micrographs of two cross-sectioned samples of KNO products. These were fairly typical of all of the concentrate products and show that the molten particles varied from completely hollow spheres to solid ones, with intermediate levels of porosity being evident between these extremes. Angular particles were also present. The field of view shown in these micrographs was scanned a second time using the X-ray detector to generate a map of the sulfur distribution. Figures 6.4(b) & 6.5(b) show that the majority of particles still contain sulfur.
Figure 6.4(a): Backscattered electron micrograph of a 45-75μm size fraction of smelted KNO products.

Figure 6.4(b): X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.4(a).
Figure 6.5(a): Backscattered electron micrograph of a >106μm size fraction of smelted KNO products.

Figure 6.5(b): X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.5(a).
Notice, however, that several of the spheres present in Figure 6.4(a) appear to have oxidised. Oxidation reduces the average atomic number of these particles making them identifiable during backscattered electron imaging by their lower signal and thus, darker colour.

EPMA and SEM examination was performed on twenty six samples of smelted KNO, AMC, MAG and UCC concentrates. Approximately thirty particles in each polished section were analysed. Iron, nickel and sulfur contents were measured, oxygen being calculated by difference. It was necessary to take care as low analysis totals occurred due to product porosity or the presence of oxide/sulfide intergrowths and contaminating silicate phases. To identify product trends with particle size some of the KNO and AMC flash smelted products were sieved into two size fractions for microscopic examination, these being 45-75μm and >106μm. Several different product types have been identified. For discussion they have been categorised into five general groups:

1. Unreacted or Unignited Particles

Despite the intensity of the heating effects in the pilot scale reactor, some particles have retained the angular shape characteristic of the unreacted concentrate. Two apparently unreacted particles appear in Figure 6.1(b), one on either side of this micrograph. Further examples
are evident in the cross-sectioned samples shown in Figures 6.4(a) and 6.5(a). These particles exhibited a wide variation in size but they were more frequently observed in the >106μm fractions of the smelted concentrates. EPMA analysis indicated that the majority of unreacted particles were pyrrhotite or pentlandite.

The second product type in this category has been labelled "unignited". Two such particles are evident on the right hand side of Figure 6.5(a), just above the dark particle of gangue material. The cross-sectioned surface of these particles looks similar to that of the unreacted particles, however, the particle shape is no longer angular. It is actually rounded or oval, yet not spherical as would be expected if melting had occurred. The sulfur X-ray scan in Figure 6.5(b) indicates that both species are relatively unoxidised. These products were invariably large (>100μm). EPMA analysis indicated stoichiometries which were similar to those of the unreacted pyrrhotite or pentlandite.

Data showing the frequency of occurrence of unreacted/unignited particles of the four sulfide minerals in the AMC, KNO, MAG and UCC smelted products have been presented in Table 6.5. The numbers of these particles in all trials of a particular concentrate have been summed in order to give a total over a range of operating conditions. The percentage each mineral comprises of the total number of unreacted/unignited
<table>
<thead>
<tr>
<th>Concentrate</th>
<th>Mineral</th>
<th>Py</th>
<th>Po</th>
<th>Vi</th>
<th>Pn</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMC (9 trials)</td>
<td>10</td>
<td>30</td>
<td>0</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>KNO (8 trials)</td>
<td>3</td>
<td>33</td>
<td>0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>MAG (5 trials)</td>
<td>0</td>
<td>22</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>UCC (4 trials)</td>
<td>4</td>
<td>21</td>
<td>0</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>TOTAL NO.</td>
<td>17</td>
<td>106</td>
<td>0</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>PERCENT</td>
<td>10%</td>
<td>65%</td>
<td>0%</td>
<td>25%</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.5: Number of unreacted/unignited particles of the four sulfide minerals remaining in the products collected after smelting AMC, KNO, MAG and UCC concentrates using the pilot scale reactor.

NOTE: Py = Pyrite Vi = Violarite
      Po = Pyrrhotite Pn = Pentlandite
particles has also been calculated.

AMC is predominantly a pyrite and violarite containing concentrate, yet no violarite was analysed in this or any of the other product samples and only a small quantity of pyrite was evident. Pyrrhotite and pentlandite were the most abundant unreacted/unignited species present in the AMC products despite the low concentration of these minerals in the original concentrate (Table 3.3). Small quantities of pyrite were analysed in the KNO and UCC products, this mineral accounting for 10% of the total number of unreacted/unignited particles analysed in all samples. Pentlandite comprised 25% of the unreacted/unignited products, while pyrrhotite comprised 65%. The latter two minerals appear to be the least reactive of the four sulfides. It must be noted, however, that 12% of the pyrrhotite particles occurred in the MAG products. This concentrate actually comprised 72% pyrrhotite by weight (Table 3.3) and hence the presence of this mineral in the products is highly probable.

The levels of pentlandite and pyrrhotite were relatively comparable in the unreacted KNO and UCC concentrates while unreacted/unignited pyrrhotite appeared far more prevalent in the smelted products. It thus seems that pyrrhotite is more resistant to ignition and melting than is pentlandite.
Further information regarding the unignited products was provided by the use of reflected light microscopy. The particle pictured in Figure 6.6(a) is approximately 150μm long. It has a morphology consistent with that of unreacted material but the corners have begun to round off. Close examination of the edges of the particle reveals the presence of a grey phase indicating that slight oxidation has commenced.

The particle pictured in Figure 6.6(b) is approximately 175μm long. Oxidation has progressed further into this particle. While the strip through the centre still appears to be unreacted, a product layer of up to approximately 25μm in thickness has formed down each side. This layer is actually comprised of fine veins of a grey oxide phase woven throughout the yellow sulfide. The development of significant porosity is also evident around the edges. This indicates that reaction has commenced with the formation of gaseous products.

Hence, it seems that these species have started to oxidise at the surface without reaction proceeding sufficiently to cause ignition of the whole particle. The rounded edges indicate that the temperature approached that necessary to melt these sulfides (>1000°C), as does the fact that veins of oxide are observed penetrating into the sulfide rather than a definite crust being formed.
Figure 6.6(a): Optical micrograph of a rounded, unignited particle showing the onset of oxidation at the particle edges (frame width = 220µm).

Figure 6.6(b): Optical micrograph of an unignited particle which exhibits a substantial degree of oxidation around the edges and the development of porosity (frame width = 220µm).
These particles may not have commenced oxidation until relatively late in their passage through the flash reactor and hence, insufficient time would have been available for complete reaction prior to quenching. The fact that many of these particles were large is consistent with this explanation as they would experience lesser heating effects due to their reduced surface area. However, smaller particles of this type were also observed. It is possible that some particles did not react because they simply did not experience a sufficient thermal environment or that the atmosphere local to them was oxygen starved.

A study on metal particle ignition (Yuasa and Takeno 1982) reported that the injection of some metal powders into a hot gas stream will not result in the simultaneous ignition of all particles at a certain position. The powder has a size distribution and the gas stream is characterised by velocity, temperature and concentration distributions. Consequently a range of products is to be expected, from those that ignite quickly to those that do not ignite at all.

Similar relatively unoxidised products have been documented in a study of copper sulfide smelting (Pignonet-Brandom, Hagni and Munroe 1986). It was reported that chalcopyrite (CuFeS$_2$) first reacted to form an intermediate solid solution (Cu$_9$Fe$_9$S$_{16}$). The stoichiometry of the latter phase was not very different
from that of the unreacted material, and the product morphology included rounded and oval grains. Some of these particles contained hollow spherical inclusions due to the formation of gas bubbles.

2. Partially oxidised nickel-iron sulfides

Partially oxidised species have been heated sufficiently to cause particle melting. Several types of these products were formed. Figures 6.7(a-d) and 6.8(a-d) show secondary electron images of cross-sectioned samples of KNO and UCC products together with X-ray maps indicating the iron, nickel and sulfur content of the particles pictured. These images were recorded using the EPMA. Nickel-containing species which have melted and reacted to a degree yet have still retained a significant quantity of sulfur can be seen. In the centre top of Figure 6.7(a) is a sphere which contains iron, nickel and sulfur distributed across the whole particle. Similar species are present in Figure 6.8(a), one example being the fragmented cenosphere in the top left corner.

An optical micrograph of a typical partially oxidised nickel-iron sulfide is evident in Figure 6.9(a). This particle comprises an intergrowth of sulfide and oxide phases, these being yellow and grey in colour respectively. Two examples of another particle type included in this product category are shown in Figure
Figure 6.7: Smelted KNO concentrate, extent of reaction = 48.9%
Magnification = X 170

(a) Secondary electron image
(b) Iron distribution
(c) Nickel distribution
(d) Sulfur distribution
Figure 6.8: Smelted UCC concentrate, extent of reaction = 49.9%
Magnification = X 160

(a) Secondary electron image
(b) Iron distribution
(c) Nickel distribution
(d) Sulfur distribution
Figure 6.9(a): A partially oxidised nickel-iron sulfide particle which contains a mixture of oxide (grey) and sulfide (yellow) phases (optical micrograph, frame width = 220μm).

Figure 6.9(b): Two partially oxidised nickel-iron sulfides showing specks of oxide throughout the sulfide spheres and around the particle edges (optical micrograph, frame width = 220μm).
6.9(b). Both of these particles have obviously melted and evolved gas as evident from the large holes which have formed but their overall extent of reaction is low. Small specks of iron oxide are seen to be dispersed throughout the nickel-iron sulfide phase and around the particle edges.

EPMA analyses confirmed that products in this category had undergone partial oxidation and crystallised from an oxide-sulfide melt in a wide variety of compositions. Many phases normally contained more iron than nickel at any point within a particle. Their nickel:iron ratios approached that expected for trevorite \((\text{Ni,Fe})\text{Fe}_2\text{O}_4\). XRD data supported this, trevorite being detected in samples of smelted KNO and AMC.

Other products in this category contained comparable levels of iron and nickel, having stoichiometries which were similar to, but slightly sulfur deficient compared with the unreacted pentlandite stoichiometry. The particles shown by Figure 6.9(b) were typical of this type. Some particles yielded a complete range of stoichiometries from low nickel and high iron containing ones to those that were comparable with unreacted pentlandite. Intermixing between the phases in the partially oxidised nickel-iron sulfides was so extensive that it was difficult to establish stoichiometries accurately as the beam area often included more than one phase.
3. Partially oxidised iron sulfides

A situation analogous to that for the nickel-iron containing sulfides arose with the smelted products of the iron sulfides. In the bottom left corner of Figure 6.8(a) is a fragmented cenosphere which contains iron and sulfur but a negligible amount of nickel. Many spherical products of this type were observed. The extent of oxidation varied widely, significant quantities of sulfur remaining in some species. A small quantity of nickel was present, usually comprising less than 5% of the analysis total. This is most likely due to the original nickel content of unreacted pyrrhotite, the presence of some nickel in pyrrhotite having been established in Section 3.3.4.

A partially oxidised iron sulfide particle is evident in the centre of the optical micrograph shown in Figure 6.10(a). This particle comprises an iron oxide phase dispersed throughout an iron sulfide sphere. At times the oxide was highly crystalline as is seen from the particle in Figure 6.10(b). Oxidation of some particles was not so readily visible. The particle on the right hand side of Figure 6.10(a) actually possesses fine veins of oxide running through the sulfide. These veins were of a similar appearance to those seen in the unignited particles. However, in contrast with the latter, oxidation appears to have progressed right across this partially oxidised particle.
Figure 6.10(a): Two partially oxidised iron sulfide particles which comprise oxide dispersed throughout the sulfide phase (optical micrograph, frame width = 220μm).

Figure 6.10(b): A partially oxidised iron sulfide particle showing skeletal crystals of oxide (optical micrograph, frame width = 220μm).
Partially oxidised iron sulfides have invariably melted and reacted to varying degrees resulting in a complete oxide-sulfide intergrowth. Similar products were reported in a chalcopyrite smelting study where skeletal crystals of oxide were observed to have developed within sulfide phases (Hagni and Vierrether 1988).

Studies on the ignition of pyrite under flash smelting conditions have also reported the formation of an oxide-sulfide melt (Huffman et al. 1989; Jorgensen 1981a; Otsuka and Soma 1980; Pignolet-Brandom, Hagni and Munroe 1986). It was found that pyrite first decomposed to pyrrhotite without allowing oxidation. Melting did not occur until after decomposition of the pyrite had been completed (Kang and Pyun 1988). Some intermediate species were quenched, these comprising angular particles having a pyrite core surrounded by a radial fibrous pyrrhotite rim (Hagni and Vierrether 1988; Jorgensen 1981a). Very few of these species were observed in the current study.

4. Oxide Species

Examination of the backscattered electron micrograph in Figure 6.4(a) and comparison with the sulfur X-ray map in Figure 6.4(b) shows that several particles do not contain any sulfur, having completely oxidised. Some oxide particles are evident in the optical micrograph presented
in Figure 6.11(a). The angular particle in the lower middle area shows the red internal reflections which are characteristic of hematite. Most oxides which have formed during the smelting process are invariably molten. Hence, they do not possess internal reflections. The value of drawing attention to this angular particle is that it allows identification of the grey colour of hematite. Consequently, the small spherical particles observed surrounding this angular one can also be recognised as hematite.

A second type of oxide is apparent on the right hand side of Figure 6.11(a). This particle comprises discrete oxide and sulfide phases. For the purpose of the present discussion the sulfide phase will not be considered. Two types of oxide are evident within this particle, the lighter phase having formed a very crystalline network on resolidification. The two particles in the top of this micrograph comprise a rather mottled mixture of oxide phases. Another example of this particle type is evident on the left hand side of Figure 6.11(b).

Figure 6.11(c) shows a small sphere which has fused to a sulfide phase. The former contains lines of what appears to be hematite within a slightly darker oxide phase. The particle in the centre of Figure 6.11(c) has the typical appearance of a partially oxidised nickel-iron sulfide species. This also contains two oxide phases. Hence, it appears that at least three types of oxides have formed
Figure 6.11(a): Oxide particles and an oxide/nickel sulfide particle. An angular hematite particle possessing red internal reflections is evident. Some of the oxides comprise two phases (optical micrograph, frame width = 220μm).

Figure 6.11(b): An oxide/nickel sulfide particle which contains two types of oxide (optical micrograph, frame width = 220μm).
Figure 6.11(c): Two oxide/nickel sulfide particles and a partially oxidised nickel-iron sulfide. All particles exhibit a mixture of oxide phases (optical micrograph, frame width = 220μm).
during the smelting process.

EPMA examination of completely oxidised particles revealed that they were predominantly iron species, some with variable, but usually low levels of nickel. Silica was also detected. Less frequently nickel oxide particles and oxides containing comparable levels of nickel and iron were observed. XRD evidence confirmed the presence of hematite and magnetite. Trevorite \((\text{Ni,Fe})\text{Fe}_2\text{O}_4\) was also identified.

5. Nickel Sulfide Species

The optical micrographs in Figures 6.11(a-c) showed that some particles contain completely separated oxide and sulfide phases. A backscattered electron micrograph of a smelted AMC sample (Figure 6.12(a)) also shows several of these species. Comparison of this micrograph with the associated sulfur X-ray map (Figure 6.12(b)) confirms that the particle in the top right hand corner, for example, contains a bleb of a bright, sulfur containing phase within an oxide sphere. Three more particles of this type are evident in this micrograph, two near the one just described, and the third in the lower right hand corner.

EPMA analysis revealed that these products comprise an iron oxide phase and a nickel sulfide phase. The range
Figure 6.12(a): Backscattered electron micrograph of smelted AMC products.

Figure 6.12(b): X-ray map showing the sulfur distribution of the group of particles photographed in Figure 6.12(a).
of stoichiometries for the latter varied, a typical nickel:sulfur ratio being 5.2:3.0 with a few percent of iron present. Some species possessed higher contents of iron, for example, a nickel:iron:sulfur ratio of 4.6:1.2:3.0 was typical.

The object of the flash smelting process is to oxidise the iron sulfide component of the concentrate, leaving the nickel sulfide component essentially unoxidised. Hence, these oxide/nickel sulfide particles are classified as completely reacted.

Oxide and sulfide phases will separate in the liquid state due to differences in surface tension and density. Wuth (1984) stated that providing there is sufficient time available, complete separation of these two phases within a particle can be expected.

Most of the products in Figures 6.11(a-c) show complete separation between the oxide and sulfide phases. The particle in Figure 6.13, however, has only partially separated. A bleb of sulfide is evident at the top of this particle and bright specks of sulfide are dispersed throughout the mixture of oxide phases.

Close examination of the particle on the right hand side of Figure 6.11(c) reveals that the nickel sulfide phase is not homogeneous. Crystals of a second, brighter phase are present. A further example of this was evident in
Figure 6.13: An oxide/nickel sulfide sphere showing specks of sulfide dispersed throughout the two oxide phases (optical micrograph, frame width = 220μm).
Figure 6.11(b). These crystals could not be resolved using EPMA. Qualitative X-ray analysis was performed using the SEM. This showed that these phases were invariably higher in nickel and lower in sulfur than the surrounding nickel sulfide phase. Hence, the stoichiometries quoted above are probably average values as the beam area most likely contained both nickel sulfide phases.

6.2.4 Product Distribution in the Smelted Concentrates

The frequency of occurrence of each of the five product categories in several of the smelted samples of AMC, KNO, MAG and UCC has been tabulated (Tables 6.6-6.9). This data was based upon the number of particles of a particular type counted. While it was possible to establish general trends, the results for some samples were anomalous. This is most likely due to the practical difficulties associated with ensuring that a representative sample was analysed. Only 1-2g of each 1-3kg smelted sample was mounted in the polished section. Furthermore, due to the time consuming nature of the EPMA exercise, only thirty particles in each sample were examined. As a result of these two factors, it is likely that bias occurred in the results.

Table 6.6 shows that the percentage of unreacted/unignited particles and partially oxidised sulfides was
<table>
<thead>
<tr>
<th>Smelting Conditions</th>
<th>Air</th>
<th>35% O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45-75</td>
<td>&gt;106</td>
</tr>
<tr>
<td>Size Fraction (µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Extent of Reaction</td>
<td>58</td>
<td>26</td>
</tr>
<tr>
<td>Unreacted/Unignited</td>
<td>17</td>
<td>23</td>
</tr>
<tr>
<td>Partially Oxidised Iron Sulfides</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Partially Oxidised Nickel-Iron Sulfides</td>
<td>13</td>
<td>64</td>
</tr>
<tr>
<td>Oxides</td>
<td>40</td>
<td>3</td>
</tr>
<tr>
<td>Nickel Sulfides</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.6: EPMA data on smelted KNO samples showing the frequency of occurrence (%) for the five classifications of product.
<table>
<thead>
<tr>
<th>Smelting Conditions</th>
<th>Air</th>
<th>35% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Extent of Reaction</td>
<td>42</td>
<td>59</td>
</tr>
<tr>
<td>Unreacted/Unignited</td>
<td>37</td>
<td>16</td>
</tr>
<tr>
<td>Partially Oxidised Iron Sulfides</td>
<td>27</td>
<td>22</td>
</tr>
<tr>
<td>Partially Oxidised Nickel-Iron Sulfides</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>Oxides</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>Nickel Sulfides</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6.7: EPMA data on smelted UCC samples showing the frequency of occurrence (%) for the five classifications of product.
<table>
<thead>
<tr>
<th>Smelting Conditions</th>
<th>Air</th>
<th>35% O&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size Fraction (μm)</td>
<td>45-75</td>
<td>&gt;106</td>
</tr>
<tr>
<td>% Extent of Reaction</td>
<td>55</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>66</td>
</tr>
<tr>
<td>Unreacted/Unignited</td>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>Partially Oxidised Iron Sulfides</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Partially Oxidised Nickel-Iron Sulfides</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>Oxides</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>37</td>
</tr>
<tr>
<td>Nickel Sulfides</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 6.8: EPMA data on smelted AMC samples showing the frequency of occurrence (%) for the five classifications of product.
<table>
<thead>
<tr>
<th>Smelting Conditions</th>
<th>Air</th>
<th>35% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Extent of Reaction</td>
<td>51</td>
<td>77</td>
</tr>
<tr>
<td>Unreacted/ Unignited</td>
<td>26</td>
<td>6</td>
</tr>
<tr>
<td>Partially Oxidised Iron Sulfides</td>
<td>56</td>
<td>18</td>
</tr>
<tr>
<td>Partially Oxidised Nickel-Iron Sulfides</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>Oxides</td>
<td>8</td>
<td>58</td>
</tr>
<tr>
<td>Nickel Sulfides</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6.9  EPMA data on smelted MAG samples showing the frequency of occurrence (%) for the five classifications of product.
generally higher in the >106μm product fractions of the KNO samples compared with the 45-75μm fractions. The latter contained a significant quantity of completely reacted species, that is, oxides and nickel sulfides, few of these species being found in the >106μm fractions. KNO primarily comprised pentlandite and pyrrhotite. These results suggest a significant decrease in reactivity with increasing particle size of these two minerals. This trend was confirmed by the data collected on the UCC products (Table 6.7). UCC was mineralogically similar to the KNO concentrate but of a coarser particle size distribution. The UCC products were dominated by partially oxidised iron sulfide and nickel-iron sulfide species. Many unreacted/unignited particles were also evident. Hence larger particles of pentlandite and pyrrhotite appear to be very resistant to smelting.

The 45-75μm fractions of the AMC products (Table 6.8) contained a significant number of nickel sulfide species, as did the >106μm fraction which had been smelted in 35% oxygen. There were relatively few partially oxidised iron sulfide and nickel-iron sulfide species compared with the KNO products, particularly when an oxygen enriched atmosphere was used. AMC is primarily comprised of violarite and pyrite. These results suggest that these two minerals are more reactive at all particle sizes than are pentlandite and pyrrhotite.

Tables 6.9 contains the product distribution for the MAG
samples. This shows an increase in the number of oxides present as the extent of reaction of the samples increased due to the use of an oxygen enriched atmosphere. There was a corresponding decrease in the number of unreacted/unignited species. The UCC products (Table 6.7) showed a similar trend with oxygen enrichment.

The smelted MAG products (Table 6.9) contained many partially oxidised iron sulfides. There was also a significant quantity of these species present in the UCC and the KNO products. However, relatively few were found in the AMC products. As the MAG, KNO and UCC concentrates contained a substantial proportion of pyrrhotite, it seems likely that this mineral ignited in the flash reactor to produce a partially oxidised species. The dominant iron sulfide present in the AMC concentrate was pyrite. Hence, the lack of a significant quantity of partially oxidised iron sulfides in the AMC products suggests that pyrite tends to ignite and react to completion in the flash reactor.

6.3 Summary

During pilot scale flash smelting in an air atmosphere AMC and KNO were the most reactive concentrates. When the intensity of the smelting conditions was increased by enriching the combustion air to a level of 35% oxygen,
MAG achieved a level of reactivity comparable with AMC. Hence, it appears that the ignition behaviour of MAG is very sensitive to the operating conditions. UCC was the least reactive concentrate under both sets of conditions. The lesser reactivity of this material compared with KNO can be attributed to its relatively coarse particle size distribution.

Larger particles exhibited a lower extent of reaction than fine ones. This effect was very noticeable in the UCC and KNO samples. The overall reactivity of the AMC concentrate was not as strongly influenced by particle size, particularly for particles smaller than 106 μm.

The KNO and AMC concentrates showed a substantial increase in particle size distribution following smelting. Microscopic examination of the products revealed that most particles were molten and that hollow spheres, or cenospheres, had formed. The temperature of the particles had obviously escalated well above the temperature of the combustion air, a value in excess of 1000°C being required to cause melting. Cenospheres were probably formed by the evolution of sulfur dioxide from the molten particles, this gas effectively acting as a blowing agent. The presence of spheres and cenospheres explains the apparent increase in the particle size distribution of the KNO and AMC samples. Analysis of the less reactive UCC samples, however, did not show a significant difference between the particle size
distributions of the unreacted and smelted samples. This implies that fewer spheres and cenospheres were formed.

The use of optical and electron microscopy allowed the identification of five main product types: 1. unreacted/unignited particles, 2. partially oxidised nickel-iron sulfides, 3. partially oxidised iron sulfides, 4. oxides and 5. nickel sulfide species. Hence, while some particles experienced sufficiently intense conditions to allow complete oxidation others did not react at all or were quenched in a state of partial oxidation. This complete distribution of product types is due to the different reactivities of the four sulfide minerals which comprise the concentrates and the variations in the conditions to which each individual particle was exposed within the smelter.

The unreacted/unignited particles were primarily pyrrhotite and pentlandite. These species were more abundant in the >106μm size fractions of the KNO and UCC products than in the 45-75μm size fractions. This indicates that pyrrhotite and pentlandite are the least reactive of the four sulfides, particularly at larger particle sizes. Prior to ignition of these two minerals oxidation was initiated at the particle surface. If the energy released by this process heats the particle rather than being lost to the surroundings, it is likely that the reaction will accelerate, further oxidation causing increased self heating until ignition and melting occur.
Alternatively, if the environment local to the particle is oxygen deficient or there is insufficient time available, the particles will be quenched before they can ignite. Once melting does occur oxidation can proceed more rapidly due to the faster kinetics associated with a gas-liquid reaction as opposed to a gas-solid one.

The predominantly pyrrhotite-containing MAG concentrate produced a large quantity of either partially oxidised iron sulfide species or oxides. The relative quantities of each species varied according to the measured extent of reaction. Once sufficiently oxidising conditions were achieved through the use of a 35% oxygen atmosphere this concentrate oxidised to a high level. Hence ignition of pyrrhotite is apparently quite sensitive to the smelting conditions.

The AMC concentrate was very reactive under all conditions and the products comprised a large number of completely reacted oxides and nickel sulfides. AMC is primarily a violarite and pyrite containing material, hence, these two minerals are the most reactive to smelting.
CHAPTER 7 CONCLUSIONS

The ignition of pyrite, pyrrhotite, pentlandite and violarite has been studied using two laboratory scale ignition techniques (TG-DTA and Isothermal TG) and a pilot scale flash reactor. All of these techniques indicated that pyrite and violarite were the most easily ignited minerals. Pyrrhotite ignited readily once sufficiently oxidising conditions had been established. Pentlandite did not exhibit ignition behaviour.

The reactivity of all minerals was reduced as particle size increased although the magnitude of this effect differed. Particle size was least important for pyrite and violarite in the laboratory studies, and also for the AMC concentrate, in which the dominant minerals were pyrite and violarite, in the pilot scale reactor. Pyrrhotite and pentlandite exhibited a more significant particle size effect. Hence, the UCC concentrate, in which pyrrhotite and pentlandite were the dominant minerals, was less reactive than the mineralogically similar, but finer, KNO material.

Large particles of pyrrhotite and pentlandite were the most commonly observed unreacted minerals in the pilot scale flash reactor products, the former being most prolific. Pentlandite particles were more likely to melt and they were included as partially oxidised nickel-iron
sulfide species. However, the extent of reaction of these species was usually low.

Increasing the oxygen partial pressure in the gas flow was found to substantially enhance the reactivity of the sulfide minerals in the laboratory and that of the concentrates in the pilot scale reactor.

The reactivity of these sulfides to ignition appears to be linked to their ability to decompose with the evolution of sulfur vapour. This vapour will react with oxygen in a rapid and very exothermic gas-phase process. This will generate heat to further increase the particle temperature, causing it to escalate well above the temperature of the surroundings. This triggers ignition, the particles melt and reaction continues as a gas-liquid process. A second consequence of sulfur vapour evolution is that porosity develops within the particles. This will allow ready access of the oxidant to the unreacted sulfide. Hence, both gas-phase reaction and morphological change are fundamental to the ignition process. There is no evidence to support the conventional "shrinking-unreacted core" mechanism which is a gas-solid process.

Ignition of pyrite is triggered by decomposition to form pyrrhotite and sulfur vapour. Violarite will decompose to form an iron sulfide species and a nickel sulfide species with significant sulfur vapour loss. This
explains the comparable level of reactivity observed for these two minerals.

During ignition of violarite iron migrates to the particle surface where it is rapidly oxidised leaving a nickel enriched sulfide core. The latter does not ignite, but rather oxidises at a higher temperature.

Ignition of pyrrhotite also appears to involve sulfur vapour evolution, although this process is far less significant than that for either pyrite or violarite. Consequently, pyrrhotite was more difficult to ignite.

Like violarite, pentlandite decomposes to form an iron sulfide species and a nickel sulfide species, however, no sulfur evolution is observed. Iron migrates to the particle surface and is oxidised, forming dense rims of oxide surrounding the nickel sulfide core. Consequently, the reaction of this mineral relies upon direct attack of oxygen at the particle surface, this being a non-ignition process consistent with the "shrinking-unreacted core" model.

The use of thermal analytical techniques to elucidate the flash smelting process has been criticised in the past because of the fundamental differences which exist between the sample configurations of the two processes. During thermal analysis experiments the particles are in contact with each other and with the sample crucible as
opposed to the gas-solid suspension which exists in the smelter. The gas flow to the smelter is also preheated, while thermal analysis experiments employ gas at ambient temperatures. Consequently the heat transfer mechanisms in operation in these two situations will differ substantially. Despite this, the current study has demonstrated that the results obtained via thermal analytical techniques show the same general trends as those observed using a pilot scale flash smelter.

The use of thermal analysis has several advantages in that it is a simple, rapid and cheap method of establishing the ignition temperatures of minerals. Another significant advantage is that only milligram quantities of sample are required. Variables such as particle size and oxygen concentration can easily be controlled and their effects on reactivity determined. On the basis of these results the relative reactivity of sulfide minerals under various conditions in a flash smelter can be correctly anticipated. Hence, thermal analysis would be a good method for predicting the smelting behaviour of new orebodies.

There are several practical implications of this study which are relevant to the Kalgoorlie Nickel Smelter. It has been established that concentrates containing pyrite and violarite will be far more reactive than those which contain pentlandite and pyrrhotite. While an increase in particle size will reduce the reactivity of all of these
sulfide minerals, this effect is most significant for pyrrhotite and pentlandite. Hence, grinding is particularly important for concentrates containing coarse particles of these two minerals.

Ignition of pyrrhotite in the flash smelter will be very dependent upon the conditions in the reaction shaft. The use of an oxygen-enriched atmosphere substantially increases the reactivity of this mineral. The reactivity of the other sulfides is also increased although to a lesser extent.
REFERENCES


