FLUIDIZED-BED SELECTIVE SULFATE ROASTING
OF COPPER, COBALT AND NICKEL SULFIDE
CONCENTRATES FROM KILEMBE MINE - UGANDA

by

Mfite Basaza A.G.
A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Metallurgical Engineering).

Signed: [Signature]

Mfite Basaza A.G.

Golden, Colorado
Date: May 27, 1975

Approved: [Signature]

G. P. Martins
Thesis Advisor

W. M. Mueller
Head, Department of Metallurgical Engineering

Golden, Colorado
Date: May 27, 1975
Dedicated To

Mama na baba, wapenzi na marafiki
yangu kwa kumvumilia kwao wakati
nirikuwa inje kwa munda kwa miaka miwili.

(My mother and father, all friends and well wishers
who endured the two years I have been away.)
ABSTRACT

The aim of this investigation was to selectively sulfate copper, cobalt and nickel while producing iron oxides at the same time. Relevant isothermal stability diagrams, constructed for 900 and 1000° K, were used to deduce the sulfating gas composition corresponding to the selective sulfation region.

The investigation was conducted on sulfide concentrates obtained from Kilembe Mine (Uganda). It was found that within the roasting temperature range of 900-1000° K, the cobalt and copper recoveries exceeded 80% while nickel recovery was about 40% and the dissolved iron was less than 3%. However, due to low quantities of the sulfatable metals, the concentration of iron in the leach solution present after four hours of leaching was almost the same as that of nickel and about half that of copper and cobalt. At roasting temperatures close to 1000° K, sintering occurred in the reactor. Of all the variables investigated, the most critical with regard to the metal recovery was the amount of sulfur dioxide and oxygen present in the reactor. The highest recoveries were obtained using high partial pressures of sulfur dioxide and lowest partial pressures of oxygen in the following pressure range:
0.06-0.15 atm. of sulfur dioxide

0.05-0.10 atm. of oxygen

The overall findings of the investigation should facilitate further understanding of the process metallurgy of the Zambian-Zairian copper belt mineralogy, Kilembe Mine being an integral part of it. It is in the light that the above belt contains more than 50% of the world's cobalt reserves that the present investigation should prove useful.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xiii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xiv</td>
</tr>
<tr>
<td><strong>CHAPTER 1</strong> INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Kilembe Mine</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1 Location</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2 History</td>
<td>4</td>
</tr>
<tr>
<td>1.1.3 Petrology-Mineralogy Relationship</td>
<td>4</td>
</tr>
<tr>
<td>1.1.4 Kilembe Mill Flow Sheet</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Scope</td>
<td>12</td>
</tr>
<tr>
<td>1.3 Objective of This Study</td>
<td>15</td>
</tr>
<tr>
<td><strong>CHAPTER 2</strong> LITERATURE SURVEY</td>
<td>17</td>
</tr>
<tr>
<td>2.1 Fluidization Technology</td>
<td>17</td>
</tr>
<tr>
<td>2.1.1 The Quality of Fluidization</td>
<td>18</td>
</tr>
<tr>
<td>2.1.2 Incipient Velocity</td>
<td>21</td>
</tr>
<tr>
<td>2.1.3 Pneumatic Transport Velocity</td>
<td>23</td>
</tr>
<tr>
<td>2.1.4 Liquid Like Behaviour</td>
<td>24</td>
</tr>
<tr>
<td>2.1.5 Mass Transfer</td>
<td>24</td>
</tr>
<tr>
<td>2.1.6 Heat Transfer</td>
<td>26</td>
</tr>
<tr>
<td>2.2 The Chemistry of Sulfate Roasting of Copper, Cobalt, Nickel and Iron Sulfides</td>
<td>28</td>
</tr>
</tbody>
</table>

vi
<table>
<thead>
<tr>
<th>Section / Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.1 Reaction Mechanics and Kinetics</td>
</tr>
<tr>
<td>2.2.2 Thermodynamic Analysis</td>
</tr>
<tr>
<td>3.1 Fluidization Technology</td>
</tr>
<tr>
<td>3.1.1 Historical Development in Fluidization Technology</td>
</tr>
<tr>
<td>3.1.2 Fluidization Phenomena</td>
</tr>
<tr>
<td>3.1.3 Fluidization Characteristics</td>
</tr>
<tr>
<td>3.1.4 Applications of Fluidization Technology</td>
</tr>
<tr>
<td>3.2 The Chemistry of Sulfate Roasting of Copper, Cobalt, Nickel and Iron Sulfides</td>
</tr>
<tr>
<td>3.2.1 The Kinetics of Oxide Formation</td>
</tr>
<tr>
<td>3.2.2 Mechanism of Sulfate Formation</td>
</tr>
<tr>
<td>3.3 Thermodynamic Analysis of Cu-, Co-, Ni-, Fe-S-O Systems</td>
</tr>
<tr>
<td>3.3.1 Co-, Cu-, Ni- and Fe-S-O Phase Diagrams</td>
</tr>
<tr>
<td>3.3.2 Selective Sulfation Temperature - Gas Composition Control Diagram</td>
</tr>
<tr>
<td>4.1 Apparatus</td>
</tr>
<tr>
<td>4.1.1 Fluidizing Gas Mixture</td>
</tr>
<tr>
<td>4.1.2 Fluidized-bed Reactor Unit</td>
</tr>
<tr>
<td>4.2 Sample Preparation</td>
</tr>
<tr>
<td>4.2.1 Experimental Techniques</td>
</tr>
<tr>
<td>Section</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.2.2 Results</td>
</tr>
<tr>
<td>4.3 Procedure</td>
</tr>
<tr>
<td>4.3.1 Roasting Procedure</td>
</tr>
<tr>
<td>4.3.2 Recovery Determination</td>
</tr>
<tr>
<td>4.4 Results</td>
</tr>
<tr>
<td>4.4.1 Results of Roasting Experiments</td>
</tr>
<tr>
<td>4.4.2 Results From Leaching Experiments</td>
</tr>
<tr>
<td>4.5 Interpretation of the Previous Observations</td>
</tr>
<tr>
<td>4.5.1 The Behavior of Sulfur Dioxide Concentration in the Reactor During Roasting</td>
</tr>
<tr>
<td>4.5.2 Sulfur Deposition</td>
</tr>
<tr>
<td>4.5.3 White, Dense Gas</td>
</tr>
<tr>
<td>4.5.4 The Leach Behavior During Recovery Tests</td>
</tr>
<tr>
<td>4.5.5 The Effect of Sulfur Dioxide and Oxygen Partial Pressures on the Metal Recovery</td>
</tr>
<tr>
<td>4.6 Experimental Limitations</td>
</tr>
<tr>
<td>4.6.1 Particle Size</td>
</tr>
<tr>
<td>4.6.2 Fluidizing-gas Velocity</td>
</tr>
<tr>
<td>4.6.3 Gas Mixture &amp; Composition</td>
</tr>
<tr>
<td>4.6.4 Roasting Temperature Range</td>
</tr>
<tr>
<td><strong>CHAPTER 5</strong> CONCLUSIONS AND RECOMMENDATIONS</td>
</tr>
<tr>
<td>5.1 Conclusions</td>
</tr>
<tr>
<td>5.1.1 The Physical Chemical Nature of the Kilembe Sulfides</td>
</tr>
</tbody>
</table>
5.1.2 Optimum Roasting Temperature and Gas Composition 175

5.2 Recommendations 177

5.2.1 Installation of a Commercial Roast-Leach Plant 177

5.2.2 Possible Source of Iron for the East African Steel Industry 181

5.2.3 The Possibility of Manufacturing Sulfuric Acid 181

APPENDICES 183

REFERENCES 218
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Number</th>
<th>Figure Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1-1</td>
<td>Kilembe Mine Location</td>
<td>3</td>
</tr>
<tr>
<td>1.1-2</td>
<td>Crushing Section</td>
<td>6</td>
</tr>
<tr>
<td>1.1-3</td>
<td>Flotation Section</td>
<td>9</td>
</tr>
<tr>
<td>3.1-1</td>
<td>Fluidization Phenomena</td>
<td>39</td>
</tr>
<tr>
<td>3.1-2</td>
<td>Schytil Diagram (for 900° K, 8% SO₂ and 5% O₂)</td>
<td>43</td>
</tr>
<tr>
<td>3.1-3</td>
<td>Shape of the Bubble and Relative Motion of the Solids (1-mm. Lead-shot Fluidized in Water)</td>
<td>51</td>
</tr>
<tr>
<td>3.3-1</td>
<td>Equilibrium P\textsubscript{SO₃} (atm.) as a Function of P\textsubscript{O₂} (atm.)</td>
<td>85</td>
</tr>
<tr>
<td>3.3-2</td>
<td>Cu-S-O Stability Diagram at 900° K</td>
<td>93</td>
</tr>
<tr>
<td>3.3-3</td>
<td>Cu-S-O Stability Diagram at 1000° K</td>
<td>94</td>
</tr>
<tr>
<td>3.3-4</td>
<td>Co-S-O Stability Diagram at 900° K</td>
<td>104</td>
</tr>
<tr>
<td>3.3-5</td>
<td>Co-S-O Stability Diagram at 1000° K</td>
<td>105</td>
</tr>
<tr>
<td>3.3-6</td>
<td>Ni-S-O Stability Diagram at 900° K</td>
<td>108</td>
</tr>
<tr>
<td>3.3-7</td>
<td>Ni-S-O Stability Diagram at 1000° K</td>
<td>108</td>
</tr>
<tr>
<td>3.3-8</td>
<td>Fe-S-O Stability Diagram at 900° K</td>
<td>113</td>
</tr>
<tr>
<td>3.3-9</td>
<td>Fe-S-O Stability Diagram at 1000° K</td>
<td>114</td>
</tr>
<tr>
<td>3.3-10</td>
<td>Co-, Ni-, Cu &amp; Fe-S-O Stability Diagram at 900° K</td>
<td>116</td>
</tr>
<tr>
<td>3.3-11</td>
<td>Co-, Ni-, Cu &amp; Fe-S-O Stability Diagram at 1000° K</td>
<td>117</td>
</tr>
<tr>
<td>3.3-12</td>
<td>Selective Sulfation Equilibria at 900° K</td>
<td>119</td>
</tr>
<tr>
<td>3.3-13</td>
<td>Selective Sulfation Equilibria at 1000° K</td>
<td>120</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.3-14</td>
<td>900-1000° K Selective Sulfation Equilibria Block Diagram</td>
<td>121</td>
</tr>
<tr>
<td>3.3-15</td>
<td>Selective-Sulfation Temperature - Gas Composition Control Diagram</td>
<td>122</td>
</tr>
<tr>
<td>4.1-1</td>
<td>Experimental Apparatus (schematic)</td>
<td>129</td>
</tr>
<tr>
<td>4.1-2</td>
<td>By-pass and In-line Circuits</td>
<td>132</td>
</tr>
<tr>
<td>4.1-3</td>
<td>Apparatus for Carbon and Sulfur Analyses</td>
<td>203</td>
</tr>
<tr>
<td>4.1-4</td>
<td>Apparatus for Carbonate Determination</td>
<td>206</td>
</tr>
<tr>
<td>4.2-1</td>
<td>Major Elements in the Kilembe Sulfide Concentrates (Microprobe Back Scatter and X-ray Fluorescence Photographs)</td>
<td>146</td>
</tr>
<tr>
<td>4.2-2</td>
<td>Major Elements in the Kilembe Sulfide Concentrates (Microprobe Back Scatter and X-ray Fluorescence) - Continued</td>
<td>147</td>
</tr>
</tbody>
</table>


LIST OF TABLES

<table>
<thead>
<tr>
<th>Number</th>
<th>Table Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1-1</td>
<td>A Comparison of Incipient Velocities Using Different Formulae</td>
<td>60</td>
</tr>
<tr>
<td>3.3-1</td>
<td>Equilibrium Partial Pressures of SO$_3$ for Different O$_2$ Potentials at 900 and 1000° K</td>
<td>86</td>
</tr>
<tr>
<td>3.3-2</td>
<td>Chemical Reactions and log K Values for Cu-O-S System at 900 and 1000° K</td>
<td>90</td>
</tr>
<tr>
<td>3.3-3</td>
<td>Chemical Reactions and log k Values for Cu-Fe-S-O System at 1000° K (Assuming that the only Iron Phase in Equilibrium with Chalcopyrite and Bornite is Ferric Oxide)</td>
<td>96</td>
</tr>
<tr>
<td>3.3-4</td>
<td>Chemical Reactions and log K Values for Co-O-S System at 900 and 1000° K</td>
<td>99</td>
</tr>
<tr>
<td>3.3-5</td>
<td>Chemical Reactions and log K Values for Ni-O-S System at 900 and 1000° K</td>
<td>106</td>
</tr>
<tr>
<td>3.3-6</td>
<td>Chemical Reactions and log K Values for Fe-O-S System at 900 and 1000° K</td>
<td>111</td>
</tr>
<tr>
<td>4.2-1</td>
<td>Dry Screen Analysis Data</td>
<td>140</td>
</tr>
<tr>
<td>4.2-2</td>
<td>Assay Results (Obtained Using AA and Gravimetric Methods)</td>
<td>142</td>
</tr>
<tr>
<td>4.2-3</td>
<td>Normalized Assay Results (Obtained Using X-ray Techniques)</td>
<td>143</td>
</tr>
</tbody>
</table>
LIST OF APPENDICES

<table>
<thead>
<tr>
<th>Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lennard Jones Parameters</td>
<td>183</td>
</tr>
<tr>
<td>2</td>
<td>List of $X_{SO_2}$, $X_{O_2}$, $X_{N_2}$, $D$ and $\mu_{mix}$</td>
<td>184</td>
</tr>
<tr>
<td>3</td>
<td>Calculation of $d_p$</td>
<td>189</td>
</tr>
<tr>
<td>4</td>
<td>Sulfate Conversion Stoichiometric Calculation</td>
<td>191</td>
</tr>
<tr>
<td>5</td>
<td>Gas Chromatograph &amp; Chromatography</td>
<td>195</td>
</tr>
<tr>
<td>6</td>
<td>Digestion Experiment</td>
<td>201</td>
</tr>
<tr>
<td>7</td>
<td>Total Carbon Analysis</td>
<td>202</td>
</tr>
<tr>
<td>8</td>
<td>Apparatus for Carbon and Sulfur</td>
<td>204</td>
</tr>
<tr>
<td>9</td>
<td>Carbonate Determination by Evolution of CO$_2$ Using 1:1 HCl Acid</td>
<td>205</td>
</tr>
<tr>
<td>10</td>
<td>Apparatus for Carbonate Determination</td>
<td>207</td>
</tr>
<tr>
<td>11</td>
<td>Sulfur Analysis</td>
<td>208</td>
</tr>
<tr>
<td>12</td>
<td>X-ray Techniques</td>
<td>210</td>
</tr>
<tr>
<td>13</td>
<td>Computer Output of the Possible Elements in the Sample</td>
<td>211</td>
</tr>
<tr>
<td>14</td>
<td>Flow Meter Calibration Graphs (Figs. 4.2-3 — 4.2-5)</td>
<td>215</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

First and foremost, the author wishes to express his deep gratitude to Dr. G. P. Martins, the academic adviser, whose guidance and assistance was immeasurable throughout the entire course of this investigation.

Further acknowledgements go to the Ugandan government, the African-American Institute and the Colorado School of Mines whose sponsorship enabled me to undertake studies leading to the M.Sc. degree in Metallurgical Engineering.

Kilembe Mine Limited (Uganda) is acknowledged for not only providing financial assistance to my dependents but also for providing samples on which the present investigation was conducted. The author also extends his thanks to John M. Mortimer (Chief Metallurgical Engineer - Falconbridge Nickel Mines Limited, Canada) for supplying previous reports on the metallurgy and the geology of the Kilembe sulfides.

The author feels indebted to the personnel Messrs W. Hazen - President, F. M. Stephens, Jr. - Vice President, Rodney Hodgeson - Senior Research Engineer, Woolly Hills - Chief Chemical Analyst) of Hazen Research Institute for their immeasurable assistance and discussion pertaining to this investigation and otherwise.

Last but not least, the author's felicitations
are extended to his brothers and sisters whose spirit of oneness was a source of inspiration and to Miss Georgia Kushman whose untiring enthusiasm, assistance and devotion proved extremely useful in the final preparation of this thesis.
CHAPTER 1 INTRODUCTION

The general subject of selective sulfate roasting of concentrates in fluidized bed reactors has received considerable attention over a number of years now. However, studies involving quantitative aspects of the process have been confined to simple systems [1,2,3,4,5,6]. In particular, literature search has not revealed any work in connection with fluidized bed roasting of a mixed sulfide concentrate of copper, cobalt and nickel with an aim of recovering all these metals.

The present investigation was initiated as a result of guidelines surrounding the AFGRAD fellowship which I was awarded in order to undertake a program of study leading to a Master of Science degree. It is required that the holder of this fellowship engage in research which would be of benefit to his country (Uganda in this case). A previous association with Kilembe Mine Ltd., during the period 1970-1975, led to a correspondence which uncovered the possibility of carrying out research on the topic ultimately chosen. An exciting aspect of this work lies in the fact
that the Zambian-Zairian copper belt, Kilembe locality inclusive, contains more than 50% of the world's cobalt reserves, and the findings should lead to a better understanding of the process metallurgy which will be needed for the exploitation of the metal values.

1.1 **Kilembe Mine**

1.1.1 **Location**

Kilembe Mine Ltd. is a copper-cobalt mining company. The mine is situated in the southeastern foothills of Rwenzori (snow-covered) mountains in Western Uganda, fourteen miles north of the equator (Fig. 1.1-1). The Rwenzori range is considered to be a tilted block, rising to 17,000 feet above the floor (3,000 feet above sea-level) of the western branch of the East African Rift Valley system. The company facilities stretch for over five miles along Nyamwanba River, the major drainage of the "Mountains of the Moon", as the Rwenzori mountains are often called. Kilembe Mine forms the extreme western terminus of the Kampala-Mombasa railway (Fig. 1.1-1). It is also linked with the rest of Uganda by a network of all-weather macadamized roads. An airport for quick business transaction is situated eight miles away from the mine site.
Fig. 1.1-1. Kilembe Mine location.
1.1.2 History

The traces of copper were first identified by Rocetti, an Italian, who led a geological expedition to the Rwenzoris in 1909 [7]. Mineralized outcrops were later confirmed by Wayland (1919), Wilson (1937) and Michot (1938) [8]. Between the years 1926 and 1937, Tanganyika Concessions, Ltd. explored the deposit. In 1947, Frobisher Ltd. resumed the exploration to further assess the extent and metal content of the orebody. By 1950, it was decided to go ahead with the project and Kilembe Mine Ltd. was formed. Full production started in July 1956.

1.1.3 Petrology-Mineralogy Relationship

The Rwenzori mountains are composed of strongly metamorphosed precambrian rocks. The orebody is found emplaced in the tremolite-actinolite amphibolite facies which constitute the lower Kilembe series (LK1) [9]. The gossan, already mined out, consisted of malachite, azurite, chrysocolla, cuprite, chalcocite, tenorite (minor) and lubeckite. The primary sulfides mainly consist of pyrite, chalcopyrite and pyrrhotite - approximately in the ratio 12:7:1, as they are mined out. Rare amounts of linnaeite, sphalerite, pentlandite, and graphite have been observed. Cobalt and nickel are found associated with octahedral and massive pyrite, pyrrhotite and chalcopyrite. Copper,
cobalt and nickel can substitute for ferrous iron only in
the octahedral crystal lattice, forming solid solutions.
This is so because their covalent and ionic radii are
within 15% of each other, as can be calculated from the
following data [10]:

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>Co</th>
<th>Co^{++}</th>
<th>Cu</th>
<th>Cu^{++}</th>
<th>Ni</th>
<th>Ni^{++}</th>
<th>Fe</th>
<th>Fe^{++}</th>
<th>Fe^{+++}</th>
</tr>
</thead>
<tbody>
<tr>
<td>RADIUS</td>
<td>1.32</td>
<td>0.72</td>
<td>1.35</td>
<td>0.72</td>
<td>1.39</td>
<td>0.69</td>
<td>1.23</td>
<td>0.74</td>
<td>0.64</td>
</tr>
</tbody>
</table>

(Å)

In pyrrhotite, cobalt and nickel occur in their commonest
compounds in the crystal lattice. Nicolas De Kun [11] has
given the following cobalt and nickel assays of the Kilimbe
Mine sulfides:

<table>
<thead>
<tr>
<th></th>
<th>% Co</th>
<th>% Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral pyrite</td>
<td>1.74</td>
<td>1.07</td>
</tr>
<tr>
<td>Massive pyrite</td>
<td>1.65</td>
<td>0.95</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>1.70</td>
<td>2.08</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.03-0.17</td>
<td>0.07-0.033</td>
</tr>
<tr>
<td>Linnaiete</td>
<td>57.96</td>
<td>17.00 (and gold)</td>
</tr>
</tbody>
</table>

1.1.4 Kilembe Mill Flow Sheet

At Kilembe Mine, the mill produces 3,000 tons of
ore daily, every day of the week. Ore from the mine is
tipped into a 450 ton trench and fed into a 5 inch fixed
grizzly by a 48 inch Telsmith pan feeder (Fig. 1.1-2).
The oversize is crushed to minus 7 inches by a 48 x 36 in.
Fig. 1.1-2. Crushing and grinding section.
Pegson-Osborne jaw crusher. The grizzly and crusher discharge is conveyed to a coarse ore stockpile, with a live capacity of 10,000 tons. The coarse ore is drawn from the stockpile by vibrating feeders and conveyed by a 30 inch belt to a hopper at the secondary crushing plant. The ore is fed by an AMSCO pan feeder onto a 3 inch vibrating grizzly, and the oversize is crushed to minus 3 inches in a 20B Pegson gyratory crusher. The undersize from the grizzly is discharged onto No. 1 rod-deck screen (3/16 in.).

The oversize is fed to two 5 1/2 ft. short-head Symmons crushers, and the product is conveyed to the fine ore silos together with the undersize from No. 2 rod-deck screen.

No. 1 rod-deck undersize is fed to a 66 in. Akins classifier. The coarse fraction joins the feed to the fine ore silos. The fines fraction is pumped to two 30 by 10 ft. thickeners, the underflow of which is subsequently fed to the Spargo pump sump.

Crushed ore from the silos is fed via three weightometer-equipped conveyor belt systems to two rod mills. The grinding section consists of two 8 x 6 ft. Allis Chalmers ball mills, a 5 x 12 ft. Allis Chalmers ball mill (regional), and a 8 x 6 ft. Allis Chalmers ball mill (middlings).

The rod mill discharge (about 80% solids) is combined with the ball mill discharge (about 70% solids).
and pumped to two 24 inch cyclones. The cyclone underflow is fed to the ball mills, and the overflow is discharged to the flotation section (Fig. 1.1-3)

There is also an extension grinding circuit which comprises a 2.2 x 3 meter Humboldt rod mill and a 2 x 8 ft. Allis Chalmers ball mill. The rod and ball mill discharges are combined and pumped to an 18 inch cyclone. The underflow is fed to the ball mill, and the overflow joins the main circuit flotation feed. The flotation feed is maintained at a density of 40% solids by weight, at 45% minus 200 mesh Tyler.

In recent years, the mill has treated sulfide ores only. A bulk sulfide concentrate containing chalcopryite and cobaltiferrous pyrite is reground, and treated by differential flotation, to produce copper and pyrite concentrates.

The flotation feed gravitates to six banks of 8, No. 24, Denver flotation machines. The froth concentrate from the first four cells on each bank forms the bulk concentrate regrind circuit. The tailings from the Denver cells flow to two banks of 16, No. 48 Agitair flotation machines. The froth from the Agitair cells is combined with that from the second 4, Denver cells, on each of the six banks noted previously, to form the middlings concentrate which is pumped to the 12 in. cyclone in the middlings regrind circuit.
Fig. 1.1-3 Flotation section.
The middlings regrind ball mill operates in closed circuit with the cyclone, and the cyclone overflow is returned to the bulk flotation distributor.

After regrinding the bulk concentrate to 90% minus 200 mesh, and adjusting the pH, the product is fed to the primary differential roughers (2, No. 48, Agitair flotation machines). The tailings from the primary cells pass to the secondary differential roughers (8, No. 48, Agitair flotation machines) and the concentrate goes to final cleaner flotation. The secondary differential rougher concentrate is fed to the primary differential cleaners (4, No. 24, Denver flotation machines). The primary differential cleaner float joins the primary differential rougher concentrate for final cleaning.

The underflow from the primary differential cleaners passes to the secondary differential cleaners (4, No. 24, Denver flotation machines), where the concentrate is returned to the head of the secondary differential roughers and the tailings join the secondary differential rougher tailing, to form the pyrite concentrate. The final cleaning stage is carried out in a bank of 4, No. 48, Agitair flotation machines.

The copper and pyrite concentrates gravitate a distance of over 7 miles in two 4 in. pipe lines to the filter plant at Kasese (Fig. 1.1-1). The copper concen-
trates are fed into a 40 x 8 ft. Dorr thickener, and the product is filtered by 6 ft. Vacuum disc filters. The filtered copper concentrates are conveyed under infra-red heater panels which reduce the moisture content to 6.5%. Copper concentrates are stockpiled in a 750 ton conical bin and fed via a weightometer into 40 ton rail cars and dispatched to the smelter at Jinja (266 miles away) (Fig. 1.1-1).

The pyrite concentrates are stockpiled in an open dam. This has been going on ever since the company went into full production in 1956. By 1965, the stockpile was estimated at 300,000 tons assaying 1.5% Co. It is these stockpile concentrates that are rich in cobalt and nickel. Some attention was given to their extraction during 1952-1956 period but the cobalt and nickel metal prices were so low that their extraction from this stockpile was not a worthwhile economic venture. However, during the last five years or so, cobalt and nickel prices have shot up considerably and, in addition, having undergone natural heap leaching by rain water, the cobalt grade has been enriched. These two factors have motivated the company to continue the search for an economic method by which cobalt, nickel and copper, in the concentrate stockpile, could be removed.
1.2 Scope

The use of fluidized bed selective sulfate roasting in roast-leach or roast-leach-electrowinning processes, such as practiced by Dowa Mining Company and CSIRO, has acquired a growing commercial interest in the last twenty years or so [1,2,3,12,13]

The success of such processes requires precise knowledge of the following factors:

(1) Physical and chemical properties of the ore or concentrates to be selectively sulfated
(2) Temperature and gas composition required to effect the sulfation selectively
(3) Fluidized bed operation and design parameters
(4) Optimum leaching conditions required to obtain the highest recovery of the soluble sulfates.

The physical and chemical properties of the ore or concentrates of interest are:

(a) Density
(b) Particle size distribution analysis
(c) Qualitative, quantitative and mineralogical analyses.

These are necessary for evaluating some of the fluidized bed parameters and to furnish information leading to the understanding of the chemistry of the roasting.

With regard to the fluidized-bed design parameters and operation, the following are necessary:
(a) Incipient fluidizing gas velocity  
(b) Pneumatic transport gas velocity  
(c) Assessment of the quality of fluidization  
(d) Transport disengagement height  
(e) Mass and heat-transfer coefficients  

The above factors are extensively covered in the literature and several empirical correlations have been formulated. It is to be noticed, however, that these formulae are not universal. They require the use of the property values of the system under investigation (e.g. solids density, the mean particle diameter, void fraction, bed pressure drop, the density and viscosity of the fluidizing gas(es)), at the possible operating temperatures. In addition, these property values have to be measured or estimated. However, since there are usually several correlations available for evaluating a particular design parameter, the choice of an acceptable result is based on the consistency between at least two approaches, as well as actual verification for the system under design. The usefulness of this prerequisite can be appreciated on reading the fluidized-bed plant practice as described, in general terms, by Thompson [14] and Thompson and Roesner [15].

Inghram [12], H. H. Kellog [16,17] and Pehlke [18] have given excellent reviews of the thermodynamic equilibria involved in sulfate roasting of metallic sulfides, while F. M. Stephens, Jr. [1] has stressed the importance of
temperature and gas composition control for the selectivity of the sulfating reactions. Ingraham, in particular, has discussed at great length thermodynamic phase diagrams and selective sulfating requirements for some metals. It is to be noticed, however, that:

(a) none of these authors has discussed the conditions for selective sulfate roasting of copper, cobalt, nickel and iron with a view to recovering copper, cobalt and nickel

(b) new thermodynamic data by Skeaff and Espellund [19] has appeared since the publication of the above literature. In particular a recent compilation (1973) of the most acceptable thermodynamic data of most inorganic substances has been published by I. Barin and O. Knacke [20]

(c) literature search has not revealed any attempt to construct a predominance area diagram for Cu-Fe-S-O system and yet chalcopyrite (CuFeS$_2$) and bornite (Cu$_5$FeS$_4$) are common mineral components of most sulfides containing copper.

(d) certain solid phases are missing on previous published phase diagrams, e.g., FeSO$_4$ and Cu$_3$S$_4$

(e) the superimposition of the phase diagrams constructed for single metal-sulfide-oxygen systems have been widely accepted as good approximations to the thermodynamic equilibria of complex ores. Yet the following gross assumptions are involved:

(i) ionic interaction during roasting, which could lead to ferrite formation and kernel roasting phenomena [21] is not considered

(ii) the existence of solid solutions either in the original material or during roasting is completely neglected. Yet, Rosenqvist [21] has pointed out Cu$_2$S and FeS may form
ternary compounds and solid solutions during roasting

(iii) the existence of double metal sulfides in the ore or double oxides in the calcine is again neglected. However, the existence of chalcopyrite, carrollite, nickel and cobalt ferrites contradict this assumption

(iv) for further discussion of other assumptions refer to section 3.1.4

(f) nickel and cobalt oxides are difficult to sulfate. Several investigators [5,22,23,24,25] have studied the use of alkali sulfates to provide sulfation enhancement. However, the mechanism as to how these sulfates act is not well understood. In addition, when used in sulfide roasting, it has not been fully established whether they influence the oxidation step or inhibit ferrite formation. Rosenqvist has suggested that they promote kernel roasting by forming eutectic melts on the particle surfaces thus facilitating the migration of copper ions to the interior of the particle where it forms Cu₂S while iron ions migrate to the particle surface where they are oxidized. This reaction is thermodynamically possible and has been experimentally observed. Thus these alkali sulfates may be detrimental to the sulfide oxidation.

1.3 Objective of this Study

Due to the above reasons and to the fact that the Kilembe sulfides are a part of a metallogenic province which contains more than 50% of the world's cobalt reserves and as yet very little specific knowledge is available, it is the purpose of this investigation

(a) to study the physical, chemical and mineralological nature of these sulfide concentrates

(b) to construct phase diagrams which are
compatible with the chemical nature of these minerals in order to elucidate the optimum temperature and gas composition required to selectively sulfate the copper, cobalt and nickel
c
to obtain design and operation parameters which will ultimately be valuable for a commercial fluidized-bed roast-leach plant, suitable for the Kilembe sulfides.
CHAPTER 2  LITERATURE SURVEY

The commercial importance of fluidized-bed, selective sulfation cannot be over emphasized. Its success as a process, entails a proper understanding of the characteristics of a fluidized bed and the chemistry of sulfate roasting as applicable to the ore or concentrate being treated. Therefore, a literature survey was organized to cover two areas:

(i) Fluidization technology

(ii) The chemistry of sulfate roasting of copper, cobalt, nickel and iron sulfides.

2.1 Fluidization Technology

Written knowledge on fluidization technology dates as far back as 1879, when a U.S.A. patent was granted to C. E. Robinson [26,27,28] for the treatment of ores containing gold and silver with the aim of recovering these noble metals to the exclusion of iron [29]. However, it was not until the period of World War II that
fluidization was revolutionized, when Esso research produced a commercial, fluidized-bed, petroleum, catalytic-cracking process for producing 100-octane jet gasoline which boosted the Western allies [28,30] airwise. Since then fluidization technology has been applied in various fields of chemical engineering [27-55] This can be judged by realizing that an average of more than one paper per week was published by 1961-1962 period or by the numerous reviews and text books on the subject edited during the last twenty years [44-50,56,57]

2.1.1 The Quality of Fluidization

The diversity of applications of fluidized beds is dependent on their inherent behavior which is characterized in terms of the quality of fluidization and determined by:

(i) Density uniformity, shape, size distribution and the degree of repose of the particles being fluidized.

(ii) The nature of the fluidizing medium and the fluidization velocity.

(iii) The nature of the gas distributor plate and the arrangement of the gas inlet holes.

(iv) The shape and diameter of the reactor.

Perhaps the best definition of the quality of fluidization is that by Morse [56]:

The quality of fluidization is . . . the uniformity of particle dispersion and the uniformity of gas velocity in
a boiling bed. The water-fluidized bed of sand approaches perfect quality. The bed that slugs or channels badly is at the other extreme quality. The bed in which the gas pockets remain small and well distributed, with a steady, even, overall boiling of the bed is intermediate in uniformity, but perhaps optimum in the balance between uniformity and the requirement of mixing and boiling in order to control the temperature.

This definition indicates that the more a fluidized bed, which is basically a heterogeneous system, resembles a homogeneous system, the greater will be its uniformity. Thus, inspite of numerous experiments, it has been difficult to define a quantitative value of the quality of fluidization.

Wilhelm and Kwauk [57] defined fluidization as being particulate or aggregative based on whether the fluidizing medium is liquid or gas. Rice and Wilhelm [58] endeavored to put the above concept into quantitative terms. Thus they developed a set of equations governing the stability of bed-fluid "interfaces", which were later modified and transformed into dimensionless groups by Romero and Johanson [58] as follows:

$$(F_{mf})(R_{mf}) \left( \frac{\rho_s - \rho_g}{\rho_g} \right) \left( \frac{L_{mf}}{dr} \right)$$

where
\[ Fr_{mf} = \frac{U_{mf}^2}{d_p g} \] is the particle Froude number,

\[ Re_{mf} = \frac{U_{mf} \rho_g d_p}{\mu} \] is the particle Reynolds number,

\[ \frac{\rho_s - \rho_g}{\rho_g} \] = the ratio of the density of the fluidized bed to that of the fluidizing medium.

\[ \frac{L_{mf}}{dr} \] = the ratio of the bed height at incipient fluidization to the reactor diameter.

Since this expression can only distinguish between particulate (<100) and aggregative (>100) fluidization phenomena, the other types of fluidization [60,61], e.g., channelling, spouting and slugging observed particularly during gas fluidization, cannot be distinguished. In fact, the terms particulate and aggregative can be misleading. Thus Sutherland [62] and Shuster [61] have approached the problem by pressure drop fluctuation studies as an indicator of the degree of bubbling of the bed since, ideally, the pressure drop across any region of a fluidized bed is directly proportional to the weight of the solids in that region but will be altered by the presence of bubbles by an amount related to the bubble volume.

As noted earlier, any quality of fluidization is associated with certain fluidized bed qualities:

(i) Incipient and pneumatic transport velocities
(ii) Liquid-like behaviour
(iii) Mass transfer
(iv) Heat transfer

2.1.2 Incipient Velocity

When a fixed bed is subjected to an increasing fluid velocity, there will be a particular velocity at which the solids will just be suspended in such a way that their overall weight balances the fluid pressure and no interparticle forces are exerted. This is called the incipient velocity. Using this definition and the Ergun semi-empirical equation [88], several correlations have been obtained [15,30,45,56]. However diverse these "incipient velocity" formulations may appear, they can be evaluated only after knowing the following parameters:

(i) The viscosity and density of the fluidizing fluid

(ii) Solids density and mean particle diameter

(iii) Void fraction and the sphelicity factor

The viscosity of a gas mixture (if it is the fluidizing fluid), is computed using Wilke's [89] semi-empirical formula:

\[ \mu_{\text{mix}} = \sum_{i=1}^{n} \frac{X_i \mu_i}{n \sum_{j=1}^{n} X_j \Phi_{ij}} \] 2.1-1

where

\[ \Phi_{ij} = 8^{-\frac{1}{2}} (1 + M_i / M_j)^{-\frac{1}{4}} \left[ 1 + (\mu_i / \mu_j)^{\frac{1}{2}} (M_j / M_i)^{\frac{1}{4}} \right]^2 \] 2.1-2
\[ \mu_i, \mu_j, X_i, X_j, M_i \text{ and } M_j = \text{ the viscosities, mole fractions and molecular weights of } n \text{ gas components.} \]

(Note: The reproducibility of \( \mu_{\text{mix}} = \pm 2\% \) of the measured value [89])

Since the viscosity of a gas is temperature dependent, its dependency is obtained using the Chapman-Enskog equation in conjunction with Lennard-Jones constants:

\[ \mu_i = 2.6693 \times 10^{-5} (M_i T/\sigma^2 \Omega_\mu) \quad 2.1-3 \]

where \( \sigma(\text{Å}) \) and \( \Omega_\mu \) are some of Lennard-Jones constants (Appendix 1).

The density of the gas mixture is computed assuming ideal gas behaviour. For instance, for SO\(_2\), O\(_2\) and N\(_2\) gas mixture at 625 mm Hg and T°K, the following expression can be derived:

\[ \rho_g = (0.64 X_{\text{SO}_2} + 0.32 X_{\text{O}_2} + 0.28 N_2)T^{-1} \quad 2.1-4 \]

where \( X \) = the gas mole fraction and T°K is the temperature of operation. Note that Appendix 2 is a list of \( X_{\text{SO}_2}, X_{\text{O}_2}, X_{\text{N}_2}, \rho_g \) and \( \mu_{\text{mix}} \) at the temperatures useful for the present investigation.

The particle mean diameter can be computed using expression available in Diazo Kunii [30]:
\[ \bar{d}_p = \left[ \sum_{i}^{\text{all}} \left( \frac{X}{d_{pi}} \right) \right]^{-1} \text{ (microns)} \]

where

\[ X_i \text{ and } d_{pi} = \text{weight fraction and diameter of sample range } i. \]

(Note: Appendix 3 is an illustration using the sample under investigation of how this equation can be applied to a sample whose size distribution is known.)

The void fraction, \( \varepsilon \), and the sphelicity factor, \( \Phi_s \), are either experimentally evaluated as suggested by Diazo Kunii [30] and Max Leva [45]. However, good approximations can be obtained using approximations suggested by Wen and Yu (eqns. 3.1-12 and 3.1-13).

2.1.3 Pneumatic Transport Velocity

The best formulations of this parameter, are those given by Diazo Kunii (eqns. 3.1-23, 3.1-24 and 3.1-25). Each of these equations is valid for a certain range of Reynolds numbers.

A graphical approach can be used as an alternative to methods (already described) for evaluating the incipient and pneumatic transport velocities. This idea, originated by Schyttil, consists of plotting particle Froude number versus particle Reynolds number and superimposing on it a grid of particle diameter versus fluidizing velocity. The grid co-ordinates are obtained by correlating the
Froude number and Reynolds number in such a way that the Froude number is expressed as a function of particle diameter or fluidizing velocity. The incipient and pneumatic transport velocities are found by the intersection between the mean particle diameter and the "incipient" curve constructed using equations 3.1-1 and 3.1-2 and the "pneumatic transport" curve constructed using equation 3.1-5.

The choice of the applicable velocity is based on the Pinchbeck and Popper criterion:

\[ u_t : u_{mf} = 90:1 - 10:1 \]  \hspace{0.5cm} 2.1-6

2.1.4 Liquid-like Behaviour

This is an important aspect of fluidized beds which has enabled operation of multistage fluidization in single or separate interconnected reactors. Its importance in reactor design is in pressure drop evaluation using the hydrodynamic assumption that fluidized beds behave as liquids, which, as pointed out by Hagyard [64], is a good approximation. Other liquid properties of fluidized beds have been reported by Diazo Kunii [30], Max Leva [45] and Nienow [66].

2.1.5 Mass Transfer

Mass transfer in fluidized beds is due to particle mixing and particle gas contacting effects.
(a) Particle mixing

Particle mixing, a phenomena responsible for establishing uniform bed temperatures and gas composition, is effected by bubble agitation [56], which creates solids circulation convectively [67]. Since bubbles rise vertically, the axial aspect of solids mixing in tapered and non-tapered reactors has been extensively studied [68, 69, 71] to evaluate the effect of baffles, the ratio of solids feed rate to the fluidizing gas velocity, particle size and reactor diameter. Massimilla and Bracale [69] found that baffles reduce solids mixing while Kavetskii experimentally concluded that the rate of particle mixing increases as the ratio of solids feed rate to gas velocity decreases. In most of these studies, pulse technique using temperature as a tracer, is employed. Sandblom, using this technique, found that an equation analogous to the diffusion-transport equation, adequately describes solids mixing.

(b) Gas-solids contacting

Two models have been postulated to calculate a mass transfer coefficient which makes it possible to evaluate the effectiveness of gas/solids contact. The earliest of these models, the two-phase model, was proposed by Shen and Johnstone [72]. This model takes into account mass exchange between bubbles and a dense
phase consisting of solids which are uniformly distributed in a gas stream. Kunii and Levenspiel [30] have modified it into a bubbling bed model. The counterpart of this model, the three-phase model, was proposed by Gwyn, Moser and Peter [73]. It considers a mass exchange between the bubble enclosed in a thin film of solids and the film itself in addition to the concepts of the two-phase model. Due to the fact that the three-phase model is more recent, most "gas/solids contact" studies [74 76] have been analysed using Shen's model. For instance, Bailie et al. [74] used it to formulate statistical instability index based on "bypassing" phenomenon.

2.1.6 Heat Transfer

For good temperature control, high heat transfer rates are necessary. In fluidized beds, the heat transfer rates are caused by:

(i) Large exposed particle surfaces
(ii) Perfect solids mixing
(iii) Excellent fluid/solids contact

Note that the high particle volumetric heat capacities compared to those of the gas is an additional factor responsible for equilibration of the gas and particle temperatures. Studies on this heat transfer have been complicated by lack of proper knowledge on most of the following phenomena:
(i) Reactor geometry and dimensions

(ii) Bed particle geometry and dimensions which change as the reaction proceeds. This is also affected by attrition and agglomeration effects.

(iii) The dynamics of particle circulation

(iv) The residence time of the particles on the reactor walls or submerged surfaces

(v) Gas and particle temperature measurements, with regard to distinguishing one from the other.

It is noteworthy that studies on this subject have been concerned only with the following phenomena:

(i) Heat transfer between the fluid and the particles

(ii) Heat transfer between the bed and the reactor walls or submerged surfaces.

(iii) Particle-particle heat transfer

Botterill and Brundrett [77] and Williams and Smith [78] have reviewed these aspects in general terms whereas Frantz [79] has limited his work to fluid-particle heat transfer. Gabor [80] and Botterill [91] have analysed bed-to-surface heat transfer while Wen and Chang [82] were concerned with particle-particle heat transfer. However, inspite of these different approaches, all these investigators have concluded that fluidized beds have high heat transfer rates.
2.2 The Chemistry of Sulfate Roasting of Copper, Cobalt, Nickel and Iron Sulfides

A literature survey on this subject was organized under two sections:

(i) Reaction mechanisms and kinetics

(ii) Thermodynamic analysis

2.2.1 Reaction Mechanisms and Kinetics

Of all the complex equilibria of sulfate roasting considered by Willis [91] in concord with the phase rule, two are thought to be involved in sulfate formation from sulfides:

(i) Oxidation of the metallic values to oxides [1,2,92], followed by

(ii) Sulfation of the oxides [4,16,93,94]

Shah and Khallafalla [95], Hocking and Alcock [96] have experimentally verified the formation of basic copper sulfate prior to the formation of copper sulfate. On the other hand Ingraham and co-workers [12,24] who have made extensive studies on cobalt and nickel systems have not reported any cobalt and nickel basic sulfates.

The sulfide-oxide conversion stage is thought to be an irreversible reaction. Its dependence on temperature, oxygen potential at the particle surface, particle surface area and the presence of catalysts have been analysed by Shelef and Jackson [25]
The mechanism of oxidation of sulfides and the subsequent sulfation have been studied by Thornhill and Pidgeon [103], Ingraham and Marie [23] besides those already mentioned. In most cases, the conclusions were based on micrographic studies of polished thin sections of the roasted material. Certain unwanted reactions have been reported. Thornhill [103] and Rosenqvist [21] have observed kernel roasting and ferrite formation. Also cobalt and nickel form protective coatings which hinder further sulfation of the oxides. To overcome this difficulty, several investigators have tried the use of alkali sulfates. Hotz, Kerby and Ingraham [109] have tried the effect of molten sodium pyrosulfate and sodium bisulfate on cobalt and nickel ferrites. They found that the sulfation is quickly achieved under such conditions. The mechanism by which alkali sulfates promote sulfation of cobalt and nickel oxides, is not well understood. And in fact, Rosenqvist has questioned this promotion effect on the basis that these alkali sulfates may form eutectic melts which may aid ionic migration thereby aiding kernel behaviour.

2.2.2 **Thermodynamic Analysis**

In order to determine conditions suitable for selective sulfation, phase diagrams are constructed at the temperature of operation. Such diagrams show that the
stability fields of the various condensed phases correspond to certain partial pressures of the gas phase components. Therefore, the species of the system, their equilibria reactions and a thermodynamic data source are necessary.

The most outstanding contributions in the field of sulfation equilibria are those by H. H. Kellog [16,17, 110,115] and T. R. Ingraham [12,24,116,118] Their data on sulfates agree very closely and either can be adopted. However, phase diagram construction requires additional free energy data. The data available in Barin and Knacke's compilation [20] supplemented by those of Rosenqvist [113], Kubaschweski [119], Skeaff and Espellund [19] and P. A. Young [112] (who reviewed and recommended free energy of formation data of chalcopyrite, bornite, cubanite and idaite) are extremely useful. In addition, Ingraham and Kerby [120] have reviewed selected papers on thermodynamics and kinetics of roasting as applied to extractive metallurgy.

Finally, selective sulfation is conducted below the decomposition temperature of the sulfate(s) under investigation, and as such is a function of the gas composition. Therefore, a temperature-gas composition control diagram is essential to show the sulfate-stability dependence on the gas composition. Diagrams of this nature have been constructed by Holland [114] for various Me-S-O systems. More recently, Thomas [13] has followed
this procedure when he considered sulfate roasting of copper and iron sulfides to selectively sulfate copper.
CHAPTER 3  THEORETICAL AND EMPIRICAL CONSIDERATIONS

In this chapter, an attempt will be made to explore facts which have made Fluidization Technology industrially successful. In particular, it will be shown how these facts are utilized, in conjunction with the knowledge of the chemistry of roasting, to selectively sulfate copper, cobalt and nickel sulfide concentrates.

Therefore, the theoretical and empirical considerations of fluidized-bed, selective sulfate roasting will consist of three headings subdivided as follows:

(1) Fluidization Technology
   (a) Historical Developments of Fluidization Technology
   (b) Fluidization Phenomena
   (c) Fluidization Characteristics
   (d) Applications of Fluidization

(2) The Chemistry of Sulfate Roasting of Copper, Cobalt, Nickel and Iron Sulfides

(3) A Thermodynamic Analysis of Cu-Co-Ni and Fe-S-O Systems in the Temperature Range
of $900-1000^\circ$ K

(a) Phase Stability Diagrams
(b) Temperature-Gas Composition Control Diagram

3.1 Fluidization Technology

The field of fluidization engineering covers all methods used to contact solids with a moving fluid, in such a way that the resulting two phase mixture exhibits fluid characteristics which make fluidization methods economically attractive. The fluidizing fluid may be a liquid or a gas. It may be a reactive or inert component. In the case where the fluid is a reactant, it is used to accomplish a heterogeneous reaction which may be catalytic or non-catalytic. If the fluid is gaseous, it is usually composed of the actual gas reactant(s) and an inert gas (usually nitrogen). The latter is used to reduce the reactant gas partial pressure to values corresponding to those under which the desired products are stable, as predicted from stability phase diagrams.

Tette and Tailby [28] have described fluidization as a perfect example where practice has gone ahead of theory. To justify this quotation, historical developments in fluidization technology will be reviewed, followed by fluidization phenomena, schematically and graphically
portrayed. Fluidization characteristics which, as noted earlier, have made fluidization technology economically attractive, thus accounting for the diversity of fluidization applications, will also be covered in this section.

3.1.1 **Historical Developments in Fluidization Technology**

The earliest recorded patent that seems to have initiated fluidization technology, is an U.S.A. patent granted to a Mr. C. E. Robinson in 1879 [26,27,28]. It is noteworthy that this invention was originally aimed at sulfide mineral roasting. This patent is well described in unpublished lecture notes of Drs. Curlook and Alcock [27] and is worthy re-quoting:

"My invention relates to an improved process and apparatus for treating ores, more particularly for desulfurizing auriferous ores, the object being to secure the desired result in a more perfect manner, in a shorter time, and with less expenditure of fuel and labour than heretofore. . In carrying out the process, a charge of pulvillized ore is admitted into the cupola, and a jet or blast of air, gas, or steam is admitted at the bottom of the cupola, and, passing up through the ore, causes it to boil or play like the waters of a fountain ."

Dr. N. J. Hasse (Department of Chemical Engineering, College Technology, Loughborough) [28] has indeed called it the father of all patents dealing with fluidization. According to the current terminology [57] the type of
fluidization described therein is the "spouted bed" fluidization. The low economic factor which has, up to now, made fluidization extremely attractive, is stressed by Mr. Robinson [26].

Max Leva [45] has made reference to a second earliest patent granted to Phillips and Bulteel in 1910. Fluidization, as a means of achieving excellent contact between a gas and a finely divided catalyst, is depicted. The catalyst is swept by the gas into a reaction chamber where the reaction occurs in the lean fluidized phase and the products carry the catalyst into a recovery vessel from where it returns to the catalyst feed point by gravity mechanism, utilizing the high catalyst density.

Until 1921, there appears to have been no commercial application of the technology described in the above patents. In 1922, a Germany patent was granted to Fritz Winkler for gasification of pulverized coal. BASF (the acronym for Badische Anilin Und Soda-Fabrik) utilized the Winkler fluidized bed gas generators to produce water and producer gases in 1926. It is recorded [30] that similar units were independently constructed in Japan.

In 1940, with the escalation of Second World War, the Western Allies' demand of 100-octane jet aviation gasoline had gone up to 40,000 barrels per day and by the end of the war, 1945, 600,000 barrels were required
every day. In response, Esso Research and Engineering Company (U.S.A.) acting on recommendations of professors W. K. Lewis and E. R. Gilliland of Massachusetts Institute of Technology, launched a successful, smoothly-operated, fluidized-bed, petroleum catalytic-cracking process in 1942. This reactor, 40 ft. in diameter, produced 15,000 barrels per day whereas other processes like the slurry technique had been producing 100 barrels per day. Three commercial plants were designed simultaneously and commissioned within a few months of one another; five more of improved design were in the stage of engineering detail even before these went into operation. Altogether, some 30 plants went into operation to supply the Western Allies' demand of high jet gasoline, and the plant capacity had jumped to 100,000 barrels per day at the close of the war. The way in which this development was scaled up from the laboratory to commercial operations was a remarkable achievement which was recognized in 1947 by the award of the Institute of Petroleum Cadman Memorial Medal to R. P. Russell [28]

Later, adoption of fluidized-bed reactors to accomplish other petroleum chemical reactions has been increasing at a tremendous rate. These other processes include fluid hydro-forming for reforming naphtha vapour, thermal cracking of petroleum feed stocks, catalytic
oxidation of naphthalene or ortho-xylene, production of alkyl chloride and others too numerous to mention.

In 1945, BASF, based on their Winkler gas generator experience, developed a commercial, fluidized-bed roaster. In 1946, Dorr-Oliver Company, Ontario, Canada, having bought the rights to Esso's fluidized-bed know-how, constructed and successfully operated a sulfide fluidized-bed roaster, at Cochenour Williams Gold Mine. Such a reactor was 6 ft. 8 in. in diameter, with a capacity of 15 tons of concentrate per day. In light of the Robinson patent, this idea was novel, it is nevertheless the first known fluidized-bed roaster for sulfide minerals applied commercially, since the BASF roaster did not go into smooth operation until 1950. In 1952, Sumitomo Chemical Manufacturing Company, independently developed roasters to produce high concentration of sulfur dioxide gas.

In the years that have followed (1950-1975), the art of fluidization has been adopted in other engineering fields besides the chemical industry. Processes like drying of solids, limestone and dolomite calcination, Pyzel process for production of cement clinker, removal of heat from nuclear reactors, and in transport (fluidized bed conveyors), are in common use today.

It is to be noted, however, that in spite of this flourishing fluidized-bed technology there were few
theoretical developments until 1950's, when such symposiums as held in Massachusetts Institute of Technology (1948), in London (1951), in New Haven (1953), and at Brooklyn Polytechnic Institute (1955), were convened. This shows, as Tailby pointed out, that fluidization is a perfect example of processes where practice has kept ahead of theory. However, the latter is being vigorously investigated as exemplified by the fact that between the years 1961 and 1962, more than 100 technical papers were published. This is at an average rate of more than one paper per week! This has been useful since there is need for data co-ordination and knowledge in cases where little or contradictory data exists, as this may lead to better designs and wider utilization of the fluidized-bed technology.

3.1.2 Fluidization Phenomena

Figure 3.1-1 is helpful in initiating this topic. Starting at the bottom, the reactor is charged with ore or concentrates. If a fluidizing fluid has not been introduced, a bed whose solids are static with respect to one another and to the reactor, is formed. This is a fixed bed which is transformed into either of the following when a fluid is allowed to flow through it:

(a) A channelling bed. The fluid may form
Fig. 3.1-1. Fluidization Phenomena.
vertical channels through which most of the flow occurs. This tendency depends on the particle shape, arrangement and interparticle forces which cause agglomeration and bridging when they exceed the forces transmitted to the particles by the fluid. The diameter of the gas distributor holes has been cited to promote channelling. Such "rat-holes" are common with finely divided powders and solids with broad size distribution. Also high fluid velocities tend to promote channelling. Channelling is disadvantageous because it decreases the surface area available for gas-solid contact; it reduces the gas residence time in the bed and improperly fluidized parts of the bed may develop into hot spots. Thus channelling must be avoided. It is circumvented by incorporation of anti-agglomerants, e.g., submicron size silica; by imparting mechanical forces large enough to overcome the interparticle forces, e.g., using mechanical agitators or by low frequency mechanical vibration of the reactor.

(b) If the fluid flow contacts the bed through a centrally situated single orifice, the fluid carries some of the solids upwards in the central core and sheds them to the sides into the freeboard of the bed. Particles at the sides of the central core then flow countercurrent to the main gas flow. The central "fountain" constitutes a lean phase while the peripheral annulus is a dense
phase. This is a spouting bed.

(c) If channelling or spouting do not occur then by increasing the superficial fluid velocity a point is reached where the vertical interparticle compressive forces are no longer exerted. At what is called the "incipient" velocity the total frictional force between the particles and the fluid equals the effective weight of the particles packed in the loosest form. The bed has expanded from a fixed bed to an incipient fluidized bed.

If the fluidizing fluid is a liquid, particulate (smooth, homogeneous) fluidization occurs. The volume concentration of the particles is uniform and time independent. If it is a gas, aggregative (heterogeneous) fluidization results. However, at high fluidizing gas partial pressures, particulate fluidization may be achieved.

Incipient, particulate and aggregative fluidization constitute a phase with a clearly definable surface or upper limit, called the dense phase. The other phase is called the dispersed phase. Aggregative fluidization transforms into this directly or may go through a phenomenon called "slugging". Reactor diameter is one of the parameters which influences slugging, a phenomenon common in reactors with small diameters. Slugging results in non-uniform temperature and yield composition and can
also increase the reactor wear. A slugging bed is characterized by the growth of a bubble whose diameter equals that of the reactor. The particles adhering to its bottom rain down as the bubble moves upwards. When the force due to pressure inside the bubble becomes less than the gravitational force due to the weight of the upward-moving particles, the bubble breaks. As this happens a new bubble is formed or is already growing.

The solids with spouting or channelling tendencies may be transformed into a dense phase or may directly go to the dispersed phase. Finally, as entrainment velocity is reached pneumatic transport of the solids occurs, the smallest particles being affected first.

Fluidization phenomena can alternatively be graphically represented by plotting particle Froude number versus particle Reynolds number. These dimensionless parameters offer excellent means of relating the particle diameter to the superficial gas velocity, two of the most important complex factors that determine the quality of fluidization. Thus a grid of particle diameter versus superficial gas velocity can be superimposed on this plot. Such diagram is called Schytil diagram (Fig. 3.1-2)

The particle Froude number at incipient fluidization (ε = 0.45) may be represented as follows:
Fig. 3.1-2. Schytil diagram (for 900°C, 8% SO₂ & 5% O₂).
\[ \text{Fr}_{mf} = \varepsilon^3 \frac{(\rho_s - \rho_g)}{(\rho_g \Psi_{Re, \varepsilon})} \] 3.1-1

where

\[ \Psi_{Re, \varepsilon} \] is a modified Fanning friction factor for beds of granular solids:

\[ \Psi_{Re, \varepsilon} = 150 (1 - \varepsilon) / \text{Re} + 1.75 \] 3.1-2

\[ \text{Re} = \frac{u d_p \rho_g}{\mu} \] 3.1-3

\[ \text{Fr} = \frac{u^2}{d_p g} \] 3.1-4

where

\[ u \] = superficial velocity (cm sec\(^{-1}\))

\[ d_p \] = particle diameter (cm)

\[ \rho_g \] = gas density (gm cm\(^{-3}\))

\[ g \] = acceleration due to gravity, 980 (cm sec\(^{-2}\))

\[ \mu \] = viscosity (g cm\(^{-1}\) sec\(^{-1}\))

\[ \rho_s \] = solids density (gm cm\(^{-3}\))

\[ \varepsilon \] = void fraction

The particle Froude number for the settling of spheres at any given void fraction is:

\[ \text{Fr}_{s, \varepsilon} = \frac{4}{3} \varepsilon^{4.65} \frac{(\rho_s - \rho_g)}{\rho_g \text{Re}} \] 3.1-5

where
\( C_{Re} \) is the drag coefficient for spheres and has the following values:

<table>
<thead>
<tr>
<th>Re</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{Re} )</td>
<td>245</td>
<td>28</td>
<td>4.4</td>
<td>1.1</td>
<td>0.46</td>
</tr>
</tbody>
</table>

By rearranging the particle Froude number and the particle Reynolds number, the coordinates of the particle diameter and the superficial gas velocity can be obtained:

For constant \( d_p \) lines:

\[
Fr = \frac{Re^2 (\mu^2/\rho g^2 g)}{d_p^{3.1-6}}
\]

For constant \( u \) lines:

\[
Fr = \frac{u^3}{Re (\rho g/\mu)}
\]

It is interesting to note that many authors have quoted and in most cases have reproduced [18] the Schytil diagram constructed by R. B. Thompson of Dorr-Oliver Inc. and G. Roesner of Lurgi Gesellschaft, Germany [15]. However, the equations for the particle diameter lines \((\log Fr = 2 \log Re + \log (\rho^2 g/d_p^{3.1-6} \mu^2 g))\) and the gas velocity lines \((\log Fr = -\log Re + \log (u^3 \mu/\rho g))\) are incorrect. But since the actual \( \mu/\rho g \) used = 1 cm\(^2\)sec\(^{-1}\), therefore the error (whether a typing error or not) should not affect
the final diagram.

In order to reduce the number of variables to three (\(d_p\), \(\mu\), and \(\varepsilon\)), \(\rho_s\), \(\rho_g\) and \(\mu\) must be known. Choosing the conditions for sulfate roasting as:

Temperature 900°K, 8% SO₂, 5% O₂

the viscosity of the gas mixture, \(\mu = 3.81245 \times 10^{-4} \text{gmcm}^{-1}\text{sec}^{-1}\)

the density of the gas mixture, \(\rho_g = 3.46312 \times 10^{-4} \text{gmcm}^{-3}\)

the density of the solids, \(\rho_s = 4.53 \text{gmcm}^{-3}\),
equations 3.1-6 and 3.1-7 reduce to:

\[\text{Fr} = 1.23665 \times 10^{-3} \left(\frac{\text{Re}^2}{d_p^3}\right)\]

and

\[\text{Fr} = 9.26909 \times 10^{-6} \left(\frac{\text{u}^3}{\text{Re}}\right)\]

[For values of \(\mu\), \(\rho_g\), refer to Appendix 2.]

On the plot the particle diameter is in mm.; the lower line corresponds to incipient fluidization (\(\varepsilon = 0.45\)), while the upper one corresponds to pneumatic transport (\(\varepsilon = 1.0\)). Between these lines lies the field of fluidization. Thus three distinct phenomena are exhibited on the diagram:
(a) Fixed bed region

(b) Dense fluidization phase

(c) Dispersed or lean phase (corresponding to pneumatic transport)

The flotation concentrates of copper, cobalt and nickel normally have particle size distribution of 50-300 microns (325-48 mesh) and void fraction of 0.45 at incipient fluidization. The dense phase fluidization of such material results in void fraction range of 0.6 - 0.8, shown by dotted lines on the Schytil diagram. The mean particle diameter lies between 100 and 225 microns and therefore operative gas velocities of 30-45 cmsec\(^{-1}\) are usually employed [15]

The Schytil plot is based on particles of uniform diameter. For solids with broad size distribution, a mean diameter should be used (eqn. 2.1-5) Therefore, the boundary line between the fixed bed and the dense phase fluidization represents a mixture of particle sizes including the coarser ones which, if they were alone, would be in the fixed bed region. For a given fluidizing velocity, all particles, in a mixture, whose diameter is smaller than the diameter located by the point of intersection between the gas velocity and the pneumatic transport line, would eventually be blown out of the reactor but illustration is not complete because, for practical gas/solids fluidization, small amounts of fines remain in
the bed voids.

For further evaluation of the bed characteristics, the gas velocity line A (37.7 cmsec\(^{-1}\)) is useful. Its lower terminus indicates that a mixture of particles with a mean particle diameter smaller than about 0.6 mm (28 mesh) would be fluidized while mixtures with larger mean particle diameters would settle to form a fixed bed. In fact, if a given mixture of particles has a large diameter range, the gas will follow "rat-holes" thus forming a channelling bed. Where the line intersects the pneumatic transport line, particles of size smaller than 0.04 (approximately 325 mesh) would be blown out but as indicated earlier, some fines remain trapped in the bed voids. Finally the gas velocity required to effect incipient fluidization of the sample under investigation (\(d_p = 0.126\) mm) has been calculated using equations 3.1-14 and 3.1-15 and found to be 1.12 cmsec\(^{-1}\); a similar value was deduced from Schytil diagram. Also, using other equations (3.1-17, 3.1-18, 3.1-19) the minimum fluidization velocity, \(u_{mf}\), lies in the range 1-2 cmsec\(^{-1}\). The entrainment velocity was found to be 17.7 cmsec\(^{-1}\) using Schytil diagram. Thus this value agrees with the Pinchbeck and Popper Criterion (eqn. 2.1-6) In this respect the Schytil diagram excells the equations given by Diazo Kunii et al. (3.1-14 - 3.1-19) (It should be clarified that the
above figures are based on operation conditions of 900°K, 8% SO₂ and 5% O₂.)

3.1.3 Fluidization Characteristics

The success of fluidization processes depends on the inherent fluidization characteristics. Thus at present they constitute the major design considerations of fluidized bed reactors. Therefore, in order to have a better understanding of fluidization, it is important that these characteristics be known.

(1) Liquid-like behavior

Fluidized beds behave as liquids: if a light object is pushed into the bed, the object pops out and floats when it is released. Fluidized beds offer resistance to the passage of solid objects. This resistance is analogous to liquid viscosity. Hagyard and Sacerdote [64] have estimated it to be of the order of 200 centi-stokes from studies made using a torsion pendulum. On being punched, the bed shoots out in a jet, a property which has made it possible to flow fluidized beds from one reactor to another when connected enabling such operations as solids circulation, countercurrent and cross-current contacting fluidized systems [30]. Fluidized beds have a definite "hydrostatic" head making pressure drop computation easier.
(2) Perfect particle mixing

Particle mixing in fluidized beds is accomplished by gas bubble agitation. It is conceptually agreed that the gas in excess to that required to effect incipient fluidization passes through in the bubble phase. As the bubble moves upwards it drags a wake of particles, pushes those at its head upwards and those at the sides outwards. Some distance away from the bubble, a compensating downward particle motion occurs [67]. Thus particles which were originally at the bottom of the reactor end up being circulated throughout the bed. A direct consequence of this phenomenon is establishment of uniform temperatures and bed composition. However, slight deviations may occur where large quantities of cold feed, cooling water and hot gases are introduced. Hot spots due to agglomeration and sintering are further manifestations of such deviations. Figure 3.1-3 illustrates particle agitation caused by bubble motion, in a bed composed of lead shot and fluidized by water [71].

(3) Gas-solids contact

Gas fluidized solids have been commonly analysed using a "two-phase" model [72]: the dense (continuous) and the dilute (discontinuous) phases. The former consists of uniformly distributed solids in close contact with and suspended by the fluidizing gas. The dilute phase, also
Fig. 3.1-3. Shape of the bubble and relative motion of the solids (1-mm. lead shot fluidized in water).
called the bubble phase, is composed of gas enclosed in a film of solids, a distinction that forms the basis for the "three-phase" model formulation used by some investigators [73]. Thus gas and solids mass transfer is an interphase phenomenon. However, a portion of gaseous matter in the bubble may pass through the bed without ever having contacted any solids. This is called bypassing. Hence inspite of the fact that bubbles promote particle mixing, which results in uniform temperatures and overall bed composition, they reduce the gas/solids contact efficiency which results in poor conversion of reactants in catalytic reactions, and poor gas utilization in roasting and reduction processes. Therefore, bubbles must be kept as small as possible using, among other things, gas velocities which are just enough to effect good fluidization. In conclusion, inspite of the bypassing effect, it is theoretically and practically agreed that fluidized beds offer the best gas/solids contact compared to any other reactors.

(4) Heat transfer

The ability to achieve uniform temperatures rapidly, has made fluidized beds economically attractive particularly in metallurgical processes where high heat transfer rates are vital. This can be accounted for by analysing heat transfer between:
(a) fluidizing medium and the particles
(b) the bed as a whole and the reactor walls, and any immersed surfaces
(c) particle and particle

The latter is considered to have insignificant contribution particularly in well fluidized beds, and will therefore not be considered any further.

**Fluid/particle heat transfer.** Heat transfer between a fluidizing medium and fluidized particles occurs by conduction. A wide spectrum of heat transfer rates has been reported [77,79,82]. However, heat transfer coefficient range of 40-100 Btu. hr.^{-1}ft.^{-2}°F^{-1} has been reported [83].

There has been discrepancy in these reports due to difficulties encountered in measuring gas and particle temperatures. Some investigators [79] have taken the gas temperature to be that recorded by a bare thermocouple inserted in the bed. Clearly, this is incorrect because such temperature is intermediate between the gas and particle temperatures. This is particularly true if fluidization is at high temperatures because heat transfer, from the particles, by radiation plays an important role. This is the view taken by Cibrowski and Rosza, Shakhova et al. [49]. Others have attempted to succumb this handicap by using certain temperature probe devices, e.g., Chang and Wen [82] have used a suction pyrometer for gas
temperature and a miniature thermocouple inserted in a particle for the solids temperature. J. F. Franz et al. [79] have analysed heat transfer in fluidized beds assuming that the particle temperature is equal to the exit gas temperature. Fritz [85] and Ferron [86] used the temperature of a collapsed bed (obtained by cutting off the fluidizing medium) as the particle temperature. However, it is noteworthy that in spite of all these difficulties, the results point to high heat transfer rates. This is expected since the volumetric heat capacities of the particles are of the order of 1000 times those of fluidizing media, particularly gases [87]. Thus solids act as heat source or sink, a phenomena which when supplemented by the high particle surface area (1000-2000 ft$^2$ ft$^{-3}$ of bed), quickly establishes thermal equilibrium between the particles and the fluidizing medium.

**Reactor of immersed surface/bed heat transfer.**

External heating of fluidizing beds, circulation of hot fluids in submerged coils or cold water to cool the bed are common procedures in fluidization technology. Their utility is attributed to high heat transfer rates that exist between such surfaces and the bed. This has been broadly attributed to continuous replacement of the particles which are close to these surfaces. In this respect the bed can be pictured behaving as a "convective
cell" — on recalling the particle mixing caused by bubbles. However, since direct particle/surface contact is minimal, this heat transfer mechanism is effected by the fluidizing medium between the particles (closest to the surface) and the surface. But the distance between the circulating particles and the surfaces is so small that the heat transfer between the reactor or submerged surfaces and the bed is not hampered by the low fluid conductivities. It is to be noted that an additional heat transfer mechanism by radiation may occur at temperatures exceeding 600°C.

(5) Minimum fluidizing velocity, $u_{mf}$

Fluidization begins at a particular gas velocity which is characteristic of the properties of the fluidizing fluid and the solids involved. This onset of fluidization occurs when the frictional force between the upward moving fluid and the particles equals the weight of the particles. In terms of pressure drop, this is expressed as follows:

$$\Delta P (A) = (A)(L_{mf}) (1-\epsilon_{mf}) (\rho_s - \rho_g) \frac{g}{g_c}$$

where

$\Delta P$ = pressure drop (gm wt. cm$^{-2}$)

$L_{mf}$ = height of the bed at incipient fluidization (cm)

$A$ = cross-sectional area of the reactor (cm$^2$)
\[ \varepsilon_{mf} = \text{void fraction at incipient fluidization} \]
\[ g = \text{gravitational acceleration, } 980 \text{ (cm/sec}^{-2}) \]
\[ g_c = \text{gravitational acceleration conversion factor, } 980 \text{ (gm cm (gm wt.)}^{-1} \text{ sec}^{-2}) \]

By rearrangement, the following equation is obtained:

\[ \frac{\Delta P}{L_{mf}} = (1-\varepsilon_{mf})(\rho_s-\rho_g)\frac{g}{g_c} \quad \text{(3.1-9)} \]

For a fixed bed of uniformly sized solids the semi-empirical Ergun equation [88] relating pressure drop and superficial velocity of the fluidizing medium, has been found to give satisfactory results when applied to incipient fluidization.

\[ \frac{\Delta P_{gc}}{L} = 150(1-\varepsilon_m)^2\mu u_o + \frac{1.75(1-\varepsilon_m)\rho_g u_o^2}{\varepsilon_m^3 \phi_s d_p^2} \quad \text{(3.1-10)} \]

where

\[ \phi_s = \text{the sphericity factor} \]
\[ L = \text{the bed height (with respect to the gas distributor level) over which the pressure drop is being considered} \]

Combining eqn. 3.1-9 with eqn. 3.1-10, subsequent rearrangement produces an equation which is quadratic with respect to \( u_{mf} \):
\[
\frac{\rho g d^3}{\mu^2} (\rho_s - \rho_g) = 150 \left( \frac{1 - \epsilon_{mf}}{\epsilon_{mf}^3 \phi_s^2} \right) \left( \frac{u_{mf} d p \rho_g}{\mu} \right) + 1.75 \left( \frac{1}{\phi_s \epsilon_{mf}^3} \right) \left( \frac{u_{mf} d p \rho_g}{\mu} \right)^2
\]

When \( \phi_s \) and \( \epsilon_{mf} \) are unknown, Wen and Yu [30] have suggested the following empirical relationships:

\[
\frac{1}{\epsilon_{mf}^3 \phi_s^3} = 14 \tag{3.1-12}
\]

\[
\frac{1 - \epsilon_{mf}}{\epsilon_{mf}^3 \phi_s^2} = 11 \tag{3.1-13}
\]

By substituting eqns. 3.1-12 and 3.1-13 into eqn. 3.1-11 and solving, the following expression is obtained:

\[
u_{mf} = \frac{\mu}{49d_p \rho_g} \left\{ -1650 + \left[ (1650)^2 + \frac{98d_p^3 \rho_g (\rho_s - \rho_g)}{\mu^2} \right]^{1/2} \right\}
\]

Such an expression is valid for the whole range of Reynolds numbers. However, for small particles and low Reynolds number, the viscous term is more important.

Therefore

\[
u_{mf} = \frac{d_p^2 (\rho_s - \rho_g) g}{1650 \mu} \quad \text{for } Re < 20 \tag{3.1-15}
\]
and

\[ u_{mf} = \sqrt{\frac{d_p (\rho_s - \rho_g) g}{2.45 \rho_g}} \]

In order to apply these formulae, a value for \(Re\) is arbitrarily assumed in order to decide the formula to use. The \(u_{mf}\) values obtained are used to calculate a corresponding \(Re\) number. If this value falls within the range earlier used, then a good approximation of \(u_{mf}\) has been obtained. If, however, the value under examination is between 20 and 1000, the general equation is used. Max Leva has given the following formula for determining the minimum fluidizing gas velocity:

\[ G_{mf} = 688 d_p^{1.82} (\rho_g (\rho_s - \rho_g))^{0.94} / \mu^{0.88} \]

where:

- \(G_{mf}\) = minimum fluidization mass flow rate (lb hr\(^{-1}\) ft\(^{-2}\))
- \(d_p\) = particle diameter (in)
- \(\rho_g, \rho_s\) = fluid and solid densities respectively (lb ft\(^{-3}\))
- \(\mu\) = fluid viscosity (cP)

Rowe (1961), using water flowing through a regular array of spheres developed the following similar equation:
\[ u_{mf} = 0.00081 \frac{gd_p^2(\rho_s-\rho_g)}{\mu} \] 3.1-18

Davison and Harrison [121], using the theory originated by Kozeny (1927) and Carman (1937), derived the following formula:

\[ u_{mf} = 0.00114 \frac{gd_p^2(\rho_s-\rho_g)}{\mu} \] 3.1-19

Finally, a comparison of the values of \( u_{mf} \) obtained using the above formulae and the experimental conditions can be used in choosing which one(s) is useful. Such a comparison is provided in Table 3.1-1. From this table, it can be seen that the formulae given by Diazo Kunii, Rowe and Davison are in close agreement whereas Max Leva's formula gives a low value. Besides this comparison method, these values can be checked experimentally to find the correct incipient fluidizing velocity for the system under investigation.

(6) Minimum entrainment or pneumatic transport velocity, \( u_t \)

Entrainment velocity is the velocity at which fluidized particles undergo pneumatic transport. This velocity depends upon particle diameter, the reactor freeboard height and the fluidizing gas flow rate. This upper limit to the desirable gas flow rate is usually estimated
### TABLE 3.1-1

**A Comparison of Incipient Velocities Obtained Using Different Formulae**

<table>
<thead>
<tr>
<th>Formula</th>
<th>umf Value (cm/sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu / 49 \cdot \frac{d \rho g}{d \rho g} - 1650 + \frac{1650^2}{d \rho g} )</td>
<td>1.12</td>
</tr>
<tr>
<td>( d \rho g (\rho - \rho g) / 1650 \mu )</td>
<td>1.12</td>
</tr>
<tr>
<td>From Schylt diagram</td>
<td>1.50</td>
</tr>
<tr>
<td>0.00814 ( g \rho (\rho - \rho g) / \mu )</td>
<td>2.11</td>
</tr>
<tr>
<td>0.00114 ( g \rho (\rho - \rho g) / \mu )</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Note: \( G_{mf} \) (lb/hr⁻¹·ft⁻²) was converted to \( umf \) (cm/sec⁻¹) as follows:

\[
G_{mf} = \frac{1000}{2.2} \left( \frac{3600}{12 \times 2.54} \right) \left( \frac{1}{1 \text{(km)}} \right)^2 \left( \frac{1}{1 \text{(in)}} \right)^2 \left( \frac{1}{1 \text{(lb/hr)}} \right)^2 \left( \frac{1}{1 \text{(ft²)}} \right)^2 \left( \frac{1}{1 \text{(cm³/gm)}^2} \right)^2
\]
using terminal free-fall velocity of the particles, as estimated from fluid mechanics:

\[ u_t = \frac{4gd_p(\rho_s - \rho_g)}{3\rho_gC_d} \]  

where

\[ C_d \] is an experimentally determined drag coefficient

\[ d_p \] is the diameter of the smallest particle

\[ C_d \text{ and Re} \] are related as

\[ \text{Re} = \frac{d_p\rho g u_t}{\mu} \]  

\[ C_d\text{Re}^2 = \frac{4gd_p^3\rho g(\rho_s - \rho_g)}{3\mu^2} \]

Diagrams of experimental correlations of \( C_d\text{Re}^2 \) versus \( \text{Re} \) have been constructed by many authors [30 p. 77] By evaluating \( C_d\text{Re}^2 \), which contains experimentally determinable parameters, and using such diagrams, values of \( \text{Re} \) number are obtained from which \( u_t \) can be computed.

Alternatively, for small particles which are approximately spherical the following equations can be used to estimate \( u_t \), for different \( \text{Re} \) numbers. By recalculating \( \text{Re} \) and ascertaining that it falls within the
range previously assumed, then the best approximation of \( u_t \) has been made.

\[
u_t = \frac{g (\rho_s - \rho_g) d_p^2}{18 \mu} \quad \text{Re}<0.4 \quad 3.1-23
\]

\[
u_t = \left( \frac{4 (\rho_s - \rho_g)^2 g^2}{225 \rho_g \mu} \right)^{1/3} d_p \quad 0.4<\text{Re}<500 \quad 3.1-24
\]

\[
u_t = \left( \frac{3.1 (\rho_s - \rho_g) d_p}{\rho_g} \right)^{1/2} \quad 500<\text{Re}<200,000 \quad 3.1-25
\]

Pinchbeck and Popper [90] derived an equation relating the minimum fluidizing gas velocity (\( u_{mf} \)) and the minimum entrainment velocity (\( u_t \)).

Using this equation, the ratio of \( u_t \) to \( u_{mf} \) is usually found to lie between 10:1 and 90:1. This signifies the range of operation of fluidized bed reactors. However, the above range is narrower for large particles than for small ones.

3.1.4 Applications of Fluidization Technology

It has already been noted that fluidization applications depend upon the characteristics of this technique.
It will be further emphasized that these characteristics are inherent in the sense that they are not limited to a single operation. Thus all the vast number of fluidization applications utilize a large combination of these characteristics, if not all, for their eventual success. On the whole these applications can be divided into two sections: chemical and physical operations. Fluidization applications are so diverse that indulging into their details is beyond the scope of this work. Moreover, they are well treated in standard text books [30, 44,45,46,121,122] on fluidization. Therefore, their enumeration will suffice.

(1) Chemical operations

(a) Coating of plastic materials on metal surfaces [31] This is used for insulation, protection or decolation purposes.

(b) Evaporation and crystallization. Solutions are injected into the reactor containing seed particles. Successful operations using sodium hydroxide, ammonium sulfate, ammonium nitrate, calcium chloride and sodium cyanide solutions have been reported [32]

(c) Separation technique using adsorption mechanism. This is especially useful for gases which are difficult to condensate; recovery and re-concentration of fluids present in small concentrations and separation of materials which have boiling points which are close to one another [33]

(d) Synthesis applications. These include some of the earliest applications of
fluidization technique. They are mainly organic reactions, a number of which are found in the petroleum industry.

(i) Manufacture of ethylene, alkyl chloride, phthalic anhydride and acrylonitrile by Sohio process [30]

(ii) Catalytic cracking and reforming of hydrocarbons, fluid coking, thermal cracking of naphtha petroleum fractions, carbonization and gasification [34]

(iii) Fischer-Tropsch process [35] and production of carbon disulfide [30]

(e) Calcining and clinkering of limestone, dolomite, phosphate rocks, kaolin clays and Pyzel process for cement production [30,36]

(f) Oxidation processes:

(i) Roasting of sulfides [6,14,15,18, 21,30,37,38,39-5] to produce metallic oxides; pyrite to produce sulfur dioxide for the manufacture of sulfuric acid [52], to take part in segregation processes; for sulfite pulp for the pulp and paper industry and also for use in:

(ii) Selective sulfate roasting, e.g., of copper, cobalt, nickel and zinc sulfides [1,2,3]

(g) Reduction processes:

(i) Reduction of iron oxides to produce iron for the steel industry or for iron carbide production in fluidized bed reactors [39,40]

(ii) Production of metallic copper from cuprous chloride, and reduction of nickel oxide using hydrogen.

(h) Pollution abatement. The purpose is to destroy toxic polluting components or to
convert them into innocuous compounds. This is accomplished by incineration of municipal sludges and refinery wastes and by oxidation and decomposition of chemical waste compounds [29]

(i) Production of christobalite from quartz [41] and the annealing of brass [42]

(j) Production of uranium tetrafluoride [43]

(2) Physical operations

(a) Transportation. Air slide conveyors utilizing pneumatic transport fluid velocities are used in cement, soda ash, fly ash, flour and resin industries [51]

(b) Heat exchange operations. In this aspect high heat transfer rates of fluidized bed reactors are being used. A few examples include air cooling of ingot moulds and heat removal from nuclear reactors.

(c) Drying. This includes circulation of silica gel in multistage fluidized bed reactors to dry air and drying of crops, e.g., peas and wheat [50]

(d) Drying and sizing. This process involves blowing away the fines while retaining the coarser materials. Fluidized bed reactors have made drying and sizing of dolomite, limestone, coal, blast furnace slag, plastics and salt a practical reality.

(e) Humidification. A recent application of relatively shallow fluidized beds is as gas-humidifier coolers. The advantage over the spray chamber humidifier is that no liquid re-circulation is necessary.
3.2 The Chemistry of Sulfate Roasting of Copper, Cobalt, Nickel and Iron Sulfides

Sulfate roasting processes are basically metal-sulfur-oxygen systems. Such ternary systems have a large number of phases and consequently the number of possible reactions is even larger. Hence, the following reactions have to be considered in order to deduce which are important under particular conditions of temperature and gas composition [91]

\[
\begin{align*}
\text{MS} \, \text{(s)} + 2\text{MO} \, \text{(s)} & = 3\text{M} \, \text{(s)} + \text{SO}_2 \, \text{(g)} \\
\text{MS} \, \text{(s)} + \text{MSO}_4 \, \text{(s)} & = 2\text{M} \, \text{(s)} + 2\text{SO}_2 \, \text{(g)} \\
\text{MS} \, \text{(s)} + 3\text{MSO}_4 \, \text{(g)} & = 4\text{MO} \, \text{(s)} + 4\text{SO}_2 \, \text{(g)} \\
\text{MS} \, \text{(s)} + 2\text{SO}_2 \, \text{(g)} & = \text{MSO}_4 \, \text{(s)} + \text{S}_2 \, \text{(g)} \\
\text{M} \, \text{(s)} + \text{MSO}_4 \, \text{(s)} & = 2\text{MO} \, \text{(s)} + \text{SO}_2 \, \text{(g)}
\end{align*}
\]

In addition to these, the metal sulfate decomposition may be considered:

\[
\text{MSO}_4 \, \text{(s)} = \text{MO} \, \text{(s)} + \text{SO}_3 \, \text{(g)}
\]

If a metal forms a number of sulfides, oxides and basic
sulfates, then the number of possible reactions becomes increasingly large. In spite of this chemical reaction complexity, there are three schools of thought as to how the sulfates are formed during roasting of metallic sulfides.

(a) The metallic oxide formation as the initial reaction \[1,2,92\]

\[
MS(s) + \frac{3}{2} O_2(g) = MO(s) + SO_2(g) \quad 3.2-7
\]

This is followed by interaction between the oxide and sulfur dioxide (or sulfur trioxide) in presence of oxygen to form the sulfates.

\[
MO(s) + SO_2(g) + \frac{1}{2} O_2(g) = MSO_4(g) \quad 3.2-8
\]

This step is thought to involve the formation of sulfur trioxide which subsequently sulfates the oxide as follows:

\[
SO_2(g) + \frac{1}{2} O_2(g) = SO_3(g) \quad 3.2-9
\]

(this reaction is thought to be catalysed by other metallic oxides as well, particularly iron oxides \[4,16,93,94\]) The actual sulfation is thus:

\[
MO(s) + SO_3(g) = MSO_4(s) \quad 3.2-10
\]

It has also been experimentally verified that some sulfate roasting reactions involve intermediate step which produces
basic sulfate(s) [95,96]

\[ 2MO(s) + SO_3(g) = MO \cdot MSO_4(s) \quad 3.2-11 \]

and then

\[ MO \cdot MSO_4(s) + SO_3(g) = 2MSO_4(s) \quad 3.2-12 \]

This behaviour is exhibited by copper, zinc and lead sulfides [24]. No such step is thought to exist with regard to sulfate roasting of cobalt and nickel sulfides [24].

(b) Direct sulfation of the sulfides

\[ MS(s) + 2O_2(g) = MSO_4(s) \quad 3.2-13 \]

Ingraham calls this a "metallurgical phallacy". His argument is based on thermodynamic stability diagrams which predicts \( P_{SO_2} \) required for such a change to occur as being unpractically high, i.e., greater than 1 atmosphere.

(c) A combination of mechanism (a) and (b)

A. F. Lozhkin et al. [6] have reported that "it has been experimentally demonstrated" that cobalt sulfate is formed in two ways during roasting of cobalt monosulfide:

\[ CoS(s) + 2O_2(g) = CoSO_4(s) \quad 3.2-14 \]
\[
\text{CoS}(s) + \frac{3}{2} \text{O}_2(g) = \text{CoO}(s) + \text{SO}_2(g) \quad 3.2-15
\]

\[
\text{CoO}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2 = \text{CoSO}_4(s) \quad 3.2-16
\]

3.2.1 **The Kinetics of Oxide Formation**

If the end products of roasting are oxides, the phenomenon is referred to as "dead" or "sweet" roasting [18]. For all metallic sulfides, this reaction is strongly exothermic with an equilibrium lying far to the right at all practical roasting temperatures (500-1200°C) [16,92]. Hence, the reaction is essentially irreversible. The rate of this reaction is of prime importance. It has been shown [25,97,98,99] that several factors influence this reaction as follows:

(a) The rate increases rapidly with increase in temperature.

(b) The rate increases with the partial pressure of oxygen at the particle surface.

(c) The initial rate is proportional to the surface area of the particles although subsequent reaction rates are influenced by this factor to a less extent.

(d) The rate may be increased by the presence of suitable catalysts. The latter may be certain metal sulfides. For instance, at Flin Flon, Canada [97] and at Kosaka, Japan [98], it is reported that copper and iron sulfides appear to catalyze the oxidation of zinc sulfides increasing the rate of reaction.

In general, the rate of sulfide oxidation decreases in the following order:
\[ \text{FeS}_2 > \text{FeS} > \text{Cu}_2\text{S} > \text{CoS} > \text{Ni}_3\text{S}_2 \]

For instance, Fletcher and Shelef [4] and Fletcher and Jackson [25] have reported that pyrite is oxidized ten times faster than chalcocite and the latter ten times faster than nickel sulfide. These relative rates were obtained in fluidized bed reactors [4].

3.2.2 Mechanism of Sulfate Formation
(1) Copper sulfate

Copper forms many sulfides:

- Chalcopyrite . . . \text{CuFeS}_2 34.6\% \text{Cu}
- Bornite . . . \text{Cu}_5\text{FeS}_4 63.3\% \text{Cu}
- Chalcocite . . . \text{Cu}_2\text{S} 79.8\% \text{Cu}
- Covellite . . . \text{CuS} 66.4\% \text{Cu}

It is also found associated with other elements in sulfide minerals, e.g.,

- Carrollite . . . \text{Co}_2\text{CuS}_4 25.9\% \text{Cu},

a major cobalt mineral in Zaire, Africa.

However, from a thermodynamic point of view, it is impossible for all these sulfides to co-exist at a given temperature. Hence isothermal phase equilibria considerations are made relatively easier than they would otherwise be. These sulfides also behave differently
during roasting. Hence, each sulfide mineral will be
analysed individually except where there is scarcity of
literature regarding its behaviour during roasting.

(a) Chalcocite

Below 400°C, the interaction between
chalcocite and air produces cuprous oxide (known as cuprite
when in a mineral form) and sulfur dioxide.

\[
\text{Cu}_2\text{S}_\text{(s)} + \frac{3}{2} \text{O}_2\text{(g)} \rightarrow \text{Cu}_2\text{O}_\text{(s)} + \text{SO}_2\text{(g)}
\]  \hspace{1cm} 3.2-17

At temperatures above 400°C, cuprite is oxidized to cupric
oxide (CuO) (called tenorite as found in nature) [96,100,
101]

\[
\text{Cu}_2\text{O}_\text{(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow 2\text{CuO}_\text{(s)}
\]  \hspace{1cm} 3.2-18

However, at higher temperatures, chalcocite is directly
oxidized to cupric oxide.

\[
\text{Cu}_2\text{S}_\text{(s)} + 2 \text{O}_2\text{(g)} \rightarrow 2\text{CuO}_\text{(s)} + \text{SO}_2\text{(g)}
\]  \hspace{1cm} 3.2-19

Judging from the stoichiometry of the above reactions and
the prevailing roasting conditions, cuprous oxide, which
is only soluble in acidified ferric sulfate solution, is
formed using a limited amount of air. With excess air
and high temperatures, cupric oxide is predominant. It
has also been shown [94] that in excess air, chalcocite
can be sulfatized directly as follows:

$$\text{Cu}_2\text{S}(s) + \frac{5}{2} \text{O}_2(g) = \text{CuSO}_4(s) + \text{CuO}(s)$$  \hspace{1cm} 3.2-20

The sulfation of cupric oxide has been experimentally demonstrated \([95,96]\) to go through an intermediate basic sulfate.

$$2\text{CuO}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{CuO} \cdot \text{CuSO}_4(s)$$  \hspace{1cm} 3.2-21

$$\text{CuO} \cdot \text{CuSO}_4(s) + \text{SO}_3(g) = 2\text{CuSO}_4(s)$$  \hspace{1cm} 3.2-22

Ingraham and Marrier \([23]\) have conclusively shown that when copper sulfate thermally decomposes, the interface (CuSO\(_4\)/CuO\(\cdot\)CuSO\(_4\)) recedes into the CuSO\(_4\) pellet at a uniform rate under isothermal conditions. Shah and Khalafalla \([95]\) have concluded that CuO\(\cdot\)CuSO\(_4\) is formed prior to the formation of copper sulfate during roasting of covellite. Alcock and Hocking \([96]\) have found the following reaction sequence during the sulfation roasting of blocks of cuprous oxide:

$$\text{Cu}_2\text{O}(s) \rightarrow \text{CuO}(s) \rightarrow \text{CuO} \cdot \text{CuSO}_4(s) \rightarrow \text{CuSO}_4(s)$$

with the phases shown being present in the above order starting with the core of the block. This sequence was deduced from microscopic observations of thin polished
sections of the roasted Cu$_2$O blocks.

Other authors [93,100,101] have postulated that copper sulfate can also be formed due to a reaction between ferric sulfate and cupric oxide if iron sulfides are present during roasting.

$$3\text{CuO}_\text{(s)} + \text{Fe}_2\text{(SO}_4\text{)}_3\text{(s)} = \text{Fe}_2\text{O}_3\text{(s)} + 3\text{CuSO}_4\text{(s)}$$

This reaction has been verified quantitatively using laboratory experiments in the temperature range of 500-600°C. Such a reaction is more favourable at temperatures below the decomposition temperature (approximately 530°C), of ferric sulfate.

(b) Chalcopyrite

Razouk, Kolt et al. [100] have reported that the oxidation of chalcopyrite at temperatures below 400°C produces cuprous sulfide and ferric sulfate as follows:

$$2\text{CuFeS}_2\text{(s)} + 6\text{O}_2\text{(g)} = \text{Cu}_2\text{S}_\text{(s)} + \text{Fe}_2\text{(SO}_4\text{)}_3\text{(s)}$$

followed by sulfation of cuprous sulfide as expressed in equation 3.2-20. Frank M. Stephens, Jr. and others [1] have summarized the oxidation of chalcopyrite as follows:
CuFeS$_2$(s) + 15 O$_2$(g) + 4CuSO$_4$(s) + 2Fe$_2$O$_3$(s) + 4SO$_2$(g)  

3.2-25

with a roasting temperature of (670-710)°C.

(c) Covellite

Perriti [102] and Razouk et al. [100], have reported that the oxidation of covellite at temperatures as low as 150°C begins by conversion to cuprous sulfide:

$$2CuS(s) + O_2(g) = Cu_2S(s) + SO_2(g),$$  

3.2-26

followed by the conversion of Cu$_2$S to CuSO$_4$. However, at higher temperatures sulfation of covellite proceeds via oxide formation. Further reactions are similar to those for chalcocite.

Before going to the roasting of other sulfides, it is worthwhile to briefly say that as roasting temperatures approach 900°C copper ferrite may be formed. Since this is insoluble in water, lower copper recovery would result.

(2) Cobalt sulfate

Cobalt forms the following natural sulfide minerals:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>% Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linnaeite</td>
<td>Co$_3$S$_4$</td>
<td>57.96%</td>
</tr>
<tr>
<td>Cattierite</td>
<td>CoS$_2$</td>
<td>47.89%</td>
</tr>
</tbody>
</table>
In addition, there are other possible cobalt sulfides although they do not occur naturally:

$$\text{Co}_9\text{S}_8 \quad 67.40\% \text{ Co}$$

$$\text{Co}_4\text{S}_3 \quad 71.02\% \text{ Co}$$

In general, the general mechanism of sulfate formation applies to cobalt sulfate as well. However, T. R. Ingraham has reported the following decomposition sequence of cobalt sulfate:

$$\beta\text{CoSO}_4 = \alpha\text{CoSO}_4$$

This beta to alpha transition occurs at 948\(^\circ\)K. Then

$$\alpha\text{CoSO}_4 = \text{CoO} + \text{SO}_3(g)$$

occurs at 1218\(^\circ\)K. By cooling cobalt monoxide in presence of oxygen, tricobalt tetroxide is formed at 1100\(^\circ\)K.

$$3\text{CoO} + \frac{1}{2} \text{O}_2 = \text{Co}_3\text{O}_4$$

(3) Nickel sulfate

Nickel forms the following natural sulfide minerals:
Heazlewoodite. \( \text{Ni}_3\text{S}_2 \) 73.31% Ni
Vaesite. \( \text{NiS}_2 \) 47.80% Ni
Polydymite \( \text{Ni}_3\text{S}_4 \) 57.86% Ni
Millerite. \( \text{NiS} \) 64.68% Ni
Pentlandite. \((\text{NiFe})_9\text{S}_8\) 41.04% Ni

Another nickel sulfide mineral which does not occur naturally has the following formula:

\[ \text{Ni}_6\text{S}_5 \] 68.72% Ni

and is often found on stability diagrams but there is no mention in the literature of its existence as a mineral.

In general the chemical reactions involved in the roasting of copper sulfides can be extended to the roasting of nickel sulfides as well. However, there are certain peculiarities which deserve mention.

Fletcher and Jackson [25] and Pannetier [104] have found that roasting of nickel monosulfide above 700°C, proceeds via \( \text{Ni}_3\text{S}_2 \) as follows:

\[ 3\text{NiS(s)} + \text{O}_2(g) \rightarrow \text{Ni}_3\text{S}_2(s) + \text{SO}_2(g) \] 3.2-30

followed by oxidation to nickel oxide:

\[ 2\text{Ni}_3\text{S}_2(s) + 7 \text{O}_2(g) \rightarrow 6\text{NiO(s)} + 4\text{SO}_2(g) \] 3.2-31

and the nickel oxide is sulfated according to the following
equation:

\[ \text{NiO} \quad \text{(s)} + \text{SO} \quad \text{3(g)} = \text{NiSO} \quad \text{4(s)} \]

However, this is a simplified picture. Direct oxidation of the monosulfide to the oxide cannot be ruled out.

Pannetier et al. found that roasting of millerite and heazlewoodite, below 650°C, proceeds as follows:

\[ \text{Ni}_3\text{S}_2\quad \text{(s)} + \frac{1}{2} \text{O}_2\quad \text{(g)} \rightarrow \text{NiO} \quad \text{(s)} + 2\text{NiS} \quad \text{(s)} \]

Delafosse et al. [105] suggested that the above reaction occurs at 260°C. The nickel monosulfide is then oxidized to NiO which is subsequently sulfatized.

\[ \text{NiS} \quad \text{(s)} + \frac{3}{2} \text{O}_2\quad \text{(g)} \rightarrow \text{NiO} \quad \text{(s)} + \text{SO}_2\quad \text{(g)} \]

\[ \text{NiO} \quad \text{(s)} + \text{SO}_3\quad \text{(g)} \rightarrow \text{NiSO}_4\quad \text{(s)} \]

As has already been said sulfate roasting of cobalt and nickel sulfides does not involve any intermediate basic sulfates. However, they are attended by other problems as exemplified by problems encountered during roasting of nickel sulfides:

(i) Although NiSO\textsubscript{4} is stable below 700°C, the rate of oxidation of nickel sulfides (which is probably the first stage in sulfate roasting) is extremely slow [24,99]
(ii) The kernel roasting phenomenon.

(iii) As in the case of cobalt, nickel oxide tends to form nickel ferrite which is not readily sulfated.

\[ \text{NiO}_\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} = \text{NiO.Fe}_2\text{O}_3\text{(s)} \]  

In the roasting of cobalt and nickel sulfides, the sulfation of the oxides is the rate determining step because these oxides are more resistant to sulfation than other metallic oxides. This is confirmed by applying the Pilling-Bedworth ratio [106]. According to the latter, both cobalt and nickel sulfates should form protective coatings on their respective oxides because the molar volumes of the sulfates are greater than those of the corresponding oxides. In the case of cobalt, Hocking [22] has confirmed this using laboratory studies. Similarly Ingraham and Marrier [23] studied sulfation of NiO and arrived at the same conclusion.

For successful sulfation of cobalt and nickel sulfides, the following solutions have been proposed:

(a) Two stage roasting:

   (i) Oxidizing at higher temperatures

   (ii) Sulfate roasting of the calcine at lower temperatures

(b) The same operation as above but executing the two stages simultaneously by differential settling of the heavier unroasted sulfides into the hotter lower zone while sulfation
occurs in the upper, supposedly cooler, region.

(c) Addition of an alkali sulfate (usually 2-6 molar % \( \text{Na}_2\text{SO}_4 \)), to the sulfide feed, which promotes sulfation of these sulfides at temperatures where sulfates are stable.

(d) A combination of (a) and (b) by first roasting to the oxide and then adding the alkali sulfate to the hot calcine and sulfate roasting in the presence of sulfur dioxide and sulfur trioxide from the calcining step.

Only proposal (c) has been practised on an industrial scale. Several explanations have been evinced to account for the action of the alkali sulfates:

(i) That the alkali metals form double sulfates in combination with the base metals, which are more thermally stable than the base metal sulfates.

(ii) That the alkali sulfates destroy the ferrites [5], e.g.,

\[
\text{NiO.} \text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 = \text{Na}_2\text{Fe}_2\text{O}_4 + \text{NiSO}_4 \quad 3.2-37
\]

(iii) That the alkali sulfates act as sulfur trioxide gas carrier. Hotz and Ingraham [24] have explained the following postulate in the case of \( \text{Na}_2\text{SO}_4 \) as follows:

That sodium sulfate reacts with sulfur trioxide to form sodium pyrosulfate

\[
\text{Na}_2\text{SO}_4 + \text{SO}_3(g) = \text{Na}_2\text{S}_2\text{O}_7 \quad 3.2-38
\]

which melts at 401°C to form a mobile fluid with a low surface tension. It can penetrate the sulfate coating
and wet any mineral surface available. However, the above reaction is reversible thus regenerating sulfur trioxide, which, since it has been formed at the oxide surface, sulfates the oxide. In spite of these different theories, advanced to explain the role of the alkali sulfates in promoting sulfation of nickel and cobalt oxides, the latter has been unmistakably and experimentally demonstrated. Fletcher and Jackson [25] have also shown experimentally that the alkali sulfates catalyze the oxidation of sulfides to oxides besides promoting sulfation. Several alkali sulfates have been tested and their relative effects have been found to vary in the following order:

\[ \text{Li} > \text{Na} > \text{Cs} > \text{Rb} > \text{K} \]

(4) Pyrite

Tor Lindstand [107] has studied fluidized-bed roasting of flotation pyrite (i.e., pyrite concentrate produced by differential flotation and whose mineral composition was:

- 0.05 - 0.1 % Cu
- 0.2 - 0.4 % Zn
- 0.02 - 0.05 % Pb

with a gangue reduced to 3-5%)

He advanced the following mechanism to explain his observations:
\[
\text{FeS}_2(s) \rightarrow \text{FeS}(s) + \text{SO}_2(g) \quad \text{3.2-39}
\]
\[
3\text{FeS}(s) + 5\text{O}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s) + 3\text{SO}_2(g) \quad \text{3.2-40}
\]
\[
\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{SO}_3(g) \quad \text{3.2-41}
\]
\[
\text{Fe}_3\text{O}_4(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) \quad \text{3.2-42}
\]

Alcock and Curlook [27] have evinced a mechanism similar to this. They contend that if ferrous sulfide is roasted at temperatures around 873 °K, the formation of magnetite is accompanied by a weight gain initially. They explain this as being due to magnetite being formed by cationic iron which has migrated from the sulfide, leaving a sulfide enriched in anionic sulfur. Since the oxide forms a coating on the sulfide, then the weight gain is only due to the oxygen which combines with the iron. A critical point is reached and the oxide cracks followed by evolution of sulfur dioxide which escapes and causes a weight loss to the system. These authors, however, do not explain what causes the initiation of the formation of the ions; and the preferential outward migration of cations to anions. Other authors believe that ferrous sulfate is formed first and then breaks down to ferric oxide as follows:
\[
\text{FeS}_2(s) + 3 \text{O}_2(g) = \text{FeSO}_4(s) + \text{SO}_2(g) \quad 3.2-43
\]

\[
2\text{FeSO}_4(s) = \text{Fe}_2\text{O}_3(s) \text{SO}_2(g) + \text{SO}_3(g) \quad 3.2-44
\]

However, R. O. Thomas [13] used Fe$_2$O$_3$, as being derived from ferric sulfate, in constructing the control chart for sulfation roasting of sulfides. Therefore, it is possible that Fe$_2$O$_3$ may be formed by the decomposition of ferrous and ferric sulfates and by oxidation of pyrite.

### 3.3 Thermodynamic Analysis of Cu-,Co-,Ni-, Fe-S-O- Systems

This analysis involves the construction of phase diagrams and their superimposition to demarcate and determine the selective sulfation region and conditions pertaining to complex ores such as the concentrates from Kilembe Mine. Most of the thermodynamic data used was taken out of Barin's and Knacke's compilation of thermochemical data of inorganic substances. In this book, the elements are taken as the standard states and a zero enthalpy is assigned them to form the basis for calculating other thermodynamic functions. In addition, a roasting control diagram was constructed, together with equilibrium yield calculations, to theoretically determine the roasting conditions that produce the highest metal(s) recovery.
3.3.1 Co-, Cu-, Ni-, and Fe-S-O Phase Diagrams

Co-, Cu-, Ni-, and Fe-S-O systems are examples of ternary systems. The following phase rule properties can be identified:

(i) The number of components, \( C = 3 \)

(ii) The intensive variables consist of temperature, pressure and two composition concentrations which are required to specify the composition of any species in the system.

(iii) Since \( F = C + 2 - P \), where \( F \) is the degree of freedom and \( P \) is the number of phases, the maximum number of phases that can co-exist in equilibrium is five (four condensed phases and a gas phase) However, if the temperature is fixed, the phase rule assumes the following form: \( F = C + 1 - P \), implying that the maximum number of phases that can co-exist in equilibrium is four (three condensed phases and a gas phase)

Generally, the condensed species can be categorized as follows: Metal (M), Metal sulfide (MS), Metal oxide (MO), and a Metal sulfate (MSO₄). The gaseous species are \( S_2 \), \( SO_2 \), \( SO_3 \) and \( O_2 \). Therefore, the following equilibrium reactions can be established:

\[
S_2 + 2 \, O_2 \quad 3.3-1
\]

\[
SO_2 + 1/2 \, O_2 = SO_3 \quad 3.3-2
\]

Considering a roasting temperature range of 900-1000° K and fluidizing gas partial pressure range of 0.01-0.1 atm. of \( SO_2 \) and \( O_2 \), the presence of sulfur gas can be neglected because of small partial pressures it exhibits at 900° K
The formation of $\text{SO}_3$ is thermodynamically favoured at low temperatures. This is well illustrated by plotting $\log P_{\text{SO}_3}$ versus $\log P_{\text{O}_2}$, Fig. 3.3-1, at 900 and 1000° K. The data used for constructing this figure is shown in Table 3.3.1. The upper set of curves is constructed for $P_{\text{SO}_3} + P_{\text{SO}_2} + P_{\text{O}_2} = 1$ atm. whereas the lower set is constructed for $\text{SO}_3$, $\text{SO}_2$ and $\text{O}_2$ accounting for 20% of the total pressure (625 mm Hg). These curves have two distinct features:

(i) A broad maximum corresponding to different oxygen partial pressure ranges. It is to be noticed that this maximum corresponds to oxygen partial pressure (0.01-0.1 atm.) used during selective sulfation. This is particularly so for the two bottom curves which represent the conditions for the present investigation.

(ii) Each of the set of curves has an asymptote corresponding to conditions where oxygen would be present alone.

Knowledge of the partial pressures of any two of the gas components in the equilibria reaction 3.3-2, is enough to fix the gas phase composition. But for a fixed gas composition, the composition of the condensed phases is fixed as noted earlier by the phases rule requirements. Therefore the ternary system phase relations at constant temperature can be described using a two-dimensional diagram incorporating partial pressures of the gaseous components in a suitable form.

Such diagrams were first constructed by Sillen and
Fig. 3.3-1. Equilibrium $P_{SO_3}$ (atm) as a Function of $P_{O_2}$ (atm).
Table 3.3-1
Equilibrium Partial Pressures of SO₃ for Different O₂ Potentials at 900 and 1000 °K

\[
\text{PSO}_3 + \text{PSO}_2 + \text{PO}_2 = 1 \text{ atm.}
\]

\[
\text{log } K = \log \left( \frac{P_{\text{SO}_3}}{1-P_{\text{SO}_3}-P_{\text{O}_2}} \right) - \frac{1}{2} \log P_{\text{O}_2}
\]

<table>
<thead>
<tr>
<th>(-\log P_{\text{O}_2})</th>
<th>(T = 900^\circ\text{K})</th>
<th>(T = 1000^\circ\text{K})</th>
<th>(T = 900^\circ\text{K})</th>
<th>(T = 1000^\circ\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\log K = 0.810)</td>
<td>(\log K = 0.257)</td>
<td>(\log K = 0.81)</td>
<td>(\log K = 0.257)</td>
</tr>
<tr>
<td>0.10</td>
<td>0.756</td>
<td>0.807</td>
<td>0.756</td>
<td>0.807</td>
</tr>
<tr>
<td>0.25</td>
<td>0.440</td>
<td>0.488</td>
<td>0.440</td>
<td>0.488</td>
</tr>
<tr>
<td>0.40</td>
<td>0.316</td>
<td>0.343</td>
<td>0.316</td>
<td>0.343</td>
</tr>
<tr>
<td>0.50</td>
<td>0.271</td>
<td>0.283</td>
<td>0.271</td>
<td>0.283</td>
</tr>
<tr>
<td>0.60</td>
<td>0.243</td>
<td>0.255</td>
<td>0.243</td>
<td>0.255</td>
</tr>
<tr>
<td>0.75</td>
<td>0.221</td>
<td>0.232</td>
<td>0.221</td>
<td>0.232</td>
</tr>
<tr>
<td>0.80</td>
<td>0.218</td>
<td>0.227</td>
<td>0.218</td>
<td>0.227</td>
</tr>
<tr>
<td>0.90</td>
<td>0.216</td>
<td>0.224</td>
<td>0.216</td>
<td>0.224</td>
</tr>
<tr>
<td>1.00</td>
<td>0.219</td>
<td>0.225</td>
<td>0.219</td>
<td>0.225</td>
</tr>
<tr>
<td>1.10</td>
<td>0.226</td>
<td>0.230</td>
<td>0.226</td>
<td>0.230</td>
</tr>
<tr>
<td>1.20</td>
<td>0.237</td>
<td>0.236</td>
<td>0.237</td>
<td>0.236</td>
</tr>
<tr>
<td>1.30</td>
<td>0.251</td>
<td>0.251</td>
<td>0.251</td>
<td>0.251</td>
</tr>
<tr>
<td>1.40</td>
<td>0.267</td>
<td>0.267</td>
<td>0.267</td>
<td>0.267</td>
</tr>
<tr>
<td>1.50</td>
<td>0.286</td>
<td>0.286</td>
<td>0.286</td>
<td>0.286</td>
</tr>
<tr>
<td>1.60</td>
<td>0.307</td>
<td>0.307</td>
<td>0.307</td>
<td>0.307</td>
</tr>
<tr>
<td>1.70</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
<td>0.330</td>
</tr>
<tr>
<td>1.80</td>
<td>0.355</td>
<td>0.355</td>
<td>0.355</td>
<td>0.355</td>
</tr>
<tr>
<td>1.90</td>
<td>0.382</td>
<td>0.382</td>
<td>0.382</td>
<td>0.382</td>
</tr>
<tr>
<td>2.00</td>
<td>0.411</td>
<td>0.411</td>
<td>0.411</td>
<td>0.411</td>
</tr>
<tr>
<td>2.50</td>
<td>0.576</td>
<td>1.035</td>
<td>1.035</td>
<td>1.035</td>
</tr>
</tbody>
</table>

Note: The reaction considered is \(\text{SO}_2 + \frac{1}{2} \text{O}_2 = \text{SO}_3\).
Anderson for Ca-S-O and Mg-S-O systems [91] and more recently by Kellog and Basu [110] and Ingraham [12]. The interphase boundary lines are obtained using chemical equations expressed as follows:

\[
\begin{align*}
M + SO_2 & \quad \overset{K_1}{=} \quad MS + O_2 \\
2M + O_2 & \quad \overset{K_2}{=} \quad 2MO \\
2MS + 3O_2 & \quad \overset{K_3}{=} \quad 2MO + 2SO_2 \\
2MeO + 2SO_2 + O_2 & \quad \overset{K_4}{=} \quad 2MSO_4 \\
MS + 2O_2 & \quad \overset{K_5}{=} \quad MSO_4
\end{align*}
\]

Therefore by assuming that:

(i) The condensed phases are present in their pure standard states, i.e., their activities are unity. However, some minerals have variable chemical composition, e.g., pyrrhotite \((Fe^{1-x}S\) where \(x = 0-0.5\).) Such minerals will therefore not be in their standard states.

(ii) There is no solubility between the various phases. Deviations from this include solid solutions of FeS and Cu\(_2\)S in mixed sulfide ores, and ferrites of nickel and cobalt.

(iii) The gas activities can be equated to their fugacities which can also be equated to gas partial pressures. This is only true if the gases behave ideally [111], the following equilibria can be obtained:

\[
\log P_{SO_2} = \log P_{O_2} - \log K_1
\]
\[
\log P_{O_2} = -\log K_2 \quad 3.3-9
\]
\[
\log P_{SO_2} = -\frac{3}{2} \log P_{O_2} - \log K_3 \quad 3.3-10
\]
\[
\log P_{SO_2} = -\frac{1}{2} \log P_{O_2} - \log K_4 \quad 3.3-11
\]
\[
\log P_{O_2} = -\frac{1}{2} \log K_5 \quad 3.3-12
\]

From these expressions, it can be seen that all the metals with the same valency, have equal slopes for the corresponding interphase boundary lines. It is the equilibrium constant which changes according to the chemical reaction being considered at a given temperature, thus shifting the position of the equilibrium lines thereby determining the size of the phase stability fields. The equilibrium constants are obtained from the following free energy expression:

\[
\Delta G^o_R = -2.303 RT \log K \quad 3.3-13
\]

where

\[
\Delta G^o_R \quad \text{is computed from thermodynamic tables [20]}
\]

For a given phase, the system is bivariant, i.e., \( P_{SO_2} \) and \( P_{O_2} \) can be changed independently. But along the boundary lines, the system is univariant, i.e., \( P_{SO_2} \) and \( P_{O_2} \) cannot be independently changed. Finally, the system
is invariant where three boundary lines intersect.

Phase diagrams are useful for various predictions such as:

(i) Reaction mechanisms. For instance, it is thermodynamically impossible for direct sulfide sulfation to occur in a fluidized bed operating at high temperatures since it would involve $P_{SO_2}$ exceeding 1 atm. whereas the reactor is run at a 1 atm. total pressure. However, this mechanism is possible at lower temperatures and oxygen potentials as shown by Rosenqvist [21] in his log $P_{O_2}$ vs $1/T$ plots.

(ii) Selective sulfation conditions. This is a process which mainly aims at producing sulfates whose metallic values may be recovered by water or acid dissolution whereas the undesired metals are produced in insoluble forms. Selective sulfation conditions are obtained from superimposed individual metal phase diagrams. This is a close approximation of the behaviour of complex ores. However, this involves the gross assumption that M-M-S and M-M-O compounds and solid solutions are not present in the ore or may not be formed in the course of the reaction.

(1) Cu-S-O Phase Diagram

The condensed species are CuS, Cu$_2$S, Cu, Cu$_2$O, CuO, CuO.CuSO$_4$ and CuSO$_4$. All the possible equilibria along with logarithmic equilibria constant values evaluated at 900° K and 1000° K are listed in Table 3.3-2. These were used to construct the Cu-S-O phase diagrams shown in Figs. 3.3-2 and 3.3-3. It can be seen that as temperatures increase, there is a corresponding shift of the diagram to the right causing the stability of copper sulfate to require high sulfur dioxide and oxygen potentials.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1000^\circ K$</td>
<td>$900^\circ K$</td>
</tr>
<tr>
<td>$Cu(s) + 1/2 O_2(g) = CuO(s)$</td>
<td>3.469</td>
</tr>
<tr>
<td>$2Cu(s) + 1/2 O_2(g) = Cu_2O(s)$</td>
<td>5.013</td>
</tr>
<tr>
<td>$CuS(s) + O_2(g) = Cu(s) + SO_2(g)$</td>
<td>13.225</td>
</tr>
<tr>
<td>$CuS(s) + 3/2 O_2(g) = CuO(s) + SO_2(g)$</td>
<td>16.694</td>
</tr>
<tr>
<td>$2CuS(s) + 5/2 O_2(g) = Cu_2O(s) + 2SO_2(g)$</td>
<td>31.463</td>
</tr>
<tr>
<td>$2CuS(s) + 7/2 O_2(g) = CuO.CuSO_4(s)$</td>
<td>6.189</td>
</tr>
<tr>
<td>$CuS(s) + 2 O_2(g) = CuSO_4(s)$</td>
<td>18.772</td>
</tr>
<tr>
<td>$2CuS(s) + O_2(g) = Cu_2S(s) + SO_2(g)$</td>
<td>16.695</td>
</tr>
<tr>
<td>Reaction</td>
<td>log K 1000° K</td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
</tr>
<tr>
<td>Cu₂S(s) + O₂(g) = 2Cu(s) + SO₂(g)</td>
<td>9.755</td>
</tr>
<tr>
<td>Cu₂S(s) + 2 O₂(g) = 2CuO(s) + SO₂(g)</td>
<td>16.693</td>
</tr>
<tr>
<td>Cu₂S(s) + 3/2 O₂(g) = Cu₂O(s) + SO₂(g)</td>
<td>14.768</td>
</tr>
<tr>
<td>Cu₂S(s) + 3/2 O₂(g) = CuO·CuSO₄(s)</td>
<td>30.693</td>
</tr>
<tr>
<td>Cu₂S(s) + 3 O₂(g) = 2CuSO₄(s)</td>
<td>-20.848</td>
</tr>
<tr>
<td>2CuO(s) + SO₂(g) + 1/2 O₂(g) = CuO·CuSO₄(s)</td>
<td>2.466</td>
</tr>
<tr>
<td>CuO(s) + SO₂(g) + 1/2 O₂(g) = CuSO₄(s)</td>
<td>2.078</td>
</tr>
<tr>
<td>Cu₂O(s) + 1/2 O₂(g) = 2CuO(s)</td>
<td>1.925</td>
</tr>
<tr>
<td>Cu₂O(s) + O₂(g) + SO₂(g) = CuO·CuSO₄(s)</td>
<td>4.391</td>
</tr>
</tbody>
</table>
Table 3.3-2 - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000° K</td>
</tr>
<tr>
<td>$\text{Cu}_2\text{O} \ (s) + \frac{3}{2} \text{O}_2 \ (g) + 2\text{SO}_2 \ (g) = 2\text{CuSO}_4 \ (s)$</td>
<td>6.081</td>
</tr>
<tr>
<td>$\text{CuO.CuSO}_4 \ (s) + \text{SO}_2 \ (g) + \frac{1}{2} \text{O}_2 \ (g) = 2\text{CuSO}_4 \ (s)$</td>
<td>1.690</td>
</tr>
</tbody>
</table>
Fig. 3.3-2. Cu-S-O Stability Diagram at 900° K
Fig. 3.3-3: Cu-S-O Stability Diagram at 1000° K.
Direct sulfide sulfation would require high sulfur dioxide pressure in excess of 1 atm. thus this mechanism is not favourable at high temperatures. Considering the fluidizing temperature range and gas composition, sulfide sulfation would seem to follow the following sequence:

\[
\text{CuS} \rightarrow \text{Cu}_2\text{S} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO} \rightarrow \text{CuO}.\text{CuSO}_4 \rightarrow \text{CuSO}_4,
\]

with increasing oxygen partial pressures and sulfur dioxide partial pressures close to 50 mm Hg [1].

It is to be noticed that an attempt was made to construct a Cu-Fe-S-O phase diagram using the data recommended by Young [112]. The condensed species are chalcopyrite (CuFeS$_2$), bornite (Cu$_5$FeS$_4$) in addition to the others considered in the Cu-S-O system. Ferric oxide was considered as the iron condensed form since this is the iron form required in selective sulfation processes. The equilibria reactions are listed along with the log K values in Table 3.3-3. However, due to thermodynamic inconsistency, the attempt was abandoned.

(2) Co-S-O Phase Diagram

The principle condensed species in this system are: CoS$_2$, CoS, Co$_3$S$_4$, Co$_9$S$_8$, CoO, Co$_3$O$_4$. Co and CoSO$_4$. It is curious to find that CoS and Co$_3$S$_4$ have not been included on any previous phase diagrams [12] and yet they occupy well defined stability fields. There is no apparent
Table 3.3-3

Chemical Reactions and log K Values for Cu-Fe-S-O System at 1000° K

(Assuming that the only iron phase in equilibrium with chalcopyrite and bornite is ferric oxide)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 11/2 \text{O}_2\text{(g)} = 2\text{Cu}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 4\text{SO}_2\text{(g)})</td>
<td>76.213 (20)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 9/2 \text{O}_2\text{(g)} = \text{Cu}_2\text{S}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 3\text{SO}_2\text{(g)})</td>
<td>72.546 (21)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 7/2 \text{O}_2\text{(g)} = 2\text{CuS}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 2\text{SO}_2\text{(g)})</td>
<td>49.763 (22)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 6 \text{O}_2\text{(g)} = \text{Cu}_2\text{O}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 4\text{SO}_2\text{(g)})</td>
<td>51.850 (23)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 13/2 \text{O}_2\text{(g)} = 2\text{CuO}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 4\text{SO}_2\text{(g)})</td>
<td>83.151 (24)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 7 \text{O}_2\text{(g)} = \text{CuO}.\text{CuSO}_4\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 3\text{SO}_2\text{(g)})</td>
<td>40.356 (25)</td>
</tr>
<tr>
<td>(2\text{CuFeS}_2\text{(s)} + 15/2 \text{O}_2\text{(g)} = 2\text{CuSO}_4\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 2\text{SO}_2\text{(g)})</td>
<td>87.307 (26)</td>
</tr>
<tr>
<td>(2\text{Cu}_5\text{FeS}_4\text{(s)} + 19/2 \text{O}_2\text{(g)} = 10 \text{Cu}\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} + 8\text{SO}_2\text{(g)})</td>
<td>145.888 (27)</td>
</tr>
</tbody>
</table>
Table 3.3-3 - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2Cu_5FeS_4(s) + 15/2 O_2(s) = 5Cu_2S(s) + Fe_2O_3(s) + 6SO_2(g)$</td>
<td>173.815</td>
</tr>
<tr>
<td>$2Cu_5FeS_4(s) + 2SO_2(g) = 10 CuS(s) + 1/2 O_2(g) + Fe_2O_3(s)$</td>
<td>14.637</td>
</tr>
<tr>
<td>$2Cu_5FeS_4(s) + 12 O_2(g) = 5CuO(s) + Fe_2O_3(s) + 8SO_2(g)$</td>
<td>171.951</td>
</tr>
<tr>
<td>$2Cu_5FeS_4(s) + 29/2 O_2(g) = 10 CuO(s) + Fe_2O_3(s) + 8SO_2(g)$</td>
<td>181.575</td>
</tr>
<tr>
<td>$2Cu_5FeS_4(s) + 17 O_2(g) = 5CuO.CuSO_4(s) + Fe_2O_3(s) + 3SO_2(g)$</td>
<td>193.905</td>
</tr>
<tr>
<td>$2Cu_5FeS_4(s) + 3SO_2(g) + 39/2 O_2 = 10 CuSO_4(s) + Fe_2O_3(s)$</td>
<td>202.988</td>
</tr>
<tr>
<td>$5CuFeS_2(s) + 9 O_2(g) = Cu_5FeS_4(s) + 2Fe_2O_3(s) + 6SO_2(g)$</td>
<td>113.907</td>
</tr>
</tbody>
</table>
explanation for this since these investigators used the same data for sulfide equilibria [113,119] as used in this analysis.

All the equilibria considered and the log K values are shown in Table 3.3-4. These were used to construct the appropriate phase diagrams shown in Figs. 3.3-4 and 3.3-5. The same reasons used in section (1) are used to discredit the direct sulfide sulfation mechanism. The following reaction sequence leading to sulfate formation may be recognized:

\[
\text{CoS}_2 \rightarrow \text{CoS} \rightarrow \text{Co}_3\text{S}_4 \rightarrow \text{CoO} \rightarrow \text{CoSO}_4. 
\]

At \(P_{\text{SO}_2}\) less than 50 mm Hg and higher oxygen potentials, tricobalt tetroxide may be included prior to sulfate formation. It is also interesting to realize that although \(\text{Co}_3\text{S}_3\) is in the same category (cobalt sulfides which do not occur naturally) as \(\text{Co}_9\text{S}_8\), it does not appear on the diagram due to thermodynamic inconsistencies. Due to lack of data carrollite (\(\text{CoCuS}_4\)) was not included on the phase diagram.

(3) Ni-S-O Phase Diagram

NiS, \(\text{Ni}_3\text{S}_2\), Ni, NiO and NiSO\(_4\) species are the principle species in this system. Table 3.3-5 shows the various equilibria considered in the construction of the required phase diagrams (Figs. 3.3-6 and 3.3-7) at 900° K.
### Table 3.3-4

Chemical Reactions and log K Values for Co-O-S System at 900 and 1000° K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>900° K</th>
<th>1000° K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 8 \text{O}_2(g) = 9\text{Co}(s) + 8\text{SO}_2(g) )</td>
<td>105.356</td>
<td>96.228</td>
<td>86.228</td>
</tr>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 17 \text{O}_2(g) + \text{SO}_2(g) = 9\text{Co}_3\text{S}_4(s) + \text{S}_2 )</td>
<td>228.163</td>
<td>190.604</td>
<td>163.366</td>
</tr>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 25/2 \text{O}_2(g) = 9\text{Co}_3\text{O}_4(s) + 8\text{S}_2 )</td>
<td>184.724</td>
<td>160.002</td>
<td>166.002</td>
</tr>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 14 \text{O}_2(g) = 3\text{Co}_3\text{O}_4(s) + \text{O}_2(g) )</td>
<td>190.791</td>
<td>-11.860</td>
<td>-143.338</td>
</tr>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 24 \text{SO}_2(g) = 3\text{Co}_3\text{S}_4(s) + 10\text{O}_2(g) )</td>
<td>-59.555</td>
<td>-52.651</td>
<td>-143.338</td>
</tr>
<tr>
<td>( \text{Co}_9\text{S}_8(s) + 10 \text{SO}_2(g) = 3\text{Co}_3\text{S}_4(s) + 4\text{O}_2(g) )</td>
<td>-158.207</td>
<td>46.293</td>
<td>51.304</td>
</tr>
<tr>
<td>Reaction</td>
<td>log K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>--------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{S}_4\text(s)} + 7 \text{O}_2\text(g) = 3\text{CoSO}_4\text(s)} + \text{SO}_2\text(g)$</td>
<td>81.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{S}_4\text(s)} + \frac{11}{2} \text{O}_2\text(g) = 3\text{CoO}_4\text(s)} + 4\text{SO}_2\text(g)$</td>
<td>72.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{S}_4\text(s)} + 6 \text{O}_2\text(g) = \text{Co}_3\text{O}_4\text(s)} + 4\text{SO}_2\text(g)$</td>
<td>72.884</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{S}_4\text(s)} + \text{O}_2\text(g) = 3\text{CoS}_4\text(s)} + \text{SO}_2\text(g)$</td>
<td>13.597</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{S}_4\text(s)} + 2\text{SO}_2\text(g) = 3\text{CoS}_2\text(s)} + 2 \text{O}_2\text(g)$</td>
<td>-30.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CoS}_2\text(s)} + 3 \text{O}_2\text(g) =\text{CoSO}_4\text(s)} + \text{SO}_2\text(g)$</td>
<td>25.507</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CoS}_2\text(s)} + 3 \text{O}_2\text(g) = \text{CoSO}_4\text(s)} + \text{SO}_2\text(g)$</td>
<td>37.107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CoS}_2\text(s)} + \frac{5}{2} \text{O}_2\text(g) = \text{CoO}_4\text(s)} + 2\text{SO}_2\text(g)$</td>
<td>34.078</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3\text{CoS}_2\text(s)} + 8 \text{O}_2\text(g) = \text{Co}_3\text{O}_4\text(s)} + 6\text{SO}_2\text(g)$</td>
<td>103.113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>10000° K</td>
<td>900° K</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2(s) + O_2(g) = \text{CO}_3(s) + \text{SO}_2(g)$</td>
<td>14.609</td>
<td>16.047</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3(s) + 2O_2(g) = \text{CO}_5(s) + \text{SO}_2(g)$</td>
<td>10.899</td>
<td>12.127</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_5(s) + 3/2O_2(g) = \text{CO}_3O_4(s) + \text{SO}_2(g)$</td>
<td>22.496</td>
<td>26.883</td>
<td></td>
</tr>
<tr>
<td>$3\text{CO}_3(s) + 5O_2(g) = 3\text{CO}_3O_4(s) + 3\text{SO}_2(g)$</td>
<td>19.470</td>
<td>22.057</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3O_4(s) + \text{SO}_2(g) + 1/2O_2 = \text{CO}_5(s) + \text{CO}_3(s)$</td>
<td>59.287</td>
<td>68.192</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_5(s) + \text{SO}_2(g) + O_2(g) = 3\text{CO}_3O_4(s)$</td>
<td>3.026</td>
<td>4.826</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_5(s) + 1/2O_2(g) = \text{CO}_3(s)$</td>
<td>8.201</td>
<td>12.457</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3O_4(s)$</td>
<td>11.597</td>
<td>14.756</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3(s)$</td>
<td>8.571</td>
<td>9.930</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.3-4 - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[ \log K ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000° K</td>
</tr>
<tr>
<td>(3\text{Co}_3\text{O}_4(s)) + (2\text{O}_2(g)) = (\text{Co}_3\text{O}_4(s))</td>
<td>26.591</td>
</tr>
<tr>
<td>(3\text{CoO}_3(s) + 1/2 \text{O}_2(g) = \text{Co}_3\text{O}_4(s))</td>
<td>0.879</td>
</tr>
<tr>
<td>(4\text{Co}_3\text{S}_8(s) + 5 \text{O}_2(g) = 9\text{Co}_3\text{S}_3(s) + 5\text{SO}(g))</td>
<td>51.473</td>
</tr>
<tr>
<td>(3\text{Co}_4\text{S}_3(s) + 7\text{SO}_2(g) = 4\text{Co}_3\text{S}_4(s) + 7\text{O}_2(g))</td>
<td>-87.359</td>
</tr>
<tr>
<td>(\text{Co}_4\text{S}_3(s) + 5\text{SO}_2(g) = 4\text{CoS}_2(s) + 5\text{O}_2(g))</td>
<td>-69.425</td>
</tr>
<tr>
<td>(\text{Co}_4\text{S}_3(s) + \text{SO}_2(g) = 4\text{CoS}(s) + \text{O}_2(g))</td>
<td>-10.991</td>
</tr>
<tr>
<td>(3\text{Co}_4\text{S}_3(s) + 17\text{O}_2(g) = 4\text{Co}_3\text{O}_4(s) + 9\text{SO}_2(g))</td>
<td>337.136</td>
</tr>
<tr>
<td>(\text{Co}_4\text{S}_3(s) + 5\text{O}_2(g) = 4\text{CoO}(s) + 3\text{SO}_2(g))</td>
<td>66.888</td>
</tr>
<tr>
<td>(\text{Co}_4\text{S}_3(s) + 3\text{O}_2(g) = 4\text{Co}(s) + 3\text{SO}_2(g))</td>
<td>32.604</td>
</tr>
</tbody>
</table>
Table 3.3-4 - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000° K</td>
</tr>
<tr>
<td>( \text{Co}_4\text{S}_3(\text{s}) + \text{SO}_2(\text{g}) + 7 \text{O}_2(\text{g}) = 4\text{CoSO}_4(\text{s}) )</td>
<td>78.994</td>
</tr>
</tbody>
</table>
Fig. 3.3-4. Co-S-O Stability Diagram at 900° K.
Fig. 3.3-5. Co-S-O Stability Diagram at 1000° K.
Table 3.3-5
Chemical Reactions and log K Values for Ni-O-S System at 900 and 1000° K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000° K</td>
</tr>
<tr>
<td>$\text{Ni}_3\text{S}_2(\text{s}) + 2 \text{O}_2 = 3\text{Ni}(\text{s}) + 2\text{SO}_2(\text{g})$</td>
<td>22.210</td>
</tr>
<tr>
<td>$\text{Ni}_3\text{S}_2(\text{s}) + \text{SO}_2(\text{g}) + 5 \text{O}_2(\text{g}) = 3\text{NiSO}_4(\text{s})$</td>
<td>57.734</td>
</tr>
<tr>
<td>$\text{Ni}_3\text{S}_2(\text{s}) + 7/2 \text{O}_2(\text{g}) = 3\text{NiO}(\text{s}) + 2\text{SO}_2(\text{g})$</td>
<td>45.745</td>
</tr>
<tr>
<td>$\text{Ni}_3\text{S}_2(\text{s}) + \text{SO}_2(\text{g}) = 3\text{NiS}(\text{s}) + \text{O}_2(\text{g})$</td>
<td>-11.397</td>
</tr>
<tr>
<td>$\text{NiS}(\text{s}) + \text{O}_2(\text{g}) = \text{Ni}(\text{s}) + \text{SO}_2(\text{g})$</td>
<td>11.202</td>
</tr>
<tr>
<td>$\text{NiS}(\text{s}) + 2 \text{O}_2(\text{g}) = \text{NiSO}_4(\text{s})$</td>
<td>23.044</td>
</tr>
<tr>
<td>$\text{NiS}(\text{s}) + 3/2 \text{O}_2(\text{g}) = \text{NiO}(\text{s}) + \text{SO}_2(\text{g})$</td>
<td>19.047</td>
</tr>
<tr>
<td>$\text{Ni}(\text{s}) + \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) = \text{NiSO}_4(\text{s})$</td>
<td>11.841</td>
</tr>
<tr>
<td>Reaction</td>
<td>log K</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td><strong>Ni(s) + 1/2 O_2(g) = NiO(s)</strong></td>
<td>7.845, 9.216 (9)</td>
</tr>
<tr>
<td><strong>NiO(s) + SO_2(g) + 1/2 O_2(g) = NiSO_4(s)</strong></td>
<td>3.996, 5.909 (10)</td>
</tr>
</tbody>
</table>
Fig. 3.3-6. Ni-S-O Stability Diagram at 900° K.
Fig. 3.3-7. Ni-S-O Stability Diagram at 1000° K.
and $1000^\circ$ K. The following conclusions illustrate the usefulness of these phase diagrams:

(a) NiO is the only oxide of nickel that can co-exist in equilibrium with NiSO$_4$.

(b) NiS-NiSO$_4$ equilibrium can occur only at P$_{SO_2}$ exceeding 1 atm.

(c) The possibility of NiS being converted to Ni$_3$S$_2$ before oxidation requires extremely low sulfur dioxide partial pressures. Thus the sulfation of NiS would seem to follow the following sequence:

$$\text{NiS} \rightarrow \text{NiO} \rightarrow \text{NiSO}_4.$$  

Vaesite (Ni$_2$S), polydymite (Ni$_3$S$_4$), pentlandite ((Ni,Fe)$_9$S$_8$) and Ni$_6$S$_5$ are not included on the phase diagrams due to lack of suitable thermodynamic data.

(4) Fe-S-O Phase Diagram

The principle condensed species are FeS$_2$, FeS, Fe, FeO, Fe$_3$O$_4$, Fe$_2$O$_3$, FeSO$_4$ and Fe(SO$_4$)$_3$. The various equilibria reactions considered are illustrated in Table 3.3-6 and the phase diagrams at 900$^\circ$ K and 1000$^\circ$ K are presented in Figs. 3.3-8 and 3.3-9.

These phase diagrams are markedly different from those previously reported by earlier investigators [12,21]. The following differences can be observed:

(a) Ferrous sulfate was not included on the previous diagrams. Perhaps this was due to lack of reliable thermodynamic data. However, Skeaff and Espelund data [19], having been found consistent with well established thermodynamic data of known species, was used in
Table 3.3-6
Chemical Reactions and log K Values for Fe-O-S System at 900 and 1000° K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000° K</td>
<td>900° K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>1000° K</th>
<th>900° K</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS₂(s) + 2 O₂(g) = Fe(s) + 2SO₂(g)</td>
<td>24.560</td>
<td>(1)</td>
</tr>
<tr>
<td>FeS₂(s) + O₂(g) = FeS(s) + SO₂(g)</td>
<td>14.637</td>
<td>15.847</td>
</tr>
<tr>
<td>FeS₂(s) + 5/2 O₂(g) = FeO(s) + 2SO₂(g)</td>
<td>35.386</td>
<td>(3)</td>
</tr>
<tr>
<td>2FeS₂(s) + 11/2 O₂(g) = Fe₂O₃(s) + 4SO₂(g)</td>
<td>78.496</td>
<td>(4)</td>
</tr>
<tr>
<td>3FeS₂(s) + 8 O₂(g) = Fe₃O₄(s) + 6SO₂(g)</td>
<td>115.010</td>
<td>128.680</td>
</tr>
<tr>
<td>2FeS₂(s) + 7 O₂(g) = Fe₂(SO₄)₃(s) + SO₂(g)</td>
<td>80.769</td>
<td>95.298</td>
</tr>
<tr>
<td>FeS(s) + O₂(g) = Fe(s) + SO₂(g)</td>
<td>9.923</td>
<td>11.162</td>
</tr>
<tr>
<td>FeS(s) + 3/2 O₂(g) = FeO(s) + SO₂(g)</td>
<td>20.748</td>
<td>23.543</td>
</tr>
</tbody>
</table>
Table 3.3-6 - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \log K )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 1000^\circ K )</td>
</tr>
<tr>
<td>( 2FeS(s) + 7/2O_2(g) = Fe_2O_3(s) + 2SO_2(g) )</td>
<td>49.221</td>
</tr>
<tr>
<td>( 3FeS(s) + 5O_2(s) = Fe_3O_4(s) + 3SO_2(g) )</td>
<td>71.097</td>
</tr>
<tr>
<td>( 2FeS(s) + SO_2(g) + 5O_2(g) = Fe_2(SO_4)_3(s) )</td>
<td>51.494</td>
</tr>
<tr>
<td>( 2FeO(s) + 1/2O_2(g) = Fe_2O_3(s) )</td>
<td>7.725</td>
</tr>
<tr>
<td>( 3FeO(s) + 1/2O_2(g) = Fe_3O_4(s) )</td>
<td>8.853</td>
</tr>
<tr>
<td>( 2FeO(s) + 3SO_2(g) + 2O_2(g) = Fe_2(SO_4)_3(s) )</td>
<td>9.998</td>
</tr>
<tr>
<td>( 3Fe_2O_3(s) = 2Fe_3O_4(s) + 1/2O_2(g) )</td>
<td>-5.470</td>
</tr>
<tr>
<td>( Fe_2O_3(s) + 3SO_2(g) + 3/2O_2(g) = Fe_2(SO_4)_3 )</td>
<td>2.417</td>
</tr>
<tr>
<td>( 2Fe(s) + 3SO_2(g) + 3O_2(g) = Fe_2(SO_4)_3(s) )</td>
<td>31.648</td>
</tr>
<tr>
<td>Reaction</td>
<td>log K</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>$\text{Fe(s)} + \frac{1}{2} \text{O}_2(g) = \text{FeO}(s)$</td>
<td>10.825, 12.381 (18)</td>
</tr>
<tr>
<td>$2\text{Fe(s)} + \frac{3}{2} \text{O}_2(g) = \text{Fe}_2\text{O}_3(s)$</td>
<td>29.375, 29.382 (19)</td>
</tr>
<tr>
<td>$3\text{Fe(s)} + 2 \text{O}_2(g) = \text{Fe}_3\text{O}_4(s)$</td>
<td>41.328, 41.350 (20)</td>
</tr>
<tr>
<td>$2\text{FeSO}_4(s) = \text{Fe}_2\text{O}_3(s) + \frac{1}{2} \text{O}_2(g) + 2\text{SO}_2(g)$</td>
<td>-0.118, 2.479 (21)</td>
</tr>
<tr>
<td>$3\text{FeSO}_4(s) = \text{Fe}_3\text{O}_4(s) + \text{O}_2(g) + 3\text{SO}_2(g)$</td>
<td>2.912, 7.159 (22)</td>
</tr>
<tr>
<td>$\text{FeS}_2(s) + 3 \text{O}_3(g) = \text{FeSO}_4(s) + \text{SO}_2(g)$</td>
<td>39.307, 45.280 (23)</td>
</tr>
<tr>
<td>$\text{Fe}_2(\text{SO}_4)_3(s) + 2\text{FeSO}_4(s) + \text{SO}_2(g) + \text{O}_2(g)$</td>
<td>2.299, 4.595 (24)</td>
</tr>
</tbody>
</table>
Fig. 3.3.8. Fe-S-O Stability Diagram at 900° K.
Fig. 3.3-9. Fe-S-O Stability Diagram at 1000° K.
conjunction with the data available in Barin and Knacke's book [20] to construct the phase diagram of Fe-S-O system.

(b) The phase diagram constructed by Rosenqvist [21] shows an interphase equilibria between FeS and FeSO$_4$ species. However, this vertical interphase requires oxygen potentials less than $10^{-2.5}$ at 900° K. Thus its possibility is very doubtful.

(c) At elevated temperatures ferrous sulfate stability field shrinks in size but it nevertheless exists under more oxidizing conditions, as temperatures increase -- contrary to Kellogg's [17] contention that it probably exists under reducing conditions. Thus the possibility of FeSO$_4$ being in the roast products cannot be ruled out completely.

(d) Ferric oxide is the only iron oxide that can possibly be in equilibrium with the iron sulfates in roast products since magnetite does not form a stable equilibrium with ferric sulfate and its equilibrium with ferrous sulfate requires sulfur dioxide partial pressures exceeding 1 atm.

(e) The roasting of pyrite under fluidizing conditions may probably follow the following sequence:

$$\text{FeS}_2 \rightarrow \text{FeS} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3.$$ 

Thus sulfur gas may be produced if the oxygen potentials are extremely low due to other oxygen consuming species, i.e., carbonaceous matter and high pyrite content in the ore.

All the phase diagrams hitherto considered were superimposed in order to locate the "selective sulfation region" as shown in Figs. 3.3-10 and 3.3-11. This region coincides with the sulfate and ferric oxide stability fields. This was enlarged and points of equilibrium
Fig. 3.3-10. Co-, Ni-, Cu & Fe-S-O Stability Diagram at 900° K.
(Shaded region shows selective sulfation region)
Fig. 3.3-11. Co-, Ni-, Cu & Fe-S-O Stability Diagram at 1000° K.  (Shaded region shows selectivsulfation region)
composition were plotted on it at the ambient pressure of 625 mm Hg. (Figs. 3.3-12 and 3.3-13) Superimposition of the last two figures followed by projections enabled deductions of the roasting conditions at 950 \(^\circ\) K as shown in Fig. 3.3-14. The projection was made assuming straight line behaviour of the free energy function of the species concerned at high temperatures as deduced by Ellingham [21] Such assumption is possible if there is no phase change of these species in the temperature range being considered.

3.3.2 Selective Sulfation Temperature - Gas Composition Control Diagram

Generally, sulfation reaction can be represented by the following reaction:

$$\text{MO}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{MSO}_4(s)$$

Therefore,

$$\log P_{\text{SO}_2} P_{\text{O}_2}^{1/2} = \frac{\Delta G^\circ}{R} / 2.303 \text{ RT.}$$

Thus, knowing the change in the standard free energy of this reaction as a function of temperature, \(\log P_{\text{SO}_2} P_{\text{O}_2}^{1/2}\) can be plotted versus the roasting temperatures for different metal sulfates.

On such plots, it is possible to superimpose operating curves (Fig. 3.3-15) which relate the logarithm
Fig. 3.3-12. Selective Sulfation Equilibria at 900° K.

- FeSO₄
- Cu₂O
- CuO
- Cu₂CuSO₄
- CuOCl₂
- Cu₂O₃
- CuSO₄
- NiSO₄
- NO

K = KELLOG DATA
Fig. 3.3-13. Selective Sulfation Equilibria at \( 1000^\circ \) K.
Fig. 3.3-15. Selective Sulfation Temperature - Gas Composition Control Diagram
to the base ten of the fluidizing sulfating gases to excess fluidizing gas ratio (a multiple of the stoichiometric fluidizing gas requirement obtained by assuming complete conversion to sulfates) Such curves can be drawn for zero sulfur dioxide addition but since log $P_{SO_2}$ attains low values compared to the value of the equilibrium constant at the temperature of interest, the temperature rise can be quite high [13,123] in this section of the reactor, sulfate decomposition can be prevented by adding sulfur dioxide to the fluidizing gas. Thus the basic operating curve can be modified accordingly (not shown) The modified curves would appear on the left hand side of the basic curve.

To obtain the operating curve, stoichiometric calculations were performed for the following reactions:

$$Co + SO_2 + O_2 = CoSO_4$$  \[3.3-16\]

$$Ni + SO_2 + O_2 = NiSO_4$$  \[3.3-17\]

$$2Fe + 3/2 O_2 = Fe_2O_3$$  \[3.3-18\]

$$Cu + SO_2 + O_2 = CuSO_4$$  \[3.3-19\]

$$Ca + SO_2 + O_2 = CaSO_4$$  \[3.3-20\]

$$S + O_2 = SO_2$$  \[3.3-21\]
\[ C + O_2 = CO_2 \] 3.3-22

The above elements were considered to be the major oxygen consumers since most of them have the highest assays (Table 4.2-2 and 4.2-3) and also constitute the major part of this investigation. Using the experimental assays of the elements shown in reactions 3.3-16 to 3.3-22, and assuming complete conversion to sulfates, sulfur dioxide and carbon dioxide respectively, it was found (Appendix that 2.5 moles of oxygen would be consumed whereas 0.81 moles of sulfur dioxide would be produced. Furthermore, assuming a fluidizing gas consisting of 21% oxygen and 78% nitrogen, the total volume of the gas required to effect this complete sulfate conversion was calculated to be 350 liters. If the reactor is closed to the atmosphere and if the fluidizing gas is shut off after supplying 350 liters of gas, for oxygen efficiency equal to 100%, the effluent gas analysis for different fluidizing gas ratios would be as follows:

<table>
<thead>
<tr>
<th>Excess gas ratio</th>
<th>% SO₂</th>
<th>% O₂</th>
<th>log ( P_{SO₂} \cdot P_{O₂}^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>8.02</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1.1</td>
<td>7.19</td>
<td>2.22</td>
<td>-2.10</td>
</tr>
<tr>
<td>1.2</td>
<td>6.51</td>
<td>4.02</td>
<td>-2.01</td>
</tr>
<tr>
<td>1.3</td>
<td>5.94</td>
<td>5.50</td>
<td>-1.98</td>
</tr>
<tr>
<td>1.4</td>
<td>5.47</td>
<td>6.75</td>
<td>-1.97</td>
</tr>
<tr>
<td>1.5</td>
<td>5.07</td>
<td>7.82</td>
<td>-1.98</td>
</tr>
</tbody>
</table>
From the above tabulation, if no excess gas is used, the oxygen potential would be zero but stability diagrams show that the sulfates would be unstable under such conditions. Hence the use of excess fluidizing gas, the practical limit of which is 1.3 since the operating curve assumes a vertical position after this value. The corresponding gas flow rate is 451 liters containing 3.24 moles of oxygen. Thus knowing a gas composition suitable for selective sulfation and assuming some reaction time, a suitable gas flow rate can be estimated. For instance, for 10% SO$_2$, 10% O$_2$ and 80% N$_2$, the approximate flow rates of 395 mls min.$^{-1}$ of SO$_2$ and O$_2$ and 3150 mls min.$^{-1}$ of N$_2$ would be required over a period of 4 hrs. at 625 mm Hg and 293° K. A final adjustment of this flow rate would be made using a Schytil diagram such as Fig. 3.1-2, constructed for the appropriate temperature and gas composition, and visual observation of the quality of fluidization produced when the bed is subjected to such gas flow.

The selective sulfation temperature - gas composition control diagram offers an excellent means of adjusting the gas composition in such a way that the required sulfates can be stable over a large range of temperatures. This is useful in reactors which have poor temperature control devices.

From equilibrium considerations, the sulfates are stable if $\log \frac{P_{SO_2}}{P_{O_2}}^{1/2}$ exceeds $\Delta G^\circ_R / 2.303 RT$. Therefore,
they are stable in the region to the left of the roasting equilibrium lines (Fig. 3.3-15). Thus a \( \log P_{SO_2} P_{O_2}^{1/2} \) value which is less than -2.5 will stabilize \( CuSO_4 \), \( CoSO_4 \) and \( NiSO_4 \) above 900°K whereas ferric sulfate will be unstable under such roasting conditions. In fact the maximum temperature to which the respective sulfates can be stabilized can be deduced from the intersections of the vertical lines, which represent different \( SO_2 \) additions, and the various sulfate equilibria lines. Line L (\( \log P_{SO_2} P_{O_2}^{1/2} = -2.5 \)) and M (\( \log P_{SO_2} P_{O_2}^{1/2} = -3.0 \)) are good demonstrations of this contention, as shown below:

<table>
<thead>
<tr>
<th>Line</th>
<th>Maximum Stability Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( CuSO_4 )</td>
</tr>
<tr>
<td>L</td>
<td>950</td>
</tr>
<tr>
<td>M</td>
<td>923</td>
</tr>
</tbody>
</table>

Finally, the accuracy of the predictions from this diagram will be limited by how a given metal compound behaves in presence of others since this diagram is drawn neglecting ionic interactions. Nevertheless, this control diagram demonstrates that it is erroneous to report experimental sulfate decomposition temperatures without specifying the gas composition. Thus most of the previous literature has insufficient information regarding sulfate decomposition temperatures.
CHAPTER 4 EXPERIMENTAL

Experimental work consisted of sample preparation, fluidized-bed roasting and analysis of the calcine to quantitatively measure the success of the selective sulfate roasting process. Therefore, this chapter will be described under four headings:

4.1 Apparatus
4.2 Sample Preparation
4.3 Procedure
4.4 Results
4.5 Interpretation
4.6 Experimental Limitations

4.1 Apparatus

The apparatus used in this investigation can be divided into three major groups:

(a) the apparatus used during sample preparation
(b) the apparatus used during roasting, and
(c) the apparatus involved in leaching the calcine and subsequent solution analysis.
The apparatus involved in part (a) is outlined in the sample preparation section and APPENDICES 8 (Fig. 4.1-3) and 10 (Fig. 4.1-4). Also the apparatus in (c) is referred to in the section on procedure while the apparatus used in roasting is presented in Fig. 4.1-1. It consisted of three units: the fluidizing gas mixture, the fluidized-bed reactor and the gas chromatograph.

4.1.1 Fluidizing Gas Mixture (1)*

The fluidizing gas mixture was obtained from cylinders of commercially pure nitrogen (I.C.C. - 3A A2 400 T 152459), oxygen (A201 K 619293) and sulfur dioxide (Dot - 4B A300 SD 179) Gas pressure regulators on each cylinder were used to reduce the pressure to an outlet pressure of about 10 psig. The outlet from each regulator was connected through Wallace Tiernan "Varea-meter glass-tube type" flow meters (2)* The outlets of the flow meters were connected to a mixing cross (3)* (The flow meters were calibrated using a constant volume/pressure-transducer, flow measuring device.)

4.1.2 Fluidized-bed Reactor Unit

This consisted of a fluidized-bed reactor, a furnace, temperature controller and temperature recorder.

(a) Fluidized-bed reactor (4)*. It was constructed using a 1 1/2 in. I.D 304 s.s. tube welded to the frustrum of a hollow cone whose smaller diameter was 5/8 in.

(Note: numbers marked with an asterisk refer to Fig. 4.1-1)
Fig. 4.1-1. Experimental Apparatus (Schematic)
A 5/8 in. O.D. stainless steel pipe with a gas distributor plate was welded into the cone so that the gas distributor consisted of 9 - 1/16 in. gas inlet holes - 5 located on top of the plate (one central hole surrounded by four other holes equidistant from the center and spaced equiangularly) and the remaining 4 holes on the outer surface of the 5/8 in. diameter pipe, just below the distributor plate. A type K (chromel-alumel) thermocouple was fastened to the outer surface of the conical section of the reactor. A strip chart recorder (8)* was used to monitor the output from the thermocouple.

(b) The furnace. This consisted of a vertically mounted electrical, tube furnace with a type K control thermocouple (10)* situated close to the winding of the furnace, and was used for heating the fluidized-bed reactor.

(c) Temperature control system (7)*. This consisted of a variac for adjusting the supply voltage to the furnace and a rheostat for shunting the current to the furnace. The Honeywell temperature controller was used in conjunction with an auxiliary relay to obtain a "high-low" control action.

4.1.3 The Gas Chromatograph Unit

The gas chromatograph unit used in this investigation consisted of the following components:
(1) Carle analytical gas chromatograph, Model 311 (GC)

(2) Omni-Scribe recorder (CR)

(3) Autolab System I Computer Integrator (A)

(4) Chromatograph process controller, CDS Model 100 (PC)

(5) A sampling pump and a source of the gas carrier

(1) Carle analytical gas chromatograph. The Carle analytical gas chromatograph had two separatory columns and a reference column (Fig. 4.1-2):

(a) Molecular Sieve 5A (MO Sieve). This was a stainless steel column - 6' by 1/8" - packed with 42-60 mesh Molecular Sieve 5A. During the analysis, it was used for oxygen and nitrogen gas separation with oxygen coming first.

(b) Porapak Q (ppQ). This was a 3' by 1/8" stainless steel column packed with 80-100 mesh Porapak Q material. It was used for the separation of sulfur dioxide from oxygen and nitrogen.

(c) OV-101 (the reference column). This was a 6' by 1/8" stainless steel column packed with 8% OV-101 material on 80-100 mesh Supricopo.

It is to be noted that some gases may be adsorbed on some packing material permanently. This not only interferes with the detection of the proper gas(es) but also spoils the packing. For instance if sulfur dioxide were adsorbed on the Molecular Sieve packing, it would eventually contaminate it. To avoid this situation, the chromatograph has two circuits (Fig. 4.1-2)
Fig. 4.1-2. By-Pass and In-Line Circuits.

- By-Pass circuit = PPQ-TCD connection
- In-line circuit = PPQ-Mo SIEVE-TCD connection

1-PPQ - 3 ft., 1/4", 80/100 mesh PORAPAK Q
2-Mo SIEVE - 6 ft., 1/8", 42/60 mesh SULFLONEX
3-0V-101 - 6 ft., 1/8", 8% SULFOCOPE
4-VR - Variable Restrictor. Adjust to match flows, for minimum baseline upset.
5-Valves shown in CCW position as viewed from shaft end.

- 5520: CCW = Series
- 5518: CW = Fill
- 5518: CW = Inject
- (.5 ml)
- CARRIER GAS (He)
(i) A by-pass or "ppQ-thermal conductivity detector" circuit. This was used during the sulfur dioxide detection only.

(ii) In-line or "ppQ-MO Sieve-thermal conductivity detector" circuit. This was used for oxygen and nitrogen detection only.

During the analysis, the in-line circuit was used initially so that sulfur dioxide was adsorbed on the ppQ while oxygen and nitrogen were adsorbed on the MO Sieve. Before the desorption of oxygen and nitrogen occurred, the by-pass circuit would be switched on. This caused the oxygen and nitrogen to be retained in the MO Sieve column during the sulfur dioxide detection. When the latter was complete, the in-line circuit would be switched on so that oxygen and nitrogen would be detected.

Besides the columns, the chromatograph used in the gas analysis had a tungsten filament in the thermal conductivity detector, a by-pass valve and sampling valve to facilitate automatic operation.

(2) Omni-Scribe recorder. This is a two pen strip chart recorder which was used to monitor the column oven temperature as well as the signal from the thermal conductivity detector (chromatogram)

(3) Autolab System I Computer Integrator. The Autolab System I Computer Integrator performed the following functions during the analysis:

(a) Integration of individual chromatograms for each gas component.
(b) Automatic calibration of each gas component based on its retention time and concentration. This was possible due to the provision of a calculator accessory.

(c) Actuation of a sampling pump, sampling valve and a by-pass valve. This is done by using its time functions in conjunction with the CDS process controller. (For a full description and operation of the chromatograph unit, the reader is referred to APPENDIX 5) The source of helium, the gas carrier, was a cylinder connected to the chromatograph.

4.2 Sample Preparation

On July 2, 1974, a shipment of 60.0 kg sample of cobaltiferrous pyrite concentrate, of the following composition, was received from Kilembe:

Element: Co   Ni   Fe   Cu   S  
% assay: 1.48  0.21  38.25  0.38  38.33
Insolubles: 11.82% and
Undetermined: 9.53%.

These pyrite concentrates are concentrates randomly picked from the pyrite-concentrate stockpile at Kasese (Fig. 1.1-1) They are the final tailings from the secondary differential roughers (Fig. 1.1-3)

To ascertain the above composition and to prepare the sample for the experiments to follow, screen and chemical analyses were made. Hence, the techniques used will be described followed by a representation and discussion of the results.
4.2.1 Experimental Techniques

(1) Dry screen analysis. Dry screen analysis was done using the Tyler system. The objective of this analysis was four fold:

(a) To find the mean particle diameter of the bulk sample so that the minimum fluidizing velocity could be calculated.

(b) To determine the size of the smallest particles for the purpose of calculating the pneumatic transport velocity.

(c) To determine the particle size-range which would have the best fluidization quality with the least particle carry-overs.

(d) To find how the mineralization varies with particle size distribution of the sample by conducting chemical analyses based on the particle size distribution.

(2) Chemical analysis. Four methods were used:

(a) Atomic absorption spectrophotometry

(b) Gravimetric analysis

(c) X-ray diffraction and fluorescence in conjunction with a computer

(d) Electron probe micro-analysis

(a) Atomic absorption spectrophotometry. A digestion experiment was performed on a portion of the sample. The solution obtained was analysed using a Perkin-Elmer Absorption Spectrophotometer, Model 107 and a Perkin-Elmer intensitron lamp, serial number 20917. This lamp has an operating current of 10 milliamperes and a capability of analyzing for six elements (Co, Ni, Cu,
Fe, Cr and Mn)

(For details of the digestion experiment and operation of the atomic absorption spectrophotometer, refer to APPENDIX 6.)

(b) Gravimetric determinations. This method was used to determine the carbonate, total carbon and sulfur content.

A standard laboratory technique, usually used to determine the carbonate content of ores and mill products, was used to determine the carbonate content of the sample under investigation. A full description of this technique is presented in APPENDIX 7 and the apparatus used is presented in APPENDIX 8, Fig. 4.1-3.

Total carbon analysis was made using a LECO gravimetric carbon determinator, Model 521-275. This method is well described in APPENDIX 9 and the apparatus is presented in APPENDIX 10, Fig. 4.1-4.

Sulfur analysis was made using a direct combustion-iodate technique. The equipment used was a slight modification of that used for carbon analysis (APPENDIX 8, Fig. 4.1-3). A discussion of this method is presented in APPENDIX 11.

(c) X-ray method. This analysis was conducted in the Crystal Research Laboratory at Colorado School of Mines. This laboratory has access to:

(i) A Corset computer program developed
by Donald A. Stephenson and later modified by Mrs. Linda Smith.

(ii) A data collection computer program developed by Dr. M. Slaughter, a professor in Chemistry Department at Colorado School of Mines.

These programs facilitate quick qualitative and quantitative analyses of ore samples. In this way, the metals with sulfate stabilities comparable to those of Co, Ni and Cu can be considered during equilibrium calculations. Also those which form toxic chemical compounds can be identified. X-ray assays were performed to provide a check on the analyses obtained using atomic absorption and gravimetric methods.

The procedures involved in the x-ray technique are described in APPENDIX 12. In particular, a Corset computer output is illustrated in APPENDIX 13.

(d) Electron probe micro-analysis. This analysis was made on a sample prepared from the sample range of 0.106-0.417 mm which is the sample range employed in the present thesis investigation.

The sample was carbon coated. Using an electron beam of 1 μ diameter, an accelerating voltage of 25 and 35 KV and a specimen current of 0.17 μ amps., line scan traverses were carried out using Philips Electronic 4500 electron microprobe instrument. Three spot analyses were done. For each of these spots, the association of certain elements was studied.
4.2.2 Results

(1) Dry screen analysis. Results of this experiment, shown in Table 4.2.1, show that 80% of the sample is minus 200 mesh (0.074 mm). Thus, in order to minimize particle entrainment without jeopardizing fluidization quality, only 20% will be used in the experiments to follow. This corresponds to a size range of 0.106-0.417 mm. In accordance with the objective of this experiment the following parameters were obtained:

(a) The mean particle diameter corresponding to the above range was calculated to be 0.461 mm as compared to 0.126 mm of the bulk sample. Note that a sample showing how to calculate the mean particle diameter is illustrated in APPENDIX 3.

(b) The minimum fluidizing velocity was found to be 29 cm sec\(^{-1}\) as compared to 1.17 cm sec\(^{-1}\).

(c) The size of the smallest particle was 0.417 cm sec\(^{-1}\). Consequently this corresponded to a pneumatic transport velocity exceeding 300 cm sec\(^{-1}\) compared to 17.7 cm sec\(^{-1}\) for the bulk sample. Note that the pneumatic transport velocity for the bulk sample was obtained from Schytil diagram (Fig. 3.1.2) using \(d_p = 0.05\) mm. This corresponds to -325 mesh (the smallest screen used in the investigation of screen analysis).

(2) Chemical analysis. The assay results obtained using atomic absorption and gravimetric methods are presented in Table 4.2.2 and can be generalized as follows:
### TABLE 4.2.1

**DRY SCREEN ANALYSIS DATA**

<table>
<thead>
<tr>
<th>Screen Mean Size</th>
<th>Weight %</th>
<th>Cumulative Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesh size</td>
<td>microns</td>
<td></td>
</tr>
<tr>
<td>-325</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>-200 + 325</td>
<td>74</td>
<td>37</td>
</tr>
<tr>
<td>-150 + 200</td>
<td>106</td>
<td>13</td>
</tr>
<tr>
<td>-100 + 150</td>
<td>147</td>
<td>4</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>212</td>
<td>2</td>
</tr>
<tr>
<td>- 48 + 65</td>
<td>300</td>
<td>1</td>
</tr>
<tr>
<td>- 35 + 48</td>
<td>417</td>
<td>1</td>
</tr>
<tr>
<td>Element</td>
<td>Assay range (%)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1-1.5</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.1-0.3</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.3-0.7</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>27-40</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>25-40</td>
<td></td>
</tr>
<tr>
<td>C (total)</td>
<td>7-13 and C\text{\textsubscript{3}}O\text{\textsubscript{3}} 0.3-1</td>
<td></td>
</tr>
</tbody>
</table>

Several conclusions can also be made using the assay results as presented in Table 4.2-2:

(a) The assays of iron and sulfur closely correspond to the stoichiometric requirements of pyrite expressed as FeS\textsubscript{2}, locating all the iron to pyrite.

(b) The elements likely to be present as sulfides are in minute quantities compared to iron. Therefore, iron sulfides may constitute approximately 60% (by wt.) of the whole sample.

(c) For all the elements analyzed, high concentrations are found in the biggest and smallest particles.

(d) The carbonate content is very small and hence carbonaceous matter, e.g., wood chips constitutes about 10% (by wt.) of the whole sample.

The assay results obtained using x-ray methods are presented in Table 4.2-3. The lower part of the table shows the same results when adjusted for carbon and carbonate contents. As there are no trace elements and oxides indicated (besides the carbonate), the adjusted values
### TABLE 4.2-2

**ASSAY RESULTS**  
(OBTAINED USING ATOMIC ABSORPTION AND GRAVIMETRIC METHODS)

<table>
<thead>
<tr>
<th>Mesh size</th>
<th>Co</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>S</th>
<th>C (Total)</th>
<th>Co\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 35</td>
<td>1.26</td>
<td>.18</td>
<td>34.13</td>
<td>.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 35 + 48</td>
<td>1.09</td>
<td>.17</td>
<td>30.29</td>
<td>.36</td>
<td>39.40</td>
<td>10.60</td>
<td>.44</td>
</tr>
<tr>
<td>- 48 + 65</td>
<td>1.00</td>
<td>.15</td>
<td>25.42</td>
<td>.47</td>
<td>36.40</td>
<td>9.91</td>
<td>.48</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>.59</td>
<td>.10</td>
<td>19.17</td>
<td>1.17</td>
<td>22.10</td>
<td>6.90</td>
<td>71</td>
</tr>
<tr>
<td>- 100 + 150</td>
<td>.64</td>
<td>.07</td>
<td>19.29</td>
<td>1.59</td>
<td>28.40</td>
<td>6.97</td>
<td>.50</td>
</tr>
<tr>
<td>- 150 + 200</td>
<td>1.25</td>
<td>.12</td>
<td>32.40</td>
<td>.43</td>
<td>32.70</td>
<td>12.45</td>
<td>.87</td>
</tr>
<tr>
<td>- 200 + 325</td>
<td>1.30</td>
<td>.18</td>
<td>38.72</td>
<td>.17</td>
<td>36.70</td>
<td>12.79</td>
<td>.18</td>
</tr>
<tr>
<td>- 325</td>
<td>1.25</td>
<td>.20</td>
<td>37.93</td>
<td>.27</td>
<td>37.50</td>
<td>12.66</td>
<td>.36</td>
</tr>
<tr>
<td>% average</td>
<td>1.05</td>
<td>.15</td>
<td>29.69</td>
<td>.56</td>
<td>33.31</td>
<td>10.01</td>
<td>.51</td>
</tr>
<tr>
<td>undetermined</td>
<td>24.72%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that the % average is based on all the tests done. It is not an average of the averages based on mesh size.
TABLE 4.2-3

NORMALIZED ASSAY RESULTS

(OBTAINED USING X-RAY TECHNIQUES)

<table>
<thead>
<tr>
<th>Mesh size</th>
<th>Co</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>V</th>
<th>Ca</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 35 + 48</td>
<td>1.596</td>
<td>.487</td>
<td>40.105</td>
<td>.939</td>
<td>.248</td>
<td>.024</td>
<td>8.940</td>
<td>44.267</td>
<td>3.188</td>
<td>.112</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>1.143</td>
<td>.338</td>
<td>29.725</td>
<td>3.081</td>
<td>.301</td>
<td>.046</td>
<td>13.947</td>
<td>32.512</td>
<td>19.227</td>
<td>.137</td>
</tr>
<tr>
<td>-150 + 200</td>
<td>1.719</td>
<td>.330</td>
<td>42.641</td>
<td>1.024</td>
<td>.220</td>
<td>.021</td>
<td>5.170</td>
<td>48.515</td>
<td>.241</td>
<td>.117</td>
</tr>
<tr>
<td>-200</td>
<td>1.741</td>
<td>.462</td>
<td>43.611</td>
<td>.462</td>
<td>.227</td>
<td>.018</td>
<td>3.605</td>
<td>48.521</td>
<td>.248</td>
<td>.103</td>
</tr>
<tr>
<td>% average</td>
<td>1.590</td>
<td>.390</td>
<td>37.486</td>
<td>1.763</td>
<td>.256</td>
<td>.031</td>
<td>9.193</td>
<td>41.606</td>
<td>6.965</td>
<td>.790</td>
</tr>
<tr>
<td>Mesh size</td>
<td>Co</td>
<td>Ni</td>
<td>Fe</td>
<td>Cu</td>
<td>Cr</td>
<td>V</td>
<td>Ca</td>
<td>S</td>
<td>Si</td>
<td>Al</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>- 35 + 48</td>
<td>1.430</td>
<td>.436</td>
<td>35.926</td>
<td>.841</td>
<td>.222</td>
<td>.022</td>
<td>8.008</td>
<td>39.654</td>
<td>2.856</td>
<td>.100</td>
</tr>
<tr>
<td>- 48 + 65</td>
<td>1.454</td>
<td>.434</td>
<td>35.740</td>
<td>1.250</td>
<td>.244</td>
<td>.028</td>
<td>8.972</td>
<td>36.189</td>
<td>5.111</td>
<td>.119</td>
</tr>
<tr>
<td>- 65 + 100</td>
<td>1.024</td>
<td>.303</td>
<td>26.628</td>
<td>2.760</td>
<td>.270</td>
<td>.041</td>
<td>12.494</td>
<td>29.124</td>
<td>17.224</td>
<td>.123</td>
</tr>
<tr>
<td>-150 + 200</td>
<td>1.540</td>
<td>.296</td>
<td>38.198</td>
<td>.917</td>
<td>.197</td>
<td>.019</td>
<td>4.631</td>
<td>43.460</td>
<td>.216</td>
<td>.105</td>
</tr>
<tr>
<td>% average</td>
<td>1.420</td>
<td>.349</td>
<td>33.580</td>
<td>1.579</td>
<td>.229</td>
<td>.028</td>
<td>8.086</td>
<td>37.271</td>
<td>6.239</td>
<td>.708</td>
</tr>
</tbody>
</table>
should still be higher than the results obtained using the atomic absorption and the gravimetric methods. However, the trend of mineralization with respect to particle size distribution is the same. Since the carbonate content is very small, it follows that limestone content is also very small but Ca is about 10% (by wt.) of the whole sample. Therefore, it must be present as amphiboles or any other Ca-bearing silicates.

The information obtained from line scan and spot analyses during electron probe micro-analysis was used in conjunction with microscopic examination and previous x-ray diffraction studies to identify the minerals present in the sample. These are shown in the primary electron back scatter probe photograph (Fig. 4.2-1). The results can be summarized as follows:

(a) The minerals are:

(i) pyrite/pyrrhotite (referred to as pyrite in Figs. 4.2-1 and 4.2-2

(ii) chalcopyrite

(iii) bornite

(iv) linnaeite

(b) Cobalt is found in pyrite, chalcopyrite and of course linnaeite. In pyrite and chalcopyrite, cobalt is disseminated.

(c) Two phases of pyrite can be identified: a very rich cobalt phase and the other contains moderate amounts of cobalt. The explanation lies in the origin of the grains studied. It is a well known fact [7,8,9,11] that
Fig 42.1 MAJOR ELEMENTS IN THE KLEMBE SULPHIDE CONCENTRATES

A = MICROPROBE BACK SCATTER PHOTO
B-F = MICROPROBE X-RAY FLUORESCENCE PHOTOS
PK = PEAK
BG = BACKGROUND
Fig 42-2 MAJOR ELEMENTS IN THE KILEMBE SULPHIDE CONCENTRATES

A = MICROPROBE BACK SCATTER PHOTO
B/F = MICROPROBE X-RAY FLUORESCENCE PHOTOS
PK = PEAK
BG = BACKGROUND
Kilembe ore contains two forms of pyrite: octahedral and massive pyrite. It has also been reported [11] that the octahedral pyrite contains more cobalt than the massive pyrite. Therefore, it can be concluded that the two phases are the octahedral and massive pyrites.

(d) The amount of cobalt found in chalcopyrite is less than that found associated with the massive pyrite (using the distinction in section (c)).

(e) Bornite contains almost no cobalt.

(f) Nickel occurs in small amounts disseminated throughout pyrite, chalcopyrite and bornite.

(g) From the above association of the elements and knowledge of the nature of the lattice structure of pyrite and chalcopyrite (virtually no vacant holes), it can be concluded that cobalt and nickel occur as substitutions for iron in pyrite. A corresponding formula would be \((\text{Fe,Co,Ni})\text{S}_2\). In chalcopyrite, it is not very clear whether cobalt and nickel are substituting for copper and/or iron. In pyrrhotite, more careful studies are required to deduce whether cobalt and nickel occur as inclusion compounds or are substituting for iron. Both situations are possible since pyrrhotite is a defect solid solution compound and has vacant holes.

(h) No conclusions can be drawn about the possible distribution of gold in linnaeite or any other minerals (Fig. 4.2-1) without more careful studies. It is to be noted that

(i) Silicates and silica are reported as silicate in Figs. 4.2-1 and 4.2-2.

(ii) Gold, uranium, lead, arsenic and zinc are possibly present as trace elements.

4.3 Procedure

This can be divided into two sections: roasting
and recovery determination.

4.3.1 Roasting Procedure

The fluidized-bed reactor was washed with concentrated nitric acid and dried. The reactor was now mounted with the furnace in place (Fig. 4.1.1) and the inlet gas line connected. The power to the furnace was turned on and the required temperature for the run set on the temperature controller. The nitrogen-oxygen-sulfur dioxide gas mixture was set up for the run by adjusting the flow meters. The temperature of the reactor was monitored by the thermocouple attached to the conical section of the reactor whose output was displayed on the strip chart recorder.

While the reactor was heating up the gas chromatograph was calibrated for nitrogen and oxygen using air, followed by the nitrogen, oxygen and sulfur dioxide fluidizing gas mixture, from which the sulfur dioxide calibration was deduced.

When the temperature of the reactor reached the temperature at which the experiment was to be conducted, 100 gm of concentrate was loaded into the reactor after recording the initial fluidizing gas composition using the chromatograph unit. The gas analysis was continued periodically throughout the experiment except during the first hour when voluminous quantities of fines were being
illustrated. The run was continued until the gas composition readings remained constant. This normally occurred after 4-6 hrs., at which time the solids were discharged into a heavy iron mold which allowed rapid quenching of the roasted material.

4.3.2 Recovery Determination

The recovery of the metals of interest was determined by leaching the roasted concentrate. Prior to leaching the calcine was digested for analysis of Co, Cu, Ni and Fe. Twenty-five gms of the roasted concentrate was leached in 750 mls of water (acidified to a pH 2) using sulfuric acid.

Samples taken every thirty minutes, were centrifuged and the clarified solution analyzed for Co, Cu, Ni and Fe using the atomic absorption spectrophotometer as described in section 4.2. This procedure was followed throughout all the runs.

4.4 Results

The results of this investigation will be discussed in two sections: results obtained from roasting experiments and those obtained from leaching experiments.

4.4.1 Results of Roasting Experiments

The results of roasting experiments to be reported
are a combination of analysis of the gas composition data, calcine analysis data and visual observations made during roasting.

Analysis of gas composition data. The gas composition analysis can graphically be represented as volumetric or mole per cent sulfur dioxide and oxygen versus time (hrs). Fig. 4.4-1 is a plot of the data obtained from a run, and is representative of the gas composition analyses obtained during roasting. From this figure several points may be noted:

(i) During the first hour of roasting, the oxygen concentration drops to negligible values for all the oxygen concentrations used during the experiments, whereas sulfur dioxide concentration increases. During the same period, it was observed that a ring of sulfur was formed on the cool parts of the reactor walls (the top part which was not in the furnace). At the same time the bed underwent some elutriation.* The initial carry-overs were golden in colour and non-magnetic. As time increased, the carry-overs became darker, voluminous, pulpy and magnetic. It is to be noted that the fluidized bed was bubbling during this period for all the fluidizing gas velocities used and at all the temperatures employed during roasting. The temperature of the reactor decreased as cold feed was introduced into the reactor.

(ii) The minimum and maximum concentration associated with oxygen and sulfur dioxide respectively, are coincident in time. The maximum value is different for different initial \( P_{SO_2} \), being higher for higher initial concentrations.

(iii) During the period of 1-2 hrs. of roasting, sulfur dioxide concentration decreases while

* It was estimated that less than 10 wt.% of the original feed material was lost.
Fig. 4.4-1. Sulfur Dioxide and Oxygen Mole During Roasting at 900° K
(Data used corresponds to run 3 (R3)).
the oxygen potential increases. Thereafter, these gases approach their initial concentrations although the final equilibrium values were consistently less than the initial values.

(iv) When roasting had been going on for 1 1/2-2 1/2 hrs., a white, dense gas was generated. The evolution of this gas was accompanied by a change in the character of the particles pneumatically transported. They were reddish brown, non-magnetic, neither voluminous nor pulpy. The time at which this gas started evolving did not seem to be a function of temperature.

The above observations were made throughout the whole range of roasting temperatures except that there was a change in the quality of fluidization at 1000° K: after three hours of roasting the bed sintered. This sintering was unique in nature in that the bed would sinter all along the reactor wall surface while a hole was formed at the center of the bed, thus defluidizing the bed. Periodic tapping of the reactor eliminated this effect.

4.4.2 Results from Leaching Experiments

As noted earlier leaching was used as a means of assessing the success of selective sulfation process. Therefore, the results are reported as percent recoveries of cobalt, copper, nickel and iron. Normally, this parameter should be based on the metal content in the fluidized-bed reactor feed. However, with the present investigation, this would not be useful due to unchecked illutriation. Therefore, the reported recoveries are based on the metal
content which was in the calcine.

During the preliminary leaching runs, the following observations were deduced by plotting metal recovery as a function of time (Fig. 4.4-2). The effect of pH is also shown. On the same plot, the variation of temperature and pH during the first four hours of leaching is shown.

(i) The pH changed from 2 to about 2.5.

(ii) Maintaining the pH at 2 caused a significant increase in recovery, compared to the recovery when the pH was unadjusted. This can be deduced from the upper curves (marked A) for each metal.

(iii) The temperature of the leaching mixture increased from 20° C to 40° C. The source of the heat was the electric motor of the magnetic stirrer. The teflon coated stirring bar was found to wear to such an extent that the metal would be exposed after three or four runs unless the side in contact with the vessel was changed.

(iv) Although the iron percent recovery is very low (<3% at most), the solution contains approximately 0.1 gpl of iron, 0.5 gpl of copper, 0.02 gpl of nickel and 0.2 gpl of cobalt (Table 5.1-1) on a relative basis.

(v) Recovery rate is highest for all metals during the first thirty minutes of leaching where 70% cobalt, 68% copper and 30% nickel are recovered when the pH is maintained at 2.

(vi) Of all the metals, the cobalt recovery shows a noticeable decrease after the first thirty minutes. It is to be noted that this decrease was corrected for by covering the leaching vessel using aluminum foil and decreasing the agitation rate which decreased the size of the vortex. Typical results are presented in Fig. 4.4-3. Under these conditions, the order of recovery with the highest first is Co, Cu, Ni and Fe (least).
Fig. 4.4-2. Metal Recovery Versus Time (At gas equilibrium composition of 6.70% SO₂ & 1.4% O₂).
Fig. 4.4-3. Metal % Recovery Versus Time (hrs)
(At gas equilibrium composition of 18% SO₂ & 5.7% O₂)
(vii) Recovery in Fig. 4.4.3 which represents metal recovery corresponding to a gas equilibrium composition of 18% SO₂ and 5.7% O₂, is higher than the recovery in Fig. 4.4.2 which is a metal recovery plot corresponding to 6.7% SO₂ and 14% O₂. For each run performed, the higher the partial pressure of sulfur dioxide in combination with the least oxygen potential, the higher the metal recovery. This is true for all temperatures within the roasting temperature range.

4.5 Interpretation of the Previous Observations

4.5.1 The Behavior of Sulfur Dioxide Concentration in the Reactor During Roasting (Fig. 4.4-1)

This relationship can only be due to the fact that initially (first hour of roasting) the rate at which oxygen was being consumed exceeded its rate of supply. This relationship was reversed as the roasting period increased.

With regard to sulfur dioxide, the rate of supply plus the rate of production exceeded its rate of consumption (if any) during the first hour of roasting. This also became reversed as roasting time increased.

There are two possible explanations of this maxima/minima sulfur dioxide/oxygen relationship:

(a) Assuming that sulfation reaction involving sulfur dioxide does not occur during the first hour of roasting, then the first hour of roasting consists of oxidation reactions whereas the ensuing period consists
of a combination of sulfation/oxidation reactions with subsequent approach to equilibrium. But the sulfation and oxidation reactions involve oxygen consumption. At first this would seem to contradict the fact that the oxygen potential increases after 1 hour of roasting. The explanation lies in the fact that more than 60% of the concentrate was iron sulfides, mainly pyrite, and the fact that the carry-overs in the first 2 hours of roasting were dark in colour and magnetic implying the presence of magnetite. Thus the predominant oxidation reaction can be represented as follows:

$$3\text{FeS}_2 + 8\text{O}_2 = \text{Fe}_3\text{O}_4 + 6\text{SO}_2$$  \hspace{1cm} 4.5-1

But after 2 hours of roasting the particles elutriated were reddish brown and non-magnetic implying the presence of ferric oxide. This transition can be represented as follows:

$$2\text{Fe}_3\text{O}_4 + 1/2\text{O}_2 = 3\text{Fe}_2\text{O}_3$$  \hspace{1cm} 4.5-2

If sulfation occurs during this period, it can be represented as follows:

$$\text{MO} + \text{O}_2 + \text{SO}_2 = \text{MSO}_4 \quad (\text{M}=\text{metal})$$  \hspace{1cm} 4.5-3

Therefore, from equation 4.5-1, it can be seen that magnetite formation requires more oxygen than ferric
oxide formation (eqn. 4.5-2) Another supplemental fact is that sulfate product layers form impervious coatings on nickel and cobalt oxides thus reducing the rate of sulfation of these oxides. Therefore, from using practical observations and theoretical considerations, the decrease in sulfur dioxide concentration and the increase in oxygen potential observed after 1 hour appears reasonable if postulate (a) is correct.

(b) The oxidation and sulfation reactions may occur simultaneously throughout the course of roasting. The facts used to support postulate (a) are still applicable to postulate (b) with the additional deduction that perhaps the sulfate layer effect on nickel and cobalt oxide is less pronounced during the first hour of roasting so that the sulfation rate is generally slower than oxidation rate. This is difficult to ascertain since the sulfatable materials (Co, Ni and Cu) are present in small amounts (Table 5.1-1)

4.5.2 Sulfur Deposition

The presence of large quantities of sulfur as sulfides in the concentrate caused high consumption of oxygen with the result that the oxygen potentials became very low. This may then have caused sulfur to act as an oxygen potential regulator due to the $S_2(g) - O_2 - SO_2$ gas
equilibrium. Thus the sulfur deposits were observed on the coolest section of the reactor.

4.5.3 White Dense Gas

Due to limited facilities, this gas was not identified. However, it is possible that it was composed of volatile sulfides. It is also thermodynamically possible that SO$_3$ was present since as can be judged from Fig. 3.3.1 the equilibrium oxygen potentials correspond to the region where $P_{SO_3}$ is a maximum (Fig. 4.4-1). The presence of these gases may be advanced to explain why the SO$_2$ and O$_2$ equilibrium potentials were less than the initial concentrations, i.e., before introducing the feed (Fig. 4.4-1). But they did not show up on the chromatograms. Another possible explanation would be that they were strongly adsorbed either on the Porapak Q or Molecular Sieve adsorbents. Unfortunately, there is no literature to support this supposition in the case of SO$_3$ and of course with regard to the unidentified gas, there were no facilities available for analyzing this gas.

4.5.4 The Leach Behavior During Recovery Tests

(a) Fig. 4.4-2 shows that the lower set of "metal recovery" curves (marked B) correspond to a pH
variation of 2.03-2.5 while the upper curves (marked A) correspond to pH maintained at 2. These upper curves show a better recovery than the lower ones. Therefore, there was a small consumption of acid (hydrogen ions). This means that the leaching was not of sulfates alone but oxides as well—although the sulfates must have been the major constituents which were leached because aquargia had to be used in order to digest the calcine.

(b) A comparison of the same figure with Fig. 4.4-3 shows that by covering the beaker and reducing the size of the vortex created by high rate of agitation, the decrease in the cobalt recovery was eliminated. One may be tempted to conclude that either the cobalt is being trapped in the lattice structure of iron hydroxides if they are precipitated or that the cobalt is precipitated as cobaltic hydroxide \((\text{Co(OH)}_3)\). However, this supposition cannot be deduced from the \(E_\text{H}^-\text{pH}\) diagrams at \(298^\circ\text{K}\) and for oxygen potentials in atmospheric air.

### 4.5.5 The Effect of Sulfur Dioxide and Oxygen Partial Pressures on the Metal Recovery

An attempt to discover a relationship of equilibrium \(P_{SO_2}, P_2\) and the equilibrium constant, expressed as \(\log \frac{P_{SO_2}}{P_2}^{1/2}\), the maximum recovery was plotted as a function of \(\log \frac{P_{SO_2}}{P_2}^{1/2}\) at \(900^\circ\text{K}\) (Fig. 4.5-1) and at \(1000^\circ\text{K}\) (Fig. 4.5-2). For certain \(P_{SO_2}\) and \(P_2\) combinations,
Fig. 4.5-1. % Maximum Metal Recovery as a Function of the log to the Base Ten of the Product of the Partial Pressure (atm.) of SO₂ and the Square Root of the Partial Pressure (atm.) of O₂ ($P_t = 625$ mm Hg) at 900° K.
Fig. 4.5-2. % Maximum Metal Recovery as a Function of the log to the Base Ten of the Product of the Partial Pressure (atm.) of SO₂ and the Square Root of the Partial Pressure (atm.) of O₂ (P_t = 625 mm Hg) at 1000° K.
it was possible to draw a straight line through the experimental points. However, as a given value of \[ \log P_{SO_2} \cdot P_{O_2} \] can have different combinations of \( P_{SO_2} \) and \( P_{O_2} \), plots of \( \log P_{SO_2} \) versus \( \log P_{O_2} \) at 900° K (Fig. 4.5.3) and at 1000° K (Fig. 4.5.4) were made to try to explain the discontinuity in the linear relationships. This is exemplified by the discontinuity between run 4 and run 6 at 900° K (Fig. 4.5.1) \( \log P_{SO_2} \cdot P_{O_2} \) for run 4 (-1.492) is almost the same as for run 6 (-1.483). Thus the two points would be plotted either vertically above each other or would correspond but analysis of \( P_{SO_2} \) and \( P_{O_2} \) shows that \( P_{SO_2} \) for run 4 exceeds that for run 6 while the oxygen for run 6 exceeds that for run 4. Therefore maximum recovery of run 6 should be less than that for run 4. This is in concord with the deduction that "the higher the \( P_{SO_2} \) (with least \( P_{O_2} \)), the higher the metal recovery. As to where run 6 would plot, with reference to the other runs and in accordance with the above deduction, can be arrived at as follows: according to its position on Fig. 4.5.3, its maximum metal recoveries should be less than those of run 5, closest to those of run 3 but exceedingly higher than those of run 2 while those of run 1 should be a little less in comparison with the maximum metal recovery of run 2. Data included on Fig. 4.5.3 clearly demonstrates this trend.
Fig. 4.5-3. Diagram Showing $\log P_{\text{SO}_2} \cdot P_{\text{O}_2}^{1/2}$
Constant Values at 900° K.
Fig. 4.5-4. Diagram Showing $\log P_{SO_2} \cdot P_{O_2}^{1/2}$

Constant Values at 1000° K.
There was no definite relationship derived but nevertheless the trend holds true for all the roasting temperatures and equilibrium gas composition investigated.

A possible explanation would be that as more oxygen is used during roasting, the predominant metallic constituents would be in the form of oxides which are least leached at pH 2. If this is supplemented by the fact that the sulfate product layers of nickel and cobalt tend to deter the sulfation of these oxides, then an oxidation/sulfation continuous mechanism seems to be operating, i.e., the more oxygen present the oxides are formed faster than they can be sulfated and thus tend to remain as oxides due to the "sulfate coating" effect. Another possibility would be that the more oxygen present the more the tendency to promote the formation of ferrites which are difficult to sulfate. However, as Rosenqvist [21] pointed out that ferrite formation is pertinent with the original nature of the sulfides, the above effect seems likely. Whatever mechanism is operating, nickel seems to be affected most since its recovery is consistently less than 50% (Fig.4.4-2 and 4.4-3). Another interesting aspect of this effect of $P_{SO_2}$ and $P_{O_2}$ on the metal recovery is that the gas composition does not seem to have much influence on the decomposition of the sulfates in the roasting range used. This seems consistent with the trend
effected by $P_{SO_2}$ and $P_{O_2}$, i.e., it is not some combination like $\log P_{SO_2} \cdot P_{O_2}^{1/2}$ that matters since a given value can be produced by suitably combining different $P_{SO_2}$ and $P_{O_2}$. Alternatively, due to the original nature of the ore, the sulfates formed were of a different nature from the conventional sulfates so that their decomposition temperatures, under the equilibrium gas compositions used, were higher than the experimental temperature range. Certainly this cannot be overruled since electron probe analysis, x-ray diffraction and fluorescence revealed intensive cobalt and nickel substitution for iron.

4.6 Experimental Limitations

The major variables involved in fluidized-bed selective sulfation of Kilembe concentrates can be enumerated as follows:

(a) Particle size distribution
(b) Fluidizing-gas velocity
(c) Gas mixture percent composition
(d) Roasting temperature range

4.6.1 Particle Size

The effect of particle size distribution on selective sulfation can be explained in terms of reaction kinetics. The smaller the particles, the larger the
surface area that is exposed to sulfating gases. Also, assuming that the sulfation occurs topochemically (particularly so if the particles are large), the diffusion of the sulfating gases may be affected by the product layer, e.g., the case of sulfating nickel and cobalt oxides. This effect would be more pronounced in the case of large particles than smaller ones. Therefore, generally speaking, the smaller the particles, the higher the reaction rate. Thus, this variable could be investigated as a function of the time required to attain equilibrium. However, attrition caused by interparticle, particle/fluid and particle/reactor wall and submerged surface interactions, will further subdivide the particles. In other cases agglomeration may occur. Another complication would be pneumatic transport of fine materials. In the present investigation, the effect of particle size on selective sulfation, was not studied due to anticipated pneumatic transport effect since 80% (by wt.) of the sample as received was minus 200 mesh (Tyler system)

4.6.2 Fluidizing-gas Velocity

First of all, it must be remarked that this velocity must exceed the incipient fluidization velocity but must be less than the pneumatic transport velocity. Secondary, the quality of fluidization is dependent upon the fluidizing velocity since it is the gas, in excess of
that required to cause incipient fluidization, that passes through the reactor as bubbles which effect the uniformity of bed temperature and composition. At the same time, the bubbles are responsible for the "by-passing" phenomenon. Therefore, there can be no doubt that fluidizing-gas velocity will affect selective sulfation.

The effect of this variable can be studied by analyzing the quantity of the "carry-overs" as a function of fluidizing-gas velocity. This entails the use of a cyclone or any suitable particle precipitator to collect the "carry-overs". In the present investigation, this was not studied because of lack of a cyclone or precipitator.

4.6.3 Gas Mixture % Composition

From isothermal stability diagrams of copper-, cobalt-, nickel- and iron-sulfur-oxygen systems, it can be seen that selective sulfate roasting is only possible under certain sulfating gas compositions as outlined in section 3.3.1. Theoretically, only these gas compositions should be investigated. However, since stability diagrams are not drawn for a mixture of systems nor for complex ores, the search for the best sulfating gas atmosphere may extend beyond the selective sulfate stability region.

However, the gas compositions that could be investigated were limited by the capacity of the flow meters
For instance, using Schytil diagram (Fig. 3.1-2) and the stoichiometric requirements (section 3.3.2), it was found that the fluidizing velocity was approximately 2000 mls min$^{-1}$. Therefore 3% O$_2$ would require 60 mls min$^{-1}$ of oxygen. If such a flow rate was used, the reaction would take a long time to reach equilibrium. Also, there is danger involved in using low oxygen and sulfur dioxide percentages because they correspond to such low P$_{SO_2}$ and P$_{O_2}$ values where metal production from sulfides cannot be ruled out and since certain metals act as cementation sites for other metals in solution (e.g., Fe cements Cu$^{++}$) from solution, this situation could cause low recovery of the cemented metals during leaching.

High percentages of SO$_2$ and O$_2$ were limited by their maximum flow through the flow meters. This is only true because of the desire to keep nitrogen flow accounting for approximately 80% since this corresponds to industrial practice where air is used. Therefore, the range of P$_{SO_2}$ and P$_{O_2}$ investigated was 5%-20%. It should also be remembered that high oxygen partial pressures could cause the bed to fuse.

### 4.6.4 Roasting Temperature Range

To selectively sulfate sulfides containing iron,
with an aim of recovering soluble metallic sulfates by leaching, the iron product must be ferric oxide instead of the soluble iron sulfates. Therefore, the roasting temperature must exceed the decomposition temperature of iron sulfates for a given $P_{SO_2}$ and $P_{O_2}$. However, the reverse of this statement is desirable with regard to recoverable metal sulfates. Therefore, the temperature range investigated was 900-1000° K. This corresponds to a temperature range applied industrially.
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

The primary aim of this investigation was to study the possibility of selectively sulfating cobalt, copper and nickel while the iron remains as ferric oxide. This sulfate roasting and leaching was conducted on Kilembe Mine (Uganda) sulfides. The conclusions which follow are therefore only applicable to these sulfides. However, it should be remembered that Kilembe sulfides are representative of the Zambian-Zairian metallogenic province which contains more than 50% of the world's cobalt reserves. Thus these results should prove extremely useful in the understanding of the process metallurgy of these Zambian-Zairian copper belt sulfides.

The conclusions to be reported are based on the author's previous geological knowledge [7] of the sulfides being studied, practical observation and data analysis from the batch tests performed in the present investigation. Therefore, their duplication is limited by the size and design of the fluidized-bed reactor employed only to a minor extent, e.g., sintering at 1000° C may have been
caused by temperature effects as well as differential gas flow caused by the gas distributor plate design and the small size of the reactor could have contributed to the effects caused by the reactor wall surface.

As can be judged from Chapter 1, kinetics of the sulfation of the kilembe sulfides was not a part of the objective of the present investigation.

However, the gas analysis data recorded as a function of time by use of the chromatogram chart can be useful for kinetic studies. Perhaps the only data unavailable is calcine analysis as a function of time although there is enough calcine analysis data recorded as a function of the equilibrium gas composition.

With regard to leaching, there was no exhaustive study of the variables involved. But the data obtained should prove useful for qualitative evaluation of a roast-leach plant.

For continuous operation of such a plant, more data is required using bench scale laboratory fluidized-bed reactor on a continuous basis. However, the present batch data does indeed show that the selective sulfation of cobalt, copper and nickel of Kilembe sulfides with subsequent leaching is indeed a viable process, since it is possible to depress the iron. Thus the author will present a conceptual, schematic roast-leach plant that could be useful for the Kilembe Mine sulfides or sulfides from
anywhere in the Zambian-Zairian metallogenic province.

5.1 Conclusions

5.1.1 The Physical, Chemical Nature of the Kilembe Sulfides

(a) The Kilembe sulfides whose density is about 5 gm/cc, consist of the following major elements: Fe, S, Si, Co, Cu, Ni, Ca, Cr and Mn.

(b) The minerals of significance as deduced from x-ray diffraction and fluorescence are: pyrite, pyrrhotite, chalcopyrite, bornite and linnaeite.

(c) From electron probe micro-analysis, it was deduced that cobalt and nickel were present as substitutions mainly for iron in pyrite and chalcopyrite.

(d) Gold, uranium, zinc and lead are present in trace amounts. This is not surprising since, in contrast to copper and cobalt which are well distributed over the Zambian-Zairian metallogenic province, gold, uranium, zinc and lead are found in localized segments of the province e.g., zinc and lead are mined in Zambia.

(e) Pyrite seems to account for more than 50% of the ore.

5.1.2 Optimum Roasting Temperature and Gas Composition

(a) Optimum temperature. In the temperature range investigated (900-1000° K) the only discriminant to be used would be the sintering effect experienced at
1000° K.

However, as this may be improved by a better gas distributor design and size of the reactor, roasting temperatures of 900-1000° K could be used if the gas composition recommended below is used.

(b) Optimum gas composition. Due to experimental limitations outlined in section 4.6, the gas composition which corresponds to the selective sulfation region at 900° K (Fig. 3.3-10) was not investigated. Nevertheless the composition investigated((0.06-0.15 atm. of SO₂) and (0.05-0.12 atm. of O₂)) resulted in an average recovery of 88% cobalt, 46% nickel, and 85% copper with 0.15 atm. of SO₂ and 0.05 atm. of O₂ having the highest overall cobalt (98%), copper (92%) and nickel (53%) recoveries (Fig. 4.5-3) while the iron recovered never exceeded 3% (Fig. 4.4-3 and 4.4-2) and Table 5.1-1 shows typical relative amounts of the metals in solution after 4 hours of leaching. Therefore the usefulness of the stability diagrams lies in predicting the possibility of selectively sulfating the desirable metals and providing a direction for the search of optimum conditions as is illustrated by the results of the present investigation.

It is to be noted that nothing much can be said about optimum gas velocities due to experimental limitations. However, velocities of about 2000 ml/min. achieve a bubbling bed of good fluidization qualities at 900° K.
The conditions for 1000° K, need not be explored since sintering constantly caused defluidization. However, it may be possible to use low frequency mechanical vibration in order to eliminate this effect.

5.2 Recommendations

5.2.1 Installation of a Commercial Roast-leach Plant

A possible flow sheet for a roast-leach plant is shown in Fig. 5.1-1. The most important aspects of this plant are as follows:

(a) Fluidizing gas mixture. For economical purposes, air should be used but it must be supplemented by SO₂ since the higher the SO₂ concentration (with least oxygen concentration), the higher the metal recovery. Separate sources of N₂ and O₂ are there for special reasons, e.g., N₂ is useful if defluidization occurs during a continuous run.

(b) Temperature control design. This consists of the following:

(i) The pre-heater to heat up the feed fluidizing gas mixture if required, e.g., in initiating the reaction.

(ii) A cooling water-jacket. An alternative would be by spray mechanism.

(iii) The Knockout (8) This could be used
Fig. 5.1.1. Sulfation roast - leach flow diagram.

Major Plant Components:
1) Preheater
2) Fluidized-bed reactor
3) Screw feeder
4) Cyclone
5) Venturi scrubber
6) Demister
7) Thickener
8) Knock-out tank
(for other plant components see p. 179)
Minor Plant Components

(From Fig. 5.1-1)

B  Burner
C  Canister
WID  Water Injection Device
CWS  Cooling Water System
GFM  Gas Flow Meter
GDP  Gas Distributor Plate
GSP  Gas Sampling Point
H  Hopper
M  Manometer
OT  Overflow Tank
P  Pump
RM  Refractory Material
S  Stack
T  Thermocouple
V  Valve
WFM  Water Flow Meter
MT  Motor
SF  Screwfeeder
F  Feeder
to cool the recirculating gases as well as reducing the amount of moisture going into the reactor as a part of the fluidizing gases.

(v) A screw feeder -- to regulate the feed concentrate for continuous operation. However, if this is blocked, feeding can be done manually from the top of the reactor.

(c) Pneumatic transport. More than 80% of Kilembe Mine concentrates are -200 mesh. Therefore, the use of a cyclone or any other particle precipitator would be especially useful.

(d) The Venturi scrubber and demister. Their use in conjunction with the thicker tank to recirculate the scrubbing water can be used for the purpose of producing impure $\text{H}_2\text{SO}_3$ which would be used for the leaching section. Another source of this acid would be the knockout tank section.

(e) The product and cyclone discharge canisters should be provided with $\text{N}_2$ safety purge lines to be used during discharge periods.

(f) Gas distributor plate. A concave gas distributor plate with T-bars is a suitable design considering expansion effects and gas distribution.

(g) Lining the reactor with a refractory material helps in preventing heat losses so that the reactor can be run autogenously.
5.2.2 Possible Source of Iron for the East African Steel Industry

Since more than 60% of Kilembe sulfides consist of pyrite, the ferric oxide residue obtained after leaching should be researched into as a possible source of iron for the steel industry in East Africa (East African Steel Corporation).

5.2.3 The Possibility of Manufacturing Sulfuric Acid

Since plenty of sulfur dioxide is produced, the possibility of manufacturing sulfuric acid should also be investigated. This acid would find a ready market since most of the sulfuric acid being used in East Africa is imported from abroad.
TABLE 5.1-1

Typical Relative Amounts of Co, Ni, Cu and Fe in Solution After 4 Hours of Leaching 25 gm of Calcine From Roasting Performed at 900°C K

<table>
<thead>
<tr>
<th>Run</th>
<th>Wt. of element in 25 gm of calcine</th>
<th>Concentration (gm/liter) of element in soln. after 4 hrs of leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>3</td>
<td>0.19</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>0.18</td>
<td>0.02</td>
</tr>
<tr>
<td>6</td>
<td>0.18</td>
<td>0.02</td>
</tr>
</tbody>
</table>
# APPENDIX 1

**LENARD JONES PARAMETERS**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mol wt</th>
<th>$\varepsilon$/K</th>
<th>$\sigma$</th>
<th>$K_T/\varepsilon$</th>
<th>$\Omega_\mu$</th>
<th>$K_T/\varepsilon$</th>
<th>$\Omega_\mu$</th>
<th>$K_T/\varepsilon$</th>
<th>$\Omega_\mu$</th>
<th>$K_T/\varepsilon$</th>
<th>$\Omega_\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>64.07</td>
<td>252</td>
<td>4.29</td>
<td>3.175</td>
<td>1.0299</td>
<td>3.373</td>
<td>1.0089</td>
<td>3.571</td>
<td>0.9951</td>
<td>3.770</td>
<td>0.9829</td>
</tr>
<tr>
<td>O$_2$</td>
<td>32.00</td>
<td>113</td>
<td>3.433</td>
<td>7.080</td>
<td>0.8712</td>
<td>7.522</td>
<td>0.8628</td>
<td>7.965</td>
<td>0.8545</td>
<td>8.407</td>
<td>0.8473</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28.014</td>
<td>91.5</td>
<td>3.681</td>
<td>8.743</td>
<td>0.8420</td>
<td>9.290</td>
<td>0.8339</td>
<td>9.836</td>
<td>0.8264</td>
<td>10.383</td>
<td>0.8226</td>
</tr>
</tbody>
</table>
## APPENDIX 2

**LIST OF MOLE FRACTIONS ($X_{SO_2}$, $X_{O_2}$, $X_{N_2}$), VISCOSITIES ($\mu_{mix}$-poise) AND DENSITIES (D - gm/cc) AT DIFFERENT TEMPERATURES (°K)**

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>800</th>
<th>850</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{SO_2}$</td>
<td>$X_{O_2}$</td>
<td>$X_{N_2}$</td>
</tr>
<tr>
<td>0.02</td>
<td>0.03</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>0.05</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Temp. (K°)</td>
<td>( x_{SO_2} )</td>
<td>( x_{O_2} )</td>
<td>( x_{N_2} )</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.89</td>
<td>3.526</td>
</tr>
<tr>
<td>0.06</td>
<td>0.10</td>
<td>0.84</td>
<td>3.556</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.79</td>
<td>3.586</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.74</td>
<td>3.616</td>
</tr>
<tr>
<td>0.08</td>
<td>0.05</td>
<td>0.87</td>
<td>3.524</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.82</td>
<td>3.553</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.77</td>
<td>3.583</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.72</td>
<td>3.613</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>0.85</td>
<td>3.521</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.80</td>
<td>3.551</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.75</td>
<td>3.580</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.70</td>
<td>3.611</td>
</tr>
<tr>
<td>Temp. (K°)</td>
<td>800</td>
<td>850</td>
<td>900</td>
</tr>
<tr>
<td>-----------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>XSO₂</td>
<td>XO₂</td>
<td>XN₂</td>
<td>Uₘix x 10⁻⁴</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.80</td>
<td>0.514</td>
<td>4.212</td>
</tr>
<tr>
<td>0.10</td>
<td>0.75</td>
<td>0.543</td>
<td>4.237</td>
</tr>
<tr>
<td>0.15</td>
<td>0.70</td>
<td>0.573</td>
<td>4.262</td>
</tr>
<tr>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.75</td>
<td>0.505</td>
<td>4.438</td>
</tr>
<tr>
<td>0.10</td>
<td>0.70</td>
<td>0.534</td>
<td>4.463</td>
</tr>
<tr>
<td>Temp. (K°)</td>
<td>X_{SO2}</td>
<td>X_{O2}</td>
<td>X_{N2}</td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>950</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.03</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>0.05</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>0.05</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Temp. (K°)</td>
<td>(X_{SO_2})</td>
<td>(X_{O_2})</td>
<td>(X_{N_2})</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>0.08</td>
<td>0.05</td>
<td>0.87</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.82</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.77</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.72</td>
<td>0.17</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>0.85</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.80</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.75</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.70</td>
<td>0.17</td>
</tr>
<tr>
<td>0.15</td>
<td>0.05</td>
<td>0.80</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.75</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.70</td>
<td>0.17</td>
</tr>
<tr>
<td>0.20</td>
<td>0.05</td>
<td>0.75</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.70</td>
<td>0.17</td>
</tr>
<tr>
<td>Cumulative Wt.</td>
<td>Diameter Smaller Than ( d_p ) in microns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>207.0</td>
<td>-325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>391.0</td>
<td>-200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>457.0</td>
<td>-150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>475.0</td>
<td>-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>483.0</td>
<td>-65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>488.0</td>
<td>-48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>493.0</td>
<td>-35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter Range (µ)</td>
<td>(d_p) (µ)</td>
<td>Wt. Fraction in Intervals ((X_i))</td>
<td>((X/d_p)_i)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------</td>
<td>---------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>50-74</td>
<td>62.0</td>
<td>(\frac{(391-207)}{493} = 0.373)</td>
<td>(0.373/62 = 0.00602)</td>
</tr>
<tr>
<td>74-106</td>
<td>90.0</td>
<td>(\frac{(457-391)}{493} = 0.134)</td>
<td>(0.134/90 = 0.00149)</td>
</tr>
<tr>
<td>106-147</td>
<td>126.5</td>
<td>(\frac{(475-457)}{493} = 0.037)</td>
<td>(0.037/126.5 = 0.00029)</td>
</tr>
<tr>
<td>147-212</td>
<td>179.5</td>
<td>(\frac{(483-475)}{493} = 0.016)</td>
<td>(0.016/179.5 = 0.00009)</td>
</tr>
<tr>
<td>212-300</td>
<td>256.0</td>
<td>(\frac{(488-483)}{493} = 0.010)</td>
<td>(0.010/256 = 0.00004)</td>
</tr>
<tr>
<td>300-417</td>
<td>358.5</td>
<td>(\frac{(493-488)}{493} = 0.010)</td>
<td>(0.010/358.5 = 0.00003)</td>
</tr>
</tbody>
</table>

\[
\sum_{i}^{\infty} \left( \frac{X_i}{d_p} \right)_i = 0.00795
\]

\[
\bar{d}_p \text{ (mean particle diameter)} = \left[ \sum_{i}^{\infty} \left( \frac{X_i}{d_p} \right)_i \right]^{-1}
\]

\[
= \frac{1}{0.00795} = 125.720\mu
\]

\[
= 0.126 \text{ mm}
\]
APPENDIX 4

(A) SULFATE CONVERSION STOICHIOMETRIC CALCULATION

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>S</th>
<th>C</th>
<th>Ca</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Wt.</td>
<td>58.933</td>
<td>58.71</td>
<td>55.847</td>
<td>63.54</td>
<td>32.064</td>
<td>12.011</td>
<td>40.08</td>
<td>15.999</td>
</tr>
<tr>
<td>Assay %</td>
<td>1.05</td>
<td>0.15</td>
<td>29.69</td>
<td>0.56</td>
<td>33.31</td>
<td>9.91</td>
<td>0.09</td>
<td>---</td>
</tr>
<tr>
<td>Moles in 100gm-Sample</td>
<td>0.0178</td>
<td>0.0026</td>
<td>0.5316</td>
<td>1.0088</td>
<td>1.0389</td>
<td>0.8251</td>
<td>0.2017</td>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Gas Requirement (Moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co + SO₂ + O₂ = CoSO₄</td>
<td>SO₂: 0.0178</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.0178</td>
</tr>
<tr>
<td>Ni + SO₂ + O₂ = NiSO₄</td>
<td>SO₂: 0.0026</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.0026</td>
</tr>
<tr>
<td>2Fe + 3/2 O₂ = Fe₂O₃</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.3987</td>
</tr>
<tr>
<td>Cu + SO₂ + O₂ = CuSO₄</td>
<td>SO₂: 0.0088</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.0088</td>
</tr>
<tr>
<td>C + O₂ = CO₂</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.8251</td>
</tr>
<tr>
<td>Ca + SO₂ + O₂ = CaSO₄</td>
<td>SO₂: 0.2017</td>
</tr>
<tr>
<td></td>
<td>O₂: 0.2017</td>
</tr>
<tr>
<td>S + O₂ = SO₂</td>
<td>SO₂: 1.0389 (Produced)</td>
</tr>
<tr>
<td></td>
<td>O₂: 1.0389</td>
</tr>
<tr>
<td></td>
<td>SO₂: 0.8080 (Produced)</td>
</tr>
<tr>
<td></td>
<td>O₂: 2.4936 (Consumed)</td>
</tr>
</tbody>
</table>
(B) CALCULATING THE FLUIDIZING GAS FLOW RATE

Assuming a fluidizing gas containing 21% O₂ and 78% N₂,
the total fluidizing gas required = \( \frac{2.4936 \times 100}{21} \)
\[= 11.8743 \text{ mols.}\]

Assuming the fluidizing gas mixture to behave ideally at 293° K and 625 mm Hg,
the total gas required = 347.1312 liters.

Therefore,
\[\text{N}_2 \text{ in effluent gas} = 0.78 \times 347.1312 \]
\[= 270.7623 \text{ liters.}\]

\[\text{SO}_2 \text{ in effluent gas} = 0.808 \text{ moles} = 23.621 \text{ liters.}\]

Therefore, effluent gas composition assuming 100% O₂ efficiency is as follows:

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>91.98</td>
</tr>
<tr>
<td>SO₂</td>
<td>8.02</td>
</tr>
<tr>
<td>O₂</td>
<td>0.00</td>
</tr>
</tbody>
</table>
From Fig. 3.3-15

The practical excess fluidizing gas ratio = 1.3.

Therefore,

the total fluidizing gas required = 1.3 x 347.1.2

= 451.271 liters.

Therefore,

\[
\begin{align*}
N_2 \text{ gas} & = 451.271 \times 0.78 \\
& = 351.991 \text{ liters.} \\
SO_2 \text{ gas} & = 23.621 \text{ liters.} \\
O_2 \text{ gas} & = (451.271 \times 0.21) - (347.1312 \times 0.21) \text{ liters} \\
& = 21.8693 \text{ liters.}
\end{align*}
\]

### Gas Analysis

<table>
<thead>
<tr>
<th>Gas</th>
<th>%Composition</th>
<th>Partial Pressure (atm.)</th>
<th>log $P_{SO_2}.P_{O_2}^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>88.56</td>
<td>0.728</td>
<td>----</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>5.94</td>
<td>0.049</td>
<td>-1.983</td>
</tr>
<tr>
<td>$O_2$</td>
<td>5.50</td>
<td>0.045</td>
<td>-1.983</td>
</tr>
</tbody>
</table>
(D) ESTIMATION OF THE GAS FLOW RATE

Assuming that the reaction will be complete in four hours, the oxygen flow rate will be in the following range:

\[
\frac{347.1312 \times 0.21}{240} \quad \text{and} \quad \frac{451.271 \times 0.21}{240}
\]

i.e., between 300 and 395 mls min.\(^{-1}\).

Therefore, knowing the gas composition suitable for selective sulfation, the flow rates of SO\(_2\) and N\(_2\) can be calculated.
APPENDIX 5

GAS CHROMATOGRAPH & CHROMATOGRAPHY

Gas chromatography is conducted in separatory columns which are packed with solid adsorbents, e.g., carbon, silica gel, etc. The sample to be separated is mixed at the inlet with the carrier gas and travels through a stationary phase, the column packing. Depending on the affinity, different gases have different retention times on a given or different adsorbent thus they can be fractionally separated. The emergent gases are fed to the detector device which measures some physical or chemical property of the separated gas components compared with that of the carrier gas. The output from the detector is fed as an electrical signal into a recorder to give a chromatogram which is a plot of detector response versus time. If the system has an Autolab System I Computer Integrator, the area of each peak is integrated and since the molar concentration is proportional to the area under the peak the Autolab reports molar concentrations and retention times of the respective gases after calibration using known amounts of these gases. By comparing this with the data obtained under similar conditions using known concentrations of suspected pure gases, the gas mixture components can be identified.
The gas chromatograph unit used in this investigation consisted of the following components:

1. Carle analytical gas chromatograph, Model 311
2. Omni-scribe recorder
3. Autolab System I Computer Integrator
4. Chromatograph process control, CDS Model 100

This can further be subdivided into the following components:

(a) Detectors
   
   (i) Thermal detectors. These are standard thermal detectors which use tungsten filaments and helium gas carrier due to its inertness, nonflammability, and high thermal conductivity. This detector indicates any change in the composition of effluent gases by comparing their thermal conductivity with that of helium. The peak of each gas component is recorded on a chromatogram and the area under the peak is integrated by the Autolab Integrator whose built-in printer gives an output comprising of gas retention times and concentrations.

   (ii) Ionisation detector. Hydrogen flame detector—hydrogen flame ionisation detection developed by McWilliam and Dewar [124] is used to analyze gases in trace amounts. It was not used during the present investigation.

(b) Temperature control panel. The unit has a column temperature controller, setable in 1° C increments up to 399° C, to effect the retention time of the component of interest in the column
(c) Columns. The gas mixture was sampled through a teflon tube - O.D. 1/8" - via a sampling valve. Since the gas mixture components expected for analysis were SO₂, O₂, and N₂, only two columns were installed. For the description of individual columns refer to Section 4.2.2.

(2) Omni-scribe recorder. Refer to Section 4.1.3.

(3) Autolab System I Computer Integrator. The Autolab System I Computer Integrator is connected to the chromatograph and the recorder. The analog signal from the chromatograph goes to the preamplifier. From here it simultaneously goes to an electrically isolated frequency voltage converter and to the input data register where the area is integrated. The frequency voltage converter provides a facsimile of the chromatograph detector signal for the strip chart recorder and since it is isolated, there is no feedback from the recorder to the Autolab Integrator. The Autolab functions can be enumerated as follows:

(a) It integrates simple resolved peaks as well as splitting fused peaks.

(b) It integrates the areas and automatically normalizes the results with an accuracy of 0.002%. By minimum area programming, the Autolab only recognizes the peaks whose areas exceed that programmed in the "minimum area" region of the parameter bar. For this purpose the reject indicator signal flashes on and off until rejection operation is over.

(c) When a calculation accessory has been added, the Autolab can compute concentrations using normalization, internal standard and external standard methods.

(d) Finally, it produces a print out report
automatically due to the built in printer.

(4) **Chromatograph process controller, Model 100.**

The chromatograph process controller, Model 100, is a "bench top" unit used with an Autolab Gas Chromatograph Integrator. The process controller outputs control signals to the Autolab, a sample pump, a sample valve, and a by-pass valve in a time programmable sequence.

The following indicates the process control connections available.

<table>
<thead>
<tr>
<th>Terminal Board Or Connector</th>
<th>Pin Number</th>
<th>Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBl</td>
<td>1</td>
<td>Sampling Pump Common</td>
</tr>
<tr>
<td>TBl</td>
<td>2</td>
<td>Sampling Pump Energize</td>
</tr>
<tr>
<td>TBl</td>
<td>3</td>
<td>Sampling Valve Common</td>
</tr>
<tr>
<td>TBl</td>
<td>4</td>
<td>Sampling Valve Sample</td>
</tr>
<tr>
<td>TBl</td>
<td>5</td>
<td>Sampling Valve Fill</td>
</tr>
<tr>
<td>TBl</td>
<td>6</td>
<td>By-Pass Valve Common</td>
</tr>
<tr>
<td>TBl</td>
<td>7</td>
<td>By-Pass Valve By-Pass</td>
</tr>
<tr>
<td>TBl</td>
<td>8</td>
<td>By-Pass Valve In-Line</td>
</tr>
<tr>
<td>TBl</td>
<td>9</td>
<td>Autolab Run</td>
</tr>
<tr>
<td>TBl</td>
<td>10</td>
<td>Autolab Standby</td>
</tr>
<tr>
<td>TBl</td>
<td>11</td>
<td>Autolab T3</td>
</tr>
<tr>
<td>TBl</td>
<td>12</td>
<td>Autolab T4</td>
</tr>
<tr>
<td>TBl</td>
<td>13</td>
<td>Autolab T5</td>
</tr>
</tbody>
</table>
(5) **Parameter programming.**

The parameter bar on the Autolab is rotated until the desired function appears. Then a parameter selection switch which is directly under the desired function is pressed. A value is entered by pressing the key of each digit in the number on the keyboard. When this is over, the number should appear on the digital display. If it is correct the load key is pressed but if it is incorrect the "clear" key is pressed and the procedure is repeated until all the parameters have been entered. The order of parameter entry is irrelevant. The following parameters must be entered before each run:

(i) "In-line → By-pass" Switch time, e.g., 50 secs.
(ii) "By-pass → In-line" switch time (T4), e.g. 170 secs.
(iii) Autolab print out period (T5), e.g. 270 secs.
(iv) Minimum area to be integrated (MA)

Other parameters programmed by default, are peak width (PW), slope sensitivity (SS), fused peak (FP), tailing peak test (TP), base line (BL), etc.

(6) **Automatic analysis sequence.**

(a) The process begins by pushing the start button on the process controller.
(b) The process controller will turn on the sample pump for an interval of time determined by the front panel adjustment. The range of the adjustment is approximately two to thirty seconds.

(c) After the sample pump has been turned off, the process controller will wait for a period of time determined by the front panel "sample delay" adjustment. This time period adjustment range is approximately two to five seconds.

(d) At the end of the sample delay time, the process controller will change the sample valve to the "sample" position and will start the Autolab.

(e) At the end of an interval defined by "T3" in the Autolab program, the process controller will change the by-pass valve to the "by-pass" position.

(f) At the end of an interval defined by "T4" in the Autolab program, the process controller will change the by-pass valve to the "in-line" position.

(g) At the end of an interval defined by "T5" in the Autolab program, the process controller will change the sample valve to the "fill" position and put the Autolab in standby.

(h) The Autolab System, when returned to standby, will print out a report on its internal printer.

(i) If the mode switch on the front panel is in the "recycle" position, the process controller will restart the process after a recycle delay interval determined by the front panel adjustment. The range of this adjustment is approximately twenty to fifty seconds.
APPENDIX 6

DIGESTION EXPERIMENT

A portion of the concentrates (1 gm) was dissolved in hot concentrated nitric acid (20 mls). Water (25 mls) was added and the mixture boiled, to expel residual nitrogen oxide gases. It was later cooled and filtered.

For reliable results when using the atomic spectrophotometer, the elemental concentrations should lie between 1 and 5 ppm. Thus due to different concentrations of Co, Ni, Cu and Fe in the sample, different filtrate dilutions* were used as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Dilution of 1 ml of Filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu &amp; Ni</td>
<td>1,000 x</td>
</tr>
<tr>
<td>Co</td>
<td>10,000 x</td>
</tr>
<tr>
<td>Fe</td>
<td>100,000 x</td>
</tr>
</tbody>
</table>

*dilutions were carried out using standard 1 ml pipette and suitable volumetric flasks.
APPENDIX 7

TOTAL CARBON ANALYSIS

A LECO Gravimetric Carbon Determinator is an ascarite-weighing tower which is mounted on the side of a LECO Induction furnace to receive carbon dioxide produced by combustion of a sample of known weight, to which two accelerator scoops, one of chip iron and another of copper metal, have been added.

Oxygen flowing at 3/2 liters min.\(^{-1}\) is introduced into the furnace via a purifying train (Fig. 4.1-3) Carbon dioxide resulting from the combustion of the sample passes through:

1. A dust collector to remove stray particles.
2. A sulfur dioxide trap containing manganese dioxide to remove sulfur dioxide.
3. A catalyst furnace.
4. A drying tube containing anhydrone.
5. An absorption tower whose weight increase is due to carbon dioxide absorption.

The practical limit of this method is .01-30% carbon with an accuracy of ±.005%. The carbon is calculated as follows:

\[
\text{wt. } \% \text{ C} = 27.27 \times \left(\frac{B}{W}\right)
\]

where
$$B = \text{the weight gain of the tower}$$

$$W = \text{the weight of the sample}$$
Fig. 4.1-3. Apparatus For Carbon and Sulfur Analysis.
APPENDIX 9

CARBONATE DETERMINATION BY EVOLUTION
OF CO₂ USING 1:1 HCl ACID

Reliability - for good results the carbonate content must exceed .10% by weight.

Outline - the equipment used is shown in Fig. 4.1-4

A weighed sample (approximately 10 gm) was treated with hydrochloric acid (1:1) in a reaction flask (500 ml Erlenmeyer flask), gently heated using a Bunsen burner and the evolved carbon dioxide was absorbed in a pre-weighed tower containing NaOH on asbestos (ascarite). The gain in weight was due to the absorption of carbon dioxide from the carbonate combustion and from the atmosphere. Thus, it was necessary to run blanks after every two sample tests to determine the atmospheric CO₂ content.

Interferences which are evolved or entrained as part of the gas flow were removed using a purifying train (Fig. 4.1-4). In this train a condenser was used to condense most of the water, followed by:

(1) A washing bottle containing copper sulfate in 5% sulfuric acid saturated with chromium oxide (CrO₃ or Na₂Cr₂O₇, etc.) to remove most of the hydrogen sulfide and sulfur dioxide.

(2) A washing bottle containing concentrated sulfuric acid for dehydration purposes.

(3) A tube filled with pumice impregnated with anhydrous copper sulfate to remove chlorine, hydrochloric acid and hydrogen sulfide.
(4) A tube filled with manganese dioxide-asbestos mixture to remove sulfur dioxide and hydrogen sulfide.

(5) A tube filled with granulated zinc to remove chlorine, etc.

(6) A drying tube filled with anhydride.

(7) A carbon dioxide absorption tower filled with ascarite and anhydride.

Finally, the results were analyzed as follows:

\[
\text{wt. \% CO}_3 = 136.36 \ (A/W)
\]

where

\[
A = \text{total weight of carbon dioxide minus the weight of atmospheric carbon dioxide}
\]

\[
W = \text{weight of the sample}
\]
FIG. 4-1-4. APPARATUS FOR CARBONATE DETERMINATION.
APPENDIX 11

SULFUR ANALYSIS

The sample was heated to a high temperature in the induction furnace in a stream of purified oxygen, flowing at 1 liter min.\(^{-1}\). The evolved sulfur dioxide was passed into a starch-iodide solution and titrated with potassium iodate solution. To avoid halide interference, an antimony trap, connected between the furnace and the titrator, was used. The following reactions are thought to occur:

\[
\text{SO}_2(g) + 2\text{H}_2\text{O}(l) + \text{I}_2(l) = \text{H}_2\text{SO}_4(l) + 2\text{HI}(l),
\]

thus the sulfur dioxide bleaches the blue colour of the starch solution, but by adding potassium iodate solution, the colour is restored.

\[
\text{KIO}_3(l) + 5\text{KI}(l) + \text{HCl}(l) = 6\text{KCl}(l) + 3\text{H}_2\text{O}(l) + 3\text{I}_2(l)
\]

The sulfur content is calculated as follows:

\[
\text{wt. \% S} = \frac{(\text{N.F} / \text{W})(\text{Titration-titration blank})}{\text{W}}
\]

where

\[
\text{N.F} = \text{normality factor of } \text{KIO}_3(l)
\]

\[
\text{W} = \text{weight of sample}
\]


Titration = volume of $\text{KIO}_3(\text{l})$ consumed

titration blank = volume of $\text{KIO}_3(\text{l})$ used to
titrante the sulfur dioxide
which evolved from the
accelerators alone

Note: (l) denotes a solution.
APPENDIX 12

X-RAY TECHNIQUES

The x-ray method consisted of qualitative and quantitative analyses. The qualitative analysis is basically the x-ray diffraction technique. The diffraction patterns showed that only pyrite peaks formed the major identifiable peaks. No other minerals could be deduced due to lack of peak distinction. The latter could be due to scattering effects or due to the factor that the minerals were present in small concentrations.

Quantitative analysis consisted of using the computer to deduce the possible elemental composition of the concentrate. The computer matches the intensities \( I(\phi) \) and \( \lambda(\phi) \) of the unknown elements in the sample with the equivalent standard intensities \( I(C) \) and \( \lambda(C) \), thus identifying the elemental composition of the sample. Judging from the intensities displayed on the computer output, the following elements were deduced to be in measurable concentrations: \( \text{Al, Si, S, Ca, V, Cr, Fe, Co, Ni and Cu} \) (APPENDIX 13)

The next operation was x-ray fluorescence performed to get the elemental assays of the sample.
# APPENDIX 13

**COMPUTER OUTPUT OF THE POSSIBLE ELEMENTS IN THE SAMPLE**

EMPTY READER, SET AND RESET SS 4  
INST. NO. 5, SAMPLE NO. 0-5  
INST. 5 DONE

<table>
<thead>
<tr>
<th>EL</th>
<th>LINE</th>
<th>I(C)</th>
<th>LAMBDA(C)</th>
<th>I(φ)</th>
<th>LAMBDA(φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>KA1,2 1</td>
<td>150</td>
<td>8.339</td>
<td>166</td>
<td>8.35</td>
</tr>
<tr>
<td>AL</td>
<td>KA1,2 1</td>
<td>150</td>
<td>8.339</td>
<td>225</td>
<td>8.37</td>
</tr>
<tr>
<td>SI</td>
<td>KA1,2 1</td>
<td>150</td>
<td>7.126</td>
<td>708</td>
<td>7.13</td>
</tr>
<tr>
<td>SI</td>
<td>KB1,2 1</td>
<td>150</td>
<td>7.126</td>
<td>787</td>
<td>7.15</td>
</tr>
<tr>
<td>SI</td>
<td>KB1  1</td>
<td>2</td>
<td>6.778</td>
<td>703</td>
<td>6.74</td>
</tr>
<tr>
<td>SI</td>
<td>KB1  1</td>
<td>2</td>
<td>6.778</td>
<td>614</td>
<td>6.81</td>
</tr>
<tr>
<td>S</td>
<td>KA1,2 1</td>
<td>150</td>
<td>5.372</td>
<td>8061</td>
<td>5.38</td>
</tr>
<tr>
<td>K</td>
<td>KA1,2 1</td>
<td>150</td>
<td>3.742</td>
<td>646</td>
<td>3.73</td>
</tr>
<tr>
<td>CA</td>
<td>KA1,2 1</td>
<td>150</td>
<td>3.359</td>
<td>4296</td>
<td>3.35</td>
</tr>
<tr>
<td>CA</td>
<td>KA1,2 2</td>
<td>37</td>
<td>3.359</td>
<td>703</td>
<td>6.74</td>
</tr>
<tr>
<td>CA</td>
<td>KB1  1</td>
<td>15</td>
<td>3.089</td>
<td>1508</td>
<td>3.08</td>
</tr>
<tr>
<td>EL</td>
<td>LINE</td>
<td>I(C)</td>
<td>LAMBDAC(C)</td>
<td>I(φ)</td>
<td>Lambda(φ)</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td>------</td>
<td>------------</td>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>TI</td>
<td>KAl,2</td>
<td>150</td>
<td>2.749</td>
<td>656</td>
<td>2.74</td>
</tr>
<tr>
<td>TI</td>
<td>KBl,3</td>
<td>30</td>
<td>2.513</td>
<td>353</td>
<td>2.50</td>
</tr>
<tr>
<td>V</td>
<td>KAl,2</td>
<td>150</td>
<td>2.504</td>
<td>353</td>
<td>2.50</td>
</tr>
<tr>
<td>V</td>
<td>KBl,3</td>
<td>30</td>
<td>2.284</td>
<td>274</td>
<td>2.28</td>
</tr>
<tr>
<td>CR</td>
<td>KAl,2</td>
<td>150</td>
<td>2.290</td>
<td>274</td>
<td>2.28</td>
</tr>
<tr>
<td>CR</td>
<td>KBl,3</td>
<td>30</td>
<td>2.084</td>
<td>112</td>
<td>2.09</td>
</tr>
<tr>
<td>CR</td>
<td>KBl,3</td>
<td>4</td>
<td>2.084</td>
<td>166</td>
<td>8.35</td>
</tr>
<tr>
<td>MN</td>
<td>KAl,2</td>
<td>150</td>
<td>2.103</td>
<td>112</td>
<td>2.09</td>
</tr>
<tr>
<td>FE</td>
<td>KAl,2</td>
<td>150</td>
<td>1.937</td>
<td>81320</td>
<td>1.93</td>
</tr>
<tr>
<td>FE</td>
<td>KAl,2</td>
<td>150</td>
<td>1.937</td>
<td>7446</td>
<td>5.82</td>
</tr>
<tr>
<td>FE</td>
<td>KAl,2</td>
<td>9</td>
<td>1.937</td>
<td>8168</td>
<td>7.78</td>
</tr>
<tr>
<td>FE</td>
<td>KBl</td>
<td>15</td>
<td>1.756</td>
<td>12986</td>
<td>1.75</td>
</tr>
<tr>
<td>FE</td>
<td>KBl</td>
<td>3</td>
<td>1.756</td>
<td>10098</td>
<td>3.50</td>
</tr>
<tr>
<td>FE</td>
<td>KBl</td>
<td>1</td>
<td>1.756</td>
<td>1017</td>
<td>5.28</td>
</tr>
<tr>
<td>CO</td>
<td>KAl,2</td>
<td>150</td>
<td>1.790</td>
<td>4715</td>
<td>1.78</td>
</tr>
<tr>
<td>CO</td>
<td>KAl,2</td>
<td>37</td>
<td>1.790</td>
<td>3990</td>
<td>3.57</td>
</tr>
<tr>
<td>CO</td>
<td>KAl,2</td>
<td>9</td>
<td>1.790</td>
<td>708</td>
<td>7.13</td>
</tr>
<tr>
<td>EL</td>
<td>LINE</td>
<td>I(C)</td>
<td>LAMBDA(C)</td>
<td>I(\phi)</td>
<td>LAMBDA(\phi)</td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>CO</td>
<td>KA1,2</td>
<td>4</td>
<td>1.790</td>
<td>787</td>
<td>7.15</td>
</tr>
<tr>
<td>CO</td>
<td>KB1</td>
<td>1</td>
<td>1.620</td>
<td>303</td>
<td>1.61</td>
</tr>
<tr>
<td>CO</td>
<td>KB1</td>
<td>2</td>
<td>1.620</td>
<td>458</td>
<td>3.22</td>
</tr>
<tr>
<td>NI</td>
<td>KA1,2</td>
<td>1</td>
<td>1.659</td>
<td>424</td>
<td>1.65</td>
</tr>
<tr>
<td>NI</td>
<td>KB2</td>
<td>1</td>
<td>1.488</td>
<td>558</td>
<td>1.47</td>
</tr>
<tr>
<td>CU</td>
<td>KA1,2</td>
<td>1</td>
<td>1.541</td>
<td>712</td>
<td>1.53</td>
</tr>
<tr>
<td>CU</td>
<td>KB3</td>
<td>1</td>
<td>1.392</td>
<td>125</td>
<td>1.39</td>
</tr>
<tr>
<td>CU</td>
<td>KB1</td>
<td>1</td>
<td>1.392</td>
<td>125</td>
<td>1.39</td>
</tr>
<tr>
<td>CU</td>
<td>KB2</td>
<td>1</td>
<td>1.381</td>
<td>125</td>
<td>1.39</td>
</tr>
<tr>
<td>GE</td>
<td>KA1,2</td>
<td>1</td>
<td>1.255</td>
<td>154</td>
<td>1.24</td>
</tr>
<tr>
<td>GE</td>
<td>KA1,2</td>
<td>1</td>
<td>1.255</td>
<td>111</td>
<td>1.26</td>
</tr>
<tr>
<td>MO</td>
<td>LA2</td>
<td>1</td>
<td>5.414</td>
<td>8061</td>
<td>5.38</td>
</tr>
<tr>
<td>MO</td>
<td>LA1</td>
<td>1</td>
<td>5.406</td>
<td>8061</td>
<td>5.38</td>
</tr>
<tr>
<td>MO</td>
<td>KA1,2</td>
<td>2</td>
<td>0.710</td>
<td>72</td>
<td>1.43</td>
</tr>
<tr>
<td>AU</td>
<td>MA2</td>
<td>1</td>
<td>5.853</td>
<td>7446</td>
<td>5.82</td>
</tr>
<tr>
<td>AU</td>
<td>MA1</td>
<td>1</td>
<td>5.839</td>
<td>7446</td>
<td>5.82</td>
</tr>
<tr>
<td>AU</td>
<td>LL</td>
<td>1</td>
<td>1.459</td>
<td>558</td>
<td>1.47</td>
</tr>
<tr>
<td>EL</td>
<td>LINE</td>
<td>I(C)</td>
<td>LAMBDA(C)</td>
<td>I(φ)</td>
<td>LAMBDA(φ)</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>AU</td>
<td>LA2</td>
<td>1</td>
<td>1.287</td>
<td>334</td>
<td>1.28</td>
</tr>
<tr>
<td>AU</td>
<td>LA2</td>
<td>2</td>
<td>1.287</td>
<td>381</td>
<td>2.55</td>
</tr>
<tr>
<td>AU</td>
<td>LA1</td>
<td>1</td>
<td>1.276</td>
<td>111</td>
<td>1.26</td>
</tr>
<tr>
<td>AU</td>
<td>LA1</td>
<td>1</td>
<td>1.276</td>
<td>334</td>
<td>1.28</td>
</tr>
<tr>
<td>AU</td>
<td>LA1</td>
<td>2</td>
<td>1.276</td>
<td>381</td>
<td>2.55</td>
</tr>
<tr>
<td>AU</td>
<td>LB1</td>
<td>3</td>
<td>1.083</td>
<td>458</td>
<td>3.22</td>
</tr>
<tr>
<td>AU</td>
<td>LB2</td>
<td>3</td>
<td>1.070</td>
<td>458</td>
<td>3.22</td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>31</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>38</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>35</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>37</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td></td>
<td>47</td>
<td>0.87</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.2-3 NITROGEN CALIBRATION CURVE
Fig. 4.2-5
SULFUR DIOXIDE CALIBRATION CURVE
REFERENCES


5. ________, The Role of Alkali Sulfates in Promoting the Sulfation and Roasting of Nickel Sulfides, Proceedings of International Symposium on Unit Processes in Hydrometallurgy, Gordon and Breach, New York, p. 946 (1964)


7. Mfite, A.G., Kilembe Mine and the Geology at Kilembe, B.Sc. Project, Makerere University, Kampala, Uganda (1973)


12. Ingraham, T.R., Applications of Fundamental Thermo-
dynamics to Metallurgical Processes, Gordon

13. Thomas, R.O. and Hopkins, D.W., Control Chart For
Sulfation Roasting of Sulfides, Trans. Sec. C

14. Thompson, R.B., A New Application of Fluidization,
Chem. Eng. Progr., V. 49, No. 5, p. 253 (May
1953)

15. Thompson, R.B. and Resner, G. Fluid Bed Roasting
Principles and Practice, in Metallurgy of
Copper, Nickel and Cobalt, AIME Symp., Inter-

16. Kellog, H.H., Equilibrium Consideration in the
Roasting of Metallic Sulfides, Journal of
Metals, V. 8, p. 1105 (1956)

17. ________, A Critical Review of Sulfation Equilibria,
Trans. of the Met. Soc. of AIME, V. 230,
p. 1622 (1964)

18. Pehlke, R.D., Unit Processes of Extractive Metallurgy,
American Elsevier Publishing Co., New York, p. 8
(1973).

for the Determination of Sulfate-Oxide Equili-
bria Results for Mg, Mn, Fe, Ni, Cu, and Zn
Systems, Canadian Met. Quart., V. 12, No. 4,
p. 455 (1973)

20. Barin, I. and Knacke, O., Thermochemical Properties
of Inorganic Substances, Springer-Verlag
Heidelberg, New York (1973)

21. Rosenvist, T. Principles of Extractive Metallurgy,
(1974)

(1962)

Decomposition of Cupric Sulfate and Cupric
Oxysulfate, Trans. of Met. Soc. of AIME, V. 233,
p. 363 (1965)


27. Alcock and Carlook, Third Tutorial Symposium on Extractive Met., University of Toronto, Ontario, Canada (1973)


48. Botteril, J.S.M., Progress in Fluidization, Brit. Chem. Eng., V. 6, p. 327 (1961); V. 8, p. 21 (1963); V. 10, p. 27 (1965); V. 13, No. 8, p. 1121 (1968)


85. Fritz, J.C., Ph.D. Dissertation, University of Wisconsin (1956)


88. Szekely, J. and Carr, Trans. AIME, V. 242, p. 918 (1968)


91. Willis, G.M., Graphical Representation of Complex Equilibria (University of Melbourne, Australia).


