THE PRODUCTION OF SYNTHETIC RUTILE AND BY-PRODUCT IRON
OXIDE PIGMENTS FROM ILMENITE PROCESSING

A THESIS PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

by

C.B. WARD B.Sc.(Hons).

School of Mathematical and Physical Sciences, Murdoch University,
Perth, Western Australia

1990
The Production of Synthetic Rutile and By-Product Iron Oxide Pigments from Ilmenite Processing

Abstract

A study has been carried out on the Becher and Summit Processes with the aim of understanding the mechanism and critical parameters required for the production of a range of pure iron oxide pigments, as well as high quality synthetic rutile from reduced ilmenite.

The Becher Process currently produces a large quantity of worthless mixed phase iron oxides. However, this study has shown that the range of iron oxides formed are all derived from the transformation of lepidocrocite (\(\gamma\)-FeOOH) through the solution phase in iron(II) solutions. The results of a kinetic study of the transformation of lepidocrocite found that the rate exhibited an induction period at low pH, was dependent on temperature and was linearly related to \(\log [H^+]\) and \(\log [Fe^{2+}]\). The rate determining step was found to be the formation of suitable product nuclei, following dissolution of the initial oxide at the surface of the crystal lattice.

An electrochemical study of these reactions showed that the product formed from the transformation of lepidocrocite was a function of the solution potential and an experimental Eh-pH diagram was constructed to predict the iron oxide phase produced from hydrolysis and transformation reactions. The results from this fundamental study were then applied on both a laboratory and plant scale to produce pure iron oxide phases.
A modified Summit Process, involving the removal of metallic iron from the porous reduced ilmenite matrix using FeCl₃, regeneration of iron(III) and the production of pure iron oxide pigments from the waste iron(II) chloride solution, was also investigated in detail.

A kinetic study of pure iron dissolution in iron(III) solutions, comparing three electrochemical techniques and a standard solution sampling method, gave consistent rate constants provided allowance was made for the reaction with the proton. The iron dissolution mechanism was found to be iron(III) diffusion controlled, while the dissolution in HCl was under mixed control. A study using both pure iron and pressed reduced ilmenite discs found that acid consumption could be minimised by the addition of citrate or by the addition of Al³⁺ or Fe²⁺, which are believed to block the adsorption of the proton. It was found that iron(III)-citrate complexes inhibited iron(III) hydrolysis in the reduced ilmenite pores and enhanced the purity of the synthetic rutile product.

A study of the oxidation of iron(II) by atmospheric oxygen using copper(II) and activated carbon catalysts found that these catalysts were inefficient for complete iron(III) regeneration. The heating of carbon in the presence of Cu²⁺ was found to enhance the initial rate of iron(II) oxidation, however it is believed that surface oxide redox couples formed on the carbon control the iron(II)/iron(III) ratio in solution, and prevent complete iron(II) oxidation. The production of iron oxide pigments under the controlled conditions afforded by the Summit Process, resulted in superior quality pigments than are presently attainable from the Becher Process. However, controlled ageing and crystal growth using waste lepidocrocite from the Becher Process would result in similar quality pigments being produced.
I declare that this thesis is my own account of my research and contains work which has not previously been submitted for a degree at any University.

Christopher Ward
April 1990
Acknowledgements

I wish to sincerely thank my supervisors Associate Professor David Muir (principal) and Professor Ian Ritchie for the interest, help and guidance afforded me during the course of this work, which helped make the life and work at Murdoch University a most rewarding experience.

Acknowledgement must also be made to a number of the staff at Westralian Sands Ltd, Capel, in particular Mr. C. Pearson, Mr. N. Bernard and Mr. C. Ryan, who helped in supplying samples and for the valued discussions held throughout this project. Financial support supplied by the company for this project and to employ Mr. G. Patrick and Miss S. Gibbons, to develop some of the commercial aspects leading from this work was appreciated. The efforts of these Research Assistants is also acknowledged for their assistance during the plant trials conducted on site at the Westralian Sands Synthetic Rutile Plant.

The assistance of the technical staff of both the Mineral Science and Chemistry programmes of the School of Mathematical and Physical Sciences is gratefully acknowledged, in particular Mr. J. Biddle and Mr. T. Osborne. Their help and technical know-how was invaluable and without them this project would not have progressed as smoothly.

Last but not least, I wish to thank my wife, Anne, for her continual support and encouragement throughout.
## CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>i</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td><strong>CHAPTER 1. The Production of Synthetic Rutile and By-Product</strong></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Iron Oxide Pigments from Ilmenite Processing.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1.2 The Need for Ilmenite Upgrading</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.2.1 The &quot;Sulfate&quot; Process</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1.2.2 The &quot;Chloride&quot; Process</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1.3 By-Products from the Upgrading of Ilmenite</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1.3.1 The Becher Process</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>1.3.2 The Summit Process</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>1.4 Scope of this Thesis</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>1.5 Purpose of this Study</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td><strong>CHAPTER 2. Methods of Production and Transformation of Iron</strong></td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Oxides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>2.2 Hydrolysis of Iron</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>2.3 Iron Oxide Transformation Reactions</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>2.3.1 Thermal Interconversions</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>2.3.2 Mechanical Interconversions</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>2.3.3 Aqueous Interconversions</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>2.4 Results and Discussion</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>2.4.1 Identification and Production of Iron Oxides from the Becher Process</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>2.4.2 Iron Oxides from Laboratory Scale Aerations</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>
2.4.3 Transformation of Aerator Test Products 34
2.4.4 Transformation of $^{59}$Fe Isotope Doped Lepidocrocite 39
2.4.5 Effect of Metallic Iron and Other Reductants on the Transformation Products 40
2.5 SEM Analysis of the Iron Oxides from Aerator Tests 43
2.5.1 Initial Products 43
2.5.2 Transformed Products 47
2.6 Experimental 55
2.6.1 Identification and Production of Aerator Iron Oxides 55
2.6.2 Transformation Experiments 55
2.6.3 X-Ray Diffraction Analysis 56
2.6.4 Scanning Electron Microscope Analysis 57
2.6.5 Transformation of $^{59}$Isotope Doped Lepidocrocite 57
2.7 Conclusions 58

CHAPTER 3. Kinetics and Mechanism of Lepidocrocite Transformations 60
3.1 Introduction 60
3.2 Experimental 61
3.2.1 X-Ray Diffraction Analysis 61
3.2.2 Thermogravimetric Analysis 62
3.3 Results 62
3.3.1 Lepidocrocite Transformation Kinetics 62
3.3.2 Effect of pH 66
3.3.3 Effect of Seeding on the Rate and Product Distribution of the Transformation Reaction 70
3.3.4 Effect of Temperature 74
3.4 Discussion 76

CHAPTER 4. Electrochemistry and Thermodynamics of Iron Oxide Transformation Reactions 81
4.1 Introduction 81
4.1.1 Electrochemistry of Iron Oxide Phases 81
4.1.2 Experimental Programme 83
4.2 Experimental 84
4.2.1 Polarization of Pressed Iron Oxide/Carbon Electrodes 84
4.2.2 Calorimetry 87
4.2.3 Carbon Paste Electrodes 88
4.2.4 Mixed Potential of Reduced Ilmenite Samples 88
4.3 Results and Discussion 89
4.3.1 Thermodynamics of the Fe-H₂O System 89
4.3.2 Calorimetric Analysis of the Transformation of Lepidocrocite 94
4.3.3 Mixed Potentials 95
4.3.3.1 Mixed Potential of Lepidocrocite/Carbon Pressed Disc Electrodes in the Presence of Solid Reductants. 95
4.3.3.2 Mixed Potential of Reduced Ilmenite Samples 97
4.3.3.3 Mixed Potential of Lepidocrocite Electrodes Upon Addition of Solution Reductants 99
4.3.4 Polarization of Pressed Iron Oxide/Carbon Electrodes 101
4.3.4.1 Lepidocrocite Electrodes 101
4.3.4.2 Magnetite, Goethite and Hematite Electrodes 107
4.3.5 Cyclic Voltammetry of Iron Oxides 110
4.3.6 Electrochemical Model of the Transformation Mechanism 116
4.4 Relevance of Transformation Reactions to Corrosion 119
4.5 Conclusions 121

CHAPTER 5. Plant Analysis and Modifications to Becher Plant Conditions to Produce Pure Iron Oxides 123

5.1 Introduction 123
5.2 Experimental 124
5.2.1 Laboratory Scale Becher Aerator Trials 124
| 5.2.2 | Plant Scale Becher Aerator Trials | 124 |
| 5.3 | Results and Discussion | 126 |
| 5.3.1 | Plant Scale Aerator Trials | 126 |
| 5.3.1.1 | Variation in Solution Potentials | 126 |
| 5.3.1.2 | Variation in Iron Oxide Products | 131 |
| 5.3.2 | Modifications to Aerator Conditions to Control Iron Oxide Formation | 132 |
| 5.3.2.1 | Production of Black Magnetite by Air Flow Control | 132 |
| 5.3.3 | Laboratory Scale Becher Aeration Trials | 134 |
| 5.3.3.1 | Production of Black Magnetite by Eh Control | 136 |
| 5.3.3.2 | Production of Red Hematite by pH Control | 138 |
| 5.4 | Particle Size Analysis of Magnetite By-Product from the Modified Plant Trial | 139 |
| 5.5 | Conclusions | 141 |

**CHAPTER 6. The Summit Process: Comparison of Corrosion Techniques to Follow Leaching of Iron by Iron(III).**

| 6.1 | Introduction | 144 |
| 6.2 | Techniques for Studying Corrosion Reactions | 148 |
| 6.2.1 | Direct Solution Sampling from a Rotating Disc | 148 |
| 6.2.2 | Chronopotentiometry | 149 |
| 6.2.3 | Evans' Diagram Method | 152 |
| 6.2.4 | Stern-Geary or Linear Polarization Method | 153 |
| 6.3 | Experimental | 154 |
| 6.4 | Results and Discussion of Rate Constants Obtained by Various Methods | 157 |
| 6.4.1 | Experimental Determination of the Diffusion Coefficient (D) of Fe$^{3+}$ in HCl | 157 |
| 6.4.2 | Chronopotentiometry | 159 |
| 6.4.3 | Evans' Diagram Method | 161 |
6.4.4 Solution Sampling Method 164
6.4.5 Stern-Geary or Linear Polarization Technique 164
6.5 Comparison of Techniques and Conclusions 167

CHAPTER 7. Dissolution of Pure Iron in Iron(III) Chloride Solutions 170

7.1 Introduction 170
7.2 Experimental 171
7.3 Results and Discussion 171
7.3.1 Dissolution Rate versus Rotation Speed 171
7.3.2 Effect of Temperature 177
7.3.3 Effect of Iron(III) and Acid Concentration 179
7.3.4 Effect of the Addition of Iron(II) 183
7.4 Investigation into the Inhibition of the Hydrogen Evolution Reaction 185
7.4.1 Effect of Iron(II) Sulfate 186
7.4.2 Effect of Other Cations on the Hydrogen Evolution Reaction 190
7.5 Effect of Background Electrolytes on Iron(III) Speciation and Rate of Iron Dissolution 193
7.6 Conclusions 196

CHAPTER 8. Kinetics of Leaching Reduced Ilmenite Using a Rotating Disc 197

8.1 Introduction 197
8.2 Experimental 199
8.3 Results and Discussion 200
8.3.1 Effect of Rotation Speed on Leaching Rate 204
8.3.2 Effect of Iron(III) and Acid Concentration 207
8.3.3 Effect of Temperature and Calculation of Activation Energies 210
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.4</td>
<td>Addition of Oxalate and Citrate to Iron(III) Solutions</td>
<td>211</td>
</tr>
<tr>
<td>8.3.4.1</td>
<td>Addition of Sodium Oxalate</td>
<td>212</td>
</tr>
<tr>
<td>8.3.4.2</td>
<td>Addition of Tri-Sodium Citrate</td>
<td>214</td>
</tr>
<tr>
<td>8.4</td>
<td>Conclusions</td>
<td>219</td>
</tr>
<tr>
<td>9</td>
<td>CHAPTER 9. Production of Synthetic Rutile by Iron(III) Leaching</td>
<td>220</td>
</tr>
<tr>
<td>9.1</td>
<td>Introduction</td>
<td>220</td>
</tr>
<tr>
<td>9.2</td>
<td>Experimental</td>
<td>221</td>
</tr>
<tr>
<td>9.2.1</td>
<td>General Procedure</td>
<td>221</td>
</tr>
<tr>
<td>9.2.2</td>
<td>Leaching with FeCl₃/Citrate</td>
<td>222</td>
</tr>
<tr>
<td>9.2.3</td>
<td>Leaching with FeCl₃/FeCl₂</td>
<td>222</td>
</tr>
<tr>
<td>9.2.4</td>
<td>Oxidative Roast/Reduction Procedure for Ilmenite Samples</td>
<td>223</td>
</tr>
<tr>
<td>9.3</td>
<td>Results and Discussion</td>
<td>223</td>
</tr>
<tr>
<td>9.3.1</td>
<td>Leaching Tests at 25 and 70°C</td>
<td>223</td>
</tr>
<tr>
<td>9.3.1.1</td>
<td>Chemical Analysis</td>
<td>224</td>
</tr>
<tr>
<td>9.3.1.2</td>
<td>Microscopic Analysis</td>
<td>226</td>
</tr>
<tr>
<td>9.3.2</td>
<td>Leaching with FeCl₃/Sodium Citrate and FeCl₃/FeCl₂ Solutions</td>
<td>233</td>
</tr>
<tr>
<td>9.3.3</td>
<td>Leach Tests with Excess FeCl₃ at 70°C</td>
<td>236</td>
</tr>
<tr>
<td>9.3.4</td>
<td>Production of Higher Quality Synthetic Rutile</td>
<td>238</td>
</tr>
<tr>
<td>9.3.5</td>
<td>Manganese Impurity Removal</td>
<td>241</td>
</tr>
<tr>
<td>9.4</td>
<td>Conclusions</td>
<td>243</td>
</tr>
<tr>
<td>10</td>
<td>CHAPTER 10. Investigation of the Catalytic Oxidation of Iron(II) by Oxygen</td>
<td>245</td>
</tr>
<tr>
<td>10.1</td>
<td>Introduction</td>
<td>245</td>
</tr>
<tr>
<td>10.2</td>
<td>Oxidation of Iron(II) with Oxygen at Ambient Pressures</td>
<td>247</td>
</tr>
<tr>
<td>10.3</td>
<td>Experimental</td>
<td>252</td>
</tr>
<tr>
<td>10.3.1</td>
<td>Oxidation of Iron(II) to Iron(III)</td>
<td>252</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>10.3.2</td>
<td>Activated Carbon</td>
<td>253</td>
</tr>
<tr>
<td>10.3.3</td>
<td>Destruction of Cyanide with Carbon</td>
<td>253</td>
</tr>
<tr>
<td>10.3.4</td>
<td>Gold Absorption Kinetics</td>
<td>254</td>
</tr>
<tr>
<td>10.3.5</td>
<td>Copper and Iron Analysis of Used Carbon Samples</td>
<td>254</td>
</tr>
<tr>
<td>10.4</td>
<td>Results and Discussion</td>
<td>254</td>
</tr>
<tr>
<td>10.4.1</td>
<td>Copper(II) Catalysis</td>
<td>254</td>
</tr>
<tr>
<td>10.4.2</td>
<td>Activated Carbon Catalysis</td>
<td>257</td>
</tr>
<tr>
<td>10.4.3</td>
<td>Effect of Temperature</td>
<td>260</td>
</tr>
<tr>
<td>10.4.4</td>
<td>Loss of Carbon Activity and Role of $\text{Cu}^{2+}$</td>
<td>260</td>
</tr>
<tr>
<td>10.4.5</td>
<td>Pretreatment of Carbon with $\text{CuCl}_2$</td>
<td>263</td>
</tr>
<tr>
<td>10.4.6</td>
<td>Effect of Iron(III) on Carbon Activity</td>
<td>266</td>
</tr>
<tr>
<td>10.4.7</td>
<td>Effect of $\text{Cu}^{2+}$ on other Carbon Properties</td>
<td>268</td>
</tr>
<tr>
<td>10.4.8</td>
<td>Mechanism of Catalysis</td>
<td>272</td>
</tr>
<tr>
<td>10.5</td>
<td>Conclusions</td>
<td>274</td>
</tr>
<tr>
<td>CHAPTER 11. Characteristics and Production of Iron Oxide Pigments</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>11.1</td>
<td>Introduction</td>
<td>277</td>
</tr>
<tr>
<td>11.2</td>
<td>Experimental</td>
<td>279</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Iron Oxide Pigment Production</td>
<td>279</td>
</tr>
<tr>
<td>11.2.2</td>
<td>Transmission Electron Microscopy</td>
<td>280</td>
</tr>
<tr>
<td>11.2.3</td>
<td>Particle Size Distribution</td>
<td>281</td>
</tr>
<tr>
<td>11.3</td>
<td>Review of Pigment Properties and Physical Factors which Determine Shade</td>
<td>281</td>
</tr>
<tr>
<td>11.3.1</td>
<td>Optical Properties</td>
<td>281</td>
</tr>
<tr>
<td>11.3.2</td>
<td>Particle Size</td>
<td>282</td>
</tr>
<tr>
<td>11.3.3</td>
<td>Particle Shape</td>
<td>283</td>
</tr>
<tr>
<td>11.4</td>
<td>Summary of Methods of Production of Synthetic Iron Oxide Pigments</td>
<td>283</td>
</tr>
<tr>
<td>11.4.1</td>
<td>Red Iron Oxide Pigments</td>
<td>284</td>
</tr>
</tbody>
</table>
11.4.2 Yellow Iron Oxide Pigments 284
11.4.3 Black Iron Oxide Pigments 285
11.4.4 Brown Iron Oxide Pigments 286
11.5 Mechanism of Precipitation of Pigments from Iron(II) Solutions 286
11.5.1 Nucleation 287
11.5.2 Ageing 288
11.5.3 Crystal Growth 288
11.6 Iron Oxide Pigment Production from Lepidocrocite and Iron(II) Chloride 289
11.6.1 Characterisation of the Pigments 292
11.6.2 Particle Size Distribution of the Precipitated Phases 302
11.7 Conclusions 305

CHAPTER 12. Recommendations 307
12.1 The Becher Process 307
12.2 The Summit Process 308

REFERENCES 309
APPENDIX 1 323
APPENDIX 2 331
Chapter 1

The Production of Synthetic Rutile and By-Product Iron Oxide Pigments from Ilmenite Processing

1.1 Introduction

Titanium, the ninth most abundant element in the earth's crust occurs in two mineral forms of commercial importance - rutile and ilmenite. Commercial grades of rutile contain about 95 percent titanium dioxide (TiO₂) while ilmenite, which is substantially ferrous titanate (FeTiO₃, theoretical 52.66 percent TiO₂) ranges from as little as 35 percent TiO₂ to as much as 65 percent. This wide range of titanium dioxide content in ilmenite is due to the presence of other elements or minerals within the ilmenite grains, and to the weathering and oxidation of iron(II) in the mineral to iron(III) (Roberts, 1971).

Ilmenite occurs naturally in three forms, in massive or rock deposits, (often in association with other ores such as hematite or magnetite), as a constituent of beach sands, and thirdly, as an accessory mineral in rocks (Deer et al., 1962). Where ilmenite occurs as an accessory mineral, the ilmenite grains are dispersed and usually make up less than 10 percent of the rock (Holmes, 1965). Therefore, the two forms of ilmenite that are commercially important are the relatively rare massive deposits and the more widely occurring beach sand deposits. Table 1.1 shows the demonstrated world economic resources of ilmenite and rutile (Towner, 1986).
Table 1.1

World Economic Demonstrated Resources of Ilmenite and Rutile (Mt)

<table>
<thead>
<tr>
<th>Country</th>
<th>Sand Deposits</th>
<th>Rock Deposits</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>41</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>South Africa</td>
<td>85</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>22</td>
<td>32</td>
<td>2</td>
</tr>
<tr>
<td>Canada</td>
<td></td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td></td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>U.S.S.R.</td>
<td>'large'</td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>India/Sri Lanka</td>
<td>60</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Finland</td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>24</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>Sierra Leone</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>232</strong></td>
<td><strong>645</strong></td>
<td><strong>29</strong></td>
</tr>
</tbody>
</table>

The titaniferous beach sands have resulted where titanium bearing rock has weathered and eroded away, with the heavy minerals being transported and accumulated into dunes by the action of rivers, ocean currents, waves and wind (Martin, 1955).

Producers of ilmenite concentrates have generally preferred sand deposits because they are the cheapest and easiest to mine. During the mining process the ore is subjected to gravity, magnetic and
electrostatic processes to produce the concentrate. Rutile, zircon, monazite and a weathered ilmenite leucoxene also occur in significant amounts in mineral sands deposits.

1.2 The Need for Ilmenite Upgrading

Rutile is the traditional feedstock of choice used in the production of titanium metal by fused salt electrolysis, but the principle consumer of all forms of titanium concentrates is the white pigment industry using either the "sulfate" or "chloride" routes of production (Kahn, 1984). Titanium dioxide pigments are most effective in imparting whiteness and brightness to paints, plastics, papers, fibres, vitreous enamels, etc. This is due to their exceedingly high reflectance. Titanium dioxide pigments are produced in two crystal forms, rutile and anatase, but rutile, with a higher refractive index than anatase (R.I. = 2.70 versus 2.55), has the higher opacity than anatase (Simpson).

Different titanium minerals are consumed by the two pigment processes. "Sulfate" pigment plants require a sulfuric acid soluble ilmenite or titania slag feedstock containing low levels of contaminants such as chromium and vanadium, which could affect the final pigment colour. "Chloride" pigment plants usually prefer a high grade feed of rutile or synthetic rutile with low levels of contaminants, such as iron, which consume chlorine. As "chloride" plants use a fluid bed process for chlorinating the impure rutile, fine-size materials cannot be processed easily (McIntyre, 1989).
1.2.1 The "Sulfate" Process

In the "sulfate" process a mixture of ground ore and sulfuric acid (85-95 percent) is agitated by compressed air while superheated steam is blown-in. When the temperature reaches about 160°C a vigorous exothermic reaction occurs and the mixture is converted to a porous cake which contains iron(II), iron(III) and titanium(IV) sulfates. This cake is extracted with water or dilute acid, and any iron(III) in the solution is reduced to iron(II) by means of scrap iron. The liquor is then clarified by sedimentation to remove insoluble residues and much of the iron removed by crystallisation as FeSO$_4$.7H$_2$O (copperas).

To produce a precipitate of hydrous titanium dioxide the liquor is hydrolysed by boiling for some hours. Nuclei in the anatase or rutile form, previously prepared from pure titanium tetrachloride, are added at this stage or during the subsequent calcination. Although precipitates from sulfate liquors are invariably in the anatase form, the type of nuclei which is added determines whether calcination will give anatase or rutile pigments (Tioxide, 1988).

The "sulfate" process is difficult to control and thus good quality TiO$_2$ pigments are not consistently produced. The process also suffers from the problems associated with the disposal of acidic iron(II) sulfate wastes which are environmentally undesirable (Ward et al., 1989a). It is generally uneconomic to process these acidic wastes to recover any by-product iron oxides or salts.
1.2.2 The "Chloride" Process

The "chloride" TiO₂ pigment process is a vapour phase system where either natural or a beneficiated ilmenite known as "synthetic rutile" is chlorinated at high temperatures in the presence of coke to form titanium tetrachloride. This is then distilled and fractionated from iron(III) chloride impurity to produce a pure intermediate condensate suitable for oxidation with O₂ to titanium dioxide. The reactions occurring in the process are shown below:

\[ \text{TiO}_{2\text{impure}} + 2\text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2 \quad 1.1 \]

\[ \text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_{2\text{pure}} + 2\text{Cl}_2 \quad 1.2 \]

For successful oxidation to occur it is necessary to bring the reagent gases together at a suitable temperature and to provide nuclei on which the pigment particles form. Although it is not impossible to produce anatase by the chloride route, the thermodynamics of the process favour the production of the more valuable rutile pigments (Tioxide, 1988). Ilmenite can be used as the feedstock for the "chloride" process but iron and other impurities are also chlorinated, causing excessive chlorine consumption and fluxing of the fluid bed, as well as the problem of iron(III) chloride disposal (Robinson et al., 1977).

As a consequence of the diminishing natural rutile reserves, extensive research has been carried out to develop processes for upgrading the more abundant ilmenite into a "synthetic rutile" to serve as a low cost feedstock for the "chloride" process (see Table 1.1). A suitable
ilmenite upgrading process should remove the ferruginous content in an environmentally acceptable manner. With this trend towards the "chloride" route the burden of iron disposal has therefore shifted from the white pigment producer to the synthetic rutile plants. If synthetic rutile plants could produce a marketable by-product, not only would it reduce the amount of waste products for disposal from synthetic rutile production but it could be a significant value added commodity (Ward et al., 1989a).

1.3 By-Products from the Upgrading of Ilmenite

In their review "By-Product Iron-Discard or Recover", Craigen et al. (1975) state that if a saleable iron product can be produced it will accomplish a number of major objectives:

(1) It will eliminate environmental problems associated with the disposal of iron residues.
(2) It will increase recoveries of primary heavy metals which will normally be lost in the iron residues.
(3) It will recover a usable by-product, and could conceivably result in making processes of recovering metal values from complex ores or bulk concentrates feasible or more economic.

The first and third points are significant for ilmenite upgrading processes and can have a bearing on process selection.

Several processes have been proposed for ilmenite upgrading but most are uneconomic for number of reasons. Processes involving the direct leaching of the natural ilmenite suffer from the high temperatures and pressures required for a product of high enough quality to be substituted successfully for natural rutile (Henn and Barclay, 1970).
Selective chlorination techniques produce very high quality TiO$_2$ products but the capital costs and energy requirements are quite high (Roberts, 1971; Kahn, 1984). The lack of commercially operated plants using chlorination technology can be attributed to the disposal problems of large quantities of iron(III) chloride (Henn and Barclay, 1970). Furthermore iron(III) chloride disposal needs particular attention due to its impact on the environment, and the industrial dechlorination of FeCl$_3$ and recycling of regenerated chlorine is yet to be proven at this scale (Henn and Barclay, 1970).

The high energy requirements and the relatively poor product quality are factors against the commercialisation of other proposed processes using ilmenite. These involve either the addition of sulfur containing compounds to form sulfides, followed by hydrometallurgical treatments (Henn and Barclay, 1970) or smelting and slagging of ilmenite concentrates (Roberts, 1971).

Most commercial activity, therefore, involves processes using either partial or total reduction of the ferruginous component to Fe(II) or metallic iron by pre-roasting the concentrate with coal or oil. Table 1.2 shows the main processes used in the industry for the upgrading of ilmenite which are also amenable for the production of saleable by-products (Ullmanns, 1979). The partial reduction processes followed by acid leaching generally produce an upgraded synthetic rutile product with lower impurity levels of elements such as manganese, magnesium and iron than do the processes requiring complete reduction of the iron. However, the costs of acid regeneration plus the problems of fines generation can be greater (Robinson et al, 1977).
### Table 1.2

**Processes for the Upgrading of Ilmenite and the Production of By-Products**

(a) Reduction Roast-Leach Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Iron Oxidation State(^1)</th>
<th>Leachant</th>
<th>By-Product</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benelite</td>
<td>(II)</td>
<td>conc. HCl</td>
<td>Fe(_2)O(_3)^2</td>
<td>Benelite, 1974</td>
</tr>
<tr>
<td>Murso</td>
<td>(II)</td>
<td>dil. HCl</td>
<td>Fe(_2)O(_3)^2</td>
<td>Sinha and Waugh, 1971</td>
</tr>
<tr>
<td>Ishihara</td>
<td>(II)</td>
<td>Waste H(_2)SO(_4) (\text{NH}_4)_2SO(_4) (\text{Fe}_2)O(_3)</td>
<td>1970</td>
<td></td>
</tr>
<tr>
<td>Becher</td>
<td>0</td>
<td>NH(_4)Cl/Air/H(_2)O</td>
<td>Range of iron oxides</td>
<td>Becher, 1963</td>
</tr>
<tr>
<td>Summit</td>
<td>0</td>
<td>FeCl(_3)</td>
<td>Fe(_2)O(_3)</td>
<td>Shiah, 1966</td>
</tr>
</tbody>
</table>

(b) Other Processes

<table>
<thead>
<tr>
<th>Chlorine Technology</th>
<th>Select. Chlorination</th>
<th>Regenerate Cl(_2) in the vapour phase and Fe(_2)O(_3)</th>
<th>Dupont, and Dupont, 1974</th>
</tr>
</thead>
<tbody>
<tr>
<td>QIT</td>
<td>Smelting</td>
<td>Metallic Iron</td>
<td>Fetterolf, 1960</td>
</tr>
</tbody>
</table>

(1) after roasting (2) after oxyhydrolysis
The processes involving metallisation require considerably milder leaching conditions but the very mild conditions used in processes such as the Becher process, necessitate long leaching times and thus larger leaching vessels are required to obtain an economical throughput.

A number of processes in Table 1.2 produce an iron(II) chloride solution which is treated by high temperature oxyhydrolysis to give hematite ($\text{Fe}_2\text{O}_3$) as a by-product with the regeneration of HCl. But even though this by-product may be of high chemical purity, the crystal growth is uncontrollable and this precludes their use as high quality iron oxides suitable for pigments. The hematite is only suitable as feed to blast furnaces and other pyrometallurgical processes, and is of little commercial value. The Murso process, on the other hand, was developed to treat ilmenites containing significant amounts of chromium and vanadium generally found in Eastern Australia.

The Becher and Summit Processes, which metallise the iron by roasting with coal then corrode it away from the matrix, offer the opportunity of producing a range of higher value differently coloured synthetic iron oxide pigments. These processes are particularly suitable for the upgrading of ilmenites which contain relatively low levels of deleterious impurities such as chromium and vanadium, as found in Western Australia.

1.3.1 The Becher Process

The Becher process is a two-step procedure for the production of synthetic rutile developed by the Western Australian Government
SYNTHETIC RUTILE PRODUCTION – BECHER PROCESS

Figure 1.1. Flow sheet for the production of synthetic rutile by the Becher Process.
Chemical Laboratories in 1961 (Becher, 1963, Becher et al., 1965) and first commercialised by Western Titanium Ltd in 1968 (Cassidy et al., 1986). It is now in operation at a number of locations in Western Australia with a combined production capacity of 270,000 tonnes/annum of synthetic rutile in 1989. This capacity is expected to increase to 500,000 tonnes/annum within the next two years with the commissioning of a further new plant at Muchea, Western Australia. The flow sheet for this process is shown in Figure 1.1. The Becher process is successful because of its low capital cost and low operating costs, and because it has relatively little energy demand.

In the Becher Process, the iron(II) and iron(III) content of the ilmenite is initially reduced to metallic iron in a rotary kiln at about 1150°C using a bituminous coal as both reductant and fuel (Farrow et al., 1987). The product from the reduction kiln, termed "reduced ilmenite", consists of a honey-combed matrix of rutile with metallic iron. The next step in the process, generally termed "aeration", involves the removal of this metallic iron from the reduced ilmenite by an accelerated corrosion reaction using air sparging into an ammonium chloride solution. The corrosion reaction with oxygen is exothermic resulting in the temperature of the system rising to about 65-75°C (Farrow et al., 1987). The aeration step is usually completed within 12-16 hours producing an upgraded ilmenite and a range of iron oxide by-products, or "rusts".

As the leaching process is mild, significant quantities of impurities such as manganese and magnesium remain in the product. To lower the manganese levels, copperas or sulfur is added during the reduction roast to form an iron-manganese sulfide product which is leached
during a final acid washing step (Rolfe, 1973). Sea water has been used as a replacement for the NH$_4$Cl, however the buffering and complexing ability of the ammonium containing solution makes NH$_4$Cl more efficient (Ramakrishna et al., 1988).

The upgraded ilmenite is finally leached with 10-20 percent (w/w) sulfuric acid to remove any remaining metallic iron and any manganous impurities leaving a product containing ca. 94 percent TiO$_2$.

The Becher process, however suffers from a number of disadvantages. These can be summarised as:

(i) slow rate of reaction to remove iron,
(ii) relatively high levels of impurities depending on the characteristics of the feed material,
(iii) disposal of the iron oxides formed as by-products during the aeration step.

If a metallic iron content of the reduced ilmenite feed to the aeration process is assumed as being 30 percent, it is estimated that approximately 240,000 tonnes of waste hydrated oxide is produced per annum from the current Becher Synthetic Rutile Plants in Western Australia.

In order to improve the economics of the process and its environmental impact, it would be ideal to market this by-product as iron oxide pigments, but unfortunately the oxides presently produced are poorly defined and consist of a range of oxides and colours depending on the process conditions. Figure 1.2 shows the range of colours possible under typical plant aeration conditions.
Figure 1.2. The range of iron oxide colours possible under typical aeration condition during the Becher Process.

1.3.2 The Summit Process

The Summit Process (Shiah, 1966) is one of four patented processes which appear in the literature using iron(III) to remove the metallic iron component (George et al., 1958; Nakazawa and Terunuma, 1958; Pike, 1959). Each offers alternative methods of iron recovery, but the Summit Process appears to have the best prospect for commercialisation.
In the Summit Process the ore is first roasted in an oxidising atmosphere to about 1050°C for 2 hours to convert the iron to the iron(III) state. The oxidised ore is then roasted at about 900°C for 2 hours under reducing conditions to convert the oxidized iron to the metallic state. The reduced ore is cooled in an inert atmosphere to avoid reoxidation of the iron, and is leached at 80°C in a chloride solution containing 70 gl⁻¹ iron(II) and 50 gl⁻¹ iron(III) (Henn and Barclay, 1970). After the reaction, the iron(II) chloride solution is decanted from the residue and iron(III) chloride is regenerated by bubbling air through the solution as shown in the following equation.

\[12\text{FeCl}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + 8\text{FeCl}_3\]  \hspace{1cm} 1.3

The solution from which the hydrated iron(III) oxide is recovered contains both iron(III) and iron(II) chlorides, and after discarding up to 5 percent of the solution to avoid other impurity build up, it is recycled to the leach step. Iron(III) oxide precipitates as a hydrate and is later calcined to produce high quality Fe₂O₃. A modification of this process involved an electrolytic iron recovery system (Shiah, 1966b), but this was not economic.

The Summit Process has advantages over the Becher Process in that its leaching reaction is intrinsically much faster and amenable to continuous operation, so that the size of reactors can be much smaller. It also offers the prospect of producing a better quality synthetic rutile.
Unfortunately, the original process did not progress past the pilot plant stage. Possible reasons include, the amount of acid consumed, the hydrogen evolved from the iron(III) leach solution and the poor pigment characteristics of the Fe₂O₃.

1.4 Scope of this Thesis

The above review has identified the Becher and Summit Processes as those most suited for producing high grade synthetic rutile and an iron oxide by-product with potential for the pigment market. The object of this thesis is to gain a better understanding of these processes and the conditions which govern iron oxide production.

Previous research on the Becher process has focussed on developing a proper understanding of the roasting and rusting processes with the object of optimising the quality of the synthetic rutile product and minimising the aeration time (Bracanin et al., 1972; Rolfe, 1973). With the increasing volumes of iron oxides being dumped, there is a need to understand the factors which control the formation of the different iron oxides and to rationalise why various oxides and colours are produced from the aeration step. The control of this step not only opens the opportunity of marketing a saleable iron oxide pigment, but also allows the dewatering circuit of the plant to operate more efficiently.

Chapters 2 and 3 therefore discuss the various types iron oxides and methods of production and report for the first time the factors which control the rate of interconversions which have direct relevance to the fields of metallurgy, colloid science, corrosion and soil science.
Chapter 4 considers in more detail, the electrochemical properties of the iron oxides and the solutions from which they are precipitated, with the aim of identifying the mechanisms and appropriate conditions of Eh and pH required in the interconversion of iron oxide phases. A comparison of plant operating conditions and recommended modifications to the aeration step of the Becher Process is then discussed in Chapter 5. From a proper understanding of the kinetics, mechanism and Eh-pH conditions it is possible to produce consistent iron oxide phases, as against a range of poorly defined and mixed oxides presently being produced under plant conditions.

The Summit Process, on the other hand, requires a better understanding of the kinetics and mechanism of the leaching step with iron(III) chloride to optimise process conditions and to minimise hydrogen evolution. The dissolution of iron is fundamental to both metallurgical and corrosion science disciplines, and the comparison and application of a number of electrochemical techniques to follow this reaction is discussed in Chapters 6. Chapter 7 and 8 then outline an investigation on the heterogeneous leaching of iron with iron(III) using rotating discs to compare both the dissolution of pure iron with iron dispersed in "reduced ilmenite" under closely controlled and well-defined hydrodynamic conditions. An important aspect of this study is the rate of reaction of iron with H⁺ and establishing the effect of background salts and complexing agents to minimise hydrogen evolution. These results are applied in Chapter 9 to formulate the best conditions for the beneficiation of reduced ilmenite and to compare the chemical compositions of the synthetic rutile produced by the Summit and Becher Processes.
As a result of a better understanding of the iron oxide precipitation and interconversion reaction a modification of the original Summit Process is proposed and investigated in this work, where the regeneration of the iron(III) and the production of the by-product iron oxides are considered as separate unit operations. This allows improvements to be made on each operation. It is proposed that the iron(II) solution be split, with one stream leading to a regeneration circuit to oxidise iron(II) to iron(III) without the precipitation of an iron oxide. The second stream would lead to a pigment production operation.

Chapter 10 therefore, considers the mechanism of the catalytic oxidation of iron(II) by molecular oxygen to regenerate the iron(III), and details a novel investigation into the possible application of activated carbon to promote the rate and efficiency of this reaction. Chapter 11 then reviews the characteristics and production of iron oxide pigments and in particular, details the experimental work developed to produce pigment quality hematite ($\alpha$-Fe$_2$O$_3$), goethite ($\alpha$-FeOOH) and magnetite (Fe$_3$O$_4$) from waste iron(II) chloride solutions.

The final chapter summarises the results and findings of this study and suggests areas requiring further research.

1.5 Purpose of this Study

The purpose of this study can therefore be summarised into the following areas:
(1) to investigate improvements to the Becher and Summit ilmenite upgrading processes in order to produce high grade synthetic rutile and marketable iron oxide pigments,

(2) to understand the formation and aqueous transformations of pure iron oxides based upon the electrochemistry and thermodynamics of the system,

(3) to provide basic knowledge on the rates of transformation of iron oxides,

(4) to apply this knowledge to rationalise and control the production of particular iron oxide pigments from the Becher Process,

(5) to compare the kinetics and mechanisms controlling the dissolution of honey-combed metallic iron from reduced ilmenite by acidic iron(III) solutions,

(6) to investigate the role of activated carbon in catalysing the oxidation of iron(II) by O₂ for the regeneration of iron(III),

(7) to understand the key properties of iron oxide pigments and to develop techniques to obtain various coloured pigments from the Becher and Summit Processes.
Chapter 2

Methods of Production and Transformation of Iron Oxides

2.1 Introduction

As discussed in the previous chapter, the Becher Process produces a variety of finely divided and differently coloured iron oxides during the aeration step. Previous research and development on the Becher Process has focussed on developing a proper understanding of the roasting and rusting reactions (Bracanin et al., 1972; Rolfe, 1973), but little work has been undertaken to understand the factors controlling the formation of the different iron oxides. In this chapter a review of the methods of producing various iron oxides, namely hydrolysis and transformation, is presented. This information is then used to produce iron oxides in a laboratory scale study of the Becher Process and to establish the mechanism by which they are formed.

2.2 Hydrolysis of Iron

Precipitation of iron(III) oxides have been studied extensively, because these compounds appear in nature as various minerals, and are used as pigments, catalysts, coatings, flocculents, etc. Furthermore, the corrosion of iron and steel results in the formation of one or more of the iron oxides or hydroxides (Matijevic and Scheiner, 1978). Thus, the hydrolysis of iron containing solutions has been reviewed in the fields of soil science (Schwertmann and Taylor, 1989), colloid science (Matijevic, 1981), process metallurgy (Dutrizac, 1980; 1987;
Flynn, 1984) and corrosion science (Misawa et al., 1974).

Controlled oxidation and hydrolysis are key steps in several hydrometallurgical processes for iron removal, e.g. the Goethite process (Davey and Scott, 1975), the Hematite process (Ohtsuka et al., 1978), the Magnetite process (Kunda and Hitesman, 1977) and in the production of synthetic iron oxide pigments (see Chapter 11). Air or oxygen is usually used to oxidise iron(II) to iron(III), as iron(II) shows only a slight tendency to hydrolyze before precipitating as Fe(OH)$_2$ above pH 7 (Dutrizac, 1980). The hydrolysis of iron(III), which occurs on addition of water to an iron(III) loaded Versatic acid solution in kerosene, has been investigated as a part of a novel solvent extraction and iron recovery process (Doyle-Garner and Monhemius, 1985).

Despite numerous investigations, relatively little is known about the mechanism of iron(III) oxide precipitation. However, ample evidence is available to show that the solid phases formed from iron containing solutions can vary considerably in chemical and structural composition, particle size, morphology, colour, magnetic and surface properties, and other characteristics. The final product of precipitation depends on the iron(III) concentration, pH, temperature, time of ageing, the nature of the anions present, and other topochemical transformations (Matijevic and Scheiner, 1978).

Table 2.1 summarizes the conditions reported in the literature for the formation of pure iron oxide phases by hydrolysis of iron(III). An analysis of the table indicates that the hydrated oxides, lepidocrocite and ferrihydrite predominate at lower temperatures whilst goethite and hematite prevail at temperatures around 80°C. At
### Table 2.1

Reported Literature Conditions for the Production of Synthetic Iron Oxides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Anion</th>
<th>Temp. °C</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated oxides</td>
<td>any</td>
<td>25-100</td>
<td>&gt;7</td>
<td>1</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>SO$_4^{2-}$</td>
<td>95-100</td>
<td>&gt;7</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe$_2$O$_3$</td>
<td>SO$_4^{2-}$</td>
<td>50-100</td>
<td>3-4.5</td>
</tr>
<tr>
<td>Maghemite</td>
<td>γ-Fe$_2$O$_3$</td>
<td>SO$_4^{2-}$</td>
<td>95-100</td>
<td>&gt;7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>α-FeOOH</td>
<td>SO$_4^{2-}$</td>
<td>80</td>
<td>2-3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akaganeite</td>
<td>β-FeOOH</td>
<td>Cl$^-$</td>
<td>80</td>
<td>2-3.5</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>γ-FeOOH</td>
<td>SO$_4^{2-}$</td>
<td>&lt;70</td>
<td>6-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feroxyhyte</td>
<td>δ-FeOOH</td>
<td>Cl$^-$</td>
<td>-</td>
<td>5-8</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>5Fe$_2$O$_3$.9H$_2$O</td>
<td>NO$_3^-$</td>
<td>25</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>
2. Callen et al., 1981.

temperatures approaching 100°C hematite predominates under acidic conditions, whilst magnetite and maghemite are formed under basic conditions.

Even though the pH is shown to be significant in determining the products from hydrolysis reactions (Table 2.1), it is an uncontrolled variable in the Becher Process in which iron(III) is produced as an intermediate in the rusting of iron. In a mechanistic study of the Becher Process, Farrow et al. (1987) found the pH was initially 5.4, then rose rapidly to about 7.5 upon addition of the reduced ilmenite. As the aeration proceeded further, the pH fell from about 7.5 to 4.5 in the first hour, and then more slowly to a pH of about 3.6 over the next 4 hours. These pH changes permit the formation of the whole range of oxides by hydrolysis according to temperature and anion (Table 2.1).
The hydrolysis of iron(III) is thought to involve the formation of monomers which grow into large polymer units and thus become the immediate precursors of precipitation (Dutrizac, 1980). It has been shown that addition of iron(III) ions to water results in the rapid formation of hydroxyl complexes:

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad & (2.1) \\
2\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}_2(\text{OH})_4^{4+} + 2\text{H}^+ \quad & (2.2)
\end{align*}
\]

These undergo slow reactions with the aqueous environment (Dousma and DeBruyn, 1978; Murphy et al., 1976). As a result of these reactions, the pH falls and the colour of the solution changes, indicating the presence of small colloidal particles. The rate at which such changes occur depends on temperature, ratio of Fe\(^{3+}\):OH\(^-\), pH, iron(III) concentration, ionic strength, as well as the specific anions and cations present (Dutrizac, 1980). At high temperatures the lifetime of these polymers is very short, whilst at 25°C the polymers may continue to change for many months (Flynn, 1984).

A number of pathways have been suggested for the growth of the polymer units. If the pH is rapidly increased, thereby increasing the OH\(^-\):Fe\(^{3+}\) ratio, large iron(III) hydroxide gel colloids are formed due to the formation of hydroxyl bridges cross linking the polymer units. The gel formation is promoted by the rapid addition of excess base, poor agitation and low temperatures which encourage the formation of hydroxyl, as opposed to oxygen bridges (Dutrizac, 1980). Oxygen and hydroxyl bridges are shown below.
The hydrolysis of iron(III) is thought to involve the formation of monomers which grow into large polymer units and thus become the immediate precursors of precipitation (Dutrizac, 1980). It has been shown that addition of iron(III) ions to water results in the rapid formation of hydroxyl complexes:

\[
\begin{align*}
Fe^{3+} + H_2O & \rightarrow Fe(OH)^{2+} + H^+ & 2.1 \\
2Fe^{3+} + 2H_2O & \rightarrow Fe_2(OH)_2^{4+} + 2H^+ & 2.2
\end{align*}
\]

These undergo slow reactions with the aqueous environment (Dousma and DeBruyn, 1978; Murphy et al., 1976). As a result of these reactions, the pH falls and the colour of the solution changes, indicating the presence of small colloidal particles. The rate at which such changes occur depends on temperature, ratio of Fe\(^{3+}\):OH\(^-\), pH, iron(III) concentration, ionic strength, as well as the specific anions and cations present (Dutrizac, 1980). At high temperatures the lifetime of these polymers is very short, whilst at 25\(^\circ\)C the polymers may continue to change for many months (Flynn, 1984).

A number of pathways have been suggested for the growth of the polymer units. If the pH is rapidly increased, thereby increasing the OH\(^-\):Fe\(^{3+}\) ratio, large iron(III) hydroxide gel colloids are formed due to the formation of hydroxyl bridges cross linking the polymer units. The gel formation is promoted by the rapid addition of excess base, poor agitation and low temperatures which encourage the formation of hydroxyl, as opposed to oxygen bridges (Dutrizac, 1980). Oxygen and hydroxyl bridges are shown below.
Of most interest to this study, is the formation of oxygen bridges (oxolation) which occur in the presence of moderate concentrations of base which neutralizes the protons generated. The stability of the oxo-bridges to acid increases with increasing temperature. The oxolation structure is the likely precursor to goethite or hematite precipitation in the Becher Process, with growth most likely occurring by the addition of the low molecular weight species such as Fe(OH)$_2^+$ or Fe$_2$(OH)$_2^{4+}$ to the polymer unit. The large polymers formed by the oxolation process are of colloidal size and appear to be at least partly crystalline (Dutrizac, 1980).

2.3 Iron Oxide Transformation Reactions

After formation by hydrolysis, iron oxides can undergo a number of transformation or interconversion reactions (Burkin, 1966), brought about by thermal, mechanical or aqueous changes. Schwertmann and Taylor (1989) have summarised the pathways for the formation and transformation of iron oxides in soils, as shown in Figure 2.1. Even though it does not show all possible processes, it is a useful guide
Figure 2.1. The system of iron oxide interconversions
(taken from Schwertmann and Taylor, 1989).
for studying the complexity of the processes governing the formation of the different iron oxide phases.

2.3.1 Thermal Interconversions

The reports of thermal interconversions are widespread in the chemical and geochemical literature (Bernal et al., 1959; Francombe and Rooksby, 1959; Brown, 1980). Hematite is the ultimate product of heating all iron oxides, oxyhydroxides and hydrous oxides in air at temperatures of 600°C or above. Hence, this is a common method for producing pigment grade hematite (Brown, 1980). Listed below are a number of the possible interconversion reactions:

(i) Lepidocrocite to Hematite

Lepidocrocite decomposes at temperatures between 230 - 280°C to produce ferromagnetic maghemite (γ-Fe₂O₃) which further transforms to hematite at 400°C (Brown, 1980).

(ii) Magnetite to Hematite

At temperatures between 600 - 800°C magnetite is oxidised in air to hematite with a resultant increase in mass (Morris et al., 1985).
(iii) Goethite to Hematite

Goethite is dehydrated to form hematite at temperatures between 230 - 280°C. It has been reported that an intermediate phase of disordered hematite is formed at ~280°C which gradually develops into well crystallised hematite with further heating to 900°C (Brown, 1980).

(iv) Feroxyhyte to Goethite

δ-FeOOH tends to be unstable in air, especially above 100°C, where it readily transforms into goethite. At higher temperatures goethite itself will be transformed into hematite, as discussed above.

(v) Spinels

Preparation of synthetic spinels such as Frankline (ZnOFe₂O₃), Trevorite (NiOFe₂O₃) and Hetaerolite (ZnOMn₂O₃) can be achieved by heating the hydroxides or oxides of the two metals in air at temperatures > 800°C (Swinkels and Ward, 1985).

2.3.2 Mechanical Interconversions

Mechanical effects have also been shown to promote transformations in iron oxides (Klissurski and Blaskov, 1983; Rendon et al., 1983). For example, mechanical dehydration of lepidocrocite was achieved by grinding the oxide in an agate mortar for 60 hours. The sample transformed directly to hematite and did not pass through the maghemite phase as observed with thermal conversions. Nakatani et al. (1983) also studied the mechano-chemical effects of grinding. In their
study, Fe₃O₄ was ground with γ-Al₂O₃ for various periods of time prior to calcination to form a γ-Fe₂O₃ starting material which was then thermally transformed to α-Fe₂O₃. The grinding was found to suppress the transformation because it was believed that aluminium ions occupied vacant iron oxide sites.

2.3.3 Aqueous Interconversions

A number of reports appear in the literature concerning the transformations of iron oxides in an aqueous environment, but generally these refer to processes occurring in soils. The majority of this literature refers to the transformation of poorly ordered ferrhydrite (5Fe₂O₃·9H₂O) into goethite or hematite (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966; Cornell, 1985; Cornell et al., 1987). The transformation into more crystalline products was believed to proceed via two competing pathways: (1) dissolution-reprecipitation leading to goethite and (2) internal aggregation and rearrangement leading to hematite (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966). The predominant end product was found to depend on the pH and temperature. As well, foreign ions and compounds influenced the nature of the reaction product and modified the product crystals. In particular, oxalate (Fischer and Schwertmann, 1975), aluminium (Lewis and Schwertmann, 1979), manganese (Cornell and Giovanoli, 1987) and cobalt (Cornell and Giovanoli, 1989) were found to influence product phase and morphology.

Cornell (1988) studied the effects of a series of divalent metal ions on the kinetics and the products of the transformation of ferrhydrite metal coprecipitates to more crystalline minerals at pH 12 and 70°C.
for up to 20 days. She found that at the lowest level of additive (9.09 mole percent), metal-ferrihydrites transformed into metal-substituted goethite with Mn, Co or Ni, into Cu-hematite (with Cu), while zinc produced a mixture of goethite and hematite. Higher levels of these additives led to replacement of goethite by a spinel phase (Cornell, 1988).

The bacterial transformation of ferrihydrite to magnetite has been studied by a number of workers (Frankel et al., 1983; Mann et al., 1984). It has been proposed that in bacteria this transformation occurs in a membrane vesicle termed the magnetosome.

Lepidocrocite, being less stable than its polymorph goethite, was found to be easily converted to goethite in the presence of alkali hydroxide (Krause et al., 1934) or iron(II) sulfate solutions (Braudisch and Albrecht, 1932). Further studies by van Oosterhout (1967), Schwertmann and Taylor (1972) and Bechine et al. (1982) suggested that lepidocrocite can dissolve and recrystallise as either hematite or goethite in both caustic and iron(II) solutions.

Schwertmann and Taylor (1972) claimed that the main steps governing the rate of transformation of lepidocrocite to goethite were (i) the dissolution of lepidocrocite and (ii) the formation of the goethite nuclei and subsequent growth, with either of these processes able to be rate determining under appropriate conditions. Nitschmann (1938) on the other hand, concluded that the reaction was a pseudomorphosis, but his method of lepidocrocite preparation left the possibility that the material inadvertently contained goethite nuclei. Hiller (1966) suggested that under alkaline conditions the transformation went
through a solution phase but in an iron(II) system the transformations were topotactic. However, Misawa et al. (1974) pointed out that it would be impossible for lepidocrocite, having a cubic close-packed structure of oxygen, to be transformed directly to hexagonal close-packed goethite by solid state reaction without the formation of any detectable intermediate species. Therefore, the transformation must proceed by dissolution of $\gamma$-FeOOH, followed by precipitation from Fe(III) solutions.

Reports also appear in the literature on the transformation of akaganeite (Blesa et al., 1986) and lepidocrocite to the lower valency oxide, magnetite, in iron(II) containing solutions (Tamura et al., 1983; 1984).

Tamura et al. (1983) found that above pH 7.3, lepidocrocite was stoichiometrically converted to magnetite. He proposed that the reaction was a topotactic reaction triggered by the adsorption of iron(II) ions onto the lepidocrocite surface with the Fe(II)-FeOOH intermediate being transformed to Fe$_3$O$_4$. In their scheme, the metal ion adsorbed on the surface of the oxide is hydrolysed and one proton is released in each step of a two step process, as shown by equations (2.3) and (2.4).

\[
\begin{align*}
2\gamma\text{-FeO(OH)} + \text{Fe}^{2+} + \text{H}_2\text{O} & \rightarrow [\gamma\text{-FeO(OH)}]_2\text{.FeOH}^+ + \text{H}^+ \quad 2.3 \\
[\gamma\text{-FeO(OH)}]_2\text{.FeOH}^+ & \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{H}^+ \quad 2.4
\end{align*}
\]
van Oosterhout (1967) identified that the iron(II) ions played a special part in transformation processes. He postulated that iron(II) could increase the dissolution rate of lepidocrocite in slightly acidic solutions. He cited an example that the dissolution of iron(III) sulfate is extremely slow but with the addition of a small amount of iron(II) the rate of dissolution is significantly increased (Barreswill, 1945). Fischer's (1973) findings support this theory, claiming that the dissolution of iron(III) compounds can be accelerated by the presence of iron(II) in solution. He claimed that the iron(II) reduced iron(III) ions exposed at crystal surfaces. Gorichev and Kipriyanov (1979) also showed that the addition of iron(II) significantly increased the rate of dissolution of magnetite and hematite. Furthermore, it was found that the initial slow stage in the photochemical dissolution of iron oxides in acid/oxalate solutions could be eliminated by the addition of up to 20 ppm of iron(II) at the start of the reaction (Cornell and Schindler, 1987). This again indicates that if the transformation reactions proceed via the solution phase, iron(II) will have a significant effect on reaction.

Thus, it appears that, initially formed iron oxides in the Becher Process could also undergo aqueous interconversion reactions in the presence of iron(II), leading to the formation of hematite, goethite and magnetite.

2.4 Results and Discussion

2.4.1 Identification and Production of Iron Oxides from the Becher Process
As discussed in the previous chapter, the Becher Process is a potential source for the production of iron oxide pigments. However, the process is clearly complicated by various oxidation, hydrolysis and aqueous interconversion reactions. Thus, it is necessary to be able to reproduce and characterise on a laboratory scale, the range of iron oxides produced on the plant and then study the process parameters and their effects in detail.

A suite of iron oxides were therefore produced in a laboratory reactor designed to simulate the Becher aerator using the design and conditions detailed in the Experimental (Section 2.6). These oxides were studied by X-ray diffraction and Scanning Electron Microscopy to characterise the differently coloured products. The oxides were also subjected to solution conditions suitable for aqueous transformation reactions to help establish whether the products were formed directly or via an intermediate, in an interconversion reaction.

Experiments were also carried out using an $^{59}$Fe tracer to clarify the mechanism controlling the transformation of lepidocrocite. If significantly greater radioactivity were to report to an iron(II) solution during the transformation of a $^{59}$Fe doped sample of lepidocrocite, compared to a control, then this is unequivocal evidence of a mechanism involving a dissolution step. Conversely, no radioactivity in solution indicates a solid state topotactic conversion.
2.4.2 Iron Oxides from Laboratory Scale Aerations

Table 2.2 shows the conditions used and the iron oxide products obtained from four laboratory scale aeration tests.

Table 2.2

<table>
<thead>
<tr>
<th>Laboratory Scale Becher Aeration Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 kg Reduced Ilmenite, 30 g NH₄Cl, 1 l H₂O, Maximum temperature 70°C, Aeration Time 8 hours)</td>
</tr>
<tr>
<td>Run Identification</td>
</tr>
<tr>
<td>--------------------</td>
</tr>
<tr>
<td>Agitation (rpm)</td>
</tr>
<tr>
<td>Air Sparging (lmin⁻¹)</td>
</tr>
<tr>
<td>Oxide Colour</td>
</tr>
<tr>
<td>Oxide Phases major</td>
</tr>
<tr>
<td>minor</td>
</tr>
</tbody>
</table>

The results indicate that with only minor changes in aeration conditions a broad spectrum of iron oxides were obtained including magnetite, goethite and hematite. Bax and Ritchie (1986) also obtained mixed oxides during a number of their aeration experiments but generally only mixtures of lepidocrocite and hematite were observed, with a higher relative proportion of hematite with longer aeration times. From their work they concluded that lepidocrocite was initially precipitated, but as the solution conditions changed and became less
favourable for lepidocrocite, hematite subsequently precipitated. Thus as the process continued, the relative proportion of hematite became greater with the subsequent decline in the proportion of lepidocrocite (Ward et al., 1989b).

In this work, small changes in aeration rate and stirring speed were sufficient to cause a change in reaction product ranging from black magnetite to red hematite mixtures. Even though red, yellow and black oxides can be accounted for by simply oxidising iron(II) solutions, it is very difficult to synthesise a crystalline green iron oxide, such as Sample C. Sample C was characterised as containing crystalline magnetite and goethite. Sample B, on the other hand, was characterised as pure lepidocrocite which is known to require iron(II) as a precursor and is generally formed upon oxidation of iron(II) solutions at ambient temperatures between pH 5 and 7 (Schwertmann, 1985). These conditions are clearly achieved during the early stages of aeration and accounts for the presence of lepidocrocite in most of the aeration products. However, it is not clear whether the other iron oxide phases are formed subsequently from direct oxidation of the iron, as proposed by Bax and Ritchie (1986), or from the aqueous transformation of lepidocrocite.

2.4.3 Transformation of Aerator Test Products

An experimental programme was then formulated to investigate if lepidocrocite could be transformed to the other phases at temperatures attained during the Becher Process. The lepidocrocite produced by aeration (Sample B) was suspended in 0.5 M FeCl₂ and heated to 80°C under a range of conditions. As discussed earlier, iron(II) salts are
believed to promote transformation reactions (van Oosterhout, 1967), therefore relatively high concentrations of iron(II) were used in this study to facilitate any reaction. The conditions used and the products obtained from this series of transformation experiments are shown in Table 2.3.

**Table 2.3**

**Experimental Conditions and Reaction Products from a Series of Transformation Experiments**

(80°C, 0.5 M FeCl₂)

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Product Colour</th>
<th>Product Composition (by XRD and TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Red</td>
<td>α-Fe₂O₃(84%), α-FeOOH(16%)</td>
</tr>
<tr>
<td>3</td>
<td>Red</td>
<td>α-Fe₂O₃(51%), α-FeOOH(49%)</td>
</tr>
<tr>
<td>4</td>
<td>Green</td>
<td>α-FeOOH(81%), Fe₃O₄(19%)</td>
</tr>
<tr>
<td>5</td>
<td>Black</td>
<td>Fe₃O₄(100%)</td>
</tr>
<tr>
<td>3+10% α-Fe₂O₃ seed</td>
<td>Red</td>
<td>α-Fe₂O₃(75%), α-FeOOH(25%)</td>
</tr>
<tr>
<td>3+50% α-Fe₂O₃ seed</td>
<td>Red</td>
<td>α-Fe₂O₃(72%), α-FeOOH(28%)</td>
</tr>
<tr>
<td>3+10% α-FeOOH seed</td>
<td>Red/Brown</td>
<td>α-FeOOH(87%), α-Fe₂O₃(13%)</td>
</tr>
</tbody>
</table>

The results in Table 2.3 conclusively confirm that the spectrum of colours and products consistently produced during the aeration process can be duplicated by transforming lepidocrocite with the variation of the solution pH conditions.
Figure 2.2. X-ray diffraction patterns collected showing the iron oxide phases present during the transformation of lepidocrocite at pH 5.0, 80°C in 0.5 M FeCl₂ (M = Magnetite).
Figure 2.3. X-ray diffraction patterns collected showing the iron oxide phases present during the transformation of lepidocrocite at pH 2.0, 80°C in 0.5 M FeCl₂.

(H = Hematite, G = Goethite).
Figure 2.2 shows the disappearance of the lepidocrocite peaks and the appearance of characteristic magnetite peaks for the reaction at pH 5.0, while Figure 2.3 shows the appearance of hematite and goethite peaks in the diffractograms of samples taken at various time intervals for the reaction at pH 2.0.

From an analysis of the compositions of the products and the solution pH, the pH regions of predominance for the formation of the three different oxides can be proposed. In 0.5 M FeCl₂ it appears that pure hematite is formed at a pH between 1 and 2, whilst goethite is predominant between pH 3 and 4 and magnetite is the sole product at pH 5 or greater.

The transformation of lepidocrocite to magnetite at a pH as low as 5.0 was not observed by Tamaura et al. (1983). They observed that in 0.2 M FeCl₂ no transformation occurred below pH 7.3, but their results may be accounted for on kinetic grounds, with insufficient time being allowed for the reaction to proceed. The kinetics of these processes will be dealt with in detail in Chapter 3.

To further relate these transformation experiments to the reactions occurring in the synthetic rutile aerator, Sample C (containing a mixture of magnetite and lepidocrocite) was also treated in iron(II) chloride, in the same way. Sample C was originally 70 percent magnetite and 30 percent lepidocrocite, suggesting that reaction conditions were not suited to the complete transformation in the time available. However, after a further 60 minutes in FeCl₂ at pH 5.0, a black solid was collected which was characterised by X-ray diffraction to be pure magnetite. It would appear from this experiment that the
iron(II) solution has aided in the completion of the transformation reaction, which had only partially occurred in the aeration tests. This is conclusive evidence that transformation reactions occur in the Becher aerator, and is the first study to verify that processes other than hydrolysis reactions determine the by-product iron oxide phases formed.

2.4.4 Transformation of $^{59}$Fe Isotope Doped Lepidocrocite

The gamma emitting $^{59}$Fe isotope has a half-life of 44.1 days and was readily incorporated into the lepidocrocite lattice by direct precipitation of lepidocrocite from a doped FeCl$_2$ solution. The fate of this $^{59}$Fe isotope upon transformation then provides a conclusive means of establishing whether the mechanism is topotactic or via the solution phase, as debated by previous workers.

The lepidocrocite used for this study was prepared by bubbling O$_2$ through 0.5 M FeCl$_2$ solution containing 500µl $^{59}$FeCl$_2$ whose radioactive concentration was 3.885 MBq ml$^{-1}$ at 25$^\circ$C and pH 6-7. After filtering and drying, one sample was subsequently transformed in 0.5 M FeCl$_2$ solution, whilst at the same time a "control" sample was kept in deionised water. It was found that after 20 hours at 80$^\circ$C and pH 3 the lepidocrocite starting material in the iron(II) solution had transformed into a red hematite/goethite material, while little change had occurred in the control. On analysis of the radioactivities, the iron(II) solution contained 72 percent of the system's total counts while the filtrate from the control contributed only 4.4 percent. This 4.4 percent was attributed to a small amount of dissolution of lepidocrocite at this pH.
The high percentage of counts in the iron(II) solution establishes that the transformation of lepidocrocite indeed involves the initial dissolution of the original oxide followed by nucleation and reprecipitation of the most favoured oxide, as suggested by Schwertmann and Taylor (1972) and van Oosterhout (1967).

2.4.5 Effect of Metallic Iron and Other Reductants on the Transformation Products

Since the transformation of lepidocrocite takes place in the Becher aerator in the presence of still unreacted reduced ilmenite containing metallic iron, a series of tests were performed to establish whether the transformation products were altered by iron and other reductants in solution. Such reductants can be expected to alter the Eh of the solution and the mixed potential for transformation, if indeed, the reaction is redox controlled.

For comparison, tests were carried out in 0.5 M FeCl$_2$ solution at 80°C and pH 4 in the presence of pure iron powder, reduced ilmenite and pure zinc powder, as well as a mixed NiCl$_2$/FeCl$_2$ solution containing iron powder in order to establish whether nickel incorporation into the lattice could be achieved. Attempts to use sodium metabisulfite as a soluble reductant, to compare with Zn$^0$ and Fe$^0$, were unsuccessful because of the immediate formation of an insoluble reddish-brown compound believed to be basic iron(II) sulfite. During the reaction it was noted that the presence of Zn$^0$ and Fe$^0$ decreased the demand for base to maintain the desired pH, since these metals react with the acid generated by transformation and introduce Fe$^{2+}$ and Zn$^{2+}$ into solution.
The results of the oxide phases produced under these conditions are summarised in Table 2.4 and show that both Fe\textsuperscript{o} and reduced ilmenite produced a single magnetite phase rather than a green goethite/magnetite mixture. Interestingly, in the presence of iron(II), it was found that Zn(II) and Ni(II) were incorporated into the iron oxide lattices. Yet Ni(II) alone, with a similar electronic configuration to iron(II), did not initiate a transformation reaction (see Chapter 3).

A dissolution-reprecipitation mechanism would therefore account for the incorporation of these cations, as both iron(II) and Ni(II) or Zn(II) will be in the solution phase and can be precipitated together. The d-spacings of the X-ray diffraction pattern for the zinc containing oxide, correspond to those of franklinite in the JCPDS cards. Franklinite is a zinc containing spinel (ZnO\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{3}), being related to magnetite (FeO\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{3}). Microanalysis using the EDAX analysis system linked to the scanning electron microscope gave elemental analysis consistent with this assignment.
Table 2.4

Oxide Phases Produced from Transformation of Lepidocrocite upon Addition of Iron(0), Zinc(0) and Nickel(II) at pH 4 and 80°C

<table>
<thead>
<tr>
<th>Addition</th>
<th>Colour</th>
<th>Oxide Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>green</td>
<td>goethite/magnetite</td>
</tr>
<tr>
<td>metallic iron</td>
<td>black</td>
<td>magnetite</td>
</tr>
<tr>
<td>reduced ilmenite</td>
<td>black</td>
<td>magnetite</td>
</tr>
<tr>
<td>metallic zinc</td>
<td>green</td>
<td>franklinite (Zn0. Fe2 O3)</td>
</tr>
<tr>
<td>Ni(II) + Fe(0)</td>
<td>green</td>
<td>iron-nickel oxyhydroxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Fe.Ni.00H)</td>
</tr>
</tbody>
</table>

By contrast, Mossbauer spectroscopy found iron(III), other than lepidocrocite in the product, that was produced in the presence of NiCl₂. This established that an iron-nickel oxyhydroxide was formed rather than a nickel spinel (trevorite). The difference may be attributed to the Eh of the solution, since Fe⁰ and Zn⁰ powder produced the lower valency magnetite and franklinite respectively, while the Ni(II)/Fe⁰ mixture resulted in the formation of an oxide more closely related to goethite. This nickel containing oxide is
related to naturally occurring nickel laterites and the processes described here probably reflects the geochemistry of these types of deposits. The incorporation of Ni(II) and Co(II) into magnetites and other oxides is also well documented in the corrosion products from nuclear reactors (Regazzoni and Matijevic, 1982; Tamura et al., 1983). Again, the products formed are a function of the redox conditions prevailing during corrosion.

The observation that the lower valency magnetite could be transformed to hematite in an iron(II) solution at 80°C and pH 2.0 also suggests that potential related processes can occur, modifying the final product. This interconversion is known to occur in air at temperatures above 600°C, but this reaction also shows that other iron oxides can be transformed at low temperatures (80°C), if the solution conditions and oxide particle sizes are suitable.

Cornell (1988) discussed the difference in product phases observed as a function of the inhibitory effect of the added cations. However, significant changes in potential would have occurred in her study, resulting in a number of the effects observed in the products shown in Table 2.4.

2.5 SEM Analysis of the Iron Oxides from Aerator Tests

2.5.1 Initial Products

Plate 2.1 shows the scanning electron micrographs of the four samples collected from the aeration tests summarised in Table 2.2.
Plate 2.1a. Scanning Electron Micrograph of aeration

Sample A (Grid bar = 1 micron)

Plate 2.1b. Scanning Electron Micrograph of aeration

Sample B (Grid bar = 1 micron)
Plate 2.1c. Scanning Electron Micrograph of aeration
Sample C (Grid bar = 1 micron)

Plate 2.1d. Scanning Electron Micrograph of aeration
Sample D (Grid bar = 1 micron)
The first micrograph shows Sample A to be cubic, typical of magnetite, and well crystalline. The predominant size is ≈0.5 microns but some crystals were as large as 1.0 micron. Sample B on the other hand, consisted of elongated platy crystals mostly 1.0 micron in length and with a width of 0.5 microns. Some of the crystals observed approached 3.0 microns in length and a number of agglomerates were also present. This is similar to the lepidocrocite described by Schwertmann and Taylor (1972) in their study. At a magnification of ≈15000 they observed platy crystals with highly serrated edges, but with the lower magnification used in this study it was difficult to observe any serration.

The third sample was characterised by X-ray diffraction as being predominantly magnetite with a second component of lepidocrocite. This micrograph is consistent with this assignment, since the major crystal observed was cubic (magnetite) with fewer plate-like crystals (lepidocrocite). The magnetite particles were generally similar in size to the magnetite crystals in Sample A, but the lepidocrocite crystals tended to be less elongated than those observed in Sample B.

The final sample of the suite was characterised as a mixture of hematite, goethite and lepidocrocite and shows very little crystallinity compared to the previous three. It appears to be predominantly small (0.25 micron) spherical crystals of presumably hematite. These crystals, being smaller than the lepidocrocite, suggest that these phases have been produced at a faster rate.
2.5.2 Transformed Products

The observation that the lepidocrocite in Sample C was less elongated, prompted a study to see if a variation could be observed in the morphology during a transformation reaction over an extended period of time. To monitor these effects, samples were collected over a 3 day period, at pH 2.0, and examined at a magnification of 5,000 times using the scanning electron microscope.

The 5 micrographs in Plate 2.2 show Sample B, followed by samples taken at intervals of 23 hours, 30 hours, 37 hours and the final sample after 60 hours.

Plate 2.2. Scanning Electron Micrographs taken of the iron oxide phases produced during the transformation of lepidocrocite at pH 2.0, 80°C and in 0.5 M FeCl₂ (a) Initial lepidocrocite (Grid bar = 1 micron)
Plate 2.2b. Collected after 23 hours (Grid bar = 1 micron)

Plate 2.2c. Collected after 30 hours (Grid bar = 1 micron)
Plate 2.2d. Collected after 37 hours (Grid bar = 1 micron)

Plate 2.2e. Final product, collected after 60 hours.
(Grid bar = 1 micron)
When analysing the shapes and sizes of the crystals in chronological order it is quite evident that the crystals slowly become smaller as the elongated plates ultimately turn into spherical hematite crystals. During the period between the 23rd hour and the 39th hour, the lepidocrocite crystals generally became more rounded as if the jagged edges have been worn off or dissolved away. The micrograph taken after 30 hours shows a greater distribution of smaller particles than appears in the micrograph after 23 hours. After 37 hours, the first evidence of discrete spherical hematite appears along with the larger lepidocrocite. The final micrograph is dominated by spheres of about 0.25 microns in diameter while the X-ray diffraction pattern of this material indicated that a minor amount of goethite was present, it was difficult to identify any in the micrograph.

The size of the spheres in the last two samples seem to be similar but only qualitative observations can be made as to the relative distribution of their sizes from these micrographs.

The micrographs in Plate 2.3 show the shape of the crystals, which were produced more rapidly at pH 4.0 and 5.0 than at pH 2.0. The first one shows the characteristic acicular crystals of goethite which was found to be the major component by XRD. Other cubic or agglomerated particles are probably magnetite, which was found to be the minor substituent of this sample. The needles in this sample were generally 0.5 microns in length with the thickness very fine at about 0.1 microns. The iron oxide product from the transformation at pH 5.0 shows very little crystallinity, with hardly any magnetite cubes being discernable.
Plate 2.3. Scanning Electron Micrographs of the iron oxide products formed from the transformation of lepidocrocite at 80°C in 0.5 M FeCl$_2$ (upper) at pH 4.0, (lower) pH 5.0.
(Grid bar = 1 micron)
In general, the crystallinity of the products was found to increase with the longer duration of the experiment. The hematite crystals formed at pH 2.0 show much more crystallinity than do the magnetite crystals formed at pH 5.0, primarily it seems, due to the slower kinetics of the process at the lower pH. Only the samples formed at pH 2.0 approaches the size required for pigmentary purposes (see Chapter 11) but with slower crystal growth or with less stringent conditions larger crystals may be possible at a higher pH. The magnetite sample from the 8 hour aeration (Sample A), is significantly more crystalline than any of the products from the laboratory transformation tests. Thus, larger crystal sizes should be possible if the recrystallisation process is controlled, as detailed in the following chapter.

Plate 2.4 presents two micrographs of the product obtained from seeding the lepidocrocite with 10 percent w/w of a commercially precipitated hematite (supplied by Ajax Ltd), and the Ajax seed material itself. The micrograph of the seed material shows it to be poorly crystalline but resembling the spherical shape observed in Figure 2.4-D. The micrographs of the hematite product however, do not resemble the shape of the original hematite crystals, but rather appear as large flakes or plates. In some cases these flakes are as large as 3.0 microns square and resemble a rare, but naturally occurring grey-red hematite known as flake or micaceous hematite. Micaceous hematite is valued as a pigment in metal protective coatings because of its lamellar nature (Patton, 1973). The flakes of such a pigment reflect the sun's radiation to a high degree, similar to metallic flake pigment, and paint film containing this oxide maintains its reflectant ability for many years. Furthermore, the plate-like or leafy structure of the micaceous iron oxide provides a physical
Plate 2.4. Scanning Electron Micrographs of the micaceous hematite formed on transformation of lepidocrocite in the presence of 10 percent hematite (Ajax Ltd) seed.
(Grid bar = 1 micron)
Plate 2.4b. Scanning Electron Micrograph of the seed material used during the formation of the micaceous hematite.

(Grid bar = 1 micron)

barrier to the penetration of moisture and reduces the chance of corrosion (Patton, 1973).

Even though the crystals obtained in this work are in the smallest size range to be considered as micaceous, and the result was an isolated phenomenon, no other reports of the low temperature formation of synthetic flake hematite have been found. Unfortunately the crystallisation process seems to be very sensitive to the environment, as the introduction of a higher level of seeds did not promote micaceous iron oxide formation. Further work is required to study the reproducibility and mode of formation of this material for commercial exploitation.
2.6 Experimental

2.6.1 Identification and Production of Aerator Iron Oxides

The simulation of the Becher Process was performed using 1 kg of reduced ilmenite in a 2 litre reactor using a 1.5 percent ammonium chloride solution with air flow rates of either 2 or 3 litres per minute sparged into the pulp from the bottom of the reactor. A cylindrical baffled reactor was used to produce a consistent pulp with stirring from an overhead driven paddle stirrer. External heating was used to maintain a maximum temperature of 70°C for the last 6 hours of the 8 hour aeration test. The oxides were separated from the remaining synthetic rutile by passing the aeration mixture through a 53 micron screen and then filtering the solution under vacuum. The crystal phases and colours produced are shown in Table 2.2 (Section 2.4.2).

2.6.2 Transformation Experiments

The pure lepidocrocite used for the transformation experiments was obtained from one of the aeration runs described in the previous section.

The transformation of lepidocrocite and other iron oxide starting materials were performed in a 250 ml three-necked round bottom reactor seated in a thermostatically controlled Rotamantle. The centre neck was connected to a condensor while pure nitrogen was sparged into the reaction mixture at a constant rate through one side. A combination glass pH electrode was inserted through the remaining port and connected to a Phillips PW9420 pH meter.
Each solution, containing a known concentration of acidic iron(II) solution, was heated to 80±1°C and sparged with nitrogen for 1 hour prior to the addition of the iron oxide. On addition of 5.0g of the iron oxide the reaction mixture was brought to the predetermined pH using NH₄OH, at which point the reaction time was recorded. The pH was maintained to ±0.1 pH by the incremental addition of dilute NH₄OH.

Samples for X-ray diffraction analysis were collected at various time intervals by the withdrawal of approximately 5 ml of the reaction mixture using a syringe. This solution was filtered hot under vacuum using three Whatman No.542 filter papers and washed with copious amounts of distilled water.

The solids were air dried at <60°C and carefully ground into a fine powder using a glass mortar and pestle.

2.6.3 X-ray Diffraction Analysis

X-ray patterns of the iron oxide products from the transformation experiments were obtained using a Phillips X-ray diffractometer connected to a Siemens X-ray generator with cobalt K-alpha radiation. Diffraction patterns were recorded on a Phillips PM8203 single pen recorder. The standard conditions were 35kV, 30mA, 2 theta/min. and 10 000 counts per second full deflection on the chart recorder.

Assignments of the phases present were made by comparing d-spacings from the diffraction patterns with those reported in the cards compiled by the Joint Committee on Powder Diffraction Standards.
2.6.4 Scanning Electron Microscope Analysis

Particle shape and size were determined using a Phillips Model 503 Scanning Electron Microscope. Samples of the finely divided iron oxide powders were smeared onto individual 13 mm diameter graphite tablets using a watch glass and acetone as a solvent. After the solvent had evaporated the samples were gold coated using standard vacuum deposition techniques.

2.6.5 Transformation of $^{59}$Fe Isotope Doped Lepidocrocite

$^{59}$Fe doped lepidocrocite was prepared by bubbling $O_2$ through 0.5 M FeCl$_2$ solution at pH 6-7 which was doped with 500µl of acidified $^{59}$Fe containing (3.885 MBq ml$^{-1}$) supplied by the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights.

The solid material was collected under vacuum and allowed to partially dry for one hour. This material was split into approximately two equal parts and the gamma activity monitored to ensure sufficient $^{59}$Fe had been precipitated as lepidocrocite.

Two three necked 250 ml round bottom reactors were set up in Rotamantles as in Section 2.6.2. One reactor contained 100 ml of 0.5 M FeCl$_2$ while the other (control) contained 100 ml of deionized water. The solids were added to each reactor and the pH adjusted to approximately 3 with additions of NH$_4$OH. The reaction mixtures were then stirred at 80 ± 1°C for 20 hours.
The solid materials were collected by vacuum filtration through 0.45 micron membrane filter papers. The activities of the two solids and the filtrates were determined by counting each sample for 30.0 seconds using a Searle 1197 Series Automatic Gamma Counting System. The percentage of the total counts in the filtrates was finally compared between the iron(II) containing solution and the control.

2.7 Conclusions

A laboratory scale study of the Becher aeration process has shown that a range of different coloured iron oxides can be produced under similar conditions. It was concluded that an oxyhydrolysis reaction results in the precipitation of lepidocrocite, which then undergoes a number of interconversion reactions to produce other phases at a relatively slow rate. This work, and subsequent tests with $^{59}$Fe doped lepidocrocite, is the first study to verify that lepidocrocite is an intermediate in the formation of goethite, hematite and magnetite through a transformation process which involves a dissolution-nucleation-reprecipitation mechanism.

A scanning electron microscope study of the products from transformation reactions has shown that those oxides formed slowly at pH 2.0, approached particle sizes of around 0.5 microns which is suitable in the pigment industry. However preliminary tests indicate that the crystallinity can be greatly modified by seeding.
To further relate these transformations to the Becher Process a detailed analysis of the kinetics of these reactions is required. A kinetic study should indicate why mixed phases containing lepidocrocite are generally produced. This may also help identify the mechanisms controlling the transformation reactions, and thus enhance the chances of controlling the Becher Process.
Chapter 3

Kinetics and Mechanism of Lepidocrocite Transformations

3.1 Introduction

In the previous chapter it was shown that the aqueous transformation of lepidocrocite into other iron oxide phases accounted for the range of products obtained from the Becher Aerator both on the plant and in the laboratory. However, because the mechanism appears to involve a complex series of dissolution, nucleation and growth steps, the kinetics of transformation is not well understood. Recent studies on the kinetics of transformation of ferrihydrite have been reported by Schwertmann and Murad (1983) and Cornell and Giovanoli (1985), but following the early reports of lepidocrocite transformation (Krause et al., 1934; Braudisch and Albrecht, 1932) no comparable definitive study has been undertaken on the kinetics of its interconversion.

Variations in the rate of transformation of lepidocrocite are important in the Becher Aerator because the reaction time is determined by the time required to remove metallic iron from the reduced ilmenite. Thus, the iron oxide product mixture at the end of the batch aeration may be governed by the rate and extent of transformation under the process conditions.

In this chapter, a fundamental study of the kinetics of lepidocrocite transformation is presented and the significance of Fe$^{2+}$ and Fe$^{0}$ on the rates and products are discussed. The aim is to establish, for the first time, the dependence of rate on process parameters such as pH,
temperature, [Fe$^{2+}$] and seed, and to further clarify the role of Fe$^{2+}$ and Fe$^{0}$ by studying the effect of other cations and metals. The effect of other anions and background electrolytes is also considered since these can be expected to affect the activity of Fe$^{2+}$ through ion-pairing or complexation and hence establish whether the activity or total concentration of iron(II) is critical to the transformation process.

Particular attention is paid to the effect of seed since van Oosterhout (1967) concluded that the transformation to goethite would proceed only if goethite nuclei were present. Later this was confirmed by Schwertmann and Taylor (1972b), who showed that silicate retarded the transformation by inhibiting the nucleation step involving goethite formation.

3.2 Experimental

3.2.1 X-ray Diffraction Analysis

The method and equipment used for the collection of X-ray diffraction data was set out in Section 2.7.2. The determination of the extent of transformation of lepidocrocite was carried out by comparing the heights of the most intense lepidocrocite peak in the withdrawn samples and the starting material.

To compare the relative rates of lepidocrocite transformation over a range of pH values, the rate of disappearance of the main X-ray peak was taken from the slope of the disappearance curves at the time when it was half its original value. In this way effects of crystallinity
changes on XRD were minimized and the rates were independent of any induction period prior to transformation taking place. It was not possible to quantitatively follow the appearance of the oxide products because of the change in the phases and the varying degree of crystallinity shown over the range of pH conditions. Therefore, quantitative determinations of the relative proportions of the oxides in the individual samples were made by thermogravimetric analysis.

3.2.2 Thermogravimetric Analysis

The analysis of the water content of the iron oxides was performed by thermogravimetric analysis. In each case approximately 10 mg of sample was accurately weighed into a platinum crucible and heated in a Stanton Redcroft TG770 furnace with an increase in temperature of 20 degrees/min under control from a Stanton Redcroft TG750 thermogravimetric analyser. The subsequent weight loss was recorded on a Rikadenki 2-pen chart recorder.

3.3 Results

3.3.1 Lepidocrocite Transformation Kinetics

The conditions used and the products obtained from a further series of transformation experiments carried out at 80°C using pure lepidocrocite (Sample B, Table 2.2) are detailed in Table 3.1.
Table 3.1

Experimental Conditions, Reaction Products and Rate Constants from a Series of Transformation Experiments at 80°C.

(5g γ-FeOOH, pH 4.0)

<table>
<thead>
<tr>
<th>Solution Conditions</th>
<th>Product Colour</th>
<th>Product Composition (by XRD and TGA)</th>
<th>k min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M FeCl₂</td>
<td>Green</td>
<td>α-FeOOH(81%), Fe₃O₄(19%)</td>
<td>1.07</td>
</tr>
<tr>
<td>0.5M FeSO₄</td>
<td>Green</td>
<td>α-FeOOH(76%), Fe₃O₄(24%)</td>
<td>1.4</td>
</tr>
<tr>
<td>0.5M Fe(ClO₄)₂</td>
<td>Black</td>
<td>Fe₃O₄(85%), α-FeOOH(15%)</td>
<td>1.7</td>
</tr>
<tr>
<td>0.25M FeCl₂</td>
<td>Green</td>
<td>α-FeOOH(86%), Fe₃O₄(14%)</td>
<td>0.63</td>
</tr>
<tr>
<td>1.0M FeCl₂</td>
<td>Green</td>
<td>α-FeOOH(79%), Fe₃O₄(21%)</td>
<td>2.9</td>
</tr>
<tr>
<td>0.05M FeCl₂</td>
<td>Red/Yellow</td>
<td>only minor transformation</td>
<td>-</td>
</tr>
<tr>
<td>0.5M NiCl₂</td>
<td>Yellow</td>
<td>no reaction</td>
<td>-</td>
</tr>
<tr>
<td>0.5M CuCl₂</td>
<td>Yellow</td>
<td>no reaction</td>
<td>-</td>
</tr>
<tr>
<td>0.5M CaCl₂</td>
<td>Yellow</td>
<td>no reaction</td>
<td>-</td>
</tr>
<tr>
<td>0.5M FeCl₃</td>
<td>Red/Yellow</td>
<td>no reaction except Fe(OH)₃</td>
<td>-</td>
</tr>
<tr>
<td>0.5M FeCl₂+2M Mg(ClO₄)₂</td>
<td>Black</td>
<td>Fe₃O₄, α-FeOOH*</td>
<td>1.7</td>
</tr>
<tr>
<td>0.5M FeCl₂+4M NaClO₄</td>
<td>Black</td>
<td>Fe₃O₄, α-FeOOH*</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Excess water not allowing accurate determination of phases.

The data shown in Table 3.1 also gives the rate of transformation of pure lepidocrocite to goethite and magnetite at 80°C and pH 4 in solutions of iron(II) as chloride, sulfate and perchlorate. Results for the similar cations Ni²⁺, Cu²⁺, Ca²⁺ and Fe³⁺ are also presented. Suprisingly, no reaction occurred in solutions containing divalent
cations other than iron(II). Even iron(III) chloride resulted in little or no transformation although the precise characterisation of this product was marred by the precipitation of iron(III) hydroxide at the pH used.

A mass balance of the reaction in the presence of FeCl₂ at pH 5.0, which showed that 1.5g Fe₃O₄ was produced per gram γ-FeOOH, and confirmed the incorporation of iron(II) into the magnetite lattice. The presence of iron(II) is therefore integral in the transformation mechanism. Furthermore, since the rate varies with iron(II) concentration, it must be involved in the rate determining step. As Figure 3.1 indicates, there is a straight line relationship between the log[iron(II)] and log k with a slope of 1.1 ± 0.2.

Reactions with 0.50 M iron(II) in chloride, sulfate and perchlorate media were carried out in order to establish whether the activity of free Fe²⁺ or the concentration of iron(II) salts determines the rate. These solutions display differing relative amounts of ion pairing between the iron(II) and the anions according to the following equilibrium constants (Sillen and Martell, 1964).

\[
\begin{align*}
Fe^{2+} + SO_4^{2-} &= FeSO_4 \\
\log \beta_1 &= 2.30 \\
Fe^{2+} + Cl^- &= FeCl^+ \\
\log \beta_1 &= 0.36 \\
FeCl^+ + Cl^- &= FeCl_2 \\
\log \beta_2 &= 0.04 \\
Fe^{2+} + ClO_4^- &= Fe(ClO_4)^+ \\
\text{no pairing} \\
\end{align*}
\]
Figure 3.1. Effect of iron (II) concentration on the rate of transformation of lepidocrocite (80°C, pH 4.0)
Clearly there is no pairing with the perchlorate ion and only minor pairing with chloride ion, thus if the activity of Fe$^{2+}$ determined the rates of lepidocrocite disappearance, they should be in the order ClO$_4^-$ > Cl$^-$ > SO$_4^{2-}$. As shown in Table 3.1 the fastest rate is indeed observed in perchlorate medium but the rate of reaction is faster in the sulfate medium than in the chloride medium.

Even though these results do not completely correlate with the activities of the iron(II) ion, they indicate that the counter ion does affect the transformation rates probably due to adsorption on the lepidocrocite surface or double layer effects. Furthermore, under the same pH and temperature conditions, the product from the perchlorate medium contained significantly more magnetite (85%) than did the products from the chloride (19%) or sulfate (24%) media.

3.3.2 Effect of pH

The effect of pH on the rate of transformation is complex because the reaction shows an induction period prior to conversion which also appears to be pH dependent. Figure 3.2 shows the typical curves obtained at pH 3.0, 4.0 and 5.0 for the transformation of lepidocrocite starting material in 0.5 M FeCl$_2$ at 80$^\circ$C.

From these curves, the effect of pH on the induction period and on the rate of disappearance of the lepidocrocite starting material was determined, as set out in Table 3.2.
Figure 3.2. Typical lepidocrocite transformation curves at pH 3.0 (●), 4.0 (■) and 5.0 (▲) (0.5 M FeCl₂, 80°C).
Clearly the induction period observed at low pH does not allow a simple first or second order rate equation to be fitted to the points. However, the initial induction period, prior to the relatively rapid disappearance of the lepidocrocite, is consistent with a period of nucleation. Once the product oxide had been nucleated and was sufficiently crystalline to be detected by the X-ray diffraction technique used, the reaction proceeded relatively rapidly, at rates which increased significantly with pH.

**Table 3.2**

*Effect of pH on Rates of Transformation of Lepidocrocite*

<table>
<thead>
<tr>
<th>pH</th>
<th>Product</th>
<th>Experiment</th>
<th>k</th>
<th>$\log_{10}(k)$</th>
<th>Oxide Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>first</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>duration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>detected</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mins)</td>
<td>(mins)</td>
<td>(min$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1380</td>
<td>3120</td>
<td>0.03</td>
<td>-1.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hematite, Goethite</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>120</td>
<td>480</td>
<td>0.17</td>
<td>-0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hematite, Goethite</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>15</td>
<td>90</td>
<td>1.07</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Goethite, Magnetite</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>4</td>
<td>20</td>
<td>3.5</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Magnetite</td>
</tr>
</tbody>
</table>
Figure 3.3. Effect of pH on the rate of transformation of lepidocrocite (80°C, 0.5 M FeCl₂)
As shown in Figure 3.3, a plot of pH versus log rate constant proves to be linear with a slope of 0.7 ± 0.1. These results are consistent with the results reported by Tamura et al. (1983) who obtained a straight line relationship of slope ≈ 1 between log rate constant and pH for the formation of magnetite between pH 8.0 and 8.6.

The first order relationship with pH supports the view that the rate determining step is the dissolution of lepidocrocite once sufficient nuclei are present for reprecipitation. Thus seeding should reduce the induction period as well as increase the rate.

3.3.3 Effect of Seeding on the Rate and Product Distribution of the Transformation Reaction

As discussed earlier, a report by van Oosterhout (1967) noted that the transformation of lepidocrocite to goethite only occurred in the presence of goethite nuclei. Therefore a series of experiments were carried out in which goethite and hematite seeds were added.

As the addition of crystalline seeds is more likely to have an effect on the growth of product crystallites, for this part of the study, the rates of transformation were determined from the rate of increase of the product crystal phase rather than the rate of disappearance of lepidocrocite. Figure 3.4 shows the appearance of the goethite δ = 4.18 Å peak for a number of experiments and graphically shows the effect of the addition of seeds on the rate of transformation of lepidocrocite. Clearly the time period for complete conversion is much less because of the lack of an induction period, unlike the unseeded
Figure 3.4. The appearance of goethite (d = 4.18Å) in the x-ray diffraction patterns of iron oxides formed from the transformation of lepidocrocite at 80°C in 0.5 M iron(II). (0 = pH 3.0 in FeCl₂, □ = pH 3.0 in FeCl₂ + 10 percent goethite seed, Δ = pH 4.0 in FeSO₄, • = pH 4.0 in FeCl₂).
experiments. These rates of formation of goethite and hematite as well as the induction periods and the relative proportions of the products of both seeded and unseeded reactions are compared in Table 3.3.

**Table 3.3**

**Effect of Seeding on Rates of Formation of Hematite and Goethite**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Formation Rates</th>
<th>Induction Periods</th>
<th>Hematite</th>
<th>Goethite</th>
<th>Hematite</th>
<th>Goethite</th>
<th>Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hematite (min^{-1})</td>
<td>Goethite (min^{-1})</td>
<td>(min)</td>
<td>(min)</td>
<td>Ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no seed pH 3</td>
<td>3.2</td>
<td>1.9</td>
<td>183</td>
<td>89</td>
<td>1:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Hematite seed</td>
<td>10</td>
<td>1.1</td>
<td>0</td>
<td>-</td>
<td>3:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Goethite seed</td>
<td>3.0</td>
<td>6.0</td>
<td>-</td>
<td>0</td>
<td>1:6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% Hematite seed</td>
<td>2.9</td>
<td>2.1</td>
<td>0</td>
<td>-</td>
<td>3:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no seed pH 2</td>
<td>1.5</td>
<td>-</td>
<td>1584</td>
<td>-</td>
<td>5.5:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>no seed pH 4</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>3</td>
<td>no hematite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
An analysis of Table 3.3 shows that the addition of seed material, as well as eliminating the induction period, had an effect on both the rate of formation of the products, as well as on their relative proportions. It appears that the type of seed chosen promotes the formation of that particular crystal phase but does not promote the one phase exclusively. For example, the addition of 10 percent by weight of goethite into the starting material increased the level of goethite from 49 percent to 86 percent. The addition of hematite seeds also increased the proportion of hematite, but not to the same extent.

The addition of 10 percent goethite and hematite seeds increased the rate of appearance of that same crystal phase by a factor of about 3 in each case, but had relatively little effect on the rate of appearance of the other phase. However the addition of 50 percent hematite seed, had little effect on the rates of the transformation and there was little or no difference in the proportions of the products once the amount of seed material added was accounted for. Why there was a decrease in the rate of formation of hematite when more hematite seed was added is not clear at this stage. It is possible that the large surface area of seed adsorbs Fe$^{2+}$ and this competes with lepidocrocite, thereby decreasing the transformation rate.

Certainly limited seeding does effect the rate and product distribution which supports a mechanism involving nucleation. This would not be expected if the lepidocrocite simply dissolved, followed by the reprecipitation of a new oxide phase, without going through a concerted nucleation phase.
3.3.4 Effect of Temperature

The effect of temperature on the transformation reaction was investigated in the range 60-80° C, where rates could be easily measured. Figure 3.5 shows the degree of conversion with time for transformation experiments at 62 and 80° C in 0.1 M FeCl₂ at pH 5.0.

The figure clearly shows that temperature has a dramatic effect on the transformation rate, with the increase in kinetics for the 18° temperature rise from 62 to 80° C being much greater than would be expected for simple chemical reactions with temperature. It is believed that the pronounced effect of temperature is due to the greater production and crystallinity of nuclei at higher temperatures which decreases any induction period. Nuclei from the hydrolysis of the FeCl₂ solution are thermodynamically favoured at higher temperatures. Sidhu et al. (1981) reported that the dissolution rate of lepidocrocite increased with temperature, and this effect would also reflect in faster transformation kinetics.
Figure 3.5. Effect of temperature on the rate of transformation of lepidocrocite (0.1 M FeCl$_2$, pH 5.0)
3.4 Discussion

The results in this, and the previous chapter show that lepidocrocite can be transformed in iron(II) solutions to hematite, goethite and magnetite, and that lepidocrocite can be considered as an intermediate in the formation of these more stable oxides. The transformation of lepidocrocite is significantly increased by raising the pH, temperature and the iron(II) concentration, but the exact role of the proton and $\text{Fe}^{2+}$ ion is not clear.

As discussed earlier, Tamaura et al. (1983) found that above pH 7.3, lepidocrocite is transformed to stoichiometric magnetite with the reaction being triggered by the adsorption of iron(II) ions. The observation that iron(II) ions are adsorbed by oxyhydroxides and oxides of iron was also reported by Tamura et al. (1980) in their study of the accelerating effect of these precipitates on the rate of oxidation of iron(II) ions. Tamura et al. (1980) found that the $\text{Fe}^{2+}$ adsorption increased logarithmically with increasing pH and a similar effect with pH was shown for the similar $\text{Co}^{2+}$ ion (Tamura et al., 1982). It is believed that as the pH rises and approaches the point of zero charge (PZC) of the iron oxide, the competition between cobalt(II) ion and the proton becomes less, and more cobalt(II) is adsorbed. The adsorption behaviour was attributed to the formation of surface complexes at neutral -FeOH iron oxide sites, which increase in number with pH. The formation of these surface complexes (equations 3.7 and 3.8) result in the release of one or two protons and are therefore favoured at higher pH.
\[
\text{Co}^{2+} + \text{-FeOH} = \text{-FeOCO}^+ + \text{H}^+ \quad 3.7
\]

\[
\text{Co}^{2+} + 2\text{-FeOH} = \text{-(FeO)}_2\text{Co} + 2\text{H}^+ \quad 3.8
\]

The transformation kinetics or the rate of dissolution of the lepidocrocite is thus determined by the amount of iron(II) adsorbed and complexed on the surface. It follows that in order to increase the number of adsorbed Fe\(^{2+}\) ions on the oxide surface, it is necessary to either increase the concentration of iron(II) ions in solution or increase the pH. Thus both of these variables are inter-related and the straight line relationships between pH and \(\log[\text{Fe}^{2+}]\) and \(\log\) rate can be directly related to Fe\(^{2+}\) adsorption on the surface.

Sato et al., (1984) reported that as the pH increases, the Eh of iron(II) and iron(III) containing solutions decreases, due to the formation of complexes between iron and the hydroxide ions as shown in equations 3.9 to 3.14.

\[
\text{Fe}^{2+} + \text{OH}^- = \text{FeOH}^+ \quad 3.9
\]

\[
\text{Fe}^{2+} + 2\text{OH}^- = \text{Fe(OH)}_2 \quad 3.10
\]

\[
\text{Fe}^{3+} + \text{OH}^- = \text{FeOH}^{2+} \quad \text{pK}_I = 11.1 \quad 3.11
\]

\[
\text{Fe}^{3+} + 2\text{OH}^- = \text{Fe(OH)}_2^+ \quad \text{pK}_{II} = 21.69 \quad 3.12
\]

\[
2\text{Fe}^{3+} + 2\text{OH}^- = \text{Fe}_2\text{(OH)}_2^{4+} \quad \text{pK}_d = 25.10 \quad 3.13
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- = \text{Fe(OH)}_3^- \quad \text{pK}_{sp} = 37.20 \quad 3.14
\]

As the solution potential conditions were shown to modify the product phase in the previous chapter, these relationships indicate that the variation of pH not only induces the effects discussed above, but also
regulates the expected product due to the changes in potential at the iron oxide interface. As the pH is increased, a lower Eh is obtained in the iron(II) solutions. This correlates with the lower valence magnetite product predominating at higher pH levels. The role Eh plays in determining the end-products of lepidocrocite transformation reactions will be discussed further in Chapter 4.

The range of products observed in this study by adding different seeds, foreign cations, or metal powders, show that if different nuclei form, a number of different iron containing oxides can be produced. These nuclei presumably form from the solution phase and are highly dependent on solution potential. The chance of producing nuclei is, of course, greater from concentrated iron(II) containing solutions and the chance of producing nuclei by hydrolysis is greater with increased pH. Therefore, it is believed that the pH does not affect the transformation rate by increasing the dissolution rate, but rather effects the formation of nuclei through adsorption of iron(II). As discussed previously, increased temperatures will also affect the rate in a similar manner. It also follows that hydrolysis reactions, which occur in the Becher Process due to air sparging, create a large number of product nuclei and enhance the kinetics.

At low pH values a significant induction period was evident prior to the transformation reaction being initiated. At pH 2.0 it was found that the crystallinity of the lepidocrocite increased prior to the observation of the transformation products. These results suggest that the rate determining step of the process is in fact the formation of the nuclei of the more stable iron oxide product or products. As the solution conditions do not change throughout the process it can be
assumed that the lepidocrocite is dissolving at essentially the same rate. In fact, Sidhu et al. (1981) showed that lepidocrocite dissolution followed a zero order rate law.

Even though the experiments at pH 2.0 and 3.0 showed no evidence of the transformation products initially, the increase in crystallinity observed can be accounted for by invoking the same mechanism. Here, the smaller sized and less crystalline particles dissolve and then reprecipitate again in a reversible process, stimulating the growth of the existing lepidocrocite crystals. The absence of an induction period with the addition of seed material, is further evidence that the nucleation of the product is the rate determining step. These observations can account for van Oosterhout’s (1967) claim that \( \gamma \)-FeOOH transforms to \( \alpha \)-FeOOH on heating in alkali hydroxide or FeSO\(_4\) solutions only in the presence of \( \alpha \)-FeOOH nuclei.

Therefore, transformation reactions can be divided into four steps:

1. Adsorption of Fe\(^{2+}\) onto the iron oxide surface,

2. Dissolution of the iron oxide,

3. Nucleation of a new iron oxide phase, and

4. Reprecipitation of iron from solution,

with step (3) being rate determining.

A better understanding of these steps is required if iron oxides of
sufficient purity to be used as pigments, are to be produced from the Becher aeration process. Control of the rate and the identification of conditions required to nucleate each phase would enable the crystallisation of particles of suitable particle size. These factors will be further discussed in Chapters 4 and 5 in relation to electrochemical and plant process conditions. Obviously, other than kinetic considerations, thermodynamics will govern if a process is to proceed and this aspect will also be expanded in Chapter 4.

3.5 Conclusion

The work presented in this chapter not only discusses the kinetics of the lepidocrocite transformation for the first time, but conclusively shows that the mechanism involves adsorption, dissolution, nucleation and reprecipitation steps.

The results show that the rate of transformation is significantly increased by raising the temperature, pH and the iron(II) or Fe$^{2+}$ concentration. The latter two parameters gave a logarithmic relationship with rate and are inter-related when considering the amount of Fe$^{2+}$ adsorbed onto the lepidocrocite surface. This influences the rate of dissolution, but evidence exists that the solution potential is also modified by the pH, which then regulates the product phase.

The results obtained upon addition of seed material indicates that the rate determining step is the formation of suitable product nuclei. Nuclei formation is promoted by higher temperatures, increased iron(II) concentrations and pH, and each of these process parameters increased the rate of lepidocrocite transformation.
Chapter 4

Electrochemistry and Thermodynamics of Iron Oxide

Transformation Reactions

4.1 Introduction

In Chapter 2 it was shown that the products from lepidocrocite transformation reactions could be altered by the addition of reducing agents which modified the solution potential conditions. It was also suggested that the potential and pH of the iron(II) solutions regulated the product composition. Hematite was formed at low pH values, where the reduction potential was higher, and magnetite at the more negative reduction potentials expected at higher pH.

In this chapter a study is presented on the electrochemistry and thermodynamics of reactions involving the iron oxide phases formed during the dissolution of iron in the Becher Process. These reactions also occur as a consequence of the rusting of iron at ambient temperatures, therefore the results can be used to rationalise more generally the formation of various iron oxide phases during corrosion processes.

4.1.1 Electrochemistry of Iron Oxide Phases

Most discussions on iron oxide electrochemistry have focussed on the dissolution of oxide phases. A comprehensive review of the electrochemistry and theory of dissolution of oxide phases has been given by Diggle (1973). Pryor and Evans (1950) showed that the dissolution rate of Fe$_2$O$_3$ depended on the potential difference between
the oxide and the electrolyte. In a more recent study on magnetite and hematite, Lu and Muir (1988) concluded that the major factor which affects the acid dissolution rate was the redox potential of the solution. Much faster rates were observed at potentials cathodic to their rest potentials, in the presence of suitable reductants.

However, according to Vermilyea (1966), oxides can behave under certain conditions as electrodes with the potential determined by $\text{H}^+$ and $\text{OH}^-$ concentrations at the surface oxide sites. Taylor and Bond (1979) successfully demonstrated these properties by preparing galvanic cells of hematite and goethite, and hematite with magnetite in 0.01 M CaCl$_2$ at pH 3.6. This indicated that the electrochemical characteristics differed for each oxide. Even though hematite and goethite contain iron in the same formal oxidation state, the potential of hematite was found to be negative with respect to goethite. During the 14 weeks of the experiment, $4.6 \times 10^{-3}$ coulombs flowed, and an unidentified yellow-brown powdery deposit formed at the hematite electrode. However, at a higher pH of 8.6, the polarities were reversed and the goethite electrode was the site of the yellow-brown formation.

The observation that iron rust layers contain various proportions of $\gamma$-FeOOH, $\alpha$-FeOOH and Fe$_3$O$_4$ has generated interest in the electrochemical properties, and in particular, the electrochemical reduction of these rust layers (Stratmann et al., 1983; Keiser et al., 1982; Suzuki et al., 1979; 1980; Okada et al., 1970). However, even though different products were observed at different pH values during polarization of these rust layers, no consideration was given to transformation reactions.
4.1.2 Experimental Programme

In this chapter an experimental programme is described which relates the electrochemistry with the thermodynamics of the iron oxide by-products from the Becher Process. Potentials were recorded for electrodes made from lepidocrocite during transformation reactions, and the products are related to calculated Eh-pH diagrams to compare the thermodynamic relationships with the experimental transformation results.

As transformation reactions involve dissolution followed by reprecipitation, the construction of an experimental diagram by polarizing lepidocrocite electrodes at different pH values is useful for the practical interpretation of the by-products from the synthetic rutile plant, where both hydrolysis and transformation reactions occur. Calorimetric analysis of transformation reactions were also performed to extend the thermodynamic data available for these systems and to relate this data to temperature changes observed on the plant during aeration.

Surprisingly, no comparative study has been found on the electrochemical properties of lepidocrocite and goethite which can be related to the studies reporting the properties of hematite and magnetite. Therefore, cyclic voltammetry and potential data were collected for the various oxide phases. This will provide more data than is available in the literature on the redox reactions occurring at the iron oxide surface, and rationalise why some oxide phases are more readily transformed than others.
4.2 Experimental

4.2.1 Polarization of Pressed Iron Oxide/Carbon Electrodes

Iron oxide electrodes were prepared by mixing 0.2g of carbon black and 0.8g of the iron oxide in a glass mortar and pestle to give an even talc-like consistency and then cold pressed in a 1 cm metal die for 60 seconds at a pressure of 30 kPa. The carbon was added to increase the conductivity of the iron oxide disc.

The wafer thin iron oxide/carbon disc was then carefully removed from the die and positioned in contact with the silver conducting epoxy in the recess of the electrode assembly, as shown in Figure 4.1. Any exposed silver epoxy was removed with a spatula, so that the only conducting surface in contact with the solution was that of the iron oxide/carbon disc. The electrode was then placed in an oven at 60°C for 1 hour to allow the epoxy to harden.

The electrode assembly had all metal connections totally insulated inside the polypropylene head and body. The raised lip of the electrode head was so designed as to fit into a metal X-ray diffraction sample holder. This allowed the iron oxide disc to be flush with the sample holder and in the correct position to collect the X-ray beam. The carbon and the pressing had no effect on the diffraction patterns of the iron oxides used.
Figure 4.1. Pressed iron oxide/carbon electrode assembly

a. conducting connection pin.  b. conducting metal encased polypropylene. c. conducting screw connection to separate electrode head from the body. d. electrode head indicating for mounting the electrode into the X-ray diffractometer. e. indentation in electrode head to allow the wafer thin carbon disc to be inserted and be positioned flush with the of the electrode head. f. polypropylene electrode body.
The choice of polypropylene and the use of clay to hold the electrode into the X-ray sample holder did result in some overlap of the goethite and lepidocrocite X-ray diffraction peaks with those of the clay. However, accurate characterisation of the products could still be made by analysis of the complete diffractogram and knowing the relative peak heights of the overlapping clay lines. The severe solution conditions to which the oxide electrode was subjected, quite often resulted in the exposure of a small area of the silver conducting epoxy. Evidence of this can be found in the diffractograms at 2θ values of 42.6 and 52.1.

The electrode was then placed in 100 ml of degassed 0.5 M FeCl₂ at 80 ± 1°C and the pH adjusted to the desired value using NH₄OH solution, while monitoring the pH with a Phillips PW9420 pH meter.

A conventional three electrode system was used, with the iron oxide/carbon as the working electrode, a platinum coil as the counter electrode and a Ag/AgCl electrode, via a KCl salt bridge, as the reference electrode (E° = -197 mV nHe). This reference electrode was used to avoid the hysteresis characteristic of calomel electrodes at higher temperatures. Results were then corrected to the hydrogen scale.

An open-circuit potential was recorded on a high impedance voltmeter prior to the electrode being polarized for 5 hours at a predetermined potential. Throughout the 5 hours of the experiment the pH was intermittently checked.
After the 5 hour period had elapsed, the cell was dismantled, the iron oxide/carbon surface wiped with paper towel to ensure that the surface was flat, and an X-ray pattern of the damp disc immediately recorded.

4.2.2 Calorimetry

The enthalpy change for the transformation of lepidocrocite to magnetite at 82.5 ± 0.1°C was recorded using a Guild Model 400 Solution Calorimeter coupled with a Rikadenki single pen chart recorder.

Initially the chart recorder was calibrated at temperature by applying a known voltage through a bank of resistors immersed in the FeCl₂ solution with a total resistance of 20.4Ω. All measurements were made with the external heating of the water bath switched off and the system slowly cooling.

The heat changes made on addition of 10 ml of concentrated NH₄OH to 250 ml of 0.4 M FeCl₂ with and without the 10.00g of pure lepidocrocite were then calculated from the known energy output monitored on the chart recorder. The calibration procedure used 22.5V through the 20.4Ω resistance for 60 seconds which related to 40.4 ± 0.8 J/division on the chart recorder. The addition of the NH₄OH to the FeCl₂ solution brought the pH to 6 and resulted in 343.7 J of heat given out. A correction was made for this heat generated on addition of the NH₄OH to the FeCl₂ solution. All measurements were made in duplicate.
4.2.3 Carbon Paste Electrodes

Cyclic voltammograms were recorded for the four pure iron oxides: hematite (Ajax Chemicals AR grade precipitated red), goethite (Bayer 920), magnetite (Bayer 318) and lepidocrocite. The iron oxides were prepared as a 20 percent mixture, by weight with carbon black, and mixed in a glass pestle and mortar with paraffin oil (spectroscopic grade). The paste was pressed into a hollow electrode holder and extruded to give a fresh surface by screw feeding. The electrochemical measurements were carried out with reference to a Saturated Calomel Electrode (SCE) using a Princeton Applied Research (PAR) Model 170 combined potentiostat and programmer with a built in Houston Omigraphic X-Y chart recorder. The cyclic voltammograms were recorded between +1.0 and -0.2 V using a supporting electrolyte of 1 M NaCl at pH 5.0 at a scan rate of 50 mV s\(^{-1}\). The electrolyte was degassed with pure nitrogen for 15 minutes prior to recording the voltammograms.

4.2.4 Mixed Potential of Reduced Ilmenite Samples

Mixed potential measurements were made on a number of reduced ilmenite samples supplied by Westralian Sands Ltd. The reduced ilmenites, sampled at different positions along the length of the reduction kiln and ranging in amounts of metallic iron, were ground in a ring mill to a talc-like consistency and prepared as carbon paste electrodes, as above.

Mixed potentials were recorded in oxygenated 0.1M NH\(_4\)Cl at 25°C whilst the electrode rotated at 1000rpm.
4.3 Results and Discussion

4.3.1 Thermodynamics of the Fe-H₂O System

Thermodynamic diagrams for the Fe-H₂O system have appeared in numerous publications in the literature since the publication of the "Atlas of Electrochemical Equilibria in Aqueous Solution" by Pourbaix (1963).

Biernat and Robins (1972) reported an extensive series of diagrams for this system up to 300°C, using the Correspondence Principle (Criss and Cobble, 1964) to obtain data at the higher temperatures. Potential-pH diagrams generally show that magnetite and hematite form at different potentials. Some diagrams include a number of the hydrated oxyhydroxides (Misawa, 1973), but no diagram has been found in the literature delineating the potential boundaries for the formation of all the oxides formed during the Becher aeration process at the same temperature, namely lepidocrocite, hematite, goethite and magnetite. Relevant thermodynamic data for the formation of iron oxide phases (Table 4.1) was therefore used to construct a conventional Eh-pH diagram for the Fe-H₂O system at 80°C, for the region of most interest to the Becher Process as shown in Figure 4.2. In Table 4.1 a number of sources of thermodynamic data were used, and in some cases a subjective judgement was made on the selection. In particular, calculations were made using the value of ΔG°⁰₂(γ-FeOOH) = 470.7 kJmol⁻¹ reported by Hashimoto and Misawa (1973), which seemed to be a refinement on the other data published. The equations for the lines delineating the regions of stability can be found in the Appendices.
Figure 4.2. Calculated Eh-pH diagram at 80°C Fe-H₂O system for the region of most interest to the Becher Process. (Fe²⁺ = 0.5M).
Table 4.1

*Calculated* and *Literature Thermodynamic Data for the Fe-H$_2$O System*

* at 25 and 80°C *

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\Delta G^\circ_f$ (298K)</th>
<th>$\Delta G^\circ_f$ (353K)</th>
<th>$S^\circ_{298K}$</th>
<th>$S^\circ_{353K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
<td>J mol$^{-1}$ deg$^{-1}$</td>
<td>J mol$^{-1}$ deg$^{-1}$</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>-1.63</td>
<td>27.2</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>-494.5$^1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-483.5$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-486.6$^2$</td>
<td>-491.9</td>
<td>87.9</td>
<td>104.1</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>-696.6$^2$</td>
<td>-703.0</td>
<td>106.7</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>-1017.5$^2$</td>
<td>-1026.4</td>
<td>146.4</td>
<td>173.4</td>
</tr>
<tr>
<td></td>
<td>-1014.2$^1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeOOH</td>
<td>-489.5$^2$</td>
<td>-494.1</td>
<td>75.3</td>
<td>89.4</td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>-496.2$^1$</td>
<td>-499.1$^1$†</td>
<td>89.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-490$^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$-FeOOH</td>
<td>-470.7$^1.6$</td>
<td>-475.2$^2$†</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-469.0$^5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-477$^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>-742.2$^2$</td>
<td>-747.6</td>
<td>87.4</td>
<td>106.2</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-84.9$^7$</td>
<td>-80.0</td>
<td>-113.4</td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>-10.6$^7$</td>
<td>3.68</td>
<td>-293.2</td>
<td></td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>-.56</td>
<td>-20.9</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>-7.32</td>
<td>205.0</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-237.2$^2$</td>
<td>-241.4</td>
<td>69.9</td>
<td>82.7</td>
</tr>
</tbody>
</table>
†,‡ Estimated from data for FeOOH. * Calculated using the Correspondence Principle (Criss and Cobble, 1964) References:
1. Misawa (1973); 2. Biernat and Robins (1972); 3. Latimer (1952);

It is important to note that the stability of the different iron oxide phases is dependent on temperature and thus, even though thermodynamic data can be calculated at different temperatures, some lines are only valid for a certain temperature range.

As the Becher Process involves the corrosion of metallic iron, a number of equations can be proposed at 25°C for the formation of the different iron oxide phases from metallic iron.

\[
\begin{align*}
\text{Fe(OH)}_2 + 2e + 2H^+ &= \text{Fe} + 2H_2O \quad E^\theta = -0.063 \text{ V} \quad 4.1 \\
\text{Fe}_3\text{O}_4 + 8H^+ + 8e &= 3\text{Fe} + 4H_2O \quad E^\theta = -0.089 \text{ V} \quad 4.2 \\
\alpha\text{-FeOOH} + 3H^+ + 3e &= \text{Fe} + 2H_2O \quad E^\theta = -0.072 \text{ V} \quad 4.3 \\
\gamma\text{-FeOOH} + 3H^+ + 3e &= \text{Fe} + 2H_2O \quad E^\theta = +0.013 \text{ V} \quad 4.4 \\
\alpha\text{-Fe}_2\text{O}_3 + 6H^+ + 6e &= 2\text{Fe} + 3H_2O \quad E^\theta = -0.061 \text{ V} \quad 4.5
\end{align*}
\]
Thus, at 25°C the order of decreasing standard potentials given by these reactions is \( \gamma\text{-FeOOH} > \alpha\text{-Fe}_2\text{O}_3 > \text{Fe(OH)}_2 > \alpha\text{-FeOOH} > \text{Fe}_3\text{O}_4 \). However, this order does not follow the convention of having the most oxidised form at the most positive potentials or the most reduced at most negative potentials, as \( \text{Fe(OH)}_2 \) appears at a higher potential than does \( \text{Fe}_3\text{O}_4 \).

When such a situation occurs, the more reduced species is generally unstable and therefore should not appear in the order quoted above.

Lepidocrocite, is shown to occur at a higher potential than its pseudomorph goethite but is known to transform to goethite, hematite and magnetite in the Becher Process. Therefore, lepidocrocite could also be considered to be unstable at lower potentials and thus give negative Gibbs free energy changes for the formation of the other three phases.

\[
2\gamma\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad \Delta G = -43.0 \text{ kJmol}^{-1} \quad 4.6
\]

\[
\gamma\text{-FeOOH} \rightarrow \alpha\text{-FeOOH} \quad \Delta G = -25.5 \text{ kJmol}^{-1} \quad 4.7
\]

\[
3\gamma\text{-FeOOH} + \text{H}^+ + \text{e} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad \Delta G = -79.8 \text{ kJmol}^{-1} \quad 4.8
\]

As \( \text{Fe(OH)}_2 \) and \( \gamma\text{-FeOOH} \) can be considered to be unstable if sufficient time is allowed for conversion, the order of decreasing standard potentials for the formation of iron oxides in contact with metallic iron is \( \alpha\text{-Fe}_2\text{O}_3 > \alpha\text{-FeOOH} > \text{Fe}_3\text{O}_4 \). This suggests that hematite is more oxidised than goethite which, in turn, is more oxidised than magnetite.
4.3.2 Calorimetric Analysis of the Transformation of Lepidocrocite

In order to extend the thermodynamic data on lepidocrocite, which is relevant to the Becher Process, measurements were made on the heat of transformation using the procedure outlined in Section 4.2.2. The enthalpy change was measured for the reaction of 10.00 g of lepidocrocite in FeCl$_2$ at a similar temperature to that encountered during the course of a Becher Aeration, namely 82.5°C (equation 4.9).

$$2\gamma\text{-FeOOH} + \text{Fe}^{2+} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+ \quad 4.9$$

It was found that the transformation to magnetite was an exothermic reaction yielding 1395 J of energy which equates to $\Delta H = -9.3 \pm 0.3$ kJ mol$^{-1}$ $\gamma$-FeOOH. As far as is known, this is the first measurement of the enthalpy of transformation and accounts for the second temperature rise observed during the Becher Aeration process, as discussed in more detail in Chapter 5. Unfortunately the measurement of $\Delta H$ for the transformation to goethite and hematite was not amenable to this technique, as the kinetics of these reactions are much slower.

The exothermic reaction is consistent with rearrangement of the iron oxide lattice to a more stable orientation and the creation of new bonds with Fe$^{2+}$ incorporation into the original lepidocrocite structure.
4.3.3 Mixed Potentials

4.3.3.1 Mixed Potential of Lepidocrocite/Carbon Pressed Disc Electrodes in the Presence of Solid Reductants

The proposition that iron oxides behave as electrodes (Vermilyea, 1966) was verified by measuring the mixed potential of lepidocrocite electrodes placed in various iron(II) solutions under open-circuit conditions. When allowed to transform to hematite, goethite and magnetite in solutions containing reductants such as hydrazine, iron powder, or reduced ilmenite (conditions detailed in Table 4.2), the potential changed significantly over the course of 1-2 hours. After this period the potential either increased or decreased to a steady value according to the product formed.

No consistent potential trends could be observed for the solutions containing solid iron powder and reduced ilmenite, as major oscillations in the mixed potential were encountered due to metallic iron intermittently coming in contact with the electrodes. Reduced ilmenite and iron were shown, in the previous chapter, to alter the product distribution of oxides from transformation reaction in favour of magnetite. The results in Table 4.2 nevertheless, emphasise the importance of solution conditions on determining the product of lepidocrocite transformation reactions, as shown by the results in Chapter 2.
Table 4.2

Solution Additions and Products for Lepidocrocite Electrodes

Transformed under various Redox Conditions

(0.5 M FeCl₂, 100 ml, 80°C)

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>pH</th>
<th>Additions</th>
<th>Atmosphere</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.0</td>
<td>none</td>
<td>Air</td>
<td>Hematite</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>none</td>
<td>Air</td>
<td>Hematite</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>none</td>
<td>N₂</td>
<td>Goethite/Hematite</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.02 moles</td>
<td>N₂</td>
<td>Magnetite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrazine hydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>0.002 moles</td>
<td>N₂</td>
<td>Magnetite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrazine hydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.0</td>
<td>0.5g iron powder</td>
<td>Air</td>
<td>Magnetite</td>
</tr>
<tr>
<td>7</td>
<td>5.0</td>
<td>0.5g reduced ilmenite</td>
<td>Air</td>
<td>Magnetite</td>
</tr>
<tr>
<td>8</td>
<td>5.0</td>
<td>0.5g γ-FeOOH</td>
<td>Air</td>
<td>Hematite/Magnetite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>trace Goethite</td>
</tr>
</tbody>
</table>
4.3.3.2 Mixed Potential of Reduced Ilmenite Samples

To show that the differing amounts of metallic iron in reduced ilmenite samples could facilitate the changes in potential required to produce the various phases discussed in the previous section, a range of different quality samples were prepared. The mixed potentials recorded in 0.1 M NH₄Cl solution are as plotted in Figure 4.3 and show that there is little change in potential above 85 percent metallisation, (i.e. the value expected for good quality reduced ilmenite). Much higher potentials were observed, however, with the lower quality reduced ilmenite or reduced ilmenite at various stages of iron removal.

Therefore the figure reveals that oxides formed in the Becher Process, and which come into contact with reduced ilmenite, will experience a range of mixed potentials, according to the degree of metallisation, which in turn, will influence the type of iron oxide by-products formed.

Furthermore, the iron in low quality reduced ilmenite will dissolve more slowly in acid solution, which would result in a lower iron(II) concentrations and higher solution potentials. Thus, the iron oxide by-products from the Becher Process will be highly dependent on the quality of the reduced ilmenite feed to the aerator.
Figure 4.3. Mixed potentials of reduced ilmenite/carbon paste electrodes versus degree of metallisation of the reduced ilmenite (oxygenated 0.1M NH₄Cl, 25°C, 1000rpm).
4.3.3.3 Mixed Potentials of Lepidocrocite Electrodes upon Addition of Solution Reductants

The lepidocrocite electrodes in Table 4.2 gave much steadier potential changes with hydrazine solution than in the presence of metallic iron (Solutions 4 and 5). The potential data recorded in Figure 4.4 at pH 5.0, with or without nitrogen and hydrazine, shows that each electrode started at a potential of \( \approx 40 \text{ mV (nHe)} \), which rose within the first 15 minutes, before falling to an essentially steady value after 1.5 hours.

The electrode in solution 1 was taken out after 1.5 hours and analysed by X-ray diffraction. The electrode was shown to be essentially unchanged lepidocrocite, but when the electrode was replaced in the solution for a further 3 hours, subsequent analysis showed that the iron oxide was predominantly hematite.

As no current was applied to these electrodes, the crystallisation of the product phases must be a function of the potential at the electrode-solution interface. It can be assumed that since the solution potential conditions did not change greatly during the 5 hour experiment, the lepidocrocite and product phases result in a different potential being recorded in the same solutions. Therefore the initial potential measured during the first 30 to 60 minutes was the mixed potential of the reacting system, which slowly subsided to an equilibrium potential of the solution upon completion of the transformation. The potentials recorded after 4.5 hours and the iron
Figure 4.4. Mixed potentials observed for lepidocrocite electrodes in 0.5M FeCl₂ solution at pH 5.0 and 80°C. A) an air atmosphere, B) nitrogen atmosphere C) a nitrogen atmosphere and 0.002 moles of hydrazine hydrate D) a nitrogen atmosphere and 0.02 mole of hydrazine hydrate.
oxide phase characterised by X-ray diffraction, correlate well with the regions of predominance estimated from the polarization of lepidocrocite electrodes (Figure 4.6), as reported in the following section.

4.3.4 Polarization of Pressed Iron Oxide/Carbon Electrodes

4.3.4.1 Lepidocrocite Electrodes

Even though thermodynamic Eh-pH diagrams provide a useful guide on the precipitation of iron oxides phases, more precise potential conditions are required for the crystallization of hematite, goethite and magnetite from iron(II) solutions in the Becher Process. To gain this information lepidocrocite electrodes were made in a similar manner to that in the previous section, subsequently polarized in iron(II) containing solutions, and then characterised by X-ray diffraction. The solution conditions used were varied with respect to pH and Eh, as shown in Table 4.3, but were within the same range as was found previously to result in the transformation reactions. From the data in Table 4.3 it can be clearly seen that only small changes in pH or Eh are required to form different products and this can be plotted onto experimental Eh-pH diagrams to ascertain actual predominance regions. It should be noted that some electrodes broke-up and crumbled during the prolonged polarization, hence these experiments were rerun.
Table 4.3

Conditions and Products Obtained from Polarizing Pressed Lepidocrocite

Discs after 5 Hours in 0.5 M FeCl$_2$

(80°C, N$_2$ Bubbling)

<table>
<thead>
<tr>
<th>pH</th>
<th>Potential</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mV (nHe)</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-----------</td>
<td>------------------------</td>
</tr>
<tr>
<td>2.0</td>
<td>+200</td>
<td>Hematite</td>
</tr>
<tr>
<td>3.0</td>
<td>+200</td>
<td>Hematite</td>
</tr>
<tr>
<td>4.0</td>
<td>+200</td>
<td>Hematite</td>
</tr>
<tr>
<td>5.0</td>
<td>+200</td>
<td>Hematite + Goethite</td>
</tr>
<tr>
<td>2.0</td>
<td>-150</td>
<td>Magnetite</td>
</tr>
<tr>
<td>5.0</td>
<td>-150</td>
<td>Magnetite</td>
</tr>
<tr>
<td>3.0</td>
<td>+400</td>
<td>Hematite</td>
</tr>
<tr>
<td>2.0</td>
<td>+25</td>
<td>Hematite</td>
</tr>
<tr>
<td>2.5</td>
<td>+75</td>
<td>Hematite</td>
</tr>
<tr>
<td>2.5</td>
<td>0</td>
<td>Goethite</td>
</tr>
<tr>
<td>3.0</td>
<td>+125</td>
<td>Hematite</td>
</tr>
<tr>
<td>3.0</td>
<td>+25</td>
<td>Goethite</td>
</tr>
<tr>
<td>3.0</td>
<td>-50</td>
<td>Magnetite/Goethite</td>
</tr>
<tr>
<td>4.0</td>
<td>+125</td>
<td>Goethite/Hematite</td>
</tr>
<tr>
<td>4.0</td>
<td>+25</td>
<td>Goethite</td>
</tr>
<tr>
<td>4.0</td>
<td>-100</td>
<td>Magnetite</td>
</tr>
<tr>
<td>5.0</td>
<td>+25</td>
<td>Goethite</td>
</tr>
<tr>
<td>5.0</td>
<td>-50</td>
<td>Magnetite/Goethite</td>
</tr>
</tbody>
</table>
Figure 4.5 shows the XRD patterns of the hematite, goethite and magnetite products at pH 5.0, obtained after lepidocrocite had been polarized for 5 hours at 200 mV (nHe), +25 mV (nHe) and -150 mV (nHe) respectively. This figure shows that all three phases can be crystallised at the same pH. Previously all reports of products from transformation and hydrolysis reactions of iron have quoted the pH at which one would expect to produce each oxide, but these results suggest that a potential would be a more significant parameter. The positioning of hematite at more positive potentials than goethite and magnetite follows the same order as was predicted by the thermodynamic calculations.

The result of plotting the data in Table 4.3 on an Eh-pH diagram, along with the lines calculated for the interconversion of magnetite, goethite and hematite in the presence of Fe$^{2+}$, is shown by Figure 4.6. This diagram differs from the conventional Eh-pH diagram, as it is produced in the presence 0.5 M FeCl$_2$, and includes ageing characteristics of oxides as against simply stating dissolution or precipitation products. Conventional Eh-pH diagrams represent iron oxide dissolution reactions with H$^+$ but not transformation reactions involving Fe$^{2+}$.

Figure 4.6 indicates that a sloped boundary exists between hematite and goethite with a positive slope. This slope is approximately 57 mV per pH unit, which is a single electron reaction, whilst the goethite-magnetite line is horizontal and unaffected by pH below pH 5.0. An equation proposed for the relationship between goethite-magnetite and is in good agreement with the experimental results.

$$8\alpha-FeOOH + Fe^{2+} + 2e^{-} = 3Fe_3O_4 + 4H_2O$$ 4.10
Figure 4.5. X-ray diffraction patterns showing the products of transformation of lepidocrocite electrodes polarized at 200, 25 and -150 mV (nHe) for 5 hours at 80°C in 0.5M FeCl₂ solutions (100ml, nitrogen atmosphere, electrode stationary). (M=Magnetite, G=Goethite, H=Hematite, S=Silver, E=Electrode).
Figure 4.6. Eh-pH diagram for the interconversion of magnetite, goethite and hematite in the presence of 0.5 M FeCl₂ at 80°C.

* = Hematite, O = Goethite, □ = Magnetite, combination of symbols indicates two phases present, brackets around symbol indicates data from Table 4.2. (— Calculated boundary, --- Experimental boundary).
Equation 4.10 is very similar to that proposed by MacLeod (1989) to rationalise the formation of Fe$_3$O$_4$ in iron concretions on shipwrecks (equation 4.11).

\[
\text{FeCl}_2 + 2\text{FeOOH} + 2e = \text{Fe}_3\text{O}_4 + 2\text{Cl}^- + \text{H}_2 \tag{4.11}
\]

Which is equivalent to

\[
\text{Fe}^{2+} + 2\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+ \tag{4.12}
\]

Followed by

\[
2\text{H}^+ + 2e \rightarrow \text{H}_2 \tag{4.13}
\]

However, the potentials in this study are not sufficiently cathodic to produce hydrogen.

The phase change from goethite to hematite usually occurs by thermal transformation with elimination of water. However, a realistic equation could not be assigned to this reaction to give a +57 mV/pH slope.

The line shown in Figure 4.6 has a negative slope of 210 mV/pH (3H$^+$ per e at 80°C) which obviously does not coincide with the experimental results. We were able to propose an equation involving goethite, hematite and Fe$^{2+}$ with a positive slope of H$^+$/e, however it involved having Fe$^{3+}$ and Fe$^{2+}$ on different sides of the equation and was therefore, considered to be invalid.

Even though positive slopes for stability regions are very unusual, it is believed that this result is conceivable as transformations of lepidocrocite have been performed in caustic solutions leading to the crystallisation of goethite at high pH values (van Oosterhout, 1967).
Even though the positioning of the lines delineating the stability regions in Figure 4.6 would contain a certain degree of uncertainty due to the number of points used and the difficulty in observing phases at lower than the 5 percent level, the results show considerable coincidence with the boundary between magnetite and goethite, predicted from the thermodynamic relationships. The results plotted in Figure 4.6 involve some ageing and thus should enable more accurate predictions to be made as to the predominant phase under a precise set of conditions. The data from Table 4.2, obtained under open-circuit conditions, is also plotted and is in very good agreement, thus reinforcing the validity of these experimentally determined stability regions.

4.3.4.2 Magnetite, Goethite and Hematite Electrodes

In conventional Eh-pH diagrams, the movement into a different stability region of the diagram should result in the conversion of a species into a more thermodynamically stable species. To test this for the iron oxide system, a programme was conducted with the aim of converting hematite, goethite and magnetite electrodes to other iron oxides by polarizing the electrode in the regions of predominance of a different phase. Initial experiments using crystalline phases proved unsuccessful, but when the electrodes were prepared from poorly crystalline oxides some transformations were observed. In some instances, up to 24 hours was required before sufficient transformation was observed.
Table 4.4 details the conditions and products obtained for the polarization of these oxide electrodes, under similar conditions to those reported in Table 4.3.

**Table 4.4**

**Polarization of Iron Oxide/Carbon Pressed Electrodes**

\[(0.5 \text{ M FeCl}_2, 80^\circ \text{C}, \text{N}_2)\]

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>pH</th>
<th>Potential</th>
<th>Time</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mV (nHe)</td>
<td>h</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>----</td>
<td>-----------</td>
<td>------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Magnetite</td>
<td>3.0</td>
<td>+400</td>
<td>22</td>
<td>Hematite</td>
</tr>
<tr>
<td>Goethite</td>
<td>5.0</td>
<td>-150</td>
<td>6</td>
<td>Goethite/Magnetite</td>
</tr>
<tr>
<td>Goethite</td>
<td>3.0</td>
<td>+400</td>
<td>9</td>
<td>Hematite/Goethite</td>
</tr>
<tr>
<td>Goethite</td>
<td>3.0</td>
<td>+400</td>
<td>22</td>
<td>Hematite/Goethite</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.0</td>
<td>-150</td>
<td>24</td>
<td>Hematite/Magnetite</td>
</tr>
</tbody>
</table>
Figure 4.7. Product from the polarization of a magnetite electrode at pH 3.0 and 400 mV (nHe) (0.5M FeCl₂, 80°C, nitrogen atmosphere).

S = Silver,  H = Hematite,  E = Electrode
As expected, these transformations did not occur as readily as those observed for lepidocrocite and the X-ray patterns collected in some cases were fairly diffuse, especially when polarizing for greater than 20 hours at -150 mV (nHe). However as can be seen in Figure 4.7 a complete transformation of magnetite to hematite was achieved at pH 3.0 and +400 mV (nHe) in accordance with the prediction (Figure 4.6). This demonstrates the reversibility of all the common iron oxide phases according to the solution conditions.

4.3.5 Cyclic Voltammetry of Iron Oxides

Figure 4.8 shows the cyclic voltammograms for the four pure iron oxide rotating discs under consideration which compares the peak potentials and currents associated with the electrochemical reactions. The peak positions observed are tabulated in Table 4.5.
### Table 4.5

**Cyclic Voltammetry Data for Iron Oxide Carbon Paste Electrodes**

(1 M NaCl, pH 5.0, 400 RPM)

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_a$ (mV)</th>
<th>$E_{c1}$ (mV)</th>
<th>$E_{c2}$ (mV)</th>
<th>Rest Potential (mV, nHe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidocrocite</td>
<td>755</td>
<td>640</td>
<td>305</td>
<td>565</td>
</tr>
<tr>
<td>Hematite</td>
<td>745</td>
<td>625</td>
<td>125</td>
<td>485</td>
</tr>
<tr>
<td>Goethite</td>
<td>775</td>
<td>640</td>
<td>185</td>
<td>495</td>
</tr>
<tr>
<td>Magnetite</td>
<td>795</td>
<td>580</td>
<td>270</td>
<td>515</td>
</tr>
</tbody>
</table>

The voltammograms collected on a stationary electrodes behaved similarly to those in Figure 4.8. Figure 4.9 shows a repeated voltammetric scan for the lepidocrocite. The other three oxides also showed a similar result.
Figure 4.8. Cyclic voltammograms of iron oxide/carbon paste electrodes recorded at 25°C in 1M NaCl of pH 5.0 with a rotation speed of 400rpm (scan rate = 50mV s⁻¹)  a = lepidocrocite, b = hematite, c = goethite, d = magnetite.
Figure 4.9. Repeat cyclic voltammogram of a lepidocrocite/carbon paste electrode. (0.1M NaCl, pH 5.0, 25°C, 400 rpm, 50 mV s⁻¹ scan rate).
The cyclic voltammetry data in Table 4.5 and in Figures 4.8 and 4.9 show that each of the oxides have an anodic ($E_a$) and cathodic peak ($E_{c1}$) close to the normal potential of the iron(III)/iron(II) couple and a second cathodic peak ($E_{c2}$) at more negative potentials. Mouhandess et al. (1985) showed a similar result in their study of hematite. They found that $E_a$ and $E_{c1}$ peaks were due to the oxidation, or reduction, of iron ions coming from the instantaneous dissolution of the finest particles.

The smaller cathodic peak is attributed to the reduction of the iron(III) oxide lattice to FeO (Lu and Muir, 1986), which readily dissolves in acid solution. The disappearance of this peak on subsequent cycles (Figure 4.9), in this system is due to the passivation of the surface, as the voltammetry was conducted in near neutral conditions. Therefore the FeO would not be dissolved and would not allow a new surface to become available for this reaction to occur on subsequent cycles. The disappearance of the $E_{c2}$ peak on repeat cycles, as shown in Figure 4.9, was also observed by Sharara et al. (1984), where the complete disappearance occurred by the third cycle. However Mouhandess et al. (1984) attributed the second peak in the $\alpha$-Fe$_2$O$_3$ voltammogram to be due to the electrodissolution of the solid oxide according to a two step scheme: dissolution of Fe$_2$O$_3$, followed by reduction of iron(III). They also found this peak to be more cathodic than the reversible iron(III)/iron(II) peak, as in this study, but strongly influenced by crystal size (Mouhandess et al., 1985). In Figure 4.8 it can be seen that the $E_{c2}$ peaks are indistinct and generally smaller than $E_{c1}$ peaks and are situated at more negative potentials than the $E_{1/2}$ for the iron(III)/iron(II) couple, so it is unlikely that this is due to the reduction of dissolved iron(III), as suggested.
In their electrochemical study of hematite, magnetite, maghemite as well as the ferrites NaFeO$_2$ and LiFeO$_2$ in carbon paste electrodes, Sharara et al. (1984) found that the $E_{c2}$ peak for magnetite occurred between 0.45 and 0.55 V (nHe) while the hematite peak occurred between the more cathodic values of -0.05 to +0.35 V (nHe). They also found the NaFeO$_2$ peak occurred at more anodic potentials than for LiFeO$_2$. Even though the values in Table 4.5 differ slightly from those reported by Sharara et al. (1984), the cathodic position of the hematite peak relative to magnetite, concurs with their results.

Since it appears that the dissolution of iron oxides is promoted by the formation of FeO, it can be predicted that the magnitude of the current of $E_{c2}$ will be related to the rate of dissolution. Even though the voltammetry data (Figure 4.8) is not quantitative, it is evident that $i_{c2}$ peak is slightly greater for lepidocrocite and magnetite. Obviously the magnitude of the $E_{c2}$ peak will be influenced by its positioning, with the oxides having the more anodic peak being more easily reduced. This was discussed by Sharara et al. (1984) in relation to NaFeO$_2$ which is more hydrolysable than LiFeO$_2$. Lu and Muir (1988) likewise found the non-oxidative acid dissolution of hematite to be significantly slower than for magnetite.

Thus one can expect that the rate of non-oxidative dissolution to decrease in the order lepidocrocite-magnetite-goethite-hematite, which correlates reasonably well with the kinetic dissolution results reported by Sidhu et al. (1981), despite the fact that sample morphology would significantly alter the dissolution rate and reaction potentials, as discussed by Mouhandess et al. (1984). If the chance of
nucleating a new phase was the same, one would therefore also expect that, under similar conditions, the rate of transformation of the different oxides to follow the same relative order.

4.3.6 Electrochemical Model of the Transformation Mechanism

The transformation mechanism can now be rationalised electrochemically by the following reactions:

$$\gamma-\text{FeOOH} + H^+ + e \rightarrow \text{Fe}^{2+} + 2OH^-$$  \hspace{1cm} \text{(4.14)}

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e$$  \hspace{1cm} \text{(4.15)}

With the nucleation and reprecipitation reactions, as follows:

$$\text{Fe}^{3+} + 2H_2O \rightarrow \alpha-\text{FeOOH} + 3H^+$$  \hspace{1cm} \text{(4.16)}

$$2\text{Fe}^{3+} + \text{Fe}^{2+} + 4H_2O \rightarrow \text{Fe}_3\text{O}_4 + 8H^+$$  \hspace{1cm} \text{(4.17)}

$$2\text{Fe}^{3+} + 3H_2O \rightarrow \alpha-\text{Fe}_2\text{O}_3 + 6H^+$$  \hspace{1cm} \text{(4.18)}

the potential at which the reactions occur will regulate which one of equations 4.16 - 4.18 predominates, and thus which product crystallises. As equations 4.14 and 4.15 are electrochemical, a schematic Evans' diagram can be drawn (as shown in Figure 4.10), with Fe$^{2+}$ the reductant being oxidised and precipitating in the new phase. Since the oxidation of the Fe$^{2+}$ will occur at different potentials depending on the pH (see Equations 3.9 to 3.14), the mixed potential for transformation will determine the product phase. Hematite (equation 4.18) predominates at more oxidative potentials than
(equation 4.16), which occurs at more oxidative potentials than magnetite (equation 4.17).

Since magnetite, hematite and goethite also transform, albeit only partially, similar Evans' diagrams as in Figure 4.10 could be constructed for these oxides. The mixed potentials at which these reactions occur, which can be deduced from an Evans' diagrams, determines the product phase. However, the initial dissolution step in the process for these oxides would be inhibited as the rest potentials of these oxides occur at lower potentials. This results in a smaller potential difference between the oxide and the electrolyte, and thus a slower dissolution rate (Pryor and Evans, 1950).
Figure 4.10. Schematic Evans' diagram for the transformation of lepidocrocite. \( a, b \& c = Fe^{2+} = Fe^{3+} + e \) where pH of \( c < b < a \); 
\( d = \gamma - FeOOH + H^+ + e = Fe^{2+} + 2OH^- \). The mixed potential where \( a, b \) or \( c \) intersect with \( d \), determines the product of the transformation reaction.
As the potential of an iron(III)/iron(II) solution decreases with pH, the potential difference between the oxide and the solution will increase and thus the rate of dissolution will increase. Therefore, the transformation of goethite and hematite will be favoured at higher pH. This is shown to occur during the production of iron oxide pigments from goethite in Chapter II.

4.4 Relevance of Transformation Reactions to Corrosion

There is clearly a close similarity between the aeration step in the Becher Process and rusting reactions. In their electrochemical study of the phase transitions in rust layers, Stratmann et al. (1983) stated that the primary reaction products formed during the corrosion of iron were hydrated iron(II) ions, which could be further oxidised by oxygen to iron(III) and then precipitated as oxides, hydroxides and oxyhydroxides. The rust layer thus formed covers the metal surface and has a large influence on the further development of the corrosion process. An X-ray analysis of the rust products by Suzuki et al. (1979) indicated that the crystalline parts of pure iron rust plate were composed of $\gamma$-FeOOH, $\alpha$-FeOOH and Fe$_3$O$_4$. Therefore the major difference in these corrosion systems from the electrochemistry of the iron oxides discussed so far in this chapter, is that the iron oxides in the rust are in contact with the metallic phase, while the iron oxides in the Becher Process are liberated from the iron surface and occur as very fine particles in a slurry.
Suzuki et al. (1979) found that in the X-ray analysis of the surface layer of the rust, the intensity of the γ-FeOOH was the strongest while that of α-FeOOH was very weak. The interior of the rust plate (100μm from the surface) consisted mainly of Fe$_3$O$_4$ and little α-FeOOH, while γ-FeOOH was not detected. Between the Fe$_3$O$_4$ and the rest of the rust, they found more α-FeOOH than in the interior. Hiller (1966) also found that Fe$_3$O$_4$ occurred under the γ-FeOOH, closer to the metallic iron.

A number of studies have been reported on the reduction of rust (Okada et al., 1970; Suzuki et al., 1979; 1980; Keiser et al., 1982) but of particular note for this work are the results of Stratmann et al. (1983). Having identified iron(II) in solution during the reduction of rust, he found that in iron(II) free solutions, reduction of γ-FeOOH to magnetite began at -165 mV (nHe) while in the presence of 2 x 10$^{-3}$ M iron(II), magnetite formation started at -65 mV (nHe).

As the different oxide phases in rust have been shown to be a function of the oxidation potential, a mechanism for their formation can be proposed involving the transformation reactions reported in this work. When Fe$^{2+}$ ions from the oxidation of the metal are in contact with the oxide a transformation reaction can occur. Close to the metal surface the concentration of Fe$^{2+}$ will be higher and the corrosion potential will be lower than the equilibrium potential at the outer layer or interior of the rust. This lower potential promotes the formation of magnetite on the iron surface, with goethite being more predominant on the exterior where the potential is higher. Hematite will occur where the oxidation potential is high, presumably when the surface is exposed to air.
Since the processes occurring are electrochemical in nature and involve the reductive dissolution of the less thermodynamically stable phase with Fe$^{2+}$, the corrosion properties of the metal will significantly affect the iron oxide phases covering its surface, as previously discussed regarding the iron in reduced ilmenite during the Becher Aeration Process.

4.5 Conclusions

The calculation of the potentials from the thermodynamic data for the dissolution of metallic iron resulted in an order of the standard potentials of the oxides being $\gamma$-FeOOH $>$ $\alpha$-Fe$_2$O$_3$ $>$ Fe(OH)$_2$ $>$ $\alpha$-FeOOH $>$ Fe$_3$O$_4$. These results suggest that lepidocrocite is the most likely oxide to form at high oxidation potentials in contact with metallic iron, which concurs with the known formation of this phase in the Becher Process and as an oxide product from the rusting of iron. The thermodynamic data also predict that the lepidocrocite phase is unstable relative to the other phases found as by-products in the Becher Process, and at lower oxidation potentials would readily transform. Thermodynamic calculations show that the transformations of lepidocrocite to hematite, goethite and magnetite all proceed spontaneously and a $\Delta H$ value of $-9.3 \pm 0.3$ kJ mol$^{-1}$ was experimentally determined for the formation of magnetite from lepidocrocite. These transformation reactions occur more readily in the presence of reducing agents such as Fe$^{2+}$ or Fe$^0$, as the lepidocrocite material must dissolve via reduction of iron(III) in the lattice, prior to the formation of the new phase.
The experimental Eh-pH diagram produced in the presence of Fe$^{2+}$ for the transformation of lepidocrocite (Figure 4.6) compares the actual regions of predominance of the transformation products of lepidocrocite. As transformation reactions involve the reprecipitation of iron oxides from the solution phase, Figure 4.6 should enable predictions to be made about products of oxidation/hydrolysis of 0.5 M iron(II) chloride solutions, as discussed in Chapter 11.

Cyclic voltammetric studies show that the iron(III) in the lattice of lepidocrocite and magnetite is more easily reduced than iron(III) in the goethite and hematite lattices. This supports the view discussed earlier that the oxides that transform are the phases that are more readily reduced and solubilised. However, it is now possible to describe the transformation reactions and mechanism from an electrochemical view and relate these studies to observations made on the corrosion products of iron.
Chapter 5

Plant Analysis and Modifications to Becher Plant Conditions to Produce Pure Iron Oxides

5.1 Introduction

The results in the previous three chapters indicate that the mixed iron oxides obtained from the Becher Aeration Process are a result of transformation reactions of initially formed lepidocrocite with the rate dependent on pH, iron(II) concentration and temperature. Furthermore, the iron oxide phase formed is dependent on the redox potential at the oxide-solution interface, with the presence of reductants such as iron metal promoting the formation of the lower valence phase, magnetite. It was firmly established that lepidocrocite formed at the cooler temperatures at the beginning of the process was the intermediate in the formation of hematite, goethite and magnetite.

In this chapter the results of the fundamental iron oxide transformation study will be applied to the Becher Process, both in the laboratory and on a plant scale. The aim is to analyse plant conditions and rationalise why certain iron oxide phases are formed under the prevailing set of conditions and then consider methods of modifying operating conditions to enable better control of the iron oxide by-product.
5.2 Experimental

5.2.1 Laboratory Scale Becher Aerator Trials

Laboratory scale aeration tests were conducted in a 1 litre reactor containing 15g NH₄Cl and 500g of reduced ilmenite. Air was sparged through a glass frit at 1 litre min⁻¹ whilst the pulp agitated using a four paddle stirrer at 300rpm. External heating was applied via a hot plate, raising the temperature from an initial 40°C to a maximum of 80°C after 2.5 hours, thus simulating the temperature profile of a plant aeration batch.

Control of potential or pH was performed by the incremental addition of either NH₄OH or HCl via a Schotte Gerate T80 Automatic burette. Oxide samples were withdrawn at set intervals, dried at <60°C prior to X-ray patterns being recorded. For these experiments no data was collected on the relative amounts of iron in the synthetic rutile.

5.2.2 Plant Scale Becher Aeration Trials

Detailed sampling exercises were conducted on site at Westralian Sands North Capel synthetic rutile plant, under predetermined process conditions.

For each trial, samples were collected at one hour intervals over the 12 hour duration of the batch process. On collection, the slurry sample was immediately quenched to <30°C in a bucket of ice. The pH of the sample was then measured, followed by the separation of the reduced ilmenite/synthetic rutile from the iron oxides by passing the
solution through a 53 micron sieve. The oversize material was washed with water and immediately dried to avoid further oxidation. It was later analysed by XRF for major elements and titrated to give a metallic iron analysis.

The iron oxide slurry was meanwhile filtered under vacuum, and both the filtrate and filter cake collected. The oxides were stored in a desiccator, then dried at <60°C to avoid any iron oxide transformations.

An iron(II) analysis was immediately recorded on the filtrate using a standard permanganate titration. The immediate analysis avoided any chance of erroneous results from subsequent air oxidation or hydrolysis of the iron(II).

Temperature readings were obtained from an on-line plant monitoring system, while Eh values were recorded by dipping a combined platinum, Ag/AgCl reference electrode in the solution at the top of the aeration tank. All potential data reported here is corrected to the hydrogen scale.

The air dried iron oxide samples were brought back to Murdoch University for X-ray diffraction, thermogravimetric and particle size determinations.
5.3 Results and Discussion

5.3.1 Plant Scale Aeration Trials

5.3.1.1 Variation in Solution Potentials

To monitor the actual changes in plant solution conditions, two aeration profiles were undertaken on site at the Westralian Sands Ltd Synthetic Rutile plant at Capel. The variables of pH, Eh, iron(II) concentration, temperature and percent iron reacted, were measured at hourly intervals over the typical batch aeration lasting 11 to 12 hours. Figure 5.1 shows the profile recorded at an air flow rate of 5200 \( m^3 \text{hr}^{-1} \) while Figure 5.2 shows the profile recorded at an air flow rate of 7000 \( m^3 \text{hr}^{-1} \). Raw data for these trials is tabulated in the Appendices.

Clearly there is a complex series of competitive and parallel reactions which take place over the course of the aeration process which cause the changes in solution parameters (Ward et al., 1989b). The parameters which exhibit the most complex changes are iron(II) concentration and pH, which pass through a series of maxima and minima, but Eh and temperature also vary considerably.

To rationalise the pH changes observed, it is proposed that there is a competition between the acid consuming rusting reaction (5.1) and the acid generating "oxyhydrolysis" of \( \text{Fe}^{2+} \) (5.2).
Figure 5.1. Profile of solution conditions during a plant scale batch aeration of reduced ilmenite with an air flow rate of 5200 m³/hr⁻¹.
Figure 5.2. Profile of solution conditions during a plant scale batch aeration of reduced ilmenite with an air flow rate of 7000 m³hr⁻¹.
\[
2\text{Fe}^0 + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad 5.1
\]
\[
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 4\text{H}^+ \quad 5.2
\]

Initially reaction 5.1 predominates and both the iron(II) concentration and pH rise (Figure 5.1). However, as the iron(II) concentration increases, the rate of reaction 5.2 increases and both the Eh and pH steadily fall. After 5 - 6 hours, when the Eh and saturated \( \text{O}_2 \) concentration are low, both the pH and iron(II) concentration increase sharply, as again reaction 5.1 predominates. The very low Eh observed at this time, presumably has the effect of making the oxide and the acid forming reaction (reaction 5.2) less favourable. Later, when the metallic iron is mostly consumed, and the potential rises, this reaction again becomes more favoured and both the pH and iron(II) concentration fall accordingly.

The solution Eh passes through a simple minimum after 7 hours as the amount of residual metallic iron falls below 12 percent. This indicates that oxygen is consumed by reaction 5.1 at a faster rate, initially, than can be transferred into the solution by aeration. Only after most of the iron has reacted, can aeration keep up with oxygen demand and restore the Eh to its initial air saturated condition of around 300 mV (nHe).

The pH and iron(II) concentration trends are similar in Figure 5.2, except that the higher air flow rate in this batch did not allow the iron(II) concentration to rise above 130 mg/l and there was always a sufficiently high oxygen partial pressure for reaction 5.2 to proceed. In this batch, the Eh showed a sharp decline between 2 and 3 hours but it seems unlikely that the solution became oxygen starved. It is
believed that these anomalous Eh values were due to the platinum electrode becoming coated with a reduced ilmenite or lepidocrocite layer and recording a mixed potential rather than a solution potential.

The other major factor influencing the final iron oxide phase is temperature, and a number of parameters affect the temperature profile during aeration since the tanks themselves have no temperature control. These include the quantity and quality of the reduced ilmenite in the reactor, and the amount of air passed through the solution. If the reduced ilmenite is not of high quality, or if an oxide film passivates the metallic iron, or if the air flow is too low the temperature rise due to the exothermic rusting reaction (reaction 5.1) can be slow and a lower peak temperature attained. However, lower temperatures are also observed using excessively high air-flow rates because of greater evaporative heat losses. This lower temperature not only affects the rate of the oxyhydrolysis reaction 5.2, but will also reduce the rate, and thus the extent of the transformation of the lepidocrocite which is initially precipitated at temperatures below 70°C. As shown in Chapter 3, the rate of transformation is critically dependent on temperature because of the need to form nuclei.

Thus, even though the second test used a considerably higher air flow rate, the temperature was lower than for that in the first test over the initial 4 hours (cf. Figures 5.1 and 5.2). A very significant feature of the temperature profile in Figure 5.1 is the extra temperature rise between the 5th and 7th hours. This period of time coincided with the exothermic transformation of lepidocrocite to magnetite (Chapter 4), indicated by the change in colour of the slurry.
5.3.1.2 Variation in Iron Oxide Products

Suprisingly the iron oxide by-products varied considerably between the two test runs. For the batch using 5200 \( \text{m}^3 \text{hr}^{-1} \) of air (Figure 5.1), only lepidocrocite was evident up to the third hour, while a trace of hematite was observed after four hours and a small amount of magnetite by the fifth hour. The transformation occurred predominantly in the sixth hour and was totally complete by the seventh hour. The trace of hematite increased during the last few hours as the Eh rose above 200 mV (nHe), but was still only a minor component on completion of the aeration. The hematite is presumably a slowly forming oxyhydrolysis product, which is more favoured at higher temperatures (reaction 5.3).

\[
2\text{Fe}^{2+} + \text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + 4\text{H}^+ \quad 5.3
\]

The presence of hematite from the transformation reaction after 4 hours is unexpected since the measured Eh was much lower in the period between the 3rd and 4th hours, than is normally required for the formation of hematite (Figure 4.5). This suggests that the potential at the surface of the oxide arising from the adsorption of oxygen may be locally higher than the average slurry or solution potential, thus allowing the nucleation of other iron oxides to take place to a minor extent.

With the batch using a higher air flow rate, no transformation occurred during the aeration. The final product was mainly lepidocrocite, with again a trace of hematite appearing after the fourth hour, and progressively increasing as the aeration proceeded. The lack of transformation is attributed to the iron(II) concentration
being significantly lower in this run (50-100 mg/l$^{-1}$ versus 150-300 mg/l$^{-1}$) so that the transformation reactions were not kinetically favoured. Thus, it can be concluded that high oxygen concentrations inhibit the transformation reactions by precipitating the iron(II) before it rises above the level required to allow the reaction to occur in the 12 hour time frame of the process. The minimum concentration of Fe$^{2+}$ appears to be around 150 ppm at pH 6.5.

5.3.2 Modifications to Aerator Conditions to Control Iron Oxide Formation

5.3.2.1 Production of Black Magnetite by Air Flow Control

From the analysis of the aerator parameters and previous laboratory scale experiments it was clear that to produce magnetite, it was necessary to minimise the chance of nucleating hematite before the transformation reaction of lepidocrocite took place. Therefore it was argued that the oxygen partial pressure should be initially low to enable the Eh to fall quickly and to increase the iron(II) concentration. A batch test was therefore carried out on the plant where the air flow rate was held at 3000 m$^3$hr$^{-1}$ for the first 7 hours, then increased to 6500 m$^3$hr$^{-1}$.

The solution parameter profiles shown in Figure 5.3 resemble those of Figure 5.1, except that the temperature increased to a higher value of 83.9°C and the iron(II) concentration rose from about 100 ppm to over 500 ppm.
Figure 5.3. Profile of solution conditions during a plant scale batch aeration of reduced ilmenite with an air flow rate of 3000 m³/hr⁻¹ for the first 7 hours and then 6500 m³/hr⁻¹ for the final 5 hours.
Again the iron(II) concentration increased sharply as the Eh approached its minimum value, and with this rapid rise in iron(II) concentration, the transformation to magnetite occurred very quickly and was complete by the 6th hour. Prior to the 5th hour, lepidocrocite was the only iron oxide phase present. The X-ray pattern of the final product (Figure 5.4) shows the material to be pure magnetite. This indicates that even though the potential is rising over the last 2 hours, the oxyhydrolysis of the iron(II) results in the crystal growth of the existing magnetite nuclei, without producing a different phase such as hematite. This mechanism is similar to the synthetic iron oxide processes which will be described later, where nucleation, crystal growth and ageing are necessary stages in the production of high quality iron oxide pigments.

The increase of the air flow after the 7th hour caused the pulp to cool by 5-8°C, and increased the iron(II) entering the solution. But after the 10th hour, the rate of the oxyhydrolysis reaction became much faster than the rusting reaction, leading to a virtual iron(II) free solution on completion of the aeration (Figure 5.3).

5.3.3 Laboratory Scale Becher Aeration Trials

As shown by the laboratory scale transformation results, a certain degree of control of the iron oxide phase can also be achieved by the use of acid or alkali to regulate the pH. In the Becher Process this regulates the iron(II) concentration, the rate of transformation, and the potential at which transformation reactions occur. However, as the Westralian Sands Ltd Synthetic Rutile Plant is a production unit, there was a reluctance to add these pH controlling chemicals to the
Figure 5.4. X-ray diffraction pattern of the iron oxide produced during the aeration in Figure 5.3, showing the material to be pure magnetite.
aeration tank prior to testing the effects on a pilot scale. Therefore, in this study, two laboratory scale aeration trials were conducted. The first with potential control and the second with pH control. This was to ascertain if the predicted products from the electrochemical and thermodynamic studies could be reproduced during aeration, to give a more consistent high purity iron oxide which could be later demonstrated on a pilot plant.

5.3.3.1 Production of Black Magnetite by Eh Control

Earlier studies have shown that to produce magnetite the lepidocrocite must be subjected to a potential of < -45 mV (nHe) or a pH > 5.0 in 0.5M FeCl₂. For this aeration trial an attempt was made to conform to both criteria for as long as possible throughout the 10 hour duration of the experiment, but in the absence of additional FeCl₂, other than that produced by dissolution of the iron.

It was found that minimal NH₄OH was required in the first 8.5 hours to maintain the required pH conditions and the Eh remained below -100 mV (nHe). However, after this time, the potential rose over 100 mV and the controller was eventually turned off. During the experiment the slurry changed colour from a red-brown to black after 4.45 hours.

X-ray patterns collected for the samples taken after 2, 4 and 5 hours are shown in Figure 5.5. Figure 5.5 shows that the material changed phase from predominantly lepidocrocite to magnetite between 4 and 5 hours. A trace of magnetite was evident after 2 hours, with a slight increase after 4 hours prior to the major transformation of
Figure 5.5. X-ray diffraction patterns showing the transformation of lepidocrocite to pure magnetite during a laboratory scale aeration under Eh control.
lepidocrocite to magnetite occurring. No other oxide phases were evident in the X-ray patterns after 5 hours. This demonstrates that pure magnetite can be produced by controlling the Eh and pH of the aerator solution. However, as discussed above, these conditions are not always met in typical plant aerations and as a consequence a range of mixed phases are produced.

5.3.3.2 Production of Red Hematite by pH Control

In contrast to the conditions required for black magnetite, hematite is slowly produced from lepidocrocite at pH < 3 and at potentials greater than 200 mV (nHe). Unfortunately this low pH would be unrealistic in the aeration tanks due to corrosion problems, and the high Eh could not be achieved until virtually all of the metallic iron had reacted. Furthermore, the transformation reaction is so slow at this pH that greater than 24 hours would be required. Thus to produce hematite, a stepped aeration was devised. Initially the pH was kept below 4.0 with the addition of acid to increase the iron(II) concentration and to slow the rate of any transformation reaction. Then after a set time of 8 hours, when the majority of metallic iron had reacted and the Eh had become positive, the pH was allowed to rise, thereby increasing the kinetics of the transformation reaction. At the same time the concentration of iron(II) was kept as high as possible by decreasing the air flow rate to minimise the acid producing oxyhydrolysis reaction which removes iron(II) from solution.

During this experiment the iron(II) concentration increased from zero to 980 mg/l on completion, while the redox potential rose from an initial value of ~-200mV (nHe) to around +400mV (nHe) after 8 hours.
The redox potential remained positive in the final 2 hours, despite the increase in pH and reduction in air flow rate.

The X-ray patterns of the samples taken after 1, 8 and 10 hours are shown in Figure 5.6. The figure shows that for the first 8 hours the iron oxide remains as predominantly lepidocrocite, but the pattern does show traces of goethite and hematite. However, after 10 hours, the iron oxide transformed into goethite and hematite, with only a trace of lepidocrocite remaining. Even though a red oxide was produced, this oxide mirrors the earlier laboratory tests (Chapter 3) where the attempts to produce hematite invariably resulted in the presence of goethite. Since, pure hematite was characterised as a product from the polarization of lepidocrocite electrodes in Chapter 4, it would seem that it is not possible to maintain sufficient oxygen on the surface of lepidocrocite in the aerator to achieve the required Eh. Addition of oxygen enriched air or lower pulp densities of lepidocrocite in the aerator should enhance hematite production.

While this experiment did not produce an oxide of sufficiently high purity to be used as a pigment, it did however confirm a mechanism by which a red oxide would be formed during aeration, and suggests further work to increase purity is required.

5.4 Particle Size Analysis of Magnetite By-Product from the Modified Plant Trial

Figure 5.4 shows the magnetite produced from the air-flow modified plant trial to be crystalline and of high purity as measured by X-ray diffraction. But for an oxide to be suitable for use as a pigment it
Figure 5.6. X-ray diffraction patterns showing the formation of a red iron oxide product during a laboratory scale aeration under pH control. (L=Lepidocrocite, G=Goethite, H=Hematite)
must also conform to certain particle size criteria as discussed in Chapter 11. The volume distribution histograms for the aeration product and a standard sample of commercial pigment (Bayer 318, magnetite) were therefore measured by a Malvern Mastersizer and shown in Figure 5.7. The two samples gave the same median size value of 1.74 \( \mu \text{m} \), however, the size range of the aeration sample was narrower than that of the Bayer 318. The figure shows a smaller range of particle sizes with the difference between the sizes for the 90 and the 10 percent passing fractions giving a non-dimensional span of 1:1 compared with 2.4 for the Bayer sample.

These results demonstrate that iron oxides of the quality required for pigmentary purposes can indeed be produced from the Becher aeration process provided proper attention is given to operating parameters. The production of pure magnetite also opens the opportunity for producing a range of red hematite pigments by calcining the magnetite and grinding to different sizes as discussed in Chapter 11.

5.5 Conclusions

The results presented in this Chapter show that in the operating plant the solution conditions of temperature, \( \text{Eh} \), \( \text{pH} \) and iron(II) concentration vary significantly during a batch aeration of reduced ilmenite and account for the range of iron oxides produced. From the previous studies on the conditions and mechanisms required for both oxyhydrolysis and transformation reactions, it is possible to modify plant operating conditions to achieve consistent high quality iron oxides by controlling \( \text{pH} \), \( \text{Eh} \) and aeration rate.
Figure 5.7. Particle size distribution histograms comparing the magnetite from a plant scale aeration (upper) with that for commercial magnetite pigment (Bayer 318, lower).
Control of the iron(II) concentration by adjusting the air flow rate during the batch run, resulted in a pure magnetite by-product being formed during the production of synthetic rutile in an aeration tank at the Westralian Sands Synthetic Rutile Plant. This material possessed both the physical purity and particle size characteristics required for use as a pigment. Acid and alkali additions enabled red and black oxides to be produced in simulated laboratory scale aeration tests which can be applied to pilot plant production of other coloured pigments. Lepidocrocite, itself, which can be used as a precursor to a range of iron oxides, was prepared in high purity by using high air flow rates and limiting the concentration of iron(II) in solution.
Chapter 6

The Summit Process:

Comparison of Corrosion Techniques to Follow

Leaching of Iron by Iron(III)

6.1 Introduction

The alternate Summit process for upgrading ilmenite to synthetic rutile is also based on reduction of the iron in the ilmenite lattice to the metallic state, but rather than "rust" out the iron, it is extracted by leaching with iron(III). Thus, to get a better understanding of the factors involved in the dissolution of iron, it is necessary to conduct a detailed study of the fundamental kinetics of pure iron corrosion in iron(III) solutions. These rates are conveniently measured electrochemically. The kinetics of electrochemical corrosion reactions can be studied by a number of transient or non-destructive methods, some of which will be used to obtain the results presented in this chapter. These electrochemically derived rate constants are compared with rate constants determined directly using a rotating disc of iron. In this system the hydrodynamics are reproducible and mass transfer in a diffusion controlled reaction is calculated from the Levich equation (1942).

Electrochemical reactions, as distinct from chemical reactions, involve electron transfer between the surface of a solid phase capable of electron conduction, and a solution containing some electroactive species. As the dissolution of metallic iron in
iron(III) solutions (equation 6.1) conforms to this definition, the use of electrochemical corrosion techniques should be of significant benefit in the study of this leaching reaction. These techniques offer not only speed of measurement, but also accuracy over the conventional techniques involving sampling and chemical analysis.

The mechanism of reaction 6.1,

\[ \text{Fe}^0 + 2\text{Fe}^{3+} = 3\text{Fe}^{2+} \]  \hspace{1cm} 6.1

can be considered to pass through the following steps: (i) diffusion of the reactant (Fe\(^{3+}\)) from the bulk of the solution to the surface of the metal; (ii) adsorption of the reactant; (iii) electron transfer from the metal to the reactant; (iv) desorption of the metal ions and the reduced species (Fe\(^{2+}\)) from the metal surface; and (v) diffusion of the metal ions and the reduced species (i.e. Fe\(^{2+}\)) from the metal surface to the bulk of the solution.

If steps (i) and (v) are rate determining, the process is said to be under diffusion control. If the processes at the metal surface described by steps (ii), (iii) and (iv) are very slow compared to the diffusion of the ions, no appreciable concentration gradient exists between the metal surface and the bulk of the solution, and the reaction is considered to be under chemical control and independent of solution agitation. However, if the solution is not stirred, the reactant concentration will drop, and the system will suffer from concentration polarization. When both the diffusion and chemical rate processes are of comparable magnitude the reaction is said to be under mixed control and the measured rate will be affected by agitation.
Iron(III) solutions have been used in a number of fundamental electrochemical studies on the dissolution of metals such as copper (Couche and Ritchie, 1984) and silver (Shamis et al., 1974). Although most electrochemical studies dealing with dissolution of metallic iron discuss acidic dissolution, or the corrosion reaction from the reduction of dissolved oxygen; several reports can be found dealing with the reaction between iron(III) and metallic iron in both chloride media (Abramson and King, 1939; Makrides et al., 1955; Bezvortnii et al., 1978) and sulfate media (Gatos, 1956; Makrides, 1960; Makrides and Stern, 1960; Tobias and Nobe, 1975). Even though acid dissolution of iron has been the subject of many reviews, most recently by Drazic (1989), very little recent literature exists for the mechanisms involved when iron(III) is also present. However, it is clear from these previous studies that there is the need for an electrochemical study to gain a better understanding of the competing reactions occurring with H\(^+\) and Fe\(^{3+}\) during the dissolution of iron in acidic iron(III) solutions.

Acidic solutions are needed to avoid hydrolysis of iron(III), so a certain amount of hydrogen evolution is expected. However, the minimisation of hydrogen production is very important for the successful use of iron(III) to remove iron from reduced ilmenite and produce a high quality synthetic rutile. This is because metallic iron is embedded in deep pores within the reduced ilmenite grain. Any reduction of hydrogen ions will cause localized pH rises to occur at the surface and within the grain which could result in the precipitation of iron(III) hydroxide.
According to Gatos (1956) possible reactions for the dissolution of iron in acid involve atomic hydrogen, which can either combine to produce $H_2$ or reduce $Fe^{3+}$ to $Fe^{2+}$, as described by the following reactions.

\[
Fe = Fe^{2+} + 2e^- \quad (6.2)
\]
\[
2H^+ + 2e^- = 2[H]_{ads} = H_2 \quad (6.3)
\]

which combined gives

\[
Fe + 2H^+ = Fe^{2+} + H_2 \quad (6.4)
\]

When iron(III) ions are present, the following two half reactions are also possible

\[
Fe^{3+} + [H]_{ads} = Fe^{2+} + H^+ \quad (6.5)
\]
\[
Fe^{3+} + e^- = Fe^{2+} \quad (6.6)
\]

where $[H]_{ads}$ is adsorbed atomic hydrogen.

Even though the rate of hydrogen evolution decreased when the iron(III) concentration was increased, or as the dissolution proceeded (Gatos, 1956), there was always a component of the dissolution reaction attributable to the acid reaction. It was proposed that both the hydrogen ion and iron(III) ion compete for sites on the metal, thus limiting the number of sites available for iron(III) reduction.

In the work described in this chapter, a number of non-destructive techniques commonly used in the fundamental study of corrosion reactions are applied to the leaching of iron with iron(III). These techniques are Chronopotentiometry (Stripping), Stern-Geary or Linear
Polarization and the Evans' Diagram Method. The rate constants obtained electrochemically are compared with that obtained by direct sampling of destructed iron and are split into the iron(III) and acid components. The methods are then contrasted to find the method most suited for a more detailed kinetic analysis. An evaluation of solution parameters to minimise hydrogen evolution is described later.

6.2 Techniques for Studying Corrosion Reactions

6.2.1 Direct Solution Sampling from a Rotating Disc

By far the simplest and most common technique for following corrosion or leaching reactions is to react the bulk solid under controlled mass transport conditions and sample the solution at set intervals to follow the appearance of a particular species by a standard analytical method.

If the iron is in the form of a rotating disc, the Levich equation can be used to give the flux \( J(\text{mol} \: \text{m}^{-2} \: \text{s}^{-1}) \) of iron(III) ions arriving at a rotating disc surface.

\[
J = 0.62 \: D^{2/3} \: \nu^{-1/6} \: \omega^{1/2} \: A \: [C] \quad 6.7
\]

In this equation, \( D \) is the diffusion coefficient of iron(III) (m\(^2\) s\(^{-1}\)), \( \omega \) is the rotation speed (rad s\(^{-1}\)), \( A \) is the geometrical area (m\(^2\)), [C] is the iron(III) concentration (mol m\(^{-3}\)) and \( \nu \) the kinematic viscosity (m\(^2\) s\(^{-1}\)).
For the leaching of iron or reduced ilmenite, the choice of analysis techniques is extremely limited as most methods such as atomic absorption spectrophotometry (AAS) do not differentiate between iron valency states and give limited information. The preferred option therefore, was to follow the increase of the iron(II) ion in solution rather than to attempt to follow the small increase in total iron by AAS or the small decrease of the iron(III) concentration. Even though the limits of detection of the titrimetric method are relatively high (±3 mg l\(^{-1}\)), it offered the advantage that samples could be analysed almost immediately, thus preventing any aerial reoxidation of the generated iron(II) ions.

6.2.2 Chronopotentiometry

Barth et al. (1973) first developed this technique for the study of cementation reactions. The method involves the deposition of a known amount of the metal of interest onto an inert electrode, followed by its dissolution in the oxidising environment. The potential of the electrode, the mixed potential, is followed as a function of time until the thin film has completely reacted, at which point the potential rises sharply to the equilibrium potential for the inert electrode. The time taken to the point of inflection is then taken as the time for complete dissolution.

This technique has been used successfully to follow the dissolution of copper in iron(III) solutions (Couche and Ritchie, 1984) and also to follow a number of cementation reactions, \(\text{Ag}^+/\text{Cu}\) (Barth et al., 1973), \(\text{Cu}^{2+}/\text{Fe}\) (Schalch et al., 1976) and \(\text{Cu}^{2+}/\text{Zn}\) (Jiang and Ritchie, 1986).
To obtain rate data from the technique for the Fe$^{3+}$/Fe reaction, a known amount of iron is first plated onto an inert platinum electrode. If iron is plated from an iron(II) solution at a constant current of $I_p$ for a time $t_p$, then the number of moles, $n$, of iron deposited is given by

$$n = \eta \frac{I_p t_p}{2F} \quad 6.8$$

where $\eta$ is the plating efficiency expressed as a fraction, and $F$ is Faraday's constant. The plated platinum electrode is transferred into the iron(III) solution and the time taken for all the iron to be dissolved, $t_d$, is measured in seconds.

The dissolution current is controlled by the rate of iron(III) reduction, which is governed in turn by the rate at which iron(III) is transported to the electrode surface since the reaction is diffusion controlled.

If it is assumed that the rate of loss of iron(III) from solution is equal to the rate at which the iron(III) ions strike the rotating disc surface, then

$$-V \frac{dC}{dt} = JA = 0.62 D^{2/3} \nu^{-1/6} \psi^{1/2} [C] A \quad 6.9$$

which may be rearranged and integrated as follows

$$-\frac{d[C]}{[C_0]} = k' dt \quad 6.10$$
\[- \ln \left( \frac{[C_o]}{[C]} \right) = - \ln \left( \frac{[C_o] - \delta[C]}{[C_o]} \right) = k't \quad 6.11\]

where \( k' = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} A \)

and \( \delta[C] \) is the amount of iron stripped (which is half that of iron(III) reduced). This can be approximated by 6.12, provided \( \delta[C] \) is small, and equated to the moles of iron deposited (equation 6.8).

\[\approx - \left( \frac{-\delta[C]}{[C_o]} \right) = \delta[C] / [C_o] \quad 6.12\]

Replacing the left hand side of 6.11 with 6.12 and including the \(1/2\) factor gives

\[\delta[C]/[C_o] = 1/2 \ k't \quad 6.13\]

Thus, the rate constant \( k \) for the amount of iron dissolved can be evaluated in terms of the time taken to dissolve the plated iron \( (t_d) \), and replacing 't' in equation 6.13 to give equation 6.14.

\[k = \eta I_p t_p V / 4 F t_d \times 0.62 \ D^{2/3} \nu^{-1/6} \omega^{1/2} [C_o] A \quad 6.14\]
6.2.3 Evans' Diagram Method

Evans' diagrams (Evans, 1960) have been extensively used (Antropov and Donchenko, 1973) in the discussion of corrosion reactions as well as for cementation reactions (Power and Ritchie, 1975; 1976). Evans' diagrams are constructed by plotting the polarization curves for the two half reactions on the same log current density versus potential scale. The intersection of the two polarization curves yields the mixed potential of the system and the current or rate of reaction. It also gives information regarding the mechanism. If the curves intersect in the limiting current region, (of either the cathodic or anodic reaction), the system is diffusion controlled. Whereas if the intersection occurs in the Tafel region, (where the current varies with potential), the system is chemically controlled.

If the reaction is diffusion controlled, the reaction current is the limiting current density for the system and can be equated to the rate by the following equation.

\[ k = \frac{I_{\text{lim}}}{nF} \]  \hspace{1cm} 6.15

where \( I_{\text{lim}} \) is the limiting current density, \( n \) is the number of electrons involved in the process and \( F \) is Faraday's number.

Although the construction of an Evans' diagram is quick and simple, and provides information about both reaction rates and reaction mechanisms, some assumptions have to be made in their construction:
i) Each half reaction is independent and the rate of the cathodic reaction is assumed to be the same on the electrode used as that on iron,

ii) The ohmic resistance between anode and cathode is negligible.

6.2.4 Stern-Geary or Linear Polarization Method

In the Stern-Geary technique, the reacting system is displaced by a few millivolts from the corrosion or mixed potential (Em), and the resulting current is measured. The ratio of the displacing potential to the resulting current density is the polarization resistance \( R_p \) as first defined by Bonhoeffer and Jena (1951).

\[
R_p = \frac{(dE/dI)_{E=Em}}{6.16}
\]

Stern and Geary (1957) later showed that a linear relationship existed between the potential and applied current at potentials slightly displaced from the corrosion potential, and derived the following equation which allows the reaction current density, \( i \), to be calculated by means of the equation which bears their names.

\[
i = \left(\frac{1}{2.303} R_p \right) \left(b_{a}^{-1} + b_{c}^{-1}\right)^{-1}
\]

where \( b_a \) and \( b_c \) are the Tafel slopes of the anodic and cathodic half reactions in the vicinity of the corrosion potential respectively.
If the reaction is diffusion controlled \( b_c \) becomes infinite and equation 6.17 then reduces to:

\[
i = \frac{b_a}{2.303 R_p}
\]

6.18

The current density, \( i \), so obtained is then substituted into equation 6.15 to yield a rate constant.

6.3 Experimental

Rate constants were determined by the four techniques described above using a solution of 0.02 M \( \text{FeCl}_3 \) in 0.10 M HCl, made up from AR grade chemicals and distilled deionized water. All rate measurements described were carried out at 25.0 ± 0.1°C in a water jacketed cell.

For the rotating disc-solution sampling technique, a mild steel disc of 29mm in diameter was secured into a bell-shaped cylinder with silastic as shown in Figure 6.1 and hand polished using 1200 grade wet and dry emery paper prior to use. The disc was rotated at 1000 rpm using a variable speed motor.
Figure 6.1. Bell-shaped rotating iron disc used for the solution sampling technique. (Diameter = 29 mm).

The iron(III) solution (500 ml) was equilibrated and deoxygenated at the reaction temperature for approximately 15 minutes by bubbling pure nitrogen through it. At set intervals throughout the experiment, 5 ml samples were withdrawn and analysed for iron(II) content by titration with standardized $5 \times 10^{-3}$ M potassium permanganate using a microburette and diphenylamine sulfonate indicator (Vogel, 1961). A Zimmermann-Reinhardt solution containing manganous sulfate and phosphoric acid was added to negate any interference from the chloride ions.
The electrochemical measurements were performed on a Princeton Applied Research (PAR) Model 170 combined potentiostat and programmer with a built-in Houston Omnigraphic X-Y chart recorder. The cell used was fitted with a luggin capillary with the tip fixed at 2 mm from the centre of the working electrode. The reference electrode used for this work was a Saturated Calomel Electrode (SCE).

The active iron electrode used in the determination of the rate constant by chronopotentiometry and the ampero-potentiometry techniques was prepared by depositing iron onto a platinum electrode (diameter of 2.013 mm). The iron was plated from a degassed 0.51 M iron(II) ammonium sulfate solution (100 ml), in a similar manner to that reported by Schalch et al. (1976), at a constant current density. Nitrogen purging was continued throughout the duration of the plating process (typically 600 s). A plating efficiency was determined for this reaction by plating and stripping the iron under constant current conditions.

The active iron electrode used for the Stern-Geary technique was made from Johnson Matthey Spec Pure Iron rod (diameter of 4.8 mm) and a specification of less than 15 ppm metallic impurity.

A gold electrode (diameter 2.906 mm) was used for the iron(III) reduction polarization curve in the construction of the Evans’ diagram. The gold electrode was used in preference to platinum as it has a hydrogen overpotential much closer to that of iron (Appleby et al., 1982). In each case the counter electrode was a spiral of platinum wire.
Immediately before using the working electrodes, the metal surface was carefully polished using 1200 grade wet and dry polishing paper and rinsed with distilled water, except for the plated iron, where no special surface treatments were found to be necessary. However precautions were required to avoid any chance of oxidation and surface passivation of the active electrode. Thus, a minimum amount of time was taken in transferring the electrode from the plating bath to the previously prepared degassed solutions in which the measurements were to be made.

6.4 Results and Discussion of Rate Constants Obtained by Various Methods

6.4.1 Experimental Determination of the Diffusion Coefficient (D) of Fe$^{3+}$ in HCl

An experimentally determined diffusion coefficient was obtained on a gold electrode. This value was subsequently substituted into equation 6.14 to yield the rate constant for the dissolution of iron by the chronopotentiometric technique.

The limiting currents for the reduction of 0.012 M Fe$^{3+}$ in 0.1 M HCl at various rotation speeds up to 1000 rpm are shown in Table 6.1.
Table 6.1

Limiting Current versus Rotation Speed for Iron(III) Reduction
(25°C, Au electrode)

<table>
<thead>
<tr>
<th>Rotation Speed (rpm)</th>
<th>Limiting Current Density $(\omega^{1/2} \text{ rad s}^{-1})^{1/2} \text{ A m}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>10.23 54.3±0.8</td>
</tr>
<tr>
<td>400</td>
<td>6.47   33.3±0.8</td>
</tr>
<tr>
<td>100</td>
<td>3.24   17.3±0.8</td>
</tr>
</tbody>
</table>

As the limiting current is a measure of the flux of ions to the electrode, the slope of the line through these points, in conjunction with the rotation speed $(\text{rad s}^{-1})^{1/2}$, were used to determine the constants in the Levich equation (equation 6.7) and in the determination of rate constants from equation 6.14. This yields a diffusion coefficient for Fe$^{3+}$ of $4.9 \pm 0.1 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ in 0.1M HCl. This value is slightly lower than the value of $5.2 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ for sulfate media quoted by Tobias and Nobe (1975) and $5.45 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ quoted by Couche (1985).
6.4.2 Chronopotentiometry

Galvanostatic dissolution of previously plated iron in 0.1 M NaCl yielded an average plating efficiency (\(\eta\)) of 90.0 ± 0.5 percent. As the efficiency was found to be reproducible, attempts to further improve the method by the use of additives or increases in temperature during the plating process were not deemed necessary.

A typical chronopotentiogram obtained from a thin film of electroplated iron dissolved by an iron(III) solution is shown in Figure 6.2. It is evident from this figure that an end-point is easily discernable in this particular system, and the results were found to be reproducible for duplicate experiments with the results being within 1 percent of the mean.

The dissolution time in 0.02 M Fe\(^{3+}\), 0.1 M HCl at 1000 rpm was found to be 175 ± 2 s, when rounded off to the nearest second. This dissolution time, substituted into equation 6.14, equates to a rate constant (\(k\)), for the dissolution of metallic iron, of:

\[
k = 3.27 ± 0.06 \times 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2}.
\]

As it was not possible to differentiate between the reaction of iron with acid and iron with iron(III) by this technique, this rate constant constitutes the rate of dissolution of metallic iron, by both acid and iron(III). However, this rate constant is a true reflection of the iron dissolution rate, and involves no mechanistic assumptions.
Figure 6.2. Typical chronopotentiogram obtained for a thin film of electro-plated iron dissolving in an iron (III) solution.
6.4.3 Evans' Diagram Method

Figure 6.3 shows the Evans' diagram constructed for the dissolution of metallic iron in the same 0.02 M Fe\textsuperscript{3+}/0.1 M HCl solution, with the polarization curves recorded at a scan rate of 5 mV s\textsuperscript{-1}. The figure shows that the iron(III) reduction curve intersects the metallic iron oxidation curve in the limiting current region and therefore this system is diffusion controlled. On the other hand, the proton reduction curve is intersected in the Tafel region, thus we would expect this system to be chemically controlled. These aspects will be discussed further in the next chapter.

From the Evans' diagram, the rates for the dissolution of metallic iron can be determined for the combination of dissolution mechanisms giving a 'total iron dissolution' rate \( k(\text{sum}) \), as well as for each individual mechanism giving an 'acid only' rate \( k(\text{H}^+) \) and an 'iron(III) only' rate \( k(\text{Fe}^{3+}) \).

From Figure 6.3, the current density was obtained for the point where the iron(III) reduction and the metallic iron oxidation curves intersect and substituted into equation 6.15. This gives a rate constant of 2.84 ± .14 x 10\textsuperscript{-4} mol s\textsuperscript{-1} m\textsuperscript{-2}, being the 'iron(III) only' rate. In a similar manner, the 'acid only' rate can be determined from Figure 6.3 but with the current density taken at the same mixed potential observed for the intersection iron(III) and iron polarization curves. However, using literature values for the hydrogen evolution reaction (Appleby et al., 1982), it was calculated that the rate of hydrogen evolution on iron would be 58 percent of that on gold.
Figure 6.3. Evan's diagram for the metallic iron oxidation reaction in iron (III) and acid.

(a) for the reaction of $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ on a gold electrode in 0.02 M $\text{Fe}^{3+}$ and 0.1 M HCl at 1000 rpm.

(b) for the reaction of $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ on a gold electrode in 0.02 M $\text{Fe}^{3+}$ and 0.1 M NaCl at 1000 rpm.

(c) for the reaction $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e$ on an iron electrode in 0.1 M NaCl at 1000 rpm.

(d) for the reaction $2\text{H}^+ + 2e \rightarrow \text{H}_2$ on a platinum electrode in 0.1 M HCl at 1000 rpm.
at this corrosion potential. Using this correction, \( k(H^+) \) was determined to be \( 0.33 \pm 0.02 \times 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2} \), which when added to \( k(Fe^{3+}) \) gives a combined rate constant of \( 3.17 \pm 0.16 \times 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2} \).

From these two rate constants, and assuming the reactions are independent, it can be predicted that 90 percent of the metallic iron rotating disc will be dissolved by the iron(III) reduction mechanism at 1000 rpm in 0.02 M Fe\(^{3+}\) and 0.1 M HCl.

Taking the current density from the point of intersection of the polarization curves for the acidified iron(III) solution, and the metallic iron oxidation, and correcting for the gold electrode gives a rate constant of \( 3.26 \pm 0.18 \text{ mol s}^{-1} \text{ m}^{-2} \). This value is in remarkably good agreement with both the rate constant determined from the sum of the individual oxidant components (\( k(\text{sum}) \)) and with that determined by chronopotentiometry. It is also within the limits of the respective experimental errors. If the rate constant determined by chronopotentiometry is used as the standard for the comparison of the techniques, the rate constant calculated from the Evans' diagram is within 1 percent of this value. This does not say that chronopotentiometry is the best technique at this stage, but it is useful to use this value for comparison as it is the only rate constant not involving mechanistic assumptions, and as such has been determined directly from experimentally determined numbers.
6.4.4 Solution Sampling Method

As the dissolution of iron by iron(III) produces more iron(II) than does the dissolution by H\(^+\) (3 moles of iron(II) per mole of iron against 1 mole for the acid mechanism) the rate constant determined by following [iron(II)] in solution, will be governed by the extent of each individual reaction. In the previous section it was calculated that in 0.02M Fe\(^{3+}\)/0.1M HCl solutions, 90 percent of the metallic iron was dissolved by the iron(III) mechanism. Using this number, the amount of iron(II) in solution, and the concentrations attributable to each mechanism can be determined. The results are shown in Figure 6.4 as the total [iron(II)], [iron(II)] dissolved by iron(III), and [iron(II)] dissolved by proton attack. The rate constants determined from this data are: \(k(Fe^{3+}) = 2.74 \pm 0.27 \times 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2}\), \(k(H^+) = 0.31 \pm 0.03 \times 10^{-4} \text{ mol s}^{-1} \text{ m}^{-2}\) and \(k(\text{sum}) = 3.05 \pm 0.30 \text{ mol s}^{-1} \text{ m}^{-2}\).

The combined rate constant calculated is less than 7 percent lower than that determined by chronopotentiometry; while both individual component rate constants are slightly lower than those calculated from the Evans' diagram.

6.4.5 Stern-Geary or Linear Polarization Technique

Due to the extremely corrosive nature of this solution towards iron, the polarization resistance for the dissolution of a massive iron electrode was determined over a 10 mV increment from the corrosion potential at a scan rate of 1 mV s\(^{-1}\) in 0.02 M Fe\(^{3+}\), 0.1 M HCl solutions.
Figure 6.4. Iron (II) concentration versus time plots for the solution sampling technique showing the total amount of iron (II) dissolved (●), the iron (II) attributable to the dissolution by the iron (III) reduction mechanism (▲) and that attributable to attack by acid (■). (25°C, 1000 rpm, 0.02 M Fe³⁺, 0.1 M HCl, mild steel disc).
Again it was not possible to calculate either \( k(\text{Fe}^{3+}) \) or \( k(\text{H}^+) \) without knowing the contribution of the \( \text{Fe}^{3+}/\text{Fe}^0 \) and \( \text{H}^+/\text{Fe}^0 \) reactions to the polarization resistance.

If it is assumed that the \( \text{Fe}^{3+}/\text{Fe}^0 \) and \( \text{H}^+/\text{Fe}^0 \) reactions proceed independently and in parallel on the iron surface, then the total polarization resistance \( R_p \), may be estimated from the equation

\[
\left( \frac{1}{R_p} \right) = \left( \frac{1}{R_p(\text{Fe}^{3+})} \right) + \left( \frac{1}{R_p(\text{H}^+)} \right)
\]

where \( R_p(\text{Fe}^{3+}) \) and \( R_p(\text{H}^+) \) are the polarization resistances of the \( \text{Fe}^{3+}/\text{Fe}^0 \) and \( \text{H}^+/\text{Fe}^0 \) reactions respectively. Both \( R_p(\text{Fe}^{3+}) \) and \( R_p(\text{H}^+) \) can be calculated from equation 6.17 using data from the Evans' diagram (Figure 6.3).

For the reaction \( \text{Fe}^{3+}/\text{Fe}^0 \), from Figure 6.3 \( i = 54.95 \text{ A m}^{-2}, b_a = 0.08 \text{ V} \) and \( b_c = \infty \). The calculated value of \( R_p(\text{Fe}^{3+}) \) is therefore \( 6.32 \times 10^{-4} \text{ \Omega m}^2 \). For the competing \( \text{H}^+/\text{Fe}^0 \) reaction \( i = 10.84 \text{ A m}^{-2}, b_a = 0.08 \text{ V} \) and \( b_c = 0.140 \text{ V} \). As the hydrogen evolution rate on iron is only 58 percent of that on gold, \( i_{\text{corrected}} = 6.29 \text{ A m}^{-2} \), which yields an \( R_p(\text{H}^+) \) of \( 3.52 \times 10^{-3} \text{ \Omega m}^2 \).

Substituting these values into equation 6.19, \( R_p \) (calculated) is \( 5.36 \times 10^{-4} \text{ \Omega m}^2 \) which is 5 percent lower than \( R_p \) (experimental) \( 5.65 \times 10^{-4} \text{ \Omega m}^2 \) determined on an iron disc.
The assumptions made for the calculation of $R_p$ (calculated) appear valid as the result is very close to the value determined experimentally on iron. The rate constant calculated from the experimentally determined $R_p$ on iron, and substituted into equations 6.17 and 6.15 is $3.2 \pm 0.2 \times 10^{-4}$ mol s$^{-1}$ m$^{-2}$, is within the experimental error of the rate constant determined by chronopotentiometry.

6.5 Comparison of Techniques and Conclusions

The rate constants determined from the four techniques are shown in Table 6.2.
Table 6.2

Comparison of Metallic Iron Dissolution Rate Constants
(0.02 M Fe\(^{3+}\), 0.1 M HCl, 25°C, 1000 rpm)

<table>
<thead>
<tr>
<th>Technique</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol s(^{-1}) m(^{-2}) x 10(^6)</td>
</tr>
<tr>
<td>Chronopotentiometry</td>
<td>3.27 ± .06</td>
</tr>
<tr>
<td>Evans' Diagram</td>
<td>3.26 ± .18</td>
</tr>
<tr>
<td>Solution Sampling</td>
<td>3.05 ± .30</td>
</tr>
<tr>
<td>Stern-Geary</td>
<td>3.2 ± .2</td>
</tr>
</tbody>
</table>

The rate constants in Table 6.2 are consistent, with only the result from the solution sampling technique lying outside one standard deviation of the mean (3.20 ± .10 x 10\(^{-4}\) mol s\(^{-1}\) m\(^{-2}\)).

While the solution sampling technique is the most conventional and widely used for these types of dissolution studies it is not as accurate as the other techniques in this case, due to the relatively high limit of detection (3 mg l\(^{-1}\)). The method suffers from the possible reoxidation of Fe\(^{2+}\) which would lower the calculated rates,
and the high limit of detection equates to approximately a 10 percent error on the initial iron(II) determination. The time consuming nature of this type of kinetic study is another feature in favour of one of the electrochemical techniques.

The stripping method was found to give very accurate results and the measurements were conveniently quick for this system. It gives a total rate constant irrespective of the relative proportions of the component mechanisms. This rate constant is desirable for an accurate kinetic study to provide information for an industrial process. The large potential rise from the corrosion potential to the equilibrium potential of the platinum electrode in the iron(III) solution allowed the determinations of the end-points to be very precise. This was considered to be the best technique for a detailed study of the kinetics of pure iron dissolution described in the next chapter.

Even though the Stern-Geary method is very useful for kinetic determinations in corroding systems. The method suffered from a deal of noise in this system which required the use of filtering techniques. Thus this rate constant has the highest uncertainty.

Whilst the Evans’ diagram method gave accurate results and provides detailed mechanistic information, it suffers from the time required to produce each diagram and therefore would not be suitable for a detailed kinetic study. In addition, there are errors associated with the use of gold, rather than iron, for the H⁺ evolution studies.
Chapter 7

Dissolution of Pure Iron in Iron(III) Chloride Solutions

7.1 Introduction

For some time it has been recognised that iron(III) chloride solutions are attractive leaching agents in the chemical processing of minerals (Dutrizac and MacDonald, 1974). Iron(III) is well known in the leaching of copper, zinc and lead sulfide concentrates (Colborn and Bayne, 1970), and patents also appear in the literature for its use in the beneficiation of chromite (Coyle and Bovey, 1969) and ilmenite (Shiah, 1966). A number of reviews appear in the literature summarising the use of iron(III) leaching in hydrometallurgy, but these mainly deal with sulfide minerals (Burkin, 1971; Monhemius, 1970; Dutrizac and MacDonald, 1974; Zuo-Mei Jin et al., 1984; Hirato et al., 1986; Warren et al., 1987 and O'Malley and Liddell, 1987).

In many systems using iron(III), an electrochemical mechanism has been reported. Zuo-Mei Jin et al. (1984) found in their study of the leaching of sphalerite that the rate determining step at low iron(III) concentrations was electrochemical, while at higher concentrations an adsorption mechanism prevailed. An electrochemical rate determining step was also proposed for the leaching of chalcopyrite (Hirato et al., 1986).

In this chapter, the effects of a number of parameters on the kinetics of iron dissolution by iron(III) and by acid in chloride solutions will be studied, as well as the mechanisms governing these processes.
As the system is essentially electrochemical by nature, an electrochemical approach is taken for this study and ways of inhibiting the hydrogen evolution reaction are explored. Knowledge developed in this chapter will be further expanded in the succeeding two chapters, which consider more specifically the dissolution of iron in reduced ilmenite to produce synthetic rutile.

7.2 Experimental

The kinetic measurements in this chapter were made using the chronopotentiometric technique described in the previous chapter (Section 6.2.2). Unless otherwise stated, all tests were carried out at a rotation speed of 1000 rpm and at temperatures between 25 and 60°C. All solutions were prepared using AR grade chemicals and made up with distilled deionized water with iron(III) concentrations between 0 and 0.04 M and HCl concentrations between 0 and 0.3 M. Solutions were degassed using a steady stream of pure nitrogen, prior to all measurements. Standard conditions observed throughout the study included a plating time of 600 s at a current density of 100 A m$^{-2}$ giving an efficiency of 90.0 percent. Details of the experimental apparatus, electrodes and electrode preparation have been described earlier.

7.3 Results and Discussion

7.3.1 Dissolution Rate versus Rotation Speed

If a reaction is under diffusion control, a plot of the rate of dissolution of a rotating disc against the square root of the angular
velocity should be a straight line passing through the origin; otherwise chemical control can be involved to a greater or lesser extent (see Section 6.1).

In Figure 7.1 the dissolution rates at varying rotation speeds are plotted against the square root of the angular velocity to confirm the linearity of this relationship in acidified FeCl₃ and in dilute HCl. The rates reported for 0.1 M HCl in the absence of iron(III) have been included for comparison with the iron(III)/HCl solutions. Unfortunately, they cannot be directly related with the rates in the previous chapter as the kinetic data was collected at a different mixed potential and the \( \text{H}^+ \) diffusion coefficient was not used for their calculation.

Both plots are linear but do not pass through the origin although they have a common intersection point. However, when the 'acid only' rate is subtracted from the iron(III) dissolution rates the line does pass through the origin to give the expected diffusion controlled relationship. To determine whether this was a realistic result and not a problem with the experimental technique, copper was plated and reacted with iron(III) in a similar manner, as described by Couche (1985). The relationship between the rate of copper dissolution and the rotation speed was again a straight line, which in this case passed through the origin, indicating that the experimental technique was indeed valid.
Figure 7.1. Iron dissolution rate versus square root of the angular velocity of a rotating iron disc at 25°C.

(*) 0.02 M Fe$^{3+}$ + 0.1 M HCl, (▲) 0.1 M HCl,

(■) k(0.02 M Fe$^{3+}$ + 0.1 M HCl) - k(0.1 M HCl).
Diffusion control for the dissolution of metallic iron by iron(III) was expected as this result has been reported by a number of workers for both chloride and sulfate systems (Makrides, 1960; Bezvornizii et al., 1978; Tobias and Nobe, 1975). However, Makrides et al. (1955) claimed that in oxygen-free solutions of non-oxidising acids, the dissolution of iron is independent of rotation speed. Figure 7.1 shows that the acid system here exhibits a dependence of rate with rotation speed, albeit less than the completely diffusion controlled iron(III) system. The Evans' Diagram (Figure 6.3) clearly indicates that the process involves some chemical control, therefore the reaction must be dependent on the diffusion of products away from, rather than towards the electrode surface. It is possible that the dependence on rotation speed is a function of the diffusion of Fe$^{2+}$ or H$_2$ away from the electrode surface, but this was not investigated further.

The fact that the lines in Figure 7.1 do not pass through the origin is consistent with all the iron leaching work described in this thesis and may be explained by the competition between Fe$^{3+}$ and H$^+$ to produce Fe$^{2+}$.

\[
2\text{Fe}^{3+} + \text{Fe} = 3\text{Fe}^{2+} \quad 7.1
\]

\[
\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \frac{1}{2}(\text{H}_2\text{ads} + \text{H}_2) \quad 7.2
\]
While a secondary reaction, involving surface adsorbed hydrogen, also produces Fe^{2+}.

\[ 2\text{Fe}^{3+} + \text{H}_{2}\text{ads} \rightarrow 2\text{Fe}^{2+} + 2\text{H}^{+} \quad 7.3 \]

(where \( \text{H}_{2}\text{ads} \) is adsorbed hydrogen on the iron surface and \( \text{H}_2 \) is unreactive hydrogen in the bulk solution).

Reaction 7.1 and the combination of reactions 7.2 and 7.3 are equivalent. However reaction 7.3 should become more significant, relative to 7.2, at slower rotation speeds where \( \text{H}_{2}\text{ads} \) is not diffused as readily into the bulk of the solution, and could thus become involved in reactions occurring at the iron electrode surface. This type of depolarising reaction (equation 7.3) has been reported previously (Makrides, 1960).

In the chronopotentiograms at slower rotation speeds, some effects of hydrogen evolution are clearly evident. At these slower rotation speeds, an initial rise in potential is usually followed by a small plateau, as shown by (a) in Figure 7.2. The reason for this plateau can be explained by considering that as the last of the plated iron dissolves, revealing areas of the platinum, the hydrogen evolution rate increases and changes the mixed potential. After this period, the potential finally rises to the equilibrium potential of iron(III) on a platinum electrode.
Figure 7.2. Chronopotentiogram of an electro-plated iron film dissolving in an iron(III) solution showing the plateau (a) observed at slow rotation speeds. (100rpm, 0.02 M Fe$^{3+}$/0.1 M HCl, 25°C).
This plateau was observed in all chronopotentiograms with added acid at 100 rpm but was not observed in iron(III) solutions at pH above 2.38. This confirms that the effect was caused by the acid, and indicates that the disc surface was covered with a layer of hydrogen for a finite period of time before the last of the iron reacted.

The study of the kinetics of the acid dissolution is not as amenable to this technique as is the iron(III) dissolution, as the corrosion potential is much closer to the equilibrium potential of the inert electrode. The vertical rise from the iron corrosion potential to the equilibrium potential of a platinum electrode in an iron(III) solution, (Chapter 6, Figure 6.2), is replaced by a much smaller and gentler rise to the equilibrium potential of platinum in an acid solution. Thus, the determination of the end-point is less definitive.

7.3.2 Effect of Temperature

The activation energy, $E_a$, of a reacting system can be used in determining the mechanism of the process. Generally, the activation energy for a diffusion controlled reaction is less than 25 kJ mol$^{-1}$, while for chemically controlled systems, values greater than 40 kJ mol$^{-1}$ are expected (Miller, 1973).

The activation energy can be obtained from the determination of the temperature dependence of the rate constants by the Arrhenius equation,

$$\ln k = -\frac{E_a}{RT} + \text{Constant}$$

7.4
where $k$ is the rate constant, $T$ the absolute temperature, $E_a$ the apparent activation energy and $R$ the gas constant.

The dissolution rates of the plated iron films were determined for both iron(III) and pure acid chloride systems in the temperature range 25-60°C and plots of $\ln k$ versus the inverse of the absolute temperature produced straight lines allowing the determination of the activation energies. The data for the two systems is shown in Table 7.1.

Table 7.1

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\ln k^a$</th>
<th>$\ln k^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-8.60</td>
<td>-8.85</td>
</tr>
<tr>
<td>40</td>
<td>-8.11</td>
<td>-8.58</td>
</tr>
<tr>
<td>60</td>
<td>-7.61</td>
<td>-8.12</td>
</tr>
</tbody>
</table>

* Data corrected by subtracting acid component of rate.
The Arrhenius plots yielded an activation energy of $23 \pm 2$ kJ mol$^{-1}$ for the 0.1 M HCl solution and $17 \pm 2$ kJ mol$^{-1}$ for the Fe$^{3+}$/HCl solution.

The activation energy for the iron(III) leaching system is consistent with a diffusion controlled reaction, but the slightly higher value for the acid leaching system indicates some mixed control. The activation energy for the iron(III) reaction with iron is similar to values reported earlier. Bezvornii et al. (1978) quoted values of 14.9 kJ mol$^{-1}$ for FeCl$_3$ solutions and 18.0 kJ mol$^{-1}$ for mixed solutions of FeCl$_3$ and FeCl$_2$, whilst Abramson and King (1939) quoted a value of 25.6 kJ mol$^{-1}$ in 0.025 M FeCl$_3$ solutions. However, it was not clear from their work whether a correction was made for the competitive reaction with acid.

7.3.3 Effect of Iron(III) and Acid Concentration

The effect of iron(III) concentration was investigated over the range 0 to 0.04 M Fe$^{3+}$ in 0.1 M HCl at 25°C at a rotation speed of 1000 rpm. The rate constants, corrected for the acid reaction, are plotted against the iron(III) concentration in Figure 7.3, whilst Figure 7.4 plots the rate constants versus H$^+$ concentration for the addition of acid to 0.02 M Fe$^{3+}$ solutions.
Figure 7.3. Iron dissolution rate versus iron(III) concentration. (0.1 M HCl, 25°C, 1000 rpm).

For complete data see Appendix 1.
Figure 7.3 shows that the dissolution rate of iron increases linearly with iron(III) concentration above 0.01 M, with the data yielding an order of reaction of 2/3 as would be expected for equation 7.1. A linear increase was also observed by Gatos (1956), who monitored the weight loss of iron in solutions with an iron(III) concentration up to \( \approx 0.08 \) M. Even though dissolution rates have been shown here to increase linearly with iron(III) concentration, Makrides and Stern (1960) noted that at critical concentrations of iron(III) passivity will occur inhibiting metal dissolution. However, the concentrations required for passivity are higher than those used in this work.

Figure 7.4 clearly shows that the addition of acid at low concentrations causes a very large increase in rate, but above 0.2 M \( H^+ \) the rate does not increase significantly in the acid range studied. Abramson and King (1939) also observed that there was no significant advantage in increasing the acid concentrations for the dissolution of iron in iron(III) containing solutions, while Gatos (1956) even observed a decrease in rate. However, Gatos (1956) did observe a far greater amount of hydrogen being evolved as the acid concentration was increased. He suggested that the direct reduction of iron(III) was gradually suppressed in favour of the direct reduction of \( H^+ \), which becomes the principle cathodic reaction in 1 N \( H_2SO_4 \).

The results presented here are consistent with those in the literature. With the higher acid concentrations, the greater hydrogen evolution appears to inhibit the iron(III) and hydrogen ions reaching the interface until a plateau in the dissolution rates is attained. Normally gas evolution would increase the rate by forced turbulent flow, but in this case the evidence suggests that hydrogen formation slows the iron dissolution rate processes.
Figure 7.4. The affect on the iron dissolution rate of adding HCl to iron(III) solutions, (0.02 M Fe$^{3+}$, 25°C, 1000 rpm).

For complete data see Appendix 1.
7.3.4 Effect of the Addition of Iron(II)

The possible effect of iron(II) ions on the dissolution rate is of interest since they are the end-product of both the iron oxidation and the iron(III) reduction processes. In this situation, the chronopotentiometric technique is much more suited to this study than a conventional solution sampling method. Chemical analysis methods would be subject to large errors as the species of interest would be in high concentrations irrespective if one was following the oxidised or reduced solution species.

Using this method, the addition of iron(II) as sulfate was studied with and without iron(III). The results are presented in Table 7.2 along with the rates of the corresponding solutions without Fe$^{2+}$. 
Table 7.2  
Effect of Iron(II) Additions on the Iron Dissolution Rates  
(25°C, 1000 rpm, iron(II) as SO₄²⁻)

<table>
<thead>
<tr>
<th>[Fe²⁺]</th>
<th>[Fe³⁺]</th>
<th>[H⁺]</th>
<th>Time</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M</td>
<td>M</td>
<td>s</td>
<td>mol s⁻¹ m⁻² x10⁴</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>0.1</td>
<td>175</td>
<td>3.27</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.1</td>
<td>160</td>
<td>3.57</td>
</tr>
<tr>
<td>0.10</td>
<td>0.02</td>
<td>0.1</td>
<td>172</td>
<td>3.32</td>
</tr>
<tr>
<td>0.50</td>
<td>0.02</td>
<td>0.1</td>
<td>183</td>
<td>3.12</td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.1</td>
<td>310</td>
<td>1.84</td>
</tr>
<tr>
<td>0.10</td>
<td>0.00</td>
<td>0.1</td>
<td>310</td>
<td>1.84</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>0.2</td>
<td>140</td>
<td>4.08</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.2</td>
<td>137</td>
<td>4.17</td>
</tr>
</tbody>
</table>
The results in Table 7.2 show that iron(II) addition has little or no effect on the dissolution rates at levels up to 25 times the concentration of the iron(III) ions and 5 times the acid levels. Minor variations can be noticed at some concentrations but these can be considered to be effects of higher concentrations of electrolytes or variations due to experimental errors.

Hirato et al. (1986) found that the leaching of chalcopyrite with FeCl$_3$ was independent of FeCl$_2$ concentration. However the addition of high concentrations of FeCl$_2$ was found to increase the rate of iron removal with HCl from ilmenite in the Murso process (Sinha, 1980). This increase is presumably as a result of the higher ionic strength which has been reported to increase the activity of the proton and the rate of iron oxide dissolution (Sidhu et al., 1981; Lu and Muir, 1986).

7.4 Investigation into the Inhibition of the Hydrogen Evolution Reaction

The Evans' diagram in the previous chapter (Figure 6.3) showed that the addition of acid to the iron corrosion system, in the presence of iron(III), leads to higher current densities (especially more negative than - 0.50 V vs SCE), higher mixed potentials and higher corrosion rates. The tailing off of the Fe$^{3+}$ reduction curve at lower potentials in the presence of acid, demonstrates that the hydrogen evolution reaction is significant. It was calculated, in the previous chapter, that in 0.02 M Fe$^{3+}$/0.1 M HCl solutions, proton attack contributed to 10 percent of the metallic iron dissolution.
As discussed earlier, minimisation of the acid loss through hydrogen
evolution is required for efficient use of iron(III) for leaching iron
from the porous reduced ilmenite. Therefore, an investigation into the
effect of various cations, anions and background salts was initiated
to try to compete with $H^+$ and either buffer or block its adsorption on
the iron surface.

7.4.1 Effect of Iron(II) Sulfate

Even though the addition of iron(II) had little effect on the rate of
iron dissolution during the chronopotentiometric study (Table 7.2),
large excesses of iron(II) salts were thought to be the cause of a pH
buffering effect, evident in some preliminary leaching experiments
with reduced ilmenite (see Chapter 9).

The effect on the hydrogen evolution reaction of adding up to about
200 times the concentration of $\text{FeSO}_4$ relative to the $H^+$ concentration
was investigated using a gold electrode. In order to make a fair
comparison, it was decided to maintain the same pH (i.e. same activity
of $H^+$) after addition of $\text{FeSO}_4$ by adding extra acid, then observe the
magnitude of the limiting current attributable to hydrogen evolution,
at potentials slightly more positive than the iron deposition
reaction.

Surprisingly, lower currents were observed on addition of iron(II)
sulfate and acid at the same pH, as shown in Figure 7.5(b). Results
from the addition of a range of iron(II) concentrations and salts are
tabulated in Table 7.3.
Table 7.3

**Effect of Iron(II) on the Hydrogen Evolution Reaction**

(0.1 M NaCl, 0.005 M HCl, 25°C, 1000 rpm, Au electrode, sweep 5 mV s⁻¹)

<table>
<thead>
<tr>
<th>[FeSO₄]</th>
<th>pH</th>
<th>(I_{lim}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td></td>
<td>mA (±0.01)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0.0</th>
<th>2.31</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.59</td>
<td>0.37</td>
</tr>
<tr>
<td>0.1</td>
<td>2.31(a)</td>
<td>0.50</td>
</tr>
<tr>
<td>0.5</td>
<td>2.31(a)</td>
<td>0.36</td>
</tr>
<tr>
<td>1.0</td>
<td>2.31(a)</td>
<td>0.35</td>
</tr>
<tr>
<td>0.5 M (\text{FeCl}_2)</td>
<td>2.31(a)</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\(a\) adjusted with acid to bring the pH to 2.31.

\(b\) at -1.0 V SCE
Figure 7.5. Polarization curves showing the effect of the addition of 0.1 M FeSO₄ (b) on the limiting current of the hydrogen evolution reaction at a constant pH. (1000 rpm, pH 2.31, sweep rate 5 mV s⁻¹, Au electrode, (a) 0.1 M NaCl, 0.005 M HCl, (b) 0.1 M NaCl, 0.1 M FeSO₄, 0.005 M HCl adjusted with HCl to pH 2.31).
The results in Table 7.3 show that even with the addition of extra acid to counteract the natural buffering of the sulfate ions and decrease in activity coefficient of $H^+$, the iron(II) ions clearly have a significant effect on the magnitude of the limiting current attributable to the hydrogen evolution reaction. At pH 2.31, with the iron(II) concentration 100 times the acid concentration, the rate of hydrogen evolution is reduced by approximately 52 percent. Further increases in the concentration of FeSO$_4$ above 0.5 M seemed to have only a minor effect, with the limiting current levelling out at about 0.35 mA.

It therefore seems that the adsorption of the positively charged Fe$^{2+}$ ion onto the negatively charged iron surface has the effect of minimising the adsorption sites available for protons which are then reduced to hydrogen. The Fe$^{2+}$ ions may also limit the sites available for iron(III) reduction, but the effect seems to be minor compared to that of the acid (Table 7.2) due to the higher charge of Fe$^{3+}$ and its greater adsorption. For an observable decrease in rate to be achieved on addition of FeSO$_4$, however, the concentration of FeSO$_4$ needs to be many times that of the proton (unlike in the solutions used in Table 7.3) due to ion-pairing of Fe$^{2+}$ with SO$_4^{2-}$ giving little free Fe$^{2+}$.

To show that the decrease in the rate of hydrogen evolution, shown in Table 7.3, was not attributable to the anions present, polarization curves were recorded for the same concentration of acid in both FeCl$_2$ and FeSO$_4$ solutions.

The results show a further decrease in chloride media which, despite the need to add base to counteract the rise in activity coefficient of
H\(^+\), is almost certainly caused by the greater number of free Fe\(^{2+}\) ions in the FeCl\(_2\) solution inhibiting the hydrogen evolution reaction. Using the speciation program ESTA (May et al., 1985), it was calculated that at the ionic concentrations used, 36 percent of the iron in the chloride solution was present as Fe\(^{2+}\) and 50 percent was present as FeCl\(^+\), whereas in the sulfate medium only 9.5 percent of the iron was present as Fe\(^{2+}\) with the remainder being in solution as the ion-paired FeSO\(_4\) form.

High concentrations of Fe\(^{2+}\) can also be an advantage in leaching with Fe\(^{3+}\) as the lower equilibrium solution potential allows higher pH values to be used without the chance of hydrolysis of Fe\(^{3+}\), according to equations 7.5 and 7.6 below. Thus, lower proton concentrations can be maintained in Fe\(^{3+}\) solutions in the presence of Fe\(^{2+}\) and consequently less hydrogen evolution would be expected.

\[
\text{Fe(OH)}_3 + 3\text{H}^+ + e^- = \text{Fe(II)} + 3\text{H}_2\text{O} \quad 7.5
\]

\[
E_{298} = 0.972 - 0.177\text{pH} - 0.059\log[\text{Fe(II)}] \quad 7.6
\]

7.4.2 Effect of other Cations on the Hydrogen Evolution Reaction

As iron(II) was found to inhibit the hydrogen evolution reaction, this study was expanded to ascertain if any other cations would show a similar effect. Only cations with reversible potentials lower than Fe/Fe\(^{2+}\) couple were considered as those more noble would most certainly cement on iron. The effect of different cations on the magnitude of the hydrogen limiting current at a constant pH of 2.31 are shown in Table 7.4.
Table 7.4
Effect of Cations on the Hydrogen Evolution Reaction
(0.1 M NaCl, 0.005 M HCl, 25°C, pH 2.31, 1000 rpm, Au electrode)

<table>
<thead>
<tr>
<th>Added Salts</th>
<th>Ionic Strength (M)</th>
<th>$I_{\text{lim}}$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.10</td>
<td>0.75</td>
</tr>
<tr>
<td>0.5 M KCl</td>
<td>0.60</td>
<td>0.74</td>
</tr>
<tr>
<td>0.5 M LiCl</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>0.5 M FeCl$_2$</td>
<td>1.60</td>
<td>0.21</td>
</tr>
<tr>
<td>0.5 M CaCl$_2$</td>
<td>1.60</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5 M MgCl$_2$</td>
<td>1.60</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5 M AlCl$_3$</td>
<td>3.10</td>
<td>0.03</td>
</tr>
<tr>
<td>0.5 M LaCl$_3$</td>
<td>3.10</td>
<td>0.27</td>
</tr>
</tbody>
</table>
The results in Table 7.4 show that all the cations tested, except $K^+$, significantly inhibited the hydrogen evolution reaction when their concentration was a hundred times greater than that of the acid. It can be argued that the addition of these salts raises the ionic strength and activity coefficient of $H^+$, thereby decreasing the concentration of HCl required to maintain a pH of 2.31. Calculations of the effects of changing the ionic strength showed that even if complete ionisation was assumed, the magnitude of the hydrogen reduction current relative to that without any added salts, would fall to 0.58 mA for a $M^+$ salt, 0.35 mA for an $M^{2+}$ salt and 0.20 mA for an $M^{3+}$ salt. Table 7.4 shows that only the transition metal cations $Al^{3+}$ and $Fe^{2+}$ significantly lowered the hydrogen evolution rate below these levels.

Various theories on the role of cations in suppressing $H_2$ evolution have been proposed in the past. Drazic and Vorkapic (1978) found that the addition of $Cd^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ ions significantly lowered the volume of hydrogen evolved on iron and explained the effect as an underpotential deposition of adatoms of these metals on iron. They likened it to previous observations of the deposition of Pb, Cd and Bi on noble metals at potentials more positive than their reversible potentials producing a monolayer of deposited adatoms (Adzic et al., 1974; 1975; 1977).

Aluminium(III) is a small ion known to adsorb onto negatively charged surfaces, and its effect supports the theory put forward here that an adsorption reaction is taking place at the surface of the metallic iron. The adsorption of $Fe^{2+}$ onto the metallic iron surface with inhibition of the hydrogen evolution reaction parallels the inhibiting
effects of cations observed for cementation reactions. Jiang (1987) found that high concentrations of Zn$^{2+}$ inhibited the cementation of cobalt on zinc and the amount of hydrogen evolution. The results were attributed to the double layer effect of the concentrated zinc sulfate. Yunus et al. (1965) also observed an inhibition for this reaction and proposed that the inhibition was due to preferential adsorption of Zn$^{2+}$ at the active zinc sites which reduced the rate of nucleation of cobalt deposition.

The degree of inhibition resulting from the addition of the electrolytes inversely reflects the amount of ion-pairing occurring. In an AlCl$_3$ solution there is virtually no ion-pairing and all the aluminium is present as Al$^{3+}$ ions. On the other hand, the ion-pairing effect with sulfate anions lowers the ionic activity of most cations.

The degree of inhibition is, therefore, presumably a complex function of the charge density, ion-pairing, and concentration of the transition metal cation of interest. These results would seem to be consistent with the findings of Drazic and Vorkapic (1978) and of the other authors studying cementation systems. Other methods for controlling the hydrogen evolution reaction will be discussed in Chapter 8.

7.5 Effect of Background Electrolytes on Iron(III) Speciation and Rate of Iron Dissolution

To monitor the effect of changing the speciation of the iron(III) complex ions on the dissolution rate of iron by the addition of
electrolytes, a solid mild steel rotating disc was used so that small changes in dissolution rates could be detected by solution analysis.

Using the published stability constants (Sillen and Martell, 1964) and the speciation computer program ESTA (May et al., 1985) the concentrations of iron(III) chloride and sulfate were varied and the percentages of particular iron(III) species are shown below.

**Case 1** 0.05M Fe$_2$(SO$_4$)$_3$

(0.1M Fe$^{3+}$ and 0.15M SO$_4^{2-}$)

<table>
<thead>
<tr>
<th>Species</th>
<th>Percentage of Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>0.2</td>
</tr>
<tr>
<td>FeSO$_4^+$</td>
<td>99.8</td>
</tr>
</tbody>
</table>

**Case 2** 0.10M FeCl$_3$

(0.1M Fe$^{3+}$ and 0.3M Cl$^-$)

**Case 3** 0.1 M FeCl$_3$ + 1.2M KCl

(0.1M Fe$^{3+}$ and 1.5M Cl$^-$)

<table>
<thead>
<tr>
<th>Species</th>
<th>Percentage of Fe$^{3+}$</th>
<th>Species</th>
<th>Percentage of Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>9.9</td>
<td>Fe$^{3+}$</td>
<td>0.4</td>
</tr>
<tr>
<td>FeCl$_2^{2+}$</td>
<td>51.1</td>
<td>FeCl$_2^{2+}$</td>
<td>14.4</td>
</tr>
<tr>
<td>FeCl$_2^+$</td>
<td>39.0</td>
<td>FeCl$^+_3$</td>
<td>84.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FeCl$^-_3$</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The effects of background KCl and K$_2$SO$_4$ on the rates of iron dissolution by 0.1 M FeCl$_3$ at pH 2.0 and by 0.05 M Fe$_2$(SO$_4$)$_3$ at pH 1.8, are shown in Table 7.5.
Table 7.5

Addition of Background Electrolytes to Iron(III) Chloride

\( ^a \) (0.1M FeCl\(_3\), 400 rpm, 25°C, pH 2.0)

\( ^b \) (0.05M Fe\(_2\)(SO\(_4\))\(_3\), 400 rpm, 25°C, pH 1.8)

<table>
<thead>
<tr>
<th>Background Electrolyte</th>
<th>Added Ionic Strength (M)</th>
<th>( k ) mol m(^{-2}) s(^{-1}) x10(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>2.88(^a)</td>
</tr>
<tr>
<td>0.15M K(_2)SO(_4)</td>
<td>0.45</td>
<td>2.69(^a)</td>
</tr>
<tr>
<td>0.4M K(_2)SO(_4)</td>
<td>1.2</td>
<td>2.60(^a)</td>
</tr>
<tr>
<td>1.2M KCl</td>
<td>1.2</td>
<td>2.84(^a)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3.25(^b)</td>
</tr>
<tr>
<td>0.4M K(_2)SO(_4)</td>
<td>1.2</td>
<td>2.67(^b)</td>
</tr>
<tr>
<td>1.2M KCl</td>
<td>1.2</td>
<td>3.19(^b)</td>
</tr>
</tbody>
</table>

These results show that the change in rates are surprisingly minor compared with the variations in concentrations of the various iron(III) complexes. It seems that the solution speciation makes little difference to the reaction of iron(III) with iron.
7.6 Conclusions

The dissolution of metallic iron in iron(III) chloride solutions has been found to be diffusion controlled with an activation energy of 17 \( \pm 2 \text{ kJ mol}^{-1} \). The dissolution rate in the presence of 0.1 M HCl increases linearly with iron(III) concentrations between 0.01 and 0.04 M, while the addition of acid above 0.2 M HCl has little effect on the rate. On the other hand, iron dissolution in HCl is under mixed control and is relatively independent of concentration above 0.1 M. It was found to have an activation energy of 23 \( \pm 2 \text{ kJ mol}^{-1} \).

The iron(III) and acid dissolution mechanisms are competing reactions for the dissolution of iron in iron(III) solutions and the minimisation of acid consumption is a requirement of an efficient iron(III) leaching system. Lower hydrogen evolution rates were found to occur on addition of a large excess of transition metal cations in particular Fe\(^{2+}\) and Al\(^{3+}\). The most effective cation was Al\(^{3+}\) due to strong adsorption of the cation on the metallic iron surface which blocks sites suitable for the reduction of the proton. It is the most effective as it is small with a large charge density to compete effectively with the proton, and exhibits virtually no ion-pairing in chloride media.

The results in this chapter show that iron(III) is a very efficient oxidant for the dissolution of iron. However, before these results could be applied to a process for upgrading ilmenite an analysis of iron removal from a porous reduced ilmenite matrix is required. In the following chapter a study of the dissolution of iron from reduced ilmenite rotating discs will be conducted to ascertain if the results from this fundamental pure iron dissolution study are applicable to the Summit Process.
Chapter 8

Kinetics of Leaching Reduced Ilmenite Using a Rotating Disc

8.1 Introduction

Reduced ilmenite has been shown by Bracanin et al. (1972) and Farrow et al. (1987) to consist of large porous grains of rutile honey-combed with metallic iron particles whose average size is 1 micron. Because of the porous nature of the reduced mineral, 99 percent of the surface area of the grain is internal. Plate 8.1 is an electron micrograph of a polished reduced ilmenite grain, showing the metallic iron nodules as the white areas and the characteristic porous morphology of reduced ilmenite. The leaching process therefore requires the dissolution of metallic iron embedded in the TiO$_2$ matrix which may alter the kinetics and cause complications, such as precipitation in the pores. Hence the results of the pure iron dissolution studies, may not properly reflect the behaviour of reduced ilmenite.

Plate 8.1. Micrograph of reduced ilmenite, X640 (Grid bar = 10μm).
Even though four patents exist for the removal of metallic iron from reduced ilmenite using iron(III) (Shiah, 1966; George et al, 1958; Nakazawa and Terunuma, 1958; Pike 1959), no work has been reported on the kinetics of this reaction. This chapter therefore reports the results of a detailed kinetic study of reduced ilmenite discs compared with the results of pure iron in the preceding two chapters. This is used to gain a better understanding of the mechanism and rate governing process for the efficient removal of iron from a porous matrix and to identify potential problems in the removal of iron not encountered on smooth iron surfaces.

As discussed in Chapter 7, the viability of an acidic iron(III) chloride leaching process for the removal of iron, is dependent on the minimisation of secondary reactions involving acid consumption. But, with the reduced ilmenite matrix, the viability of the process also depends on minimising the precipitation of $\text{Fe(OH)}_3$ in the pores of the grain, caused by localised increases in pH. In the previous chapter, it was shown that the reaction of $\text{H}^+$ with metallic iron could be inhibited by adding suitable cations, such as $\text{Al}^{3+}$ or $\text{Fe}^{2+}$ to compete for sites on the iron surface. Of course another approach is to increase the pH of a iron(III) solution, but there is a limit to the increase in pH of the solution without precipitating iron(III) hydroxide, unless the activity of the iron(III) ions is reduced. The focus of this chapter is therefore to examine the effectiveness of two well-known iron(III) complexing agents, namely oxalate and citrate which inhibit the precipitation of iron(III) hydroxides.
The use of inexpensive di- and tri-carboxylic acids for iron(III) ion complexation has been known and used for many years. George et al. (1958) used citric and tartaric acid additions in their patent to avoid ferric ion hydrolysis during the plating of iron. Citric and oxalic acid are also involved in many methods for removing iron(III) stains. Oxalic acid has the added advantage in Western Australia of being available in large quantities as a waste product from the Bayer process for alumina production.

8.2 Experimental

The reduced ilmenite (-180 + 250 micron) supplied by Westralian Sands Limited was first pulverised in a ring mill to a talc like consistency. This finely pulverised material (10.0g) was then transferred to a 29 mm die and pressed using a hydraulic press at 400 kPa pressure and held for 60 seconds. The solid pressed disc was then removed and placed in a tube furnace under a stream of nitrogen while the temperature was slowly brought up to 700°C. This temperature was held for 3 hours and then the furnace and disc were allowed to cool to room temperature under a nitrogen atmosphere. Leaching experiments were performed on 29 mm diameter reduced ilmenite discs secured in a teflon bell-shaped cylinder with Silastic as shown in Figure 6.1.

The discs were polished by hand using 1200 grade wet and dry emery paper. The rotation speed of the motor driven shaft was set by an adjustable controller. The experimental equipment and analytical techniques used here have been outlined in Section 6.3.
In this work the acid concentration was the same as the iron(III) concentration, which resulted in slightly lower pH values (0.1M Fe$^{3+}$ = pH 1.35, 0.1M HCl = pH 1.06), however, experimentally this was found to be the optimum concentration due to difficulties in the analysis of the iron(II) at lower concentrations and the excessive hydrogen evolution at higher acid concentrations. Even so, hydrogen generated from the acid seeping through the surface layer and dissolving some iron below the surface caused "blow-outs" which, in some cases, resulted in large portions of the discs being dislodged.

8.3 Results and Discussion

Figure 8.1 shows the concentration profile of iron(II) dissolved from a reduced ilmenite disc leached in 0.1M FeCl$_3$ at 25°C over a period of 5 hours at a rotation speed of 400 rpm. It is evident from the profile that the curve deviates from linearity after the first hour. This progressive slowing of the rate with time is expected as it becomes increasingly more difficult for the oxidant to diffuse through the voids in the TiO$_2$ matrix and to come in contact with the underlying metallic iron. This is unlike the cementation results of copper on iron and zinc reported by Strickland and Lawson (1970; 1971), where increased surface roughness enhanced the rate of reaction through turbulence. The difference in the two systems is essentially the size of the cavities created by metal dissolution. Much smaller cavities occur during the corrosion of reduced ilmenite iron, while large pores are characteristic of cementation and rusting.
Figure 8.1. Iron(II) concentration versus time for the dissolution of a reduced ilmenite rotating disc leached in 0.1 M FeCl$_3$. (25°C, 400 rpm, pH 1.35).
During long term leaching the reduced ilmenite disc is susceptible to crumbling, so that pieces may fall away exposing new surfaces. Thus the kinetics may not follow a simple rate law. Leaching systems which leave a porous solid residue and whose rate determining step is diffusion of the reagent through a solid layer obey the Parabolic Rate Law.

For a system to obey the Parabolic Rate Law the rate of leaching varies with the square of the thickness of the solid layer (I), as in equation 8.1.

\[ I^2 = 2kt + \text{constant} \quad 8.1 \]

More conveniently, the number of moles reacted can be substituted for the thickness of the layer which for this system yields equation 8.2

\[ [\text{Fe}^{2+}]^2 = 2kt' + \text{constant} \quad 8.2 \]
Figure 8.2. Square of the iron(II) concentration versus time for the dissolution of a reduced ilmenite rotating disc leached in 0.1 M FeCl$_3$ (25°C, 400 rpm, pH 1.35).
Figure 8.2 shows that the square of the concentration of Fe$^{2+}$ against time is indeed linear after an initial period, which is consistent with parabolic kinetics. The turbulence caused by the surface cavities is probably the cause of the small deviation observed from real parabolic kinetics over the whole duration of the experiment. However, the slowing of the rate is not as great as might be expected, indicating that the developed pores are relatively large, enabling greater solution turbulence to offset any slowing of iron(III) diffusion. To be consistent with the results in the previous chapter, the rate constants in this study were taken from the linear portion of the concentration profiles over a maximum period of 60 minutes, giving a pseudo zero order rate constant.

8.3.1 Effect of Rotation Speed on Leaching Rate

The leaching rate data for three different rotation speeds are shown in Table 8.1 and plotted against the square root of the rotation speed in Figure 8.3 in order to test the Levich equation (equation 6.7). The dissolution rate data for pure iron discs from the previous chapter is also superimposed onto Figure 8.3.
Figure 8.3. Rate of iron dissolution versus rotation speed.

• Reduced ilmenite disc, 25°C, 0.1 M FeCl$_3$

(Δ Pure iron disc, 25°C, 0.02 M Fe$^{2+}$/0.1 M HCl) from Figure 7.1.
Table 8.1

Effect of Rotation Speed on the Initial Leaching Rate

(25°C, 0.1M FeCl₃, pH 1.35)

<table>
<thead>
<tr>
<th>Rotation Speed</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>rpm</td>
<td>rad s⁻¹</td>
</tr>
<tr>
<td>100</td>
<td>10.47</td>
</tr>
<tr>
<td>400</td>
<td>41.88</td>
</tr>
<tr>
<td>900</td>
<td>94.25</td>
</tr>
</tbody>
</table>

The linear relationship observed in Figure 8.3 confirms that the initial rate is essentially diffusion controlled, but again the line of best fit does not pass through the origin because of the reaction of H⁺ with iron at the pH of 1.35 used. This result is consistent with that obtained for the pure iron system (Chapter 7).
In Chapter 7 (Figure 7.1), the relationship with rotation speed was found to pass through the origin if the acid component was subtracted from the rate constants representing both the acid and iron(III) dissolution processes. As Figure 8.3 shows that the results for the dissolution of the reduced ilmenite discs and the pure iron discs have very similar rates at zero rotation speed, it can be assumed that these two systems involve similar acid dissolution components and therefore the \( \text{FeCl}_3 \) concentrations used in this chapter (0.1 M) are suitable for comparing the two experimental programmes. In Chapter 6 it was found that at 1000 rpm in 0.02 M \( \text{Fe}^{3+} \)/0.1 M HCl solutions at 25°C, acid attack contributed to 10 percent of the iron dissolution.

8.3.2 Effect of Iron(III) and Acid Concentration

The results of changing the iron(III) concentration on the leaching rate in chloride solutions, as well as the dissolution rates for 0.05 M \( \text{Fe}_2(\text{SO}_4)_3 \) and 0.1 M HCl solutions, are shown in Table 8.2 at 25°C and their natural pH. Other rate data collected on an iron disc showed that the minor pH changes required to bring the solutions to the same pH level had a negligible effect on the rates of reaction.
Table 8.2

Iron Leaching Rates for Iron(III) and Acid Solutions
(400 rpm, 25°C)

<table>
<thead>
<tr>
<th>Iron(III) Concentration</th>
<th>pH</th>
<th>Leaching Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td></td>
<td>mol m⁻² s⁻¹ x10⁴</td>
</tr>
<tr>
<td>0.05</td>
<td>1.55</td>
<td>6.00</td>
</tr>
<tr>
<td>0.10</td>
<td>1.35</td>
<td>8.59</td>
</tr>
<tr>
<td>0.20</td>
<td>1.33</td>
<td>17.31</td>
</tr>
<tr>
<td>0.05M Fe₂(SO₄)₃</td>
<td>1.48</td>
<td>10.76</td>
</tr>
<tr>
<td>0.1M HCl</td>
<td>1.06</td>
<td>8.39</td>
</tr>
</tbody>
</table>

The leaching data shows a linear relationship with iron(III) ion concentration, again consistent with the pure iron dissolution study reported in section 7.3.3. For comparison, the leaching rates for the dissolution of iron from reduced ilmenite discs in 0.1 M HCl and 0.05 M Fe₂(SO₄)₃ are also shown in Table 8.2.
The faster leaching rate shown for Fe₂(SO₄)₃ in Table 8.2 was also shown to occur for iron discs in the previous chapter. It is believed that this is due to the faster diffusion of Fe³⁺ in sulfate media, as the species of interest would be a sulfato-complexed rather than in the chloride system, where little ion-pairing occurs and the ferric species of interest would be considerably more hydrated.

The practical importance of minimising reactions involving protons in the honey-comb structure of the reduced ilmenite is that a pH gradient will be established in these cavities promoting hydrolysis of Fe³⁺. This process not only consumes the iron(III) leachant, but more importantly can result in iron(III) hydroxide precipitating in the reduced ilmenite pores and blocking further leaching, thereby giving poor quality synthetic rutile. Thus, on the one hand, the addition of acid is required to avoid hydroxide formation, but on the other hand this severely affects the viability of the process (Ward et al., 1989a).
8.3.3 Effect of Temperature and Calculation of Activation Energies

The effect of temperature on the leaching rate was determined for iron(III) ion in both chloride and sulfate media and for 0.1M HCl solutions. The rate data and the activation energies determined from the slopes of the Arrhenius plots are shown in Table 8.3.

Table 8.3

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0.1M FeCl₃</th>
<th>0.05M Fe₂(SO₄)₃</th>
<th>0.1M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>mol m⁻² s⁻¹ x10⁴</td>
<td>mol m⁻² s⁻¹ x10⁴</td>
<td>mol m⁻² s⁻¹ x10⁴</td>
</tr>
<tr>
<td>5</td>
<td>4.86</td>
<td>6.85</td>
<td>3.71</td>
</tr>
<tr>
<td>25</td>
<td>8.59</td>
<td>10.76</td>
<td>8.39</td>
</tr>
<tr>
<td>50</td>
<td>21.14</td>
<td>21.44</td>
<td>22.05</td>
</tr>
<tr>
<td>E_a (kJ mol⁻¹)</td>
<td>24 ± 3</td>
<td>19 ± 3</td>
<td>30 ± 2</td>
</tr>
</tbody>
</table>
As expected, the activation energies are very similar to those determined for the pure iron electrode dissolution, although the results here are slightly higher in each case reflecting small changes in the diffusion characteristics of the leachant to the reacting surface. However, the iron(III) leaching systems again have activation energies marginally lower than that of the acid leaching system.

The rate increases shown in Table 8.3 confirm that the iron in porous reduced ilmenite reacts in a very similar manner to pure iron discs and that the activation energies for reactions with $\text{Fe}^{3+}$ or $\text{H}^+$ are sufficiently similar that the relative amount of acid consumption should not be affected by temperature.

8.3.4 Addition of Oxalate and Citrate to Iron(III) Solutions

The activity of the free iron(III) ion in solution can be significantly altered by the addition of strong complexing ligands such as oxalate and citrate. Association constants reported in the literature (Sillen and Martell, 1964) for the respective iron(III) complexes with oxalate and citrate at $25^\circ\text{C}$ are $\log K_1 = 7.56$ and $\log K_1 = 10.24$, $\log K_2 = 5.70$ respectively.

The dissociation constants for the corresponding acids are (Weast, 1984): Oxalic Acid $pK_1 = 1.23; pK_2 = 4.19$, and Citric Acid $pK_1 = 3.14; pK_2 = 4.77; pK_3 = 6.39$
Since their association with iron(III) is stronger than with H\(^+\), it can be assumed that pH has little effect on complexation and that only stoichiometric amounts of oxalate are required for complete reaction.

8.3.4.1 Addition of Sodium Oxalate

**Table 8.4**

<table>
<thead>
<tr>
<th>Na(_2)C(_2)O(_4) conc. (M)</th>
<th>pH</th>
<th>Leaching Rate (mol m(^{-2}) s(^{-1})x10(^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1.35</td>
<td>8.59</td>
</tr>
<tr>
<td>0.05</td>
<td>1.65</td>
<td>6.51</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>3.97</td>
</tr>
<tr>
<td>0.15</td>
<td>2.70</td>
<td>2.50</td>
</tr>
<tr>
<td>0.15</td>
<td>1.35 (adjusted)</td>
<td>2.11</td>
</tr>
<tr>
<td>0.20</td>
<td>3.25</td>
<td>0.92</td>
</tr>
<tr>
<td>0.30</td>
<td>5.80</td>
<td>Below Experimental Method</td>
</tr>
</tbody>
</table>
As expected, the activation energies are very similar to those determined for the pure iron electrode dissolution, although the results here are slightly higher in each case reflecting small changes in the diffusion characteristics of the leachant to the reacting surface. However, the iron(III) leaching systems again have activation energies marginally lower than that of the acid leaching system.

The rate increases shown in Table 8.3 confirm that the iron in porous reduced ilmenite reacts in a very similar manner to pure iron discs and that the activation energies for reactions with Fe$^{3+}$ or H$^+$ are sufficiently similar that the relative amount of acid consumption should not be affected by temperature.

8.3.4 Addition of Oxalate and Citrate to Iron(III) Solutions

The activity of the free iron(III) ion in solution can be significantly altered by the addition of strong complexing ligands such as oxalate and citrate. Association constants reported in the literature (Sillen and Martell, 1964) for the respective iron(III) complexes with oxalate and citrate at 25°C are $\log K_1 = 7.56$ and $\log K_1 = 10.24$, $\log K_2 = 5.70$ respectively.

The dissociation constants for the corresponding acids are (Weast, 1984): Oxalic Acid $pK_1 = 1.23$; $pK_2 = 4.19$, and Citric Acid $pK_1 = 3.14$; $pK_2 = 4.77$; $pK_3 = 6.39$
Since their association with iron(III) is stronger than with $H^+$, it can be assumed that pH has little effect on complexation and that only stoichiometric amounts of oxalate are required for complete reaction.

8.3.4.1 Addition of Sodium Oxalate

**Table 8.4**

**Effect of Sodium Oxalate on Iron(III) Chloride Leaching Rates**

$(25{\degree}C$, $0.1M$ $FeCl_3$ and Rotation Speed = 400 rpm)

<table>
<thead>
<tr>
<th>$Na_2C_2O_4$ conc.</th>
<th>pH</th>
<th>Leaching Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td></td>
<td>$mol m^{-2} s^{-1}x10^4$</td>
</tr>
<tr>
<td>-</td>
<td>1.35</td>
<td>8.59</td>
</tr>
<tr>
<td>0.05</td>
<td>1.65</td>
<td>6.51</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>3.97</td>
</tr>
<tr>
<td>0.15</td>
<td>2.70</td>
<td>2.50</td>
</tr>
<tr>
<td>0.15 (adjusted)</td>
<td>1.35</td>
<td>2.11</td>
</tr>
<tr>
<td>0.20</td>
<td>3.25</td>
<td>0.92</td>
</tr>
<tr>
<td>0.30</td>
<td>5.80</td>
<td>Below Experimental Method</td>
</tr>
</tbody>
</table>
The effect of the addition of sodium oxalate to iron(III) chloride on the rates of iron dissolution are shown in Figure 8.4, whilst Table 8.4 details the calculated iron dissolution rates for varying concentrations of sodium oxalate up to 100 percent excess (0.30 M) at the equilibrium pH of solution. Figure 8.4 also shows the results for oxalic acid alone and for an iron(III)-oxalate solution at pH 1.35 which is the natural pH of the 0.1M FeCl₃ solutions without the addition of complexing agents. This figure clearly demonstrates that an increase in the concentration of oxalate has a significant effect on slowing the iron leaching rate. With a 3:1 ratio of oxalate:iron(III), leaching is essentially stopped (Table 8.4). At this ratio an Eh of 265 mV (nHe) was measured against a value of 925 mV in the absence of the oxalate.

On the other hand, much higher pH values can be obtained on addition of oxalate without iron(III) hydrolysing. As expected, pH has very little effect on the leaching rate with iron(III) in the presence of oxalate, but the addition of oxalate has obviously little value if the kinetics of iron removal are to be optimised.

These results are consistent with results presented by Subrahmanyanam and Hoey (1977) who claimed that potassium oxalate is an effective inhibitor for the corrosion of mild steel at pH 2.5 in sulfuric acid solutions containing iron(III). They claimed that the inhibition was due to the formation of a thin film of $\beta$-FeC₂O₄.2H₂O, which was identified by X-ray diffraction analysis.
However, the results presented here suggest that the iron(III) oxalate complex takes little or no part in the dissolution processes. As evidenced by the drop in Eh of the solution, the decrease in the rate is attributable to the decrease in concentration or activity of Fe$^{3+}$. If an iron(II) oxalate solid species were formed, one would expect a very dramatic slowing of the rate upon formation of a passivating layer, which is not observed (Figure 8.4).

8.3.4.2 Addition of tri-Sodium Citrate

The effect on the iron dissolution rate with the addition of citrate was again studied up to a ligand concentration of twice that required for 1:1 complexation. Experimentally determined iron dissolution rates for varying concentrations of citrate at equilibrium pH are shown in Figure 8.5, whilst the calculated rate constants and solution colour at various pH are summarised in Table 8.5.
Figure 8.4. Effect of the addition of sodium oxalate to iron(III) solutions on the rate of iron dissolution from reduced ilmenite rotating discs. (25°C, 0.1 M FeCl₃, ■ = FeCl₃ only at pH 1.35, ○ = 0.05 M oxalate at pH 1.65, ▲ = 0.10 M oxalate at pH 2.00, • = 0.15 M oxalate at pH 2.70, ■ = 0.15 M oxalate at pH 1.35, ▲ = 0.10 M oxalic acid pH 1.20).
Figure 8.5. Effect of the addition of tri-sodium citrate to iron(III) solutions on the rate of iron dissolution from reduced ilmenite rotating discs (25°C, 0.1 M FeCl₃).

- FeCl₃ only at pH 1.35, ▲ = 0.05 M citrate at pH 1.30,
- O = 0.10 M citrate at pH 2.00, ● = 0.10 M citric acid at pH 1.60.
Table 8.5

**Effect of the Addition of tri-Sodium Citrate on the Leaching Rate**

(400 rpm, 25°C, 0.1M FeCl₃)

<table>
<thead>
<tr>
<th>Ligand Concentration</th>
<th>pH</th>
<th>Colour of Solution</th>
<th>Leaching Rate $\text{mol m}^{-2} \text{s}^{-1} \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1.35</td>
<td>Orange</td>
<td>8.59</td>
</tr>
<tr>
<td>0.025</td>
<td>1.35</td>
<td>Red/Orange</td>
<td>9.00</td>
</tr>
<tr>
<td>0.05</td>
<td>1.30</td>
<td>Red/Orange</td>
<td>11.53</td>
</tr>
<tr>
<td>0.10</td>
<td>2.00</td>
<td>Green</td>
<td>6.22</td>
</tr>
<tr>
<td>0.10 Adjusted to 1.35</td>
<td></td>
<td>Red/Orange</td>
<td>11.96</td>
</tr>
<tr>
<td>0.20</td>
<td>5.04</td>
<td>Green</td>
<td>4.25</td>
</tr>
<tr>
<td>Citric Acid(0.1M)</td>
<td>1.60</td>
<td></td>
<td>3.53</td>
</tr>
</tbody>
</table>
The results show that with citrate addition, the pH of the solution plays a more important role in protonating citrate ion and determining the complex formed. Citric acid itself also reacts directly with iron more readily than oxalic acid and at a rate approximately half that of FeCl₃ alone.

At half the concentration of citrate to iron(III), a rate enhancement of 34 percent was observed with only a minor change in pH. This rate increase can be attributed to protonation of the citrate ion and lack of complexation with Fe³⁺. Thus, the observed rate is a combination of the rates of dissolution for iron(III) and citric acid. However, when the citrate concentration and pH increased, the solution changed to a green colour, with the obvious formation an iron(III) complex, and the leaching rate fell. But, whereas the rate fell to < 10 percent of the initial rate with oxalate, the rate only fell to half that observed for 0.1M FeCl₃ without any added complexing agents. Table 8.5 also shows that the green complex formed at pH 2.00 with equimolar citrate and iron(III), is broken by acidification to pH 1.35, leading to a rate enhancement.

Despite the apparent shortcomings of citrate ion addition it would appear from the kinetic results presented here that the addition of citrate to iron(III) could be a useful additive for the dissolution of iron from reduced ilmenite for a number of reasons. At pH < 2 the citrate will be protonated and the iron dissolution rate by iron(III) will be enhanced by the reaction of iron with citric acid. But as the pH rises in the bulk solution or in the cavities of the reduced ilmenite, the formation of citrate complexes at pH ≥ 2 would inhibit the hydrolysis of iron(III). Assuming this pH rise is localised in the
reduced ilmenite matrix, as the iron(III) citrate complex diffused back into the bulk solution, the complex would revert to release Fe$^{3+}$ with the protonation of the citrate.

Even though considerable discussion has been paid to the minimisation of iron dissolution through reaction with acid, it would seem that in the presence of citrate this reaction would not be detrimental to the process. However, the confirmation of this requires the chemical analysis of synthetic rutile produced in the presence of citrate.

8.4 Conclusions

The results of the dissolution of iron from a reduced ilmenite matrix show that after the first hour, the rate progressively slows to be approximately half the initial rate by the fifth hour as it becomes increasingly more difficult for the oxidant to diffuse through the voids. Despite the difference in morphology between the reduced ilmenite and pure iron discs, the rates and activation energies observed here were similar. No unusual effects were observed for the porous matrix indicating that the iron dissolution study previously preformed on pure iron discs is directly applicable to the reduced ilmenite system.

The reversible formation of complexes with iron and citrate indicate that this ligand may be useful for controlling the dissolution of iron by acid, however iron analyses of synthetic rutile samples produced in the presence of citrate are required to verify its suitability for the process. This data is presented in the following chapter along with the practical application of the methods discussed so far for the minimisation of acid consumption.
Chapter 9

Production of Synthetic Rutile by Iron(III) Leaching

9.1 Introduction

In the previous three chapters the emphasis has been placed on gaining an understanding of the factors which effect the rate of iron dissolution from reduced ilmenite to produce synthetic rutile. In this chapter microscopic characterisation, and the chemical composition of the synthetic rutile is used to assess the merits of the various iron(III) leaching media used. The significance of conducting a quantitative iron dissolution study is because reduced ilmenite has a complex morphology and any precipitated Fe(OH)₃ inside the grains would inhibit further corrosion and lower the overall quality of the synthetic rutile product.

As discussed in Chapter 1, leaching of reduced ilmenite with iron(III) has been the subject of four patents, which claim that the titaniferous material can be beneficiated to between 90 and 94 percent TiO₂. However, none of the patents or reports discuss acid consumption levels or discuss the problems which prevented these processes becoming commercialised. In this chapter, the conclusions derived from rotating disc studies will be applied to batch leaching of reduced ilmenite to determine whether specifications can be met and assess practical limits for subsequent development.
The results to be presented in this chapter are from a number of batch leaching exercises where the effects of temperature, iron(III) concentration, as well as citrate, $\text{FeCl}_2$ and $\text{AlCl}_3$ addition are compared. Due to the speed of the reactions, only minor kinetic observations were made from these experiments, with the emphasis being placed on the quality of the synthetic rutile product. As most interest centred on the iron(III) leaching, only a mild acid washing was conducted on the final product to remove any precipitated or adsorbed iron and iron oxides, formed during the leaching process. But this was not of sufficient strength to remove the oxide forms left in the ilmenite lattice during the reduction step.

9.2 Experimental

9.2.1 General Procedure

100 g samples of sized (-180 +125) micron reduced ilmenite supplied from the Westralian Sands Limited reduction kiln were leached at a pulp density of 10 percent in a 1 litre round bottom reactor immersed in a thermostatted water bath. The slurry containing the reduced ilmenite and the iron(III) solution was stirred by a four bladed paddle using an overhead stirrer motor.

The pH of the solution was monitored throughout the duration of each experiment. In some runs, a pH controller was programmed to add acid if the pH rose above a set point. Even though most of the iron(III) ions had been reduced within the first 15 minutes, all solutions were stirred at temperature for a total of two hours.
After washing and product recovery, a sample was taken for acid washing. Acid washing involved the stirring of 20g of the product in 250 ml of 2 M HCl for 2 hours at room temperature. This material was then washed with more water and dried at 110°C.

Both the acid washed product and leached products were analysed by XRF for major elements, with the residual metallic iron being determined by titrimetric analysis of dissolved Fe$^{2+}$, using potassium dichromate and diphenylamine sulfonate indicator.

9.2.2 Leaching with FeCl$_3$/Citrate

This leach was performed in 1 litre of 1.2 M iron(III) chloride and 0.6 M sodium citrate at 25°C. Initially the pH was 0.63, but with the addition of 100g of reduced ilmenite this rose quickly to pH 3 within the first minute. A pH controller then held this pH constant throughout the duration of the experiment. Although a significant amount of iron(III) was present after 3 minutes; after ten minutes the reaction was essentially complete. The temperature of the solution peaked at 38°C after 1.5 minutes then fell steadily back to 25°C.

9.2.3 Leaching with FeCl$_3$/FeCl$_2$

This leach was carried out in 1.2 M iron(III) chloride and 1.2 M iron(II) chloride solution at 25°C. In this system the pH rose very slowly from the initial pH 0.6 to 1.7 after 10 minutes. Eventually the pH rose to 3.0 and a few drops of acid were required prior to the controller being switched off. The temperature for this run similarly reached a maximum of 37.2°C.
9.2.4 Oxidative Roast/Reduction Procedure for Ilmenite Samples

A 1 kg sample of ilmenite was heated to 950°C whilst being rotated in a muffle furnace for 2 hours with air passing over the sample at a flow rate of 2 litres min\(^{-1}\). The oxidised material was then mixed with 1 kg of coal char and 400 ml of water (to help coat the ilmenite onto the char) and packed into a metal vessel. The vessel was then placed into a muffle furnace with a thermostat inserted into the ilmenite charge. The charge was heated to 1150°C for 3 hours then allowed to cool slowly in the muffle furnace to avoid any chance of reoxidation. The reduced ilmenite was recovered by screening it through a 500 micron screen, with any reduced ilmenite agglomerates remaining with the char being collected at a later stage with the aid of an electromagnet. A similar procedure was performed on a sample of the same ilmenite, but without the oxidative roast step to act as a control.

9.3 Results and Discussion

9.3.1 Leaching Tests at 25°C and 70°C

In these preliminary tests the product quality was assessed, in both chloride and sulfate media, at room temperature and at 70°C. However, as the reactions are exothermic, higher temperatures were experienced for a limited time during the initial stages of the process.
9.3.1.1 Chemical Analysis

The chemical compositions of the products obtained from the leach runs, conducted at 25°C and 70°C in 1.2 M iron(III) chloride, and for a run at 70°C in 0.6 M iron(III) sulfate, are given in Table 9.1. Results for a 25°C leach in iron(III) sulfate are not shown, as only marginal iron removal occurred. The typical Becher product analysis, also shown in Table 9.1, is the product of similar quality reduced ilmenite after aeration and acid washing in 20 percent H₂SO₄.

Table 9.1

<table>
<thead>
<tr>
<th>Chemical Analysis of Synthetic Rutile Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.2 M Fe³⁺, 10 % w/v pulp density)</td>
</tr>
<tr>
<td>(Temp=) 70°C 25°C 70°C Becher Product</td>
</tr>
<tr>
<td>(Anion=) Cl⁻ Cl⁻ SO₄²⁻</td>
</tr>
<tr>
<td>Analysis % % % %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>70°C</th>
<th>25°C</th>
<th>70°C</th>
<th>Becher Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_t</td>
<td>3.7</td>
<td>7.8</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe_m</td>
<td>1.7</td>
<td>0.4</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>91.2</td>
<td>83.8</td>
<td>92.4</td>
<td>92</td>
</tr>
<tr>
<td>MnO</td>
<td>1.06</td>
<td>1.9</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.1</td>
<td>0.95</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>S</td>
<td>0.72</td>
<td>0.72</td>
<td>0.83</td>
<td>0.9</td>
</tr>
</tbody>
</table>
During these experiments the pH was kept below 1.0 by the addition of acid as required. Both leaches in the chloride media required the addition of greater than 50 ml of 2 M HCl, while the natural buffering of the sulfate system kept the solution at pH 1.0 without acid additions.

Westralian Sands typically produce an acid washed synthetic rutile from their Becher plant containing around 1.0 percent metallic iron and 2.5 percent total iron. The analysis of the three iron(III) leached products shows that the metallic iron contents are < 2 percent, which is commercially acceptable. On this criteria, the synthetic rutile can be considered as saleable. But the material from the chloride containing solutions contained a considerable amount of total iron, as oxides. The higher oxide content of around 7.8 percent from the 25°C leach caused the product to be extremely difficult to filter, leaving a very fine black oxide on the filter pad. The higher total iron analyses for the chloride system reflect more hydrolysis of Fe$^{3+}$ in the grains compared to the sulfate system. The higher activity of the iron(III) and the lack of natural pH buffering in the chloride system, resulted in the hydrolysis reaction being more facile. In other analyses, the MnO was slightly over the specification of 1.0 percent while the sulfur levels are significantly higher than the 0.4 percent specification in all three products.
9.3.1.2 Microscopic Analysis

To investigate the locations of the iron phases associated with the synthetic rutile grains, polished sections were made using the reduced ilmenite and the two synthetic rutile samples produced from the iron(III) chloride solutions. The samples were embedded in an epoxy resin and examined under both the optical and the scanning electron microscopes. Photographs taken through the optical microscope of the reduced ilmenite are presented in Plates 9.1 (a) and (b), whilst the products leached by FeCl₃ at 70 and 25°C are presented in Plates 9.1 (c), (d) and 9.1 (e), (f) respectively.

Plate 9.1(a). Reduced ilmenite viewed through an optical microscope, X100.
Plate 9.1(b). Reduced ilmenite viewed through an optical microscope, X400.

Plates 9.1 (a) and (b) show a number of reduced ilmenite grains, in which the metallic iron shows up quite vividly as the overexposed white areas due to the reflection of the light. Photograph 9.1(b), taken at a higher magnification, shows how the iron forms into nodules at the surface of the TiO$_2$ grains on reduction at 1150°C, as reported by Farrow et al. (1987).
Plate 9.1(c). Synthetic rutile produced from 1.2 M FeCl₃ at 70°C viewed through an optical microscope, X100.

Plate 9.1(d). Synthetic rutile produced from 1.2 M FeCl₃ at 70°C viewed through an optical microscope using polarised light, X400.
Plate 9.1(c) shows the general topography of a number of leached grains, and when compared to Plate 9.1(a) indicates the high degree of metallic iron removal, with only one or two shiny specks discernable in this area. The grains are generally dull white with a large number of voids or craters left after metallic iron removal. Some brighter white areas can be seen in some other photographs, such as in Plate 9.1(d) taken at a higher magnification under polarised light.

Plate 9.1(e). Synthetic rutile sample produced in 1.2 M FeCl₃ at 25°C viewed through an optical microscope, X100.
Plate 9.1(f). Synthetic rutile sample produced in 1.2 M FeCl₃ at 25°C viewed through an optical microscope using polarised light, X400.

Photograph 9.1(e) appears very similar to that in 9.1(c). However, under higher magnification, and with the aid of polarised light, a number of red areas similar to that shown in Plate 9.1(f) were observed. These reddish areas are iron oxides and indicate that some oxide precipitation had occurred within the pores and around the synthetic rutile grains, after the oxidation of the metallic iron had taken place. This photograph illustrates one of the main problems associated with the iron(III) leaching process for reduced ilmenite.

The Scanning Electron Microscope (SEM) micrographs of the same materials (Plates 9.2(a)-(c)) reinforce these optical observations.
Plate 9.2(a). Micrograph of reduced ilmenite, X640 (Grid bar = 10 μm).

Plate 9.2(b). Micrograph of a synthetic rutile grain leached at 70°C, X640 (Grid bar = 10 μm).
Plate 9.2(c). Micrograph of acid washed synthetic rutile leached at 70°C, X320 (Grid bar = 10 μm).

The first micrographs shows the metallic iron particles and indicate that they can exist up to 15 microns thick on the perimeter of the TiO$_2$ grains. Plate 9.2(b) shows a thin bright rim around a synthetic rutile grain. EDAX microanalysis of these rims indicated very high values of iron and manganese, and significant differences to nodules of metallic iron in Plate 9.2(a). The acid washed particles from this particular leach (Plate 9.2(c)) showed little evidence of these rims, and the chemical analysis confirmed that more than half of the original iron and MnO had been removed.†

† Footnote: It should be noted that even though the manganese is reported to be present as an iron-manganese sulfide (Rolfe, 1973), resulting from reaction with FeSO$_4$.7H$_2$O in the reduction kiln, the removal of over 50 percent of the manganese was not accompanied by a significant lowering of the sulfur level.
These preliminary results show that leaching with FeCl₃ at 25°C involves problems associated with the precipitation of iron oxides or hydroxides both on and in the craters of the synthetic rutile left after the removal of the metallic iron, giving a lower quality product. These iron oxides clearly precipitate on the metallic iron, thus passivating the surface and not allowing complete metallic iron reaction. Therefore, leaching at elevated temperatures would seem to be desirable.

9.3.2 Leaching with FeCl₃/ Sodium Citrate and FeCl₃/FeCl₂ Solutions

As discussed in the previous two chapters, citrate and iron(II) additions showed promise in minimising hydrogen evolution and acid consumption. The chemical analyses for the leach products and the acid washed materials, produced in the presence of these compounds, are shown against those obtained with no additions in Table 9.2.
Table 9.2

Chemical Analysis of FeCl$_2$ Leach Products
(1.2 M Fe$^{3+}$, 25°C)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Citrate Leach</th>
<th>Acid$^a$ Washed</th>
<th>Iron(II) Leach</th>
<th>Acid$^a$ Washed</th>
<th>No Addition Leach</th>
<th>Acid$^a$ Washed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Fe$_t$</td>
<td>7.0</td>
<td>2.2</td>
<td>7.0</td>
<td>2.9</td>
<td>7.8</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe$_m$</td>
<td>4.4</td>
<td>0.9</td>
<td>1.8</td>
<td>1.0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>85.7</td>
<td>93.3</td>
<td>85.7</td>
<td>91.9</td>
<td>83.8</td>
<td>88.8</td>
</tr>
<tr>
<td>MnO</td>
<td>1.81</td>
<td>0.91</td>
<td>1.77</td>
<td>0.92</td>
<td>1.9</td>
<td>0.88</td>
</tr>
<tr>
<td>S</td>
<td>0.62</td>
<td>0.20</td>
<td>0.72</td>
<td>0.51</td>
<td>0.72</td>
<td>0.61</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.1</td>
<td>1.03</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
<td>0.94</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$Washed in 2 M HCl.
The results prove to be very similar to each other and to the results obtained from the iron(III) chloride leach (Table 9.1). However, significantly more iron removal was achieved during the acid washing step for the samples leached in the presence of citrate and iron(II) than was the case for the product from leaching in pure 1.2 M FeCl₃. This suggests that iron oxide passivating rims were not present in these two samples to the same extent, and supports the view that both iron(II) and citrate suppresses the precipitation of these films in the reduced ilmenite pores.

Significantly higher levels of metallic iron were left in the sample leached in the presence of citrate at pH 3, because of the formation of iron(III)-citrate complexes. However, this higher metallic iron content did result in a lower sulfur level due to the formation of H₂S during acid washing. High levels of metallic iron removal during the acid washing step is not practical on a plant scale as the large volumes of hydrogen evolved from the reaction can cause explosions. Thus, it is recommended that future leaching in the presence of citrate is carried out at slightly lower pH values, around pH 2. This would allow more metallic iron to be removed with the complexing power of the citrate only being invoked if localised pH rises were encountered within the reduced ilmenite matrix. This should also lower the amount of metallic iron required to be removed during the acid leaching.

Despite the successful use of citrate addition the, addition of FeCl₂ is preferable as it is both the product from iron(III) reduction and metallic iron oxidation, and gives a product of comparable quality. As both the acid washed products are basically saleable quality synthetic
rutiles after leaching at 25°C, it is expected that further improvement would be observed by leaching at 70°C and with slightly higher concentrations of iron(III) in the final solution.

9.3.3 Leach Tests with Excess FeCl₃ at 70°C

The two leaches in this set were conducted at 70°C in the presence of 1.2 M FeCl₂ with iron(III) concentrations of 1.2 and 1.32 M (10 and 20 percent excess of iron(III) ions respectively). In each case the pH remained constant below 1 for the 2 hour duration of the leach, whilst the temperature rose to 90°C within the first minute before returning to 70°C within 20 minutes. The chemical analysis of the two leach products and their respective acid washed samples (Table 9.3), show that these products are again very close to the specifications required for a saleable synthetic rutile.

The main impurity of concern is sulfur. Even though some of the manganese has been removed little if any of the sulfur has been leached during the process. Carbon disulfide extractions conducted on synthetic rutile samples produced in iron(III) solutions, have shown significant levels of elemental sulfur. It is believed that the excess iron(III) in the final leach liquor oxidises residual MnS and FeS in the lattice to leave elemental sulfur, which is unattacked by acid. As shown earlier, sulfur can be brought down to acceptable levels during acid washing if sufficient metallic iron is left and also removed in this stage.
Table 9.3

**Effect of Excess Iron(III) Levels on Synthetic Rutile Products**

(70°C and 1.2 M Fe²⁺)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>10% Excess Iron(III)</th>
<th>20% Excess Iron(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Leach</td>
<td>Acid²</td>
</tr>
<tr>
<td></td>
<td>Washed</td>
<td>Washed</td>
</tr>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe_t</th>
<th>Fe_m</th>
<th>TiO₂</th>
<th>MnO</th>
<th>S</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.3</td>
<td>0.9</td>
<td>93.2</td>
<td>0.96</td>
<td>0.86</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>10%</td>
<td>2.3</td>
<td>0.9</td>
<td>93.5</td>
<td>0.96</td>
<td>0.80</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Excess</td>
<td>3.0</td>
<td>1.0</td>
<td>92.5</td>
<td>0.95</td>
<td>0.86</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Iron(III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>2.3</td>
<td>0.8</td>
<td>93.2</td>
<td>0.93</td>
<td>0.84</td>
<td>1.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*Washed in 2 M HCl.
The results in Table 9.3 reveal that there is no advantage in terms of the product quality in increasing the iron(III) concentration, and that there is only a marginal improvement by raising the temperature. The process, therefore, requires the addition of different reagents or modified solution conditions to lower the residual metallic iron level.

9.3.4 Production of Higher Quality Synthetic Rutile

As Al\(^{3+}\) has been shown to be the most effective cation for controlling hydrogen evolution (Chapter 8), a leach was conducted with 1.2 M FeCl\(_3\) at 70\(^\circ\)C in the presence of 0.3 M Al\(^{3+}\), to see if a higher quality synthetic rutile could be produced. Table 9.4 shows the chemical analysis results for the leached material and the acid washed material. Also included are the analyses for the synthetic rutile produced without Al\(^{3+}\) (Table 9.3) and a typical Becher product (Table 9.1).
Table 9.4

Production of Synthetic Rutile in the Presence of Al$^{3+}$

(70°C, 1.2 M FeCl$_3$, 0.3 M AlCl$_3$)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Leach</th>
<th>Acid$^a$</th>
<th>Synthetic$^a$</th>
<th>Becher Aeration$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Washed</td>
<td>Rutile</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(No Al$^{3+}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Fe$_t$</td>
<td>2.9</td>
<td>2.3</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe$_m$</td>
<td>0.2</td>
<td>0.2</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>91.8</td>
<td>92.6</td>
<td>93.5</td>
<td>92</td>
</tr>
<tr>
<td>MnO</td>
<td>0.96</td>
<td>0.91</td>
<td>0.96</td>
<td>0.9</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.75</td>
<td>0.76</td>
<td>0.86</td>
<td>1.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.44</td>
<td>1.44</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>S</td>
<td>0.39</td>
<td>0.34</td>
<td>0.34</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^a$Washed in 2 M HCl. $^b$Leaching conditions do not apply to this analysis
The synthetic rutile produced in the presence of Al\(^{3+}\) is of very high quality with greater than 99 percent of the available iron being removed in the leaching step, compared with the Becher process where 5 percent total iron level is typical prior to the acid washing step.

Table 9.4 shows that in the presence of Al\(^{3+}\) ions, the metallic iron level of 0.2 is significantly lower than the 0.8-0.9 percent obtained from similar solutions. This indicates that passivating films did not occur on the iron, enabling efficient metallic iron removal. Even though lower pH levels occurred with Al\(^{3+}\) present, which would inhibit hydrolysis, it is more likely that Al\(^{3+}\) blocked the attack by protons. As discussed in Chapter 7, this would lessen the chances of pH rises at the iron surface which cause hydrolysis of the leachant and passivation of the corroding iron.

The lower sulfur level, shown in Table 9.4, can also be attributed to the suppression of the hydrogen evolution reaction. Hydrogen evolution in the pores leads to H\(_2\)S evolution at localised MnS/FeS sites which precipitates as S\(^0\) as it contacts iron(III). With the suppression of hydrogen evolution, there is less chance of forming S\(^0\). Thus, after the metallic iron has been removed, with the subsequent reduction of the iron(III), the MnS/FeS compound will be dissolved in the acidic solution with little chance of the sulfides being oxidised.

The results indicate that the iron removal has been extremely efficient. If a higher grade is to be obtained the degree of metallisation in the reduction kiln must be improved (presently 95.7 percent metallisation) to increase the percentage of the iron available for iron(III) attack.
Even though this process produces a high grade synthetic rutile, the addition of $\text{Al}^{3+}$ to the process would require an extra unit operation if it were to be incorporated into the cyclic process proposed.

9.3.5 Manganese Impurity Removal

It is possible that sulfur, added as copperas $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the Becher Process to help lower the manganese levels, is not a desirable addition in iron(III) leaching processes due to the formation of acid insoluble $\text{S}^0$. One possible alternative to the addition of copperas is the use of an oxidative roast prior to the reduction roast. This step is present in a number of ilmenite upgrading techniques and is reported to cause defects in the ilmenite lattice, thus allowing better impurity removal (Rolfe, 1973).

To investigate if the manganese content could be lowered without the addition of sulfur containing compounds, an oxidative roast prior to the reduction of an ilmenite sample was conducted using the procedure outlined in Section 9.2.3. The two reduced ilmenite samples produced were subsequently leached at 70$^\circ$C in a 1 litre reactor in 1.2 M $\text{FeCl}_3$, 1.2 M $\text{FeCl}_2$ solutions. Chemical analysis results for the products are tabulated in Table 9.5.
Table 9.5
Effect of a Prior Oxidative Roast on Manganese Impurity Levels
(1.2 M FeCl₃, 1.2 M FeCl₂, 70°C)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Reduction Onlyᵃ</th>
<th>Preoxidation/Reductionᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reduced Ilmenite</td>
<td>Syn.Rutile</td>
</tr>
<tr>
<td>TiO₂</td>
<td>59.7</td>
<td>82.0</td>
</tr>
<tr>
<td>Fe₄₇</td>
<td>35.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe₈₇</td>
<td>34.8</td>
<td>2.4</td>
</tr>
<tr>
<td>MnO</td>
<td>1.84</td>
<td>2.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.6</td>
<td>2.2</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

ᵃ Reduction at 1150°C with coal char.
ᵇ Preoxidation at 950°C with air.
From the analyses shown in Table 9.5 it can be seen that in the absence of copperas, much lower sulfur levels were obtained but the preoxidation had a very minor effect on the manganese levels. The 2.2 percent MnO remaining is well over the specification required for synthetic rutile. It was concluded that the addition of a sulfur containing compound is necessary for the removal of manganese and that the iron(III) leached product may well require further treatment to reduce the residual sulfur level. A treatment such as calcination at 200°C to burn off elemental sulfur may be required, if the material was not produced in the presence of Al³⁺ or similar cations, as discussed in Section 9.3.4.

9.4 Conclusions

The chemical analysis results of the synthetic rutile samples produced by leaching with iron(III) solutions confirmed that the product quality could be affected by the precipitation of iron oxides in the pores and on the surface of synthetic rutile particles. Preliminary leaching results showed that these problems were more evident at room temperature and that leaching should preferably be performed at higher temperatures around 70°C. The cause of this phenomenon is believed to be the slower diffusion of the ions at the lower temperatures and the pH gradients formed in the pores due to some acid consumption.

The synthetic rutile produced in the presence of citrate and in the presence of FeCl₂ showed less residual iron. However, a higher metallic iron level was obtained from the iron(III)-citrate leach at pH 3 due to the decrease in iron(III) activity resulting from complexation. If citrate were to be used in this process a lower pH is
recommended. The results in this chapter confirm the hypotheses put forward in the previous chapters that $\text{Al}^{3+}$ and $\text{Fe}^{2+}$ would have a beneficial effect on the product quality.

It can be concluded that iron(III) leaching is a very efficient method for producing high quality synthetic rutile. This process is amenable to a continuous leaching operation as leaching at a 10 percent pulp density was found to be essentially complete within 15 minutes. With the efficient removal of iron metal by leaching, any further increase in product quality would require the degree of metallisation in the reduction kiln to be improved to increase the percentage of iron available for iron(III) attack.

To efficiently utilise the iron values in a cyclic process using iron(III) as a lechant, iron(III) regeneration and iron by-product recovery unit operations are also required. These steps in the modified Summit Process are addressed in the following two chapters.
Chapter 10

Investigation of the Catalytic Oxidation of Iron(II) by Oxygen

10.1 Introduction

In Chapter 9 it was shown that iron(III) chloride efficiently dissolves metallic iron from a reduced ilmenite matrix, leaving an iron(II) solution. Thus, it is necessary to choose the most suitable method to re-oxidise iron(II) and recycle iron(III), as well as remove the excess dissolved iron, in order to completely evaluate the potential of the Summit Process.

Several methods exist for the oxidation of iron(II) to iron(III) (Dutrizac and MacDonald, 1974; Sato et al., 1984). These include

(i) electrolytic oxidation,

(ii) use of chlorine gas,

(iii) use of sulfur dioxide and oxygen mixtures,

(iv) use of strong oxidising agents,

(v) use of oxygen under pressure,

(vi) use of thiobacillus ferrooxidans bacteria in the presence of oxygen, and

(vii) use of oxygen at ambient pressure with a catalyst.

Electrolytic regeneration has previously been used in ilmenite beneficitation processes (George et al., 1958; Shiah, 1966b) producing an electrolytically deposited iron by-product. However, the production of metallic iron requires high overpotentials and a diaphragm cell. The generation of hydrogen and the high Tafel parameters involved in
the reduction of iron(II) result in this regeneration process being relatively expensive.

While chlorine efficiently oxidises iron(II) to iron(III), the production of pigments from waste FeCl₂ would be required to maintain an iron balance. Furthermore, the process requires a chloralkali cell to produce chlorine, or chlorine would need to be purchased and this would significantly increase the cost of running such a process.

Sulfur dioxide/oxygen mixtures rapidly oxidise 0.02 M iron(II) at 50°C with 99 percent conversion to the sulfate anion (Sato et al., 1984). This process is therefore more applicable to sulfate systems using waste gases from base metal sulfide smelting. Thus, this method of oxidation can be neglected.

The use of strong oxidising agents such as chlorates, manganese dioxide or permanganate to oxidise iron(II) is also clearly limited by the high cost of such reagents. Although high temperature and pressure oxyhydrolysis of iron(II) is accepted practice in some industries, it is again limited by the high capital cost of the autoclaves required to oxidise iron(II) (Dutrizac and MacDonald, 1974).

Therefore, the processes most attractive for an ilmenite beneficiation plant seem to be either the use of bacterial oxidation or catalysed oxidation using air or oxygen under ambient pressure. Bacterial strains can function in chloride media (Mayling, 1974), and indeed bacteria of the type Thiobacillus ferrooxidans, cause oxidation of iron(II) to proceed orders of magnitude faster than for the same solution without bacteria. However, the reaction is still relatively
slow and further inhibition occurs at relatively low iron(III) concentrations, around 5 g l\(^{-1}\) (Kelly et al., 1977). This would use very large ponds or reactors, and would produce iron(III) at much lower concentrations than required in this work.

Therefore, to have an economically viable ilmenite beneficiation process, attention was focussed on studying the regeneration of iron(III) using oxygen at atmospheric pressure with catalysts.

10.2 Oxidation of Iron(II) with Oxygen at Ambient Pressures

Even though the oxidation of iron(II) with O\(_2\) is thermodynamically favourable, in practice the oxidation rate is slow in acidic solutions with a rate constant of 1.7 \times 10^{-5} \text{ mol l}^{-1} \text{ min}^{-1} at pH 2 and 25\(^\circ\)C (Muir et al., 1983). A description of the rate equations has been reported by a number of authors (Mathews and Robins, 1972; Colborn and Nicol, 1973; Lowson, 1982; Dreisinger and Peters, 1989). For sulfate media it has generally been found that the reaction is second order in [Fe\(^{2+}\)], first order in p(O\(_2\)) or [O\(_2\)], and an inverse fractional order in [H\(^+\)] (Pound, 1939; Mathews and Robins, 1972; Keenan, 1969; Verbaan and Crundwell, 1986). While, for the chloride system, the rate equations are consistently reported as being first order in both [Fe\(^{2+}\)] and p(O\(_2\)) (Posner, 1953), with first order dependencies on both the activity of the proton and the chloride ion sometimes included (Iwai et al., 1979; Awakura et al., 1986). Other workers have reported that, like the sulfate system, iron(II) chloride oxidation is second order with respect to iron(II) concentration (Colborn and Nicol, 1973;
Yano et al., 1974). However the apparent second order dependence on \([\text{Fe}^{2+}]\) at high iron concentrations and moderate acid levels is attributed to the change in activity of the hydrochloric acid (Iwai and Majima, 1979).

Activation energies reported by a number of workers in the different media generally lie between 50 and 90 kJ mol\(^{-1}\) (Dressinger and Peters, 1989). This indicates that the iron(II) oxidation reaction is chemically controlled and that an increase in temperature or use of catalysts would significantly promote the reaction rate.

Catalysis has been achieved by the surface catalysts palladium, platinum, gold and coconut charcoal, and the solution catalyst copper(II) (Mellor, 1935). However, to overcome the inherently slow nature of the iron(II) to iron(III) oxidation using oxygen on a commercial scale, a relatively cheap reusable catalyst, such as copper(II) or activated carbon, would be required.

The catalytic properties of copper(II) for the iron(II) oxidation in acidic solutions has been reported widely (George, 1954; Cher and Davidson, 1955; Huffman and Davidson, 1956; McKay and Halpern, 1958; Thomas and Ingraham, 1965; Mathews and Robins, 1972; Colborn and Nicol, 1973; Swamvinathan et al., 1981; Muir et al., 1983; Awakura et al., 1986; Dreisinger and Peters, 1989). The catalytic mechanism is usually considered to be the redox reaction between iron(II) and copper(II):
\[
\text{Cu}^{2+} + \text{Fe}^{2+} \rightarrow \text{Cu}^{+} + \text{Fe}^{3+} \tag{10.1}
\]

followed by the rapid oxidation of copper(I) by \(O_2\).

\[
\text{Cu}^{+} + \frac{1}{2}O_2 + H^+ \rightarrow \text{Cu}^{2+} + \frac{1}{2}H_2O \tag{10.2}
\]

Unfortunately, the degree of catalysis reported varies widely. George (1954) reported a 2.5 fold increase in rate between pH 0 and 2, using up to 0.2M \(\text{Cu}^{2+}\) in perchlorate media; with a similar catalysis reported by Mathews and Robins (1972) in sulfate media. But this is slower than the 14 fold increase reported by Thomas and Ingraham (1965). McKay and Halpern (1958) showed the initial rate to be proportional to the square root of the copper concentration, and this was recently confirmed by Dreisinger and Peters (1989), who determined the following empirical function (equation 10.3).

\[
k_t(Cu) = k_t^o(1.0 + 5[\text{CuSO}_4])^{0.5} \tag{10.3}
\]

where \(k_t^o\) is the rate without copper.

Muir et al. (1983) showed that the presence of \(Cl^-\) and acetonitrile complexed copper(I) and further enhanced the rate of iron(II) oxidation by displacing reaction 10.1 to the right. However the rate of iron(III) production was inhibited as the iron(III) concentration increased.

The catalytic oxidation of iron(II) by molecular oxygen in the presence of powdered gas mask charcoal, was first studied by Lamb and Elder (1931), who found that the rate of oxidation was about 200 times
faster in the presence of charcoal. They reported that the accelerating effect was proportional to the amount of carbon added (≤20 g l⁻¹). First order relationships with oxygen and carbon were also quoted by Thomas and Ingraham (1965) and Posner (1953). Saito (1976) reported the rate to be unimolecular with respect to carbon addition within the range 2 to 20 g l⁻¹, but found that the rate varied considerably with the type of activated carbon used.

Both, Thomas and Ingraham (1965) and Puri and Kalra (1972), showed that in the presence of activated carbon the oxidation reaction had a much lower activation energy, around 25 kJ mol⁻¹, indicating that the reaction rate was much less sensitive to temperature changes. Above 60°C, no detectable increase in rate was observed (Thomas and Ingraham, 1965), presumably because the increase in rate constant was offset by a decrease in the solubility of dissolved oxygen.

Various mechanisms for the catalysis by carbon have been put forward. Lamb and Elder (1931) attributed the catalytic oxidation by carbon to surface peroxide groups, whilst Garten and Weiss (1957) proposed a more detailed mechanism based on the chromene-carbonium ion couple. Posner (1953) suggested that the oxidation involved adsorption of iron(II) and H⁺ ions onto the carbon surface and subsequent oxidation of the complex with oxygen to iron(III) ions, which desorbed immediately. This is similar to the view of Thomas and Ingraham (1965) that the catalytic activity was simply related to the surface area of the carbon. However, Puri and Kalra (1972) found that the catalytic activity was related to the nature, and not the area, of the surface. They found the catalytic performance increased with surface "unsaturation" resulting from degassing the carbon at increasing
temperatures. Maximum activity was found for carbons degassed at 1000°C which were essentially free of oxygen. Therefore, the activity could not be attributed to peroxide or chromene groups. They proposed that the function of the catalyst was to provide sites where oxygen could be dissociatively chemisorbed, and then react with iron(II) and a proton to yield iron(III), as in reaction 10.4.

\[ 2\text{Fe}^{2+} + (\text{O}) + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \quad \text{10.4} \]

They proposed that it was likely that the dissociative chemisorption of oxygen at the "unsaturated" sites occurred first, and that this was primarily responsible for the lowering of the activation energy.

Thus an investigation of the literature to study the applicability of these catalysts to ilmenite beneficiation, has found that activated carbon is especially attractive as it has been reported that there is little loss in efficiency in subsequent use. Furthermore carbon can be recovered from pulps or slurries by flotation or mechanical means (Dutrizac and MacDonald, 1974), and is widely used in the gold industry where it is regularly recycled and reactivated. Activated carbon has also been used for the catalysis of cyanide oxidation. The rate is dependent on the surface area and surface activity of the carbon and is further enhanced by the presence of Cu\(^{2+}\) in solution (Hoecker and Muir, 1987).

The elucidation of the mechanism and the catalytic properties of activated carbon for the oxidation of iron(II), is therefore worthy of further study for possible application to the Summit Process. This chapter therefore reports on the catalytic effects of activated carbon
on the rate of iron(II) oxidation with air and oxygen, using carbons employed in the local gold industry. The catalysis of iron(II) oxidation by activated carbon and Cu$^{2+}$ is compared, while the role of Cu$^{2+}$ in further activating the carbon surface for iron(II) oxidation is discussed. This surface activation was further studied using two model systems, namely the adsorption of Au(CN)$_2^-$ and the oxidation of cyanide with oxygen, to give a further insight into the mechanism of this activation.

10.3 Experimental

10.3.1 Oxidation of Iron(II) to Iron(III)

The reactor used was an air lift percolator, similar to that used by Mathews and Robins (1972). The percolator had a capacity of 1 litre with the air or oxygen being supplied through a glass tube connected to the base, and sparged through a 5 cm diameter glass frit. The flow rate was controlled by a needle valve and monitored by a rotameter. The gas flow was used as both the oxidant and to suspend and circulate the activated carbon in the solution.

The temperature was maintained at the set level by immersion of the whole percolator system in a deep plastic drum fitted with a temperature controller ($\pm 0.2^\circ$C). A condenser was fitted to the top to minimise water losses through evaporation. The pH of the solution was maintained at 1.0 $\pm 0.1$ using the pH control equipment described in Chapter 11.
Samples of the solution were withdrawn at set intervals, filtered under vacuum, and analysed for iron(III) content using freshly standardised 0.01 M EDTA solutions with Variamine Blue indicator. On completion of each experiment, the activated carbon was collected under vacuum and dried at 60°C. The same system was used for the comparative study of CN⁻ oxidation and gold adsorption kinetics.

10.3.2 Activated Carbon

The activated carbon used in all the experiments was the coconut Pica G210AS carbon. This material was used either "as received" or ground in a ring mill and screened to collect a -180 +106 micron fraction. As it is well known that oxidation rates are dependent on the amount and external surface area of carbon used, a constant amount (100 g l⁻¹) of screened carbon was used for this study. The activated carbon was soaked in 1 M HCl and was washed with water prior to use in all experiments.

10.3.3 Destruction of Cyanide with Carbon

Oxidation of 225 mg l⁻¹ CN⁻ solutions were performed in the reactor using an oxygen flow rate of 300 ml min⁻¹ at pH 10.5, 25°C in the presence of 5 g l⁻¹ carbon (-180 +106 micron).

Samples (10 ml) were withdrawn over the 24 hour duration of the experiment and analysed for CN⁻ using 0.0096 M AgNO₃ with Rhodamine as the indicator.
10.3.4 Gold Adsorption Kinetics

Gold(I) cyanide solutions containing 100 mg l\(^{-1}\) Au as KAu(CN)\(_2\) in 2.5 g l\(^{-1}\) NaCN at pH 10.5, were agitated using an oxygen flow rate of 1 litre min\(^{-1}\) in the presence of 1 g samples of ground carbon (-180 +106 micron).

Gold(I) cyanide solutions were extracted with DIBK containing 1 percent of Aliquat 336 and analysed for gold using atomic absorption spectrophotometry at a wavelength of 242.8 nm.

10.3.5 Copper and Iron Analysis of Used Carbon Samples

Accurately weighed samples of used and unused carbon samples were placed in preweighed crucibles in a muffle furnace at 650°C overnight, and digested using a minimum volume of aqua regia. The solutions were then analysed for copper and iron content using atomic absorption spectrophotometry.

10.4 Results and Discussion

10.4.1 Copper(II) Catalysis

For comparison, Figure 10.1 shows the rate of iron(III) production at 70°C for the oxidation of 0.2 M FeCl\(_2\) solutions at pH 1.0 with air, oxygen, and with oxygen in the presence of 0.01 M CuCl\(_2\). After 48 hours, 9.8 percent of the iron(II) was oxidised by air, while 29.7 percent was oxidised by oxygen and 50.0 percent when 0.01 M copper(II) was also present.
Figure 10.1. Rate of iron(III) production with (●) air, (▲) oxygen and (■) oxygen in the presence of 0.01 M CuCl₂ (pH 1.0, 0.2 M FeCl₂, 70°C, Gas flow rate 1 lmin⁻¹).
For the two uncatalysed solutions, a linear relationship was observed between iron(III) concentration and time for the 48 hour duration of the experiments. However, as can be seen in Figure 10.1, for the solution containing the 0.01 M CuCl₂, two linear regions could be distinguished, between 0 - 4 hours and 5 - 48 hours. The rates calculated for these regions and for the two uncatalysed experiments are shown in Table 10.1

Table 10.1

Iron(II) Chloride Oxidation Rates

(70°C, pH 1.0, 0.2 M FeCl₂, Gas Flow Rate 1 litre min⁻¹)

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Cu(II)</th>
<th>Time Period</th>
<th>Rate k x 10⁵ mol ⁻¹ l⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>0</td>
<td>0 - 48</td>
<td>0.71</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0</td>
<td>0 - 48</td>
<td>2.14</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.01</td>
<td>0 - 4</td>
<td>7.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 - 48</td>
<td>3.19</td>
</tr>
</tbody>
</table>

The data in Table 10.1 shows that a threefold increase in rate was achieved by using oxygen rather than air, even though oxygen contains five times more O₂ than air.
Mathews and Robins (1972) only studied the first 3 hours of the oxidation reaction and found that a 2.8 fold increase could be obtained by the addition of 0.01 M copper(II). With this work, a similar increase was achieved in the first four hours of the experiment, but over the remaining 43 hours, only a 1.5 fold increase in rate was observed.

The change in rate is attributed to all the initial copper(II) oxidant being used by the fourth hour, and thus further oxidation of the iron(II) would rely on the reoxidation of the copper(I). Even though this reaction is approximately 1000 times faster than the iron(II) oxidation reaction (Muir et al., 1983), it is diffusion controlled and dependent on the dissolved oxygen and copper concentration (Tran and Swinkels, 1986). However, as the concentration of iron(III) increases as a result of oxidation, equilibrium reaction 10.1 is driven to the left, thus decreasing the concentration of copper(I) and the rate of further oxidation of iron(II). Thus, for complete oxidation of iron(II), it is necessary to remove the iron(III). As a result, this type of catalysis is not efficient for producing high concentrations of iron(III).

10.4.2 Activated Carbon Catalysis

Figure 10.2 shows the rate of oxidation of iron(II) to iron(III) catalysed by 100 gl⁻¹ carbon with and without the addition of 0.01 M CuCl₂. These two experiments resulted in 49.7 percent and 62.6 percent oxidation of the iron(II) chloride after 48 hours at 70°C respectively, as against 29.7 and 50.0 percent oxidation observed in the similar solutions, without the addition of carbon. A comparison of
the data in Figures 10.1 and 10.2 show that besides more iron(II) being oxidised, a 3.5 fold increase in rate was observed in the first 10 hours as against 1.5 times overall.

For the period between the 10th and the 48th hour the carbon catalysed oxidation of iron(II) at pH 1.0 was slightly slower ($k = 2.39 \times 10^{-5}$ mol l$^{-1}$ min$^{-1}$) than when 0.01 M Cu$^{2+}$ was also present ($k = 3.18$ mol l$^{-1}$ min$^{-1}$). This rate data is in remarkably good agreement with the initial rates shown in Table 10.1 and shows that even though considerable catalysis is observed with carbon in the first 10 hours, after this period, the carbon loses its catalytic activity and plays no further part in the oxidation reaction.

These encouraging results, with activated carbon, warranted further investigation to try to improve the conditions for oxidation and to minimise the loss of carbon activity. Subsequent experiments, therefore, focussed on monitoring the relative rates of iron(II) oxidation over the first 10 hours in order to estimate differences in carbon activity.
Figure 10.2. Rate of oxidation of iron(II) to iron(III) catalysed by activated carbon, (▲) no CuCl₂, (●) 0.01 M CuCl₂. (pH 1.0, 0.2 M FeCl₂, 70°C, 100 g l⁻¹ carbon, O₂ flow rate 1 l min⁻¹).

10.4.3 Effect of Temperature

The effect of temperature on the oxidation of iron(II) was observed in the presence of 0.01 M CuCl₂ and 100 gl⁻¹ of ground activated carbon at 35, 70 and 90°C. The amount of iron(II) oxidised during the first 10 hours of these experiments was 21.0, 27.0 and 17.1 percent respectively. Thomas and Ingraham (1965) indicated that no detectable increase in oxidation rate occurred above 60°C, therefore the decrease in oxidation of iron(II) observed at 90°C is consistent with their results and indicates that the rate is dependent on the concentration of dissolved oxygen. The solubility of oxygen decreases considerably above 70°C (Speller, 1951). At 70°C the oxygen concentration is approximately 3.8 mg⁻¹ while at 90°C it falls to ≈1.7 mg⁻¹.

10.4.4 Loss of Carbon Activity and Role of Cu²⁺

For a process to successfully use an activated carbon, the carbon should not degrade, but it is clear from this work that this is not the case. Thomas and Ingraham (1965) also noted that the catalytic activity of carbon declined on subsequent usage before reaching a steady value, whilst Puri and Kalra (1972) found that the activity continuously declined.
The cause of the decline in catalytic activity is not clear. It would seem that continuous use of carbon modifies the surface properties or changes the functional groups, in some way and that Cu$^{2+}$ plays a role in enhancing the activity of fresh carbon only. Carbon itself adsorbs a wide variety of molecules and is readily fouled by a number of inorganic and especially organic reagents (LaBrooy et al., 1986). In this work, fouling could occur from the deposition of basic iron or copper oxides on the surface, or from trace organics in the air or water, or from reaction of chemisorbed oxygen on the surface. Tests were therefore carried out on a variety of carbons which had been previously used or acid washed or pre-oxygenated, in order to compare their relative activities. Results were also compared in the presence of Cu$^{2+}$ in solution.
Table 10.2

**Oxidation of Iron(II) in the Presence of Activated Carbon**

(100 g l⁻¹ carbon, 70° C, 0.2 M FeCl₂, O₂ Flow Rate 1 l min⁻¹, pH 1.0)

<table>
<thead>
<tr>
<th>Carbon History</th>
<th>Percent Iron(II) Oxidised over 10 hours (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>21.7</td>
</tr>
<tr>
<td>Used</td>
<td>17.7</td>
</tr>
<tr>
<td>Fresh + 0.01M Cu²⁺</td>
<td>27.0</td>
</tr>
<tr>
<td>Fresh + 0.02M Cu²⁺</td>
<td>26.4</td>
</tr>
<tr>
<td>Used⁺ + 0.01M Cu²⁺</td>
<td>37.6</td>
</tr>
<tr>
<td>Used⁺(acid washed) + 0.01M Cu²⁺</td>
<td>33.4</td>
</tr>
<tr>
<td>Preoxygenated (16 hrs) + 0.01M Cu²⁺</td>
<td>21.2</td>
</tr>
</tbody>
</table>

*Used in previous oxidation experiments with iron(II).*
The results in Table 10.2 indicate that in the absence of copper(II), the catalytic activity of the carbon is lower on subsequent use. In the presence of fresh carbon, 21.7 percent of the iron(II) was oxidised in 10 hours, while when the same carbon was used again only 17.1 percent oxidation occurred.

However, the carbon which had been previously used in the presence of Cu$^{2+}$, then dried prior to use, showed enhanced activity with 37 percent iron(II) oxidised. Acid washing of the carbon to remove any excess copper or iron before drying gave only a slightly less reactive carbon. This enhanced activity could not be attributed to adsorbed oxygen, as a sample of carbon preoxygenated for 16 hours prior to the addition to the iron(II) chloride solution, resulted in a lower activity than would normally be achieved for the fresh carbon. It is concluded that Cu$^{2+}$ reacts with the carbon surface functional groups upon heating and drying, to produce a surface more conducive for iron(II) oxidation. Thus, pretreatment of the carbon with copper(II) salts is likely to enhance the carbon activity even further.

10.4.5 Pretreatment of Carbon with CuCl$_2$

In an attempt to activate carbon further, carbon samples were soaked in 0.5 M CuCl$_2$ for 5 hours, filtered, dried at various temperatures, acid washed, then used to catalyse the iron(II) oxidation reaction. Most carbon samples were dried for 16 hours, however, at 150°C the presence of copper promoted the ignition of the carbon during this length of time. Thermogravimetric analysis later showed that copper lowered the ignition temperature of the carbon by ~100°C, and that calcium, iron or zinc did not have the same effect. This supports the
Figure 10.3. Rate of iron(II) oxidation in the presence of (●) fresh activated carbon, (▲) presoaked carbon but not dried, (■) presoaked carbon and dried at 110°C. (pH 1.0, 0.01 M CuCl₂, 0.2 M FeCl₂, 70°C, 100 g l⁻¹ carbon, O₂ flow rate 1 l min⁻¹).
view that copper promotes the oxidation by oxygen of some of the functional groups on carbon by oxygen in the drying oven.

Figure 10.3 shows the rate of iron(II) oxidation in the presence of a fresh carbon, a presoaked carbon dried at 110°C, and that for the presoaked carbon not dried prior to use. The figure clearly shows that a great difference in the rate of iron(II) oxidation occurs within the first hour but that, after the second hour, the rate of increase in iron(III) is essentially the same for each experiment. The total amount oxidised in each case is shown in Table 10.3, along with the results for fresh and used carbon quoted earlier.

**Table 10.3**

<table>
<thead>
<tr>
<th>Carbon History</th>
<th>Oxidised (over 10 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>27.0</td>
</tr>
<tr>
<td>Used, in 0.01M Cu$^{2+}$, dried at 60°C</td>
<td>33.4</td>
</tr>
<tr>
<td>Presoak$^a$, no drying</td>
<td>24.4</td>
</tr>
<tr>
<td>Presoak$^a$, dried at 60°C</td>
<td>32.3</td>
</tr>
<tr>
<td>Presoak$^a$, Dried at 110°C</td>
<td>35.8</td>
</tr>
<tr>
<td>Presoak$^a$, Dried at 150°C (2 hrs)</td>
<td>36.1</td>
</tr>
</tbody>
</table>

$^a$Presoaked in 0.5 M CuCl$_2$. 
The results in Table 10.3 concur with the view that whilst the concentration of CuCl₂ used is not significant, traces of copper create active peroxides or free radicals on dry carbon which subsequently decompose in aqueous solution.

10.4.6 Effect of Iron(III) on Carbon Activity

As most of the iron(II) oxidation occurred within the first two hours and resulted in the degradation of the carbon activity, a stepwise oxidation of 0.2 M FeCl₂ was conducted. The aim was to totally oxidise the iron by three successive additions of CuCl₂ presoaked carbon, with removal of the used carbon by filtration prior to the addition of the new carbon. However the formation of iron(III) appeared to be one of the factors causing the degradation of carbon activity.

Figure 10.4 shows the iron(III) concentration with successive carbon additions, and clearly indicates that the addition of the new carbon results in the reduction of some of the previously oxidised iron. After reduction, the oxidation of iron(II) continued, but with a carbon catalytic activity much lower than that observed for the addition of the carbon to an iron(III) free solution.

This effect was further investigated using a 0.12 M FeCl₃ solution which was oxygenated at pH 0.5. The addition of the carbon resulted in the concentration initially dropping by ~3.5 g/l within the first 30 minutes, before increasing and giving a linear iron(III) rise in the period between 1.5 and 10 hours.
Figure 10.4. Iron(III) concentration with successive carbon additions to an iron(II) chloride solution. (pH 1.0, 0.01 M CuCl$_2$, 0.2 M FeCl$_2$, 70°C, $O_2$ flow rate 1 l min$^{-1}$, 3 x 100 gl$^{-1}$ carbon).
The reducing ability of activated carbon for iron(III) has been investigated by a number of workers (Vasatko, 1928; Heymann et al., 1930; Puri and Mahajan, 1962). Results reported by Puri and Mahajan (1962) indicate that the reaction ultimately reached a limiting value. They suggested that the carbon was participating in the reaction and that its surface was being modified during the course of the reaction, making it ineffective for further reaction. These results are in agreement with the results observed in their study.

10.4.7 Effect of Cu$^{2+}$ on other Carbon Properties

To further investigate the mechanism of the observed catalysis, two other model systems were studied which involve carbon, namely the adsorption of Au(CN)$_2^-$ and the oxidation of cyanide with oxygen. These two different systems were used to compare the effects of a Cu$^{2+}$-presoaked and an untreated carbon which had similar B.E.T. surface areas of 445 and 460 m$^2$ g$^{-1}$. The cyanide oxidation reaction involves surface groups, where both CN$^-$ and oxygen are adsorbed (Hoecker, 1987). The amount of Au(CN)$_2^-$ adsorption on the other hand is related to the surface area and pore structure of the carbon and may not involve oxygen or surface functional groups to the same extent (Klauber, 1988).
Figure 10.5. \( \text{Au(CN)}_2 \) - equilibrium loadings on carbon samples.

(■) \( \text{CuCl}_2 \) presoaked carbon, (○) fresh carbon. (100 mg l\(^{-1}\) Au, 2.5 g l\(^{-1}\) NaCN, pH 10.5, 1 g l\(^{-1}\) carbon, \( \text{O}_2 \) flow rate 1 l min\(^{-1}\), 25°C).
Figure 10.5 shows that the CuCl₂ treated carbon gave a slightly lower equilibrium Au(CN)₂⁻ loading than did the untreated carbon which suggests that basic copper salts like malachite on the carbon (0.96 percent Cu) were blocking the pores. On the other hand, CuCl₂ treated carbon shows a significantly increased rate of CN⁻ destruction (Figure 10.6). The presoaked carbon resulted in 73.3 percent oxidation of CN⁻ in the first hour, and 96.4 percent oxidation over a 24 hour period, compared with 15.6 percent and 31.1 percent oxidation for the untreated carbon. As observed for the iron(II) oxidation, the majority of the CN⁻ oxidation occurs in the first hour, with similar oxidation rates thereafter.

Hoecker (1987) similarly showed that the addition of 100 mg/l copper(II) to the CN⁻ solution significantly increased the rate of cyanide oxidation, but did not oxidise the cyanide as quickly as the CuCl₂ presoaked carbon. Thus the enhanced oxidation rate could not be attributed to copper(II) in solution.
Figure 10.6. Rate of carbon catalysed destruction of cyanide.

(■) CuCl₂ presoaked carbon, (★) fresh carbon. (225 mg l⁻¹ CN⁻, 25°C, pH 10.5, 5 g l⁻¹ carbon, O₂ flow rate 300 ml min⁻¹).
10.4.8 Mechanism of Catalysis

These results, therefore, support a mechanism where oxygen and iron(II) are adsorbed onto the carbon, and certain groups on the carbon catalyse the electron transfer between the iron(II) species and oxygen, resulting in oxygen being reduced and iron(II) being oxidised to iron(III). The carbon, itself, does not oxidise the iron(II), as evidenced by the differing initial rates observed when using air and oxygen as the oxidant (Table 10.1). The functional groups are, however, changed by oxygen as shown by the change in activity after the first hour and the lower activity observed for a carbon which had previously been sparged with oxygen for 16 hours. Even trace amounts of copper(II) appear to catalyse this surface oxidation. It is proposed that the role of copper is to initiate and stabilise oxygen free radicals at the surface.

The autoxidation of organic materials is not an unusual reaction. At moderate temperatures, low conversions (<1%) are common (Howard, 1973). These autoxidation reactions involve free radical intermediates (hydroperoxides), and the final products are non-radical and result from the decompositions of the hydroperoxidic intermediates (Ammon, 1979). Therefore, the reactions involving these radicals in this system can be proposed as follows:

\[
\begin{align*}
\text{Cu}^+ \text{O}_2 \cdot + \text{Fe}^{2+} & \xrightarrow{H^+} \text{Fe}^{3+} + \text{Cu}^+ + \text{H}_2\text{O} & 10.5 \\
\text{Cu}^+ \text{O}_2 \cdot & \xrightarrow{H^+} \text{Cu}^{2+} + \text{H}_2\text{O} & 10.6 \\
\text{Cu}^+ \text{O}_2 \cdot & \xrightarrow{H^+ / CO_2} \text{Cu(OH)}_2 \text{CuCO}_3 & 10.7
\end{align*}
\]
Some loss of activity is therefore attributed to the formation of basic copper salts on the carbon surface, such as malachite and azurite, due to adsorption and interaction of CO₂ from the air. There is also evidence for free radicals being formed upon activating carbon in a kiln at high temperatures (Siedlewski, 1967), and these too can be expected to react at the carbon surface with oxygen and disappear with time in solution.

Even though Puri and Kalra (1972) discuss the catalytic nature of activated carbon as a function of "unsaturation," an earlier work noted that the catalytic efficiency for oxidation of iron(II) by O₂ could be enhanced by surface oxidation with concentrated nitric acid (Puri and Bansal, 1966). This oxidation could be similar to that occurring in this study on heating with copper salts in air.

The ability of activated carbon to effect both the oxidation of iron(II) and reduction of iron(III) clearly indicates the presence of redox couples on the surface of the activated carbon. Jankowska (1981) believed the redox potential to arise from the oxygen couple (10.8), while Kinoshita (1973) proposed a quinone/hydroquinone couple (10.9).

\[
\begin{align*}
O₂ + 2H₂O + 4e^- & = 4OH^- & E_o &= 1.23V & 10.8 \\
\text{oxidation} & + H₂O + 2e^- & = & \text{reduction} & + 2OH^- & E_o &= 0.69V & 10.9
\end{align*}
\]

In a potentiometric study of the adsorption of Au(CN)₂⁻ and Ag(CN)₂⁻ onto activated carbon, Tsuchida and Muir (1986) found that the potential of the carbon used was -0.68 V at pH 2 and decreased with increasing pH by 0.059 V per pH unit. With this being very close to
the quinone couple, shown above, they concluded the observed potentials and carbon chemistry could be more logically rationalised by the presence of these quinone-type groups and free radical peroxide groups rather than by an oxygen couple.

The iron(III)/iron(II) couple \( E^\circ = 0.73V \) in \( Cl^- \) is, therefore, similar to the potential of the carbon and can explain the reversible redox role of carbon. It also explains why there is a limit to the Eh of the solution in which carbon is present. This limits the concentration of iron(III) which can be produced as there will be an equilibrium iron(III)/iron(II) ratio established according to the quinone/hydroquinone ratio. However, the nature of the surface oxide groups is dependent on the temperature at which oxygen reacts with the surface, and there is little doubt that oxygen plays a significant role in determining the nature and activity of the activated carbon in solution (Tsuchida, 1985). No physical technique is yet available to categorically prove the presence of specific functional groups and, until this is achieved the exact nature of the active sites must remain speculative and based upon observations and characteristics of the carbon.

10.5 Conclusions

A study of the oxidation of iron(II) with \( O_2 \), using copper(II) and activated carbon as catalysts, show that both have a limited catalytic function and are inefficient catalysts for complete iron(II) oxidation at concentrations \( \geq 0.1 \) M. The increase in initial rate observed in the presence of 0.01 M copper(II) was only 3.5 fold and decreased after 4 hours to values smaller than previously reported.
The results presented here also show that activated carbon is not a practically useful catalyst for complete oxidation of iron(II) to iron(III) for the Summit Process. It is proposed that peroxide or quinone/hydroquinone-like couples are formed on the activated carbon, which determine the iron(II)/iron(III) ratio in solution according to the Eh of the carbon surface. Whilst no appreciable oxidation of carbon seems to occur with oxygen bubbling in solution, the catalytic activity of the carbon was significantly enhanced on heating in the presence of copper(II). This enhancement was attributed to the formation of radical species on dry carbon which are believed to react with oxygen to form hydroperoxidic intermediates and surface oxide groups such as quinones in solution, which temporarily increase the rate of iron(II) oxidation. These radicals can also decompose with acid or carbon dioxide which result in the loss of activity.

From the results reported in this chapter, it is highly unlikely that a process could be developed for the regeneration of concentrated solutions of iron(III) at ambient oxygen pressures using copper(II), carbon or mixtures of both to catalyse the oxidation of iron(II).

However, the use of bacteria in the presence of oxygen to oxidise iron(II) is one alternative that should be further investigated. Even though the usual bacteria tolerate only about 5 g l\(^{-1}\) of iron(III), it may be possible to adapt strains to tolerate higher concentrations.
At the present time, the only viable iron(III) regeneration method suitable for the Summit Process considered in this study, appears to be high temperature/pressure oxidation of iron(II) in an autoclave. This would involve a separate bleed of FeCl₂ solution for pigment production (see Chapter 11) to maintain an iron balance in the recirculating liquors.
Chapter 11

Characteristics and Production of Iron Oxide Pigments from Iron(II) Chloride

11.1 Introduction

The dissolution of the metallic iron in the reduced ilmenite matrix by iron(III) chloride leaves a solution of iron(II), which is then partially regenerated to iron(III) for further leaching. Ideally a saleable iron by-product should be produced from the remaining iron(II) liquor. The review of the processes amenable to by-product production (Chapter 1), indicate that the precipitation of iron oxide pigments are achievable from these solutions, even though almost all current synthetic pigment precipitation processes use sulfate media.

Australian domestic production of synthetic and natural iron oxide pigments is around 5,000 tpa, which only satisfies approximately 30 percent of the domestic market (Benbow, 1989). As the demand is not satisfied locally, it would appear that there is scope for the production and marketing of cheap pigments to satisfy this demand.

Iron oxide pigments constitute an important sector of the inorganic pigment industry due to their low cost, their permanency against fading and good hiding power. During the last 50 years, synthetic iron oxides have taken over from natural iron oxides, which are inconsistent in their properties, as a result of the large quantities of waste iron salt solutions which have become available from metal pickling operations (Rama Sastry et al., 1976). The overwhelming
majority of iron oxide pigments used today are manufactured synthetically. Numerous patents exist describing processes for the production of pigmentary oxides, but generally they can be classified into similar groupings as the patents use the same basic methods with only slight variations in pH, temperature, iron(II) concentration and equipment (Benbow, 1989).

Synthetic iron oxide pigments can be manufactured in three primary colours red, black and yellow, which correspond to the minerals hematite (\(\alpha-\text{Fe}_2\text{O}_3\)), magnetite (\(\text{Fe}_3\text{O}_4\)) and goethite (\(\alpha-\text{FeOOH}\)) in composition and structure. By combining these three primary colours, iron oxide browns can also be made with the colour shade depending upon the mixture ratio of the three components (Bayer, 1974). However, shades and pigment properties are also dependent upon a number of physical factors. Strict control of particle size and shape, as well as the oxide phase, are required to meet the specifications of the pigment industry.

Aqueous precipitation processes which have been reported, invariably quote a number of seed generation techniques and pH values for the production of different phases (Callen et al., 1981). On the other hand, precipitation of particles of the required size distribution involves a proper understanding of the processes of nucleation, ageing and crystal growth of the iron oxide phase. In this chapter, the essential characteristics and physical properties of iron oxides are reviewed together with an outline of various methods currently available for producing synthetic iron oxide pigments, particularly from iron(II) solutions.
As a result of the better understanding of transformation reactions gained in this study, a novel approach to pigment production has been developed which includes nucleation, ageing and crystal growth which is directly applicable to a synthetic rutile plant. It is shown that innoculation of solutions with the same lepidocrocite seed followed by transformation to the desired product by control of the solution Eh, gives products which are suitable as pigments.

11.2 Experimental

11.2.1 Iron Oxide Pigment Production

Pigment products were prepared in a 1 litre round bottom reactor seated in a temperature controlled (± 1°C) oil or waterbath. Iron(II) chloride (laboratory grade) was dissolved in deionised water and made up to 0.5 M in a volumetric flask. This solution (200 ml) was adjusted to pH 6.5 - 7.0 with concentrated \( \text{NH}_4\text{OH} \) solution whilst being sparged with air \( (1 \text{ l}\text{min}^{-1}) \) at room temperature to prepare the lepidocrocite seed material (see Table 2.1). The seed preparation lasted for approximately 15 minutes, in which time the slurry changed from a green to an orange colour.

The slurry was then added to the remaining iron(II) solution in the reactor and stirred with a four-paddle stirrer at 300 rpm with the aid of an overhead stirrer. The potential was controlled using a Ag/AgCl reference and a platinum coil and recorded, corrected to the hydrogen scale. A circuit linked to a Schotte Gerate T80 Automatic Burette added 0.01 ml aliquots of concentrated \( \text{NH}_4\text{OH} \) when the potential rose above the predetermined value. Measurements of pH were taken using a
combination glass pH electrode connected to a Phillips PW9420 pH meter.

Samples were withdrawn at set intervals and analysed for iron(II) using a standard permanganate solution, as described previously, while solid samples were analysed by X-ray diffraction.

On completion of each experiment, the solid material was collected under vacuum and dried at <60°C. This material was broken up in a glass mortar and pestle and analysed by X-ray diffraction and thermogravimetric techniques. In some instances, Transmission Electron Microscopy and analysis of particle size distribution were performed.

11.2.2 Transmission Electron Microscopy

Particle shape and size determinations were made using a Phillips 301 Transmission Electron Microscope. A minute amount (~0.1 mg) of each finely divided sample was smeared onto the adhesive side of a copper grid. This was best achieved by sprinkling a small amount of the iron oxide onto clean paper, touching the paper with the tip of a finger then touching the grid leaving a few particles of the oxide on the grid.
11.2.3 Particle Size Distribution

Particle size distribution data was obtained from the Curtin University Particle Analysis Centre. Each sample was dispersed in sodium polyphosphate and analysed using a Malvern Mastersizer. For these very fine materials a comparison of the volume distribution data with that of a commercial pigment (Bayer 318 Magnetite) was found to be most appropriate. This technique assumes the material to perfectly spherical and thus does not give an exact measure of the particle size, but does prove useful for an analysis of the relative distribution of particle sizes.

11.3 Review of Pigment Properties and Physical Factors which Determine Shade

The main properties affecting the performance of a pigment, which are relevant to this study, are the optical properties or colour, the particle size, and the particle shape (Bax and Ritchie, 1986).

11.3.1 Optical Properties

The main optical properties of a pigment are its colour, tinting strength and opacity. Colour is produced by selective absorption of specific wavelengths of visible light (400 - 700 nm). When almost all light is reflected from a surface it appears white; and when all light is absorbed, the surface appears black. Surfaces appear coloured when some of the wavelengths of normal light are absorbed and others are reflected. The specific colour which is seen corresponds to the wavelengths which are reflected.
The light scattering efficiency of a pigment is the main factor in its hiding power and opacity. In a paint film, the refractive index of the binder will interact with the refractive index of the pigment in such a way that the greater the difference in the refractive indices, the more opaque the film becomes.

Coloured pigments also scatter incident light, but in addition, they absorb selected wavelengths, and therefore they usually have a better hiding power than white pigments. Hiding power, therefore, is affected by pigment concentration, pigment particle size, the difference in the refractive index between the pigment and the binder, and the light absorption characteristics of the pigment.

11.3.2 Particle Size

For the optical properties of a pigment to be fully developed, it is necessary to keep the particle sizes within a certain narrowly defined range, which for iron oxides extends from 0.1 to 1.0 micron. In this range, the scattering constant, which is critical for the optical properties, passes through a maximum. Furthermore the particle size distribution of the iron oxides should be narrow due to the strong dependence of colour, shade and brightness on particle size (Bayer, 1974).

The tinctorial strength of red pigments decreases, whereas that of black pigments increases with a decrease in particle size. The colour shade of red pigments tends towards blue with increasing particle size, and that of black pigments tends to a greyish brown. Smaller red particles promote a yellow shade and a higher tinting strength.
Therefore, a large range of pigment shades can be produced by varying the amount of grinding to give different size distributions.

11.3.3 Particle Shape

The properties of iron oxides which determine colour, are highly dependent on their respective particle shapes. Iron oxide reds and blacks generally possess particles which are cubic to spherical in shape. The only exception is the iron oxide red produced by dehydration of yellow iron oxides. The particles of iron oxide yellow pigments have a more or less pronounced needle-shaped structure (acicular) which is measured by the ratio of length to cross-section. Iron oxide yellows with very slim needles have a pure greenish colour shade, while broader needles show a change of colour shade to orange.

In contrast to the spherical iron oxide red and iron oxide black pigments, the needle-shaped iron oxide yellows are sensitive to grinding. If the needles are broken during grinding the colour shade changes to a duller yellow (Bayer, 1974).

11.4 Summary of Methods of Production of Synthetic Iron Oxide Pigments

The common methods used to produce various coloured iron oxides synthetically are described below.
11.4.1 Red Iron Oxide Pigments

Red iron oxides can be generated by four methods:

(1) Thermal decomposition and oxidation of iron(II) sulfate or iron(II) chloride at temperatures between 700 and 800°C.

(2) Oxidation of magnetite to hematite at temperatures between 700 and 800°C.

(3) Calcination of iron oxide yellows to produce hematite.

(4) Precipitation of red iron oxide from an aqueous iron(II) sulfate solution. However, goethite is generally present with the hematite at temperatures less than 100°C.

This pigment type is the most important in terms of volume sales and a wide range of shades can be produced by these processes.

11.4.2 Yellow Iron Oxide Pigments

Synthetic iron oxides are currently produced by three processes; namely the Penniman-Zoph Process, Direct Precipitation Process and the Aniline Process.

(1) Penniman-Zoph Process. This was originally patented in 1921 and utilises scrap iron as a feedstock for the continuous generation of iron(II) sulfate which is then reacted with an alkali, (usually sodium hydroxide) in the presence of oxygen. Fine seed crystals generated during the initial reaction are used as nuclei to grow yellow iron oxide particles. The reaction is arrested when the desired particle size and shape is produced.
(2) **Direct Precipitation Process.** In common with the previous method, this modification uses seed crystals and differs from the Penniman-Zoph Process in that the iron(II) solution is used directly from the pickling of steel or sources of waste iron(II) sulfate such as the TiO₂ Sulfate Process.

(3) **Aniline Process.** This process is a combined organic/inorganic method, utilising nitrobenzene and metallic iron as the principle raw materials. During the process the nitrobenzene is reduced to form aniline, and the metallic iron is oxidised into either iron oxide yellow or black.

All three precipitation methods produce comparable grades of yellow oxide, Colour shade is determined by the particle size, which in turn is a function of the reaction time (Benbow, 1989).

11.4.3 Black Iron Oxide Pigments

Synthetic black oxides can be manufactured by three processes very similar to those employed in the production of synthetic yellow oxides. In summary these are:

(1) Oxidation and precipitation from an iron(II) salt solution using an alkali for pH control at higher pH than for yellows.

(2) Reduction of synthetic yellows with heat in an reducing atmosphere.
(3) Aniline Process. By altering the raw materials and the addition of additives, such as iron(II) salts and aluminium salts, a wide variety of black shades can be produced. Particle shape is normally spherical, and crystals with a diameter of 0.5 microns create a bluish shade (Benbow, 1989).

11.4.4 Brown Iron Oxide Pigments

These compounds can be produced by three methods:
(1) Mechanical blending of synthetic red, yellow and black pigments.
(2) Direct precipitation of mixed phases.
(3) Controlled oxidation of synthetic yellow oxides to produce $\gamma$-Fe$_2$O$_3$ below 400°C.

Both blending and direct precipitation have sufficient inherent versatility to be able to offer an extensive range of shades, from pale tans to dark chocolate shades. These two methods are used to produce the majority of the synthetic brown iron oxides (Benbow, 1989).

11.5 Mechanism of Precipitation of Pigments from Iron(II) Solutions

Of most significance to the study on the Summit Process is the formation of iron oxides by precipitation from iron(II) solutions. The precipitated iron oxides and their properties will depend on the rates and mechanisms of the major processes involved in their formation, namely nucleation, ageing and crystal growth.
11.5.1 Nucleation

Nucleation is the formation of small particles from a supersaturated solution. A supersaturated solution may be either labile (i.e. undergoing spontaneous precipitation through nucleation and subsequent growth in a short period of time), or metastable, in which case no observable precipitate is formed in a relatively long period. In a metastable supersaturated solution, crystal growth is initiated by inoculation with added seeds (Nancollas and Reddy, 1974).

If supersaturation is sufficient for nucleation to occur, while crystal growth is limited by the availability of the crystallising material, a sol can be formed. If the formation of new nuclei (secondary nucleation) and growth of established nuclei occur at the same time, the size distribution of the resulting particles covers a wide range and the sol is said to be poly-dispersed. If the formation of new nuclei is restricted to a short period at the beginning, a mono-dispersed sol is formed, one in which the particles are of uniform size. This may be achieved either by inoculation with added seeds or by raising the solution concentration above the metastable limit for a short time (Bax and Ritchie, 1986). Both these practices have been used for the initiation of crystal growth in pigment processes.
11.5.2 Ageing

Ageing includes all irreversible structural changes which occur in a precipitate after it has formed. These changes may include Ostwald ripening (growth of large particles at the expense of small), thermal ageing (growth of more perfect crystals) and transformation of metastable phases (the conversion of a less stable phase which precipitates first to a more stable phase) (Bax and Ritchie, 1986).

Transformation processes which are of particular significance to the pigment production in this work have been discussed in Chapters 3 and 4. A seed of one phase can be used to nucleate the process, which will transform into a more stable phase with subsequent crystal growth producing an oxide of the desired crystal size (Callen et al., 1981).

11.5.3 Crystal Growth

In the absence of secondary nucleation, the growth of seed crystals from metastable supersaturated solutions has been found for many salts to follow a rate law of the form:

\[ \text{Rate of crystal growth} = -\frac{d m}{d t} = k s (m - m_0)^n \]  \hspace{1cm} 11.1

where \( m \) is the concentration of the species at time \( t \), \( \frac{d m}{d t} \) the rate of crystal growth, \( k \) the crystal growth rate constant, \( s \) the crystal surface area available for growth, and \( n \) a constant.
The overall growth process of a crystal consists of:

(1) Diffusion of the depositing molecule or ion in the bulk of the solution up to the crystal surface.

(2) Adsorption at the crystal surface.

(3) Surface diffusion process to a step (since two surfaces of the particle in contact with the crystal faces offer additional stabilisation).

(4) Further one-dimensional diffusion along to kink site (which enables the molecule or ion to be incorporated into the crystal lattice).

Experimental evidence points to a surface reaction such as (2), (3) or (4) as being rate determining rather than bulk diffusion of the material to the growing crystal surface (Nancollas and Reddy, 1974).

11.6 Iron Oxide Pigment Production from Lepidocrocite and Iron(II) Chloride

The Eh-pH diagram constructed in Figure 4.6 predicts the iron oxide pigment which should be obtained from a combination of transformation and oxyhydrolysis reactions of lepidocrocite according to solution conditions. To test this in practice, three experiments were conducted to produce red, yellow and black iron oxide pigments when the solution Eh was controlled at +300mV, +150mV and -50mV (nHe) respectively. Lepidocrocite seed was initially produced from a sample of iron(II) chloride solution in the manner described in Section 11.2.1 and then transformed in the remaining 0.5 M FeCl₂ solution at 80°C, with attendant precipitation of iron(II). The iron(II) concentration profiles for these experiments are shown in Figure 11.1.
Figure 11.1. Precipitation of iron oxide pigments at controlled Eh. ● Red hematite/goethite at +300 mV (nHe). ■ Yellow goethite at +150 mV (nHe). ▲ Black magnetite at -50 mV (nHe). (80°C, Air flow rate 50 ml min⁻¹, 1 litre of 0.5 M FeCl₂, 200 ml used for seed generation).
The product formed at a potential of -50mV (nHe) was characterised by X-ray diffraction as pure magnetite. Figure 11.1 shows the rate of removal of iron(II) from solution during the precipitation of this magnetite is essentially linear with complete removal by the 6th hour. X-ray patterns also indicated that the lepidocrocite seed material had totally transformed to magnetite within 2.5 hours, allowing a further 3.5 hours for crystal growth.

The solution controlled at +150 (nHe) produced pure goethite. It started at pH 4.0 but quickly fell to pH 3.0 for the 25 hour duration of the experiment. As expected, the rate of iron(II) oxidation and removal from solution also followed this trend, as the rate is reported to be dependent on pH (Goto et al., 1971). Again the lepidocrocite seed in this solution was not evident by the 5th hour, and the oxide quickly developed into a bright yellow colour.

At the controlled potential of +300mV (nHe) the complete removal of iron(II) took 30 hours, with the pH equilibrating close to 2.8. In this case it took 25 hours or more to transform the lepidocrocite seed and precipitate a red oxide of mainly hematite. However X-ray diffraction and thermogravimetric analysis showed the material was not pure and that it contained 3.7 percent combined water, which represents 36 percent goethite. This concurs with the results of the fundamental transformation kinetic study reported in Chapter 3.
11.6.1 Characterisation of the Pigments

a) Yellow Pigment

As discussed earlier, the shape and size of the iron oxide crystals are significant parameters in determining their suitability for pigmentary purposes. Plate 11.1 shows a transmission electron micrograph of the pure goethite phase obtained from these experiments. This plate shows the material to have a broad needle structure with a predominant size of 0.3 microns x 0.1 microns. Even though the micrographs show a range of sizes, the crystals have very regular boundaries and can be considered to be very crystalline.

Plate 11.1. Transmission electron micrograph of pure goethite pigment produced at + 150 mV (nHe) × 110,000 .
The shape of these crystals imparts an orange shade to this oxide. However, it was observed that the material originally imparted a greenish tinge to the solution which progressively decreased as the oxidation process continued. Presumably, finer crystals were more predominant early, with the subsequent growth producing broader crystals.

b) Red Pigments

Plates 11.2(a) and (b) are the micrographs taken at different magnifications for the red oxide which clearly shows the spherical hematite and the needle or acicular shape of goethite. The goethite crystals in this product (0.5 x 0.05 μm) are longer and narrower than those shown in Plate 11.1. The hematite particles are very crystalline with sizes between 0.3 and 0.35 microns, which is the optimum size for iron oxide pigments and midway in the range of sizes offered by Bayer AG(0.1 - 0.7 μm) for its calcined reds. However, the lack of physical purity limits the applications of this product to the lower quality markets. The light red colour has no blue shading and could be considered to be midway between a yellow and blue shade.
Plate 11.2. Transmission electron micrographs showing two phases in the red pigment produced at + 300 mV (nHe). (a) upper × 49000 (b) lower × 110,000.
In order to try to produce a purer red pigment from lepidocrocite, a further 21 pigment precipitation experiments were conducted ranging in duration from 1 to 4 days. The variables changed are set out below:

Seed: 4.4 - 8.8g l\(^{-1}\), precipitated and a commercial oxide.

Air Flow rates: 0 - 100 ml min\(^{-1}\)

Iron(II) Concentration: 0.25 - 0.5 M

Anion: Cl\(^-\), SO\(_4\)^{2-}\)

Potential: +300 - +600mV (nHe)

Temperature: 80 - 100°C

Thermogravimetric and X-ray data collected for all these experiments however showed a certain amount of coprecipitated goethite. Even when a commercial sample of "Ajax" precipitated hematite was used as a seed, goethite appeared in the product oxide.

The most significant variable which affected the goethite content was temperature. Temperatures of 95 - 100°C produced oxides of a blue-red shade with the lowest water content (1.54 percent) equating to 15.2 percent goethite.

As most of the processes for the production of pigments appear in patents, little or no characterisation of the products is reported. One patent using standard technology however, reports that a light shade of red oxide is developed in 24 hours and the deepest shade of maroon in less than a week. A typical light-red oxide had a composition of Fe\(_2\)O\(_3\)-0.88·H\(_2\)O (9.1 percent water) whilst the dark maroon had a composition of Fe\(_2\)O\(_3\)-0.22·H\(_2\)O (2.4 percent water) (Bennetch, 1956).
No reports have been found in the literature quoting the production of totally dehydrated hematite at temperatures less than 100° C from iron(II) solutions. It is therefore highly unlikely that such a phase is achievable at these temperatures. Even though rapid iron removal from iron(II) solutions is required by the Hematite processes used by the Akita Zinc and Ruhr Zinc Companies, it is significant that temperatures greater than 180° C are used (Dutriza, 1987).

The inability to produce a pure hematite phase from solution is, however, inconsistent with the results observed for transformations of lepidocrocite electrodes in Chapter 4. This may be explained in terms of the mechanism of the replacement reaction involving Fe\(^{2+}\). When electron transfer takes place between Fe\(^{2+}\) and iron(III) in the lattice, a drop in potential is observed at the interface which allows the Fe\(^{2+}\) being oxidised to crystallise at a lower potential and thus form goethite. This effect would not be observed at the interface of the electrode, when its potential is controlled externally. Thus, the hematite phase will solely crystallise at a higher fixed potential within the stability region of hematite.

Even though pure hematite was not observed at temperatures below 100° C, the phases produced under these conditions could still have applications as pigments since a range of shades can be produced. However there is less control over the shade produced.
Plate 11.3. Transmission electron micrograph of pure black magnetite pigment produced at -50 mV (nHe) × 108,500.

c) Black Pigments

The micrograph of the pure black magnetite formed over a period of 6 hours at -50mV (nHe) is shown in Plate 11.3. It can be seen that small hexagonal shape particles are agglomerating into chains because of the ferromagnetic nature of the magnetite. Even though it is difficult to distinguish individual crystals, sizes were found to range from 0.05 to 0.1 microns which agglomerated to particle sizes of 0.5 to 10 microns. The hexagonal shape is a two dimensional representation of a dodecahedral crystal (Hulbut and Klein, 1987). Unfortunately, these sized particles are too small to be suitable for pigments. The small particle size is due to the relatively high pH of 5.0 needed to maintain the solution at the required potential. This resulted in secondary nucleation as the concentration rose above the metastable limit for the precipitation of Fe(OH)$_2$ at this pH.
This secondary nucleation would have substantially increased the number of seeds available for growth above that added by inoculation with the lepidocrocite, and resulted in a faster decline of the iron(II). Thus, smaller crystals were formed than were observed for the slower transformations at higher potentials and lower pH, forming hematite and goethite respectively.

In order to produce a more crystalline magnetite, a regime was developed in which goethite crystals were grown at 80°C, at a higher Eh, until there was a 2:1 ratio of iron in the oxide compared to the solution phase. The remaining iron(II) was then precipitated as Fe(OH)$_2$ by the addition of NH$_4$OH, and the temperature raised to 95°C for a further 6 hours to aid in the recrystallisation of the magnetite. On raising the pH to 7.5 the Eh decreased and the solution and colloids immediately changed from the bright yellow to a green colour, attributable to the Fe(OH)$_2$. As the temperature rose, this colour slowly turned black and after the 28 hour period had elapsed, a very easily filtered black product was collected.

Plate 11.4 shows the micrographs of samples withdrawn after 22 hours, just before and after addition of NH$_4$OH and the final product after 28 hours. The initial micrograph shows a similar crystal size and shape to that of goethite in Plate 11.1, but after the addition of NH$_4$OH, the crystals are smaller and not as regular (Plate 11.4b). It appears as though in a number of places the Fe(OH)$_2$ has transformed portions of the crystals, as evidenced by the crystals having irregular shapes. Plate 11.4c shows the particles to be crystalline, hexagonally shaped magnetite, with sizes between 0.2 and 0.25 microns of the quality required for pigmentary purposes.
Plate 11.4a. Transmission electron micrograph of the iron oxide withdrawn after 22 hours. × 110,600 .

Plate 11.4b. Transmission electron micrograph showing the change in crystal shape after the addition of NH₄OH at the 22nd hour mark. × 111,000 .
Plate 11.4c. Transmission electron micrograph showing pure hexagonally shaped magnetite crystals produced from goethite after 28 hours. 
\times 108,500.

This regime therefore allows the production of much fewer crystals than the method used initially because the \( \text{Fe(OH)}_2 \) species adsorbs onto the goethite. The rapid transformation induced by this adsorption leads to a smaller number of crystals. The increased temperature not only aids in the transformation process but also promotes the dehydration step, as observed for the red oxides.

d) Brown Pigment

Brown pigments can be produced by physically blending the other phases, or by directly precipitating two phases. For the purpose of this study, a deep red-brown pigment was produced from a modification of the process previously described for the production of magnetite from goethite. To achieve this, the solution was controlled at +150mV
Figure 11.2. X-ray patterns showing the transformation of lepidocrocite to hematite and magnetite to produce a brown pigment. (95°C, 0.5 m FeCl₂, 200 ml used for seed generation, Air flow rate 50 ml min⁻¹). (L=Lepidocrocite, G=Goethite, M=Magnetite, H=Hematite)
(nHe), and at a higher temperature of 95°C in order to produce a mixed hematite-goethite phase from the transformation and oxyhydrolysis reactions. Temperature is an important factor since at 80°C a pure goethite product is produced at the same potential, but the higher temperature shifts the equilibrium in favour of the dehydrated hematite phase.

Figure 11.2 shows the X-ray patterns of the samples withdrawn after intervals of 1, 22 and 25 hours after addition of NH₄OH. After 1 hour the sample was predominantly lepidocrocite, with a small amount of goethite and a trace of hematite. After 22 hours, prior to the precipitation of the Fe(OH)₂, the oxide was a mixture of hematite and goethite, while after 25 hours hematite and magnetite were the only phases evident.

11.6.2 Particle Size Distribution of the Precipitated Phases

The particle size distribution data shown in Figure 11.3, show similar histograms to that shown for the commercial product (Bayer 318 Magnetite, See Figure 5.7), for all except the hematite sample. Even though the micrograph in Plate 11.2 indicates that the hematite was fairly crystalline, with spheres in the range 0.3 - 0.35 microns, the histogram is very broad with a high proportion of the material reporting to the very small size ranges. This is not unexpected as Figure 11.1 shows that lepidocrocite was still unreacted in the product even after 24 hours, when less than 20 percent of the iron(II) remained for crystal growth. As growth of the lepidocrocite is not
Figure 11.3. Particle size histograms for iron oxide pigments.

(A) Hematite, (B) Magnetite, (C) Magnetite produced from geothite,
(D) Goethite.
expected, the growth of hematite is taking place on relatively fewer nuclei. For a more uniform particle size distribution, the transformation of lepidocrocite would need to occur much more quickly for the crystal growth to occur evenly on all added seeds.

As expected, the histograms of the two magnetite samples show that the sample produced from the slow growth of goethite, followed by transformation to magnetite, gave a more uniform particle size than that produced directly from lepidocrocite. The histograms also show these precipitated magnetites have very narrow size distributions and thus are well suited for use as high quality pigments.

The size distribution of the goethite sample (same as for Plate 11.1) generally shows the characteristic Gaussian shape, except tailing was observed at the high particle size end. This is probably attributable to the needle shape of the crystals affecting the algorithms, which assume the material to be perfectly spherical. However, the Gaussian shape is very similar to that recorded for the commercial product and, therefore, this sample can be considered useful as a pigment.

These results show that microscopy can give misleading information about the sizes of particles (cf. Plate 11.2), and that a distribution histogram more adequately shows the suitability of an oxide for use as a pigment. The particles shown in Plate 11.2 are obviously the larger material from the sample which would have had sufficient time to grow after transformation, and the sampling technique for the preparation of the grids introduced a bias.
11.7 Conclusions

A review of the properties affecting the performance of pigments has shown that the quality of the pigment is dependent on the colour, particle size and particle shape. It is evident from this review that to optimise these properties there is a need for a greater understanding of the nucleation, ageing and crystal growth steps in the formation of pure iron oxide phases so these oxides can be produced from waste iron(II) chloride solutions.

High quality pigments are achieved by a process involving nucleation of an iron(II) chloride solution with lepidocrocite, ageing and transforming the seed material at controlled potentials and subsequent crystal growth to the required particle size. Lepidocrocite seed can be previously prepared from the same iron(II) chloride solution.

Pure goethite, produced at a controlled potential of 150 mV (nHe), had the desired physical properties required for pigment use, but the crystal size of pure magnetite formed at -50mV (nHe) was too small. Larger crystals were achieved by the slow growth of goethite, followed by a rapid dissolution/reprecipitation process involving Fe(OH)$_2$ at pH $> 7$.

The aqueous transformation methods used did not produce a physically pure hematite phase, with some goethite always present in the final product. Higher temperatures favoured hematite precipitation from
iron(II) chloride solutions and a range of bright red oxides of varying shades were produced at 95 - 100°C. A product containing 1.54 percent water (15.2 percent goethite) was precipitated under the best conditions.

The processes described allows the production of yellow, black, red and brown pigments of varying shades from waste iron(II) chloride solutions. Therefore, a process involving iron(III) chloride dissolution of the metallic iron in reduced ilmenite has the potential for producing saleable by-products as well as synthetic rutile. Equally the same processes can be applied to lepidocrocite produced from the Becher Process. In this case the appropriate pigment is produced in a separate reactor vessel with the addition of iron(II) at controlled Eh and pH.
Chapter 12

Recommendations for Further Work

12.1 The Becher Process

This study has shown that the range of iron oxides formed during the Becher Process are all derived from the transformation of lepidocrocite through the solution phase in iron(II) solutions. The electrochemistry of these reactions was studied and it was found that the transformation products were a function of the solution potential. These results were applied on both laboratory and plant scales to produce a range of iron oxide phases, hence showing the potential of this mechanism for producing high quality value added by-products from this process.

A detailed pilot plant study is required on the formation of physically pure hematite and goethite from the aeration process. Using the knowledge gained from this study the effects of air flow rates, iron(II) addition, temperature and reduced ilmenite quality are required before the by-product process can be commercialised. The results from the plant scale study reported here, show that pure magnetite can be produced but more plant process control is required to maintain the solution conditions needed to reproducibly form the other phases exhibiting the physical properties required for pigments.

It is recommended that further attention should also be paid to the development of a process where lepidocrocite is removed from the aeration tanks prior to any transformation reactions occurring, and is used as a seed in the production of iron oxide pigments in separate reactors. This method has the potential for the production of very
high quality iron oxide pigments.

12.2 The Summit Process

A modified Summit Process involving the removal of iron from reduced ilmenite was studied and was found to produce very high quality synthetic rutile, plus have the advantage of recovering iron values as pigments. The iron dissolution mechanism was found to be iron(III) diffusion controlled, however acid dissolution of the iron limited the quality of the product. This study showed that this competing reaction could be minimised by the addition of citrate or by the addition of Al$^{3+}$ or Fe$^{2+}$. These ions are believed to block the adsorption of the proton.

Very high quality iron oxide pigments were produced from the iron(II) solutions generated in the Summit Process using the mechanisms of lepidocrocite transformation, ageing and controlled crystal growth.

Whilst this study has largely resolved the process chemistry, a detailed cost analysis is clearly needed, particularly with regard to iron(III) regeneration methods. It is possible that research is required to develop a relatively cheap method for the regeneration of iron(III), which would also leave waste iron(II) for the production of pigments. Possible alternatives include the use of bacteria in large ponds or the use of catalysts in the presence of oxygen under pressure. When this unit operation has been developed, a detailed programme of work is required, on both laboratory and pilot scales, to link the three steps and monitor the product quality and build-up of trace elements in the recirculating liquors.
References


Dutrizac, J.E.; World Symposium on Metallurgy and Environmental Control, 1980, pp532-64.


Frankel, R.B., Papaeftymiov, G.C., Blakemore, R.P. and O'Brien, W.;


Mann, S., Moench, T.T. and Williams, R.J.P.; *Proc. R. Soc. Lond.*, 221B, 1984, pp385-93.


Vasatko, J.; *Z. Zuckerind.*, 52, 1928, p221.


Appendix 1

Experimental Results

Section 8.3.3 Arrhenius Plot Data for Reduced Ilmenite Discs

<table>
<thead>
<tr>
<th>$1/T$ x10$^3$</th>
<th>0.1M FeCl$_3$ ln(rate)</th>
<th>0.05M Fe$_2$(SO$_4$)$_3$ ln(rate)</th>
<th>0.1M HCl ln(rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.595</td>
<td>-7.63</td>
<td>-7.29</td>
<td>-7.90</td>
</tr>
<tr>
<td>3.354</td>
<td>-7.06</td>
<td>-6.83</td>
<td>-7.08</td>
</tr>
<tr>
<td>3.094</td>
<td>-6.16</td>
<td>-6.15</td>
<td>-6.12</td>
</tr>
</tbody>
</table>

Section 5.7.3.1 Dissolution of Iron versus Rotation Speed

(0.02 M FeCl$_3$, 0.1 M HCl, 25°C)

<table>
<thead>
<tr>
<th>Rotation Speed (rpm)</th>
<th>Time (s)</th>
<th>$k$ (mole s$^{-1}$ m$^{-2}$ x 10$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>12.94</td>
<td>4.23</td>
</tr>
<tr>
<td>1000</td>
<td>10.23</td>
<td>3.27</td>
</tr>
<tr>
<td>400</td>
<td>6.47</td>
<td>2.43</td>
</tr>
<tr>
<td>100</td>
<td>3.24</td>
<td>1.66</td>
</tr>
</tbody>
</table>
Section 7.3.1  Dissolution of Iron in Acid versus Rotation Speed

(0.1 M HCl, 25°C)

<table>
<thead>
<tr>
<th>Rotation Speed rpm</th>
<th>( \omega^{1/2} )</th>
<th>Time s</th>
<th>( k ) moles s(^{-1}) m(^{-2}) x10(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>12.94</td>
<td>265</td>
<td>2.16</td>
</tr>
<tr>
<td>1000</td>
<td>10.23</td>
<td>310</td>
<td>1.84</td>
</tr>
<tr>
<td>400</td>
<td>6.47</td>
<td>370</td>
<td>1.54</td>
</tr>
<tr>
<td>100</td>
<td>3.24</td>
<td>490</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Section 7.3.3

Effect of Iron(III) Concentration on the Dissolution of Iron

(0.1 M HCl, 1000 rpm, 25°C)

<table>
<thead>
<tr>
<th>([\text{Fe}^{3+}]) M</th>
<th>Time s</th>
<th>( k ) mol s(^{-1}) m(^{-2}) x10(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>310</td>
<td>1.84</td>
</tr>
<tr>
<td>0.01</td>
<td>211</td>
<td>2.71</td>
</tr>
<tr>
<td>0.02</td>
<td>175</td>
<td>3.27</td>
</tr>
<tr>
<td>0.03</td>
<td>157</td>
<td>3.64</td>
</tr>
<tr>
<td>0.04</td>
<td>141</td>
<td>4.05</td>
</tr>
</tbody>
</table>
Section 7.3.3  *Acid Addition versus Iron Dissolution Rate*

*(0.02 M Fe\(^{3+}\), 1000 rpm, 25\(^\circ\)C)*

<table>
<thead>
<tr>
<th>[H(^+)]</th>
<th>Time</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>s</td>
<td>mol s(^{-1}) m(^{-2}) x10(^4)</td>
</tr>
<tr>
<td>0.0</td>
<td>490</td>
<td>1.17</td>
</tr>
<tr>
<td>0.05</td>
<td>227</td>
<td>2.52</td>
</tr>
<tr>
<td>0.10</td>
<td>175</td>
<td>3.27</td>
</tr>
<tr>
<td>0.20</td>
<td>140</td>
<td>4.08</td>
</tr>
<tr>
<td>0.30</td>
<td>137</td>
<td>4.17</td>
</tr>
</tbody>
</table>
Eh-pH Diagram Equations

1) \[ \text{Fe}^{2+} + 2e = \text{Fe}^0 \]

\[ E_{353} = -0.368 + \log[\text{Fe}^{2+}] \]

2) \[ \text{FeOOH} + 3\text{H}^+ + e = \text{Fe}^{2+} + 2\text{H}_2\text{O} \]

\[ E_{353} = 0.610 - 0.210\text{pH} - 0.070\log[\text{Fe}^{2+}] \]

3) \[ \text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe(OH)}_2 + 2\text{H}^+ \]

\[ 2\text{pH} = 9.219 - \log[\text{Fe}^{2+}] \]

4) \[ \text{Fe(OH)}_3 + 3\text{H}^+ + e = \text{Fe}^{2+} + 3\text{H}_2\text{O} \]

\[ E_{353} = 0.997 - 0.210\text{pH} - 0.070\log[\text{Fe}^{2+}] \]

5) \[ \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e = 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \]

\[ E_{353} = 0.873 - 0.28\text{pH} - 0.035\log[\text{Fe}^{2+}] \]

6) \[ 3\text{FeOOH} + \text{H}^+ + e = \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \]

\[ E_{353} = 0.085 - 0.070\text{pH} \]

7) \[ \text{Fe(OH)}_3 + \text{H}^+ + e = \text{Fe(OH)}_2 + \text{H}_2\text{O} \]

\[ E_{353} = 0.276 - 0.070\text{pH} \]
8) \[ \text{Fe(OH)}_2 + 2\text{H}^+ + 2e = \text{Fe}^0 + 2\text{H}_2\text{O} \]

\[ E_{353} = -0.077 - 0.070\text{pH} \]

9) \[ \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e = 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \]

\[ E_{353} = 0.658 - 0.210\text{pH} - 0.070\log[\text{Fe}^{2+}] \]

10) \[ \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8e = 3\text{Fe} + 4\text{H}_2\text{O} \]

\[ E_{353} = -0.110 - 0.070\text{pH} \]

11) \[ 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2e = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \]

\[ E_{353} = 0.228 - 0.070\text{pH} \]
PROFIE 1

Batch 2720  Charge: 47t RI, 80m$^3$ 1.2% NH$_4$Cl liquor
Air Flow Rate: 5200 m$^3$/hr

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Temperature ($^\circ$C)</th>
<th>Slurry pH</th>
<th>Eh mV</th>
<th>Fe$^{2+}$ conc. ppm</th>
<th>Fe$_{met}$ Wt %</th>
<th>Oxide Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.0</td>
<td>6.60</td>
<td>-</td>
<td>28.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>55.1</td>
<td>6.80</td>
<td>127</td>
<td>24.7</td>
<td>γ-FeOOH</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>66.6</td>
<td>6.70</td>
<td>variable</td>
<td>148</td>
<td>24.5</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>3</td>
<td>74.6</td>
<td>6.50</td>
<td>+100</td>
<td>184</td>
<td>22.6</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>4</td>
<td>77.3</td>
<td>6.20</td>
<td>45</td>
<td>137</td>
<td>20.6</td>
<td>γ-FeOOH + trace α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>5</td>
<td>77.8</td>
<td>6.30</td>
<td>5</td>
<td>127</td>
<td>17.9</td>
<td>γ-FeOOH + trace α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>6</td>
<td>78.9</td>
<td>6.10</td>
<td>-80</td>
<td>238</td>
<td>15.7</td>
<td>Fe$_3$O$_4$ + trace γ-FeOOH, trace α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>7</td>
<td>80.7</td>
<td>6.75</td>
<td>-110</td>
<td>350</td>
<td>11.9</td>
<td>Fe$_3$O$_4$ + some α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>8</td>
<td>79.9</td>
<td>6.70</td>
<td>-30</td>
<td>373</td>
<td>8.4</td>
<td>Fe$_3$O$_4$ + some α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>9</td>
<td>78.9</td>
<td>6.10</td>
<td>40</td>
<td>381</td>
<td>5.0</td>
<td>Fe$_3$O$_4$ + some α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>10</td>
<td>77.4</td>
<td>5.30</td>
<td>160</td>
<td>275</td>
<td>2.8</td>
<td>Fe$_3$O$_4$ + some α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>11</td>
<td>74.0</td>
<td>340</td>
<td></td>
<td></td>
<td>1.1</td>
<td>Fe$_3$O$_4$ + some α-Fe$_2$O$_3$</td>
</tr>
</tbody>
</table>
### PROFILE 2

**Batch 742**  
**Charge:** 47t RI, 80m³ 1.3% NH₄Cl liquor  
**Air Flow Rate:** 7000 m³/hr

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Temperature (°C)</th>
<th>Slurry pH</th>
<th>Eh mV</th>
<th>Fe²⁺ conc. ppm</th>
<th>Fe₄⁺ met Wt %</th>
<th>Oxide Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.0</td>
<td>6.55</td>
<td>-</td>
<td>-</td>
<td>27.8</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>54.9</td>
<td>6.06</td>
<td>200</td>
<td>70</td>
<td>25.5</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>2</td>
<td>69.5</td>
<td>6.33</td>
<td>210</td>
<td>103</td>
<td>23.1</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>3</td>
<td>75.1</td>
<td>6.40</td>
<td>-250</td>
<td>102</td>
<td>21.4</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>4</td>
<td>76.0</td>
<td>6.25</td>
<td>-200</td>
<td>95</td>
<td>19</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>5</td>
<td>75.9</td>
<td>6.29</td>
<td>-160</td>
<td>81</td>
<td>16.7</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>6</td>
<td>75.5</td>
<td>5.85</td>
<td>-120</td>
<td>64</td>
<td>14.3</td>
<td>γ-FeOOH, more α-Fe₂O₃ (trace)</td>
</tr>
<tr>
<td>7</td>
<td>75.1</td>
<td>6.68</td>
<td>-100</td>
<td>126</td>
<td>11.4</td>
<td>γ-FeOOH, more α-Fe₂O₃</td>
</tr>
<tr>
<td>8.5</td>
<td>73.9</td>
<td>6.62</td>
<td>30</td>
<td>109</td>
<td>7.5</td>
<td>γ-FeOOH, more α-Fe₂O₃</td>
</tr>
<tr>
<td>9.5</td>
<td>72.1</td>
<td>6.06</td>
<td>100</td>
<td>36</td>
<td>5.5</td>
<td>γ-FeOOH, more α-Fe₂O₃</td>
</tr>
<tr>
<td>10.5</td>
<td>69.6</td>
<td>6.52</td>
<td>100</td>
<td>11</td>
<td>4.0</td>
<td>γ-FeOOH, α-Fe₂O₃</td>
</tr>
<tr>
<td>11.5</td>
<td>67.2</td>
<td>6.72</td>
<td>160</td>
<td>2</td>
<td>2.2</td>
<td>γ-FeOOH, α-Fe₂O₃</td>
</tr>
</tbody>
</table>
**PROFILE 3**

Batch 2173  
Charge: 47t RI  
80m³, 1.2% NH₄Cl liquor

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Slurry (pH)</th>
<th>Eh (mV)</th>
<th>[Fe²⁺] (mg/l⁻¹)</th>
<th>Fe₅₇et (Wt %)</th>
<th>Oxide Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29.2</td>
<td>6.52</td>
<td>-</td>
<td>0</td>
<td>28.8</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>1</td>
<td>47.6</td>
<td>6.29</td>
<td>185</td>
<td>94</td>
<td>26.9</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>2</td>
<td>61.3</td>
<td>6.05</td>
<td>235</td>
<td>100</td>
<td>25.1</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>3</td>
<td>73.4</td>
<td>5.95</td>
<td>50</td>
<td>97</td>
<td>23.8</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>4</td>
<td>79.7</td>
<td>5.95</td>
<td>115</td>
<td>97</td>
<td>22.0</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>5</td>
<td>81.9</td>
<td>6.06</td>
<td>-125</td>
<td>137</td>
<td>20.5</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td>6</td>
<td>83.9</td>
<td>6.50</td>
<td>-185</td>
<td>334</td>
<td>17.4</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>7</td>
<td>82.8</td>
<td>6.75</td>
<td>-310</td>
<td>389</td>
<td>15.2</td>
<td>Fe₃O₄</td>
</tr>
</tbody>
</table>

**AIR FLOW RATE 3000 m³/hr**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Slurry (pH)</th>
<th>Eh (mV)</th>
<th>[Fe²⁺] (mg/l⁻¹)</th>
<th>Fe₅₇et (Wt %)</th>
<th>Oxide Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>77.0</td>
<td>6.67</td>
<td>-280</td>
<td>489</td>
<td>12.9</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>9</td>
<td>75.5</td>
<td>6.55</td>
<td>-205</td>
<td>498</td>
<td>9.5</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>10</td>
<td>74.6</td>
<td>6.10</td>
<td>-80</td>
<td>492</td>
<td>6.6</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>11</td>
<td>73.9</td>
<td>5.15</td>
<td>130</td>
<td>395</td>
<td>2.3</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>11.75</td>
<td>72.0</td>
<td>6.80</td>
<td>430</td>
<td>12</td>
<td>1.1</td>
<td>Fe₃O₄</td>
</tr>
</tbody>
</table>

**AIR FLOW RATE 6500 m³/hr**
Appendix 2
Publications from this Work

Transformations of Iron Oxide By-products During the Becher Process.
C.B. WARD\textsuperscript{1}, S.L. GIBBONS\textsuperscript{2}, I.M. RITCHIE\textsuperscript{3} AND D.M. MUIR\textsuperscript{4}

ABSTRACT

Fundamental studies on the transformations of iron oxides have been carried out and related to the solution conditions in the Becher Process. The results show that a number of iron oxide interconversion reactions occur in the aeration reactor with the products depending on the pH, temperature and oxidation potential of the aeration liquor. It is concluded that the lack of process control in the aeration reactor of the Becher Process significantly hinders the ability to predict and produce high quality single phase iron oxides of a consistent colour.

1. INTRODUCTION

a) Background and development of the Becher Process

Since the introduction of the 'chloride' process in 1959 for making pigment grade titanium dioxide (TiO\textsubscript{2}), pigment producers have moved away from the conventional 'sulfate' process when considering the construction of new plants. In the 'sulfate' process (Henn and Barclay, 1970) ilmenite (FeTiO\textsubscript{3}) is pyro-roasted with concentrated sulfuric acid to form a solid sulfate cake which is then dissolved in dilute sulfuric acid and any Fe(III) in solution is reduced with scrap iron. Ferrous sulfate is partially crystallised out from the cooled solution as FeSO\textsubscript{4}.7H\textsubscript{2}O (coppers) whilst hydrous titanium dioxide is subsequently precipitated by hydrolysis of the Ti(IV) solution. The hydrous TiO\textsubscript{2} is finally calcined and conditioned to produce white pigment. The 'chloride' process (Ullmanns, 1979), on the other hand, is a vapour phase reaction in which either natural or synthetic rutile (TiO\textsubscript{2}) is chlorinated at high temperatures to form titanium tetrachloride vapour which is then fractionated from the FeCl\textsubscript{3} impurity and oxidised to white pigment.

The 'chloride' process not only offers a lower capital cost plant with a superior quality pigment product, but also eliminates the environmentally troublesome acidic ferrous sulfate effluent liquors associated with the 'sulfate' route.

Coupled with the increasing use of the 'chloride' process, there has been a world-wide increase in demand for rutile or a cheaper synthetic substitute. A synthetic rutile product can be produced from ilmenite by a variety of methods including the Benelite, Murao, Ishiihara, Becher and Summit Processes (Benelite Corp., 1974; Sinha and Waugh, 1971; Yamada, 1976; Becher et al., 1965; Shibli, 1966). All these processes involve firstly, partial or complete reduction of the iron oxidation state in the ilmenite crystal lattice by roasting with coal, followed by selective leaching of the iron with HCl, H\textsubscript{2}SO\textsubscript{4}, FeCl\textsubscript{3} or aerated water. These processes upgrade the TiO\textsubscript{2} content from around 55 percent in the ilmenite to around 92 percent in the synthetic rutile and ultimately reject the iron as an iron oxide by-product. Thus the problem of disposing of the waste iron from the ilmenite has shifted from the white pigment producer to the synthetic rutile producer, who is forced to pay greater attention to the disposal and nature of the iron oxide waste.

In Western Australia, the preferred method of upgrading ilmenite is the Becher Process which was first developed by the Western Australian Government Chemical Laboratory in 1961, and subsequently piloted and further developed by Western Titanium N.L. in conjunction with C.S.I.R.O. (Becher, 1963; Becher et al., 1965). Commercial production of synthetic rutile from the Becher Process started around 1969 at a rate of 10,000 tonnes/year and is now running at greater than 250,000 tonnes/year with output from Westralian Sands and Associated Minerals Consolidated at Capel and Narungga.

In the current process, outlined in Figure 1, the iron in the ilmenite is reduced to the metallic state with coal in a rotary kiln at around 1150°C. A small amount of sulfur or copperas is added to the charge along with the coal reductant to convert any manganese impurity to a mixed iron-manganese sulfide which is

SYNTHETIC RUTILE PRODUCTION - BECHER PROCESS

![Diagram of the Becher Process](image)

Figure 1

1Graduate Ph.D. Student, Murdoch University
2Graduate Research Assistant, Murdoch University
3Professor of Chemistry, Murdoch University
4Associate Professor of Mineral Science, Murdoch University, Murdoch 6150 Australia.

Recovery of by-product iron oxides from the upgrading of ilmenite to synthetic rutile

C.B. Ward B.Sc.(Hons.), Grad. R.A.C.I.
D.M. Muir B.Sc., Ph.D., F.R.A.C.I., F.Aus.I.M.M.
I.M. Ritchie M.A., Ph.D., F.R.A.C.I.
School of Mathematical and Physical Sciences, Murdoch University, Murdoch, Australia

SYNOPSIS
The current ilmenite upgrading processes are reviewed with emphasis on the Becher and Summit Processes and the conditions and relevant chemistry most suited to the production of various iron oxide by-products are considered.

Results of fundamental kinetic studies on the transformation of iron oxides are presented which are related to the solution conditions. These results show that a number of oxide interconversion reactions occur in the aeration reactor of the Becher Process. Changes in pH, temperature and oxidation potential significantly alter the product distribution of the iron oxide phases. The role of ferrous ions and of solution Eh on the transformation of different oxides is discussed with a mechanism proposed for the transformation reactions. It is concluded that the lack of process control in the aeration reactor of the Becher Process significantly hinders the ability to predict and produce single phase iron oxides which are necessary for high grade pigments. The Summit ferric chloride leaching process therefore offers better process control and the opportunity to produce high quality iron oxides. The results from preliminary leaching tests with FeCl₃ on fully reduced ilmenite and pure iron are presented.