TRACE ELEMENT REMOVAL TECHNIQUES WITH IRON OXYHYDROXIDES AND THE ADSORPTION/CO-PRECIPITATION REMOVAL MECHANISM

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A Thesis Presented for the Degree of Doctor of Philosophy

at

The University of Newcastle

School of Environmental and Life Sciences
The University of Newcastle
Callaghan, New South Wales
Australia

August, 2011
DECLARATION

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Suzanne Lisa Laucht
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title</td>
<td>i</td>
</tr>
<tr>
<td>Declaration</td>
<td>ii</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>xi</td>
</tr>
<tr>
<td>Abstract</td>
<td>xii</td>
</tr>
<tr>
<td>Publications</td>
<td>xv</td>
</tr>
<tr>
<td>Glossary of Abbreviations and Terms</td>
<td>xvi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xvii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xix</td>
</tr>
<tr>
<td>List of Images</td>
<td>xxviii</td>
</tr>
<tr>
<td>List of Plates</td>
<td>xxx</td>
</tr>
</tbody>
</table>

## CHAPTER ONE: INTRODUCTION

1.1 ASH WASTE WATER STORAGE AND FLY ASH CONSTITUENTS 1

1.2 FLY ASH EFFLUENT CONSTITUENTS AND TRACE ELEMENTS OF CONCERN TO THE ENVIRONMENT 5

1.3 TOXICITY AND WATER QUALITY GUIDELINES FOR SELENIUM AND TRACE ELEMENTS DISCHARGED TO ESTUARINE AQUATIC ENVIRONMENTS 8

1.3.1 Selenium 8
1.3.2 Arsenic 11
1.3.3 Vanadium 12
1.3.4 Chromium 13
1.3.5 Antimony 14
1.3.6 Aluminium 14
1.3.7 Molybdenum 16

1.4 BACKGROUND STUDIES OF TRACE ELEMENT (SELENIUM) INPUT INTO LAKE MACQUARIE NSW AND EFFECT ON AQUATIC FAUNA AND FLORA 16
<table>
<thead>
<tr>
<th>1.5</th>
<th>SUMMARY OF SELENIUM AND TRACE ELEMENT TREATMENT PROCESSES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5.1 Precipitation – Coagulation / Flocculation</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>1.5.2 Reverse Osmosis</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>1.5.3 Brine Concentrator</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>1.5.4 Ion Exchange</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>1.5.5 Constructed Wetlands</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>1.5.6 Bioreactors</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>1.5.7 Sirofloc</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>1.5.7 Metallic Iron</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1.6</th>
<th>INVESTIGATION OF ASH WATER TREATMENT PROCESSES FOR VALES POINT POWER STATION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>REMOVAL OF TRACE ELEMENTS WITH IRON OXIDES</td>
<td>33</td>
</tr>
<tr>
<td>1.8</td>
<td>AIMS AND RESEARCH OUTLINE</td>
<td>37</td>
</tr>
<tr>
<td>1.9</td>
<td>REFERENCES</td>
<td>38</td>
</tr>
</tbody>
</table>

CHAPTER TWO: IRON OXIDES: A BACKGROUND

<table>
<thead>
<tr>
<th>2.1</th>
<th>INTRODUCTION</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>CHARACTERISATION OF IRON OXIDES</td>
<td>46</td>
</tr>
<tr>
<td>2.2.1 Iron Oxide Formation and Transformation Pathways</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>2.2.2 Colour of Iron Oxides</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>2.2.3 Crystal Structures of Iron Oxides</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>2.2.3.1 Goethite</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>2.2.3.2 Lepidocrocite</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>2.2.3.3 Hematite</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>2.2.3.4 Magnetite</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>2.2.4 Iron Oxide Surface Area and Porosity</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>2.2.4.1 The Goethite Surface</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>2.2.4.2 The Lepidocrocite Surface</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>2.2.4.3 The Hematite Surface</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>2.2.4.4 The Magnetite Surface</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>2.2.5 X-Ray Diffraction Patterns of Iron Oxides</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>CO-PRECIPITATION/ADSORPTION OF IONS ON IRON OXIDES AND OXYHYDROXIDES</td>
<td>77</td>
</tr>
</tbody>
</table>
2.3.1 Adsorption, Co-precipitation and Mobility Isotherms 77
2.3.2 Anion Adsorption 79
2.3.3 Cation Absorption 81
2.3.4 Surface Complexation Models 83
2.3.5 Modes of Coordination 83

2.4 Sorption, Absorption and/or Coprecipitation of Trace Elements from Wastewater Utilising Iron Oxides and Oxyhydroxides 85
2.4.1 Selenium 85
2.4.2 Arsenic 94
2.4.3 Vanadium 99
2.4.4 Chromium 102
2.4.5 Antimony 105
2.4.6 Aluminium 106
2.4.7 Molybdenum 108

2.5 Kinetics and Efficiency of Trace Element Removal from Wastewater 111
2.5.1 Selenium 111
2.5.2 Arsenic 113
2.5.3 Vanadium 116
2.5.4 Chromium 117
2.5.5 Antimony 118
2.5.6 Aluminium 119
2.5.7 Molybdenum 120

2.6 Leachability of Trace Elements Absorbed/Coprecipitated with Iron Oxides and Oxyhydroxides 121

2.7 References 124

CHAPTER THREE: VALES POINT POWER STATION: Selenium and Trace Metal Reduction Pilot Plant Trials 133
3.1 Introduction 133
3.2 Vaales Point Power Station Ash Water Treatment: 2002 Pilot Plant Trial 136
3.2.1 Study Objectives 136
3.2.2 Pilot Plant Design and Materials 137
3.2.2.1 Design 137
### 3.2.2.2 Materials

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilot Plant Operating Conditions</td>
<td>139</td>
</tr>
<tr>
<td>Trial Process Observations</td>
<td>140</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>141</td>
</tr>
<tr>
<td>Selenium Removal Trial Results</td>
<td>141</td>
</tr>
<tr>
<td>Discussion</td>
<td>143</td>
</tr>
</tbody>
</table>

#### 3.3 VALES POINT POWER STATION ASH WATER TREATMENT: 2004/05 PILOT PLANT TRIAL

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Study Objectives</td>
<td>144</td>
</tr>
<tr>
<td>Pilot Plant Design and Materials</td>
<td>145</td>
</tr>
<tr>
<td>Design</td>
<td>145</td>
</tr>
<tr>
<td>Materials</td>
<td>147</td>
</tr>
<tr>
<td>Pilot Plant Operating Conditions</td>
<td>148</td>
</tr>
<tr>
<td>Trial Process Observations</td>
<td>151</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>152</td>
</tr>
<tr>
<td>Selenium</td>
<td>155</td>
</tr>
<tr>
<td>Arsenic</td>
<td>157</td>
</tr>
<tr>
<td>Antimony</td>
<td>159</td>
</tr>
<tr>
<td>Aluminium</td>
<td>161</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>162</td>
</tr>
<tr>
<td>Discussion</td>
<td>163</td>
</tr>
</tbody>
</table>

#### 3.4 VALES POINT POWER STATION ASH WATER TREATMENT: 2008 PILOT PLANT TRIAL

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Study Objectives</td>
<td>165</td>
</tr>
<tr>
<td>Pilot Plant Design and Materials</td>
<td>166</td>
</tr>
<tr>
<td>Design</td>
<td>167</td>
</tr>
<tr>
<td>Materials</td>
<td>168</td>
</tr>
<tr>
<td>Pilot Plant Operating Conditions</td>
<td>169</td>
</tr>
<tr>
<td>Trial Process Observations</td>
<td>170</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>170</td>
</tr>
<tr>
<td>Selenium</td>
<td>172</td>
</tr>
<tr>
<td>Arsenic</td>
<td>173</td>
</tr>
<tr>
<td>Antimony, Vanadium and Chromium</td>
<td>173</td>
</tr>
<tr>
<td>Molybdenum and Aluminium</td>
<td>175</td>
</tr>
<tr>
<td>Discussion</td>
<td>176</td>
</tr>
</tbody>
</table>

#### 3.5 FORMATION OF IRON OXIDES AND OXYHYDROXIDES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>177</td>
</tr>
</tbody>
</table>
3.6 CONCLUSIONS

3.7 REFERENCES

CHAPTER FOUR: LEACHABILITY STUDIES

4.1 INTRODUCTION

4.2 LEACHABILITY EXPERIMENTS ON STORED CORROSION PRODUCTS

4.2.1 Samples Stored in Ash Water

4.2.1.1 Results

4.2.1.2 Discussion

4.2.2 Samples Stored in Demineralised Water

4.2.2.1 Results

4.2.2.2 Discussion

4.2.3 Samples Stored in Domestic Water

4.2.3.1 Results

4.2.3.2 Discussion

4.3 LEACHATE OF CORROSION PRODUCTS STORED IN PILOT PLANT TROUGHS

4.3.1 TCLP Leachate Analysis

4.3.1.1 Results

4.3.1.2 Discussion

4.4 CONCLUSIONS

4.5 REFERENCES

CHAPTER FIVE: CHARACTERISATION OF SYNTHETIC IRON OXIDES AND OXYHYDROXIDES AND APPLICATION IN TRACE ELEMENT REMOVAL

5.1 INTRODUCTION

5.2 SYNTHESES AND CHARACTERISATION STUDIES OF
IRON OXIDES AND OXYHYDROXIDES

5.2.1 Iron Oxides and Oxyhydroxides Procured and Synthesised for Laboratory Trials

5.2.1.1 Goethite
5.2.1.2 Lepidocrocite
5.2.1.3 Hematite
5.2.1.4 Magnetite

5.2.2 Iron Oxide and Oxyhydroxide Colours

5.2.2.1 Goethite
5.2.2.2 Lepidocrocite
5.2.2.3 Hematite
5.2.2.4 Magnetite
5.2.2.5 Pilot Plant Iron Oxide Samples

5.2.3 Structure Identification with X-ray Diffraction and Scanning Electron Microscope Imaging

5.2.3.1 Pilot Plant Oxide Sample 1
5.2.3.2 Pilot Plant Oxide Sample 2
5.2.3.3 Pilot Plant Oxide Sample 3
5.2.3.4 Pilot Plant Oxide Sample 4
5.2.3.5 Synthetic Goethite
5.2.3.6 Lepidocrocite
5.2.3.7 Synthetic Hematite
5.2.3.8 Magnetite
5.2.3.9 Discussion

5.2.4 Surface Area and Porosity of Iron Oxides and Oxyhydroxides

5.2.4.1 Adsorption Isotherms
5.2.4.2 Cumulative and Incremental Volume
5.2.4.3 Cumulative and Incremental Area
5.2.4.4 Discussion

5.3 LABORATORY TRIALS OF TRACE METAL ADSORPTION AND/OR COPRECIPITATION

5.4.1 Removal of Trace Metals with Iron Oxides and Oxyhydroxides in Variant Matrices and Solution pH

5.3.1.1 Selenium Adsorption/Co-precipitation

5.3.1.1.1 Selenium Removal with Goethite
5.3.1.1.2 Selenium Removal with Hematite
5.3.1.3  Selenium Removal with Lepidocrocite  248

5.3.1.4  Selenium Removal with Magnetite  249
5.3.1.5  Discussion  251

5.3.1.2  Arsenic Adsorption/Co-precipitation  251
  5.3.1.2.1  Arsenic Removal with Goethite  252
  5.3.1.2.2  Arsenic Removal with Hematite  253
  5.3.1.2.3  Arsenic Removal with Magnetite  254
  5.3.1.2.4  Discussion  254

5.3.1.3  Vanadium Adsorption/Co-precipitation  255
  5.3.1.3.1  Vanadium Removal with Goethite  255
  5.3.1.3.2  Vanadium Removal with Hematite  256
  5.3.1.3.3  Vanadium Removal with Magnetite  256
  5.3.1.3.4  Discussion  257

5.3.1.4  Chromium Adsorption/Co-precipitation  258
  5.3.1.4.1  Chromium Removal with Goethite  258
  5.3.1.4.2  Chromium Removal with Hematite  259
  5.3.1.4.3  Chromium Removal with Magnetite  260
  5.3.1.4.4  Discussion  261

5.3.1.5  Antimony Adsorption/Co-precipitation  261
  5.3.1.5.1  Antimony Removal with Goethite  261
  5.3.1.5.2  Antimony Removal with Hematite  262
  5.3.1.5.3  Antimony Removal with Magnetite  263
  5.3.1.5.4  Discussion  264

5.3.1.6  Aluminium Adsorption/Co-precipitation  264
  5.3.1.6.1  Aluminium Removal with Goethite  265
  5.3.1.6.2  Aluminium Removal with Hematite  266
  5.3.1.6.3  Aluminium Removal with Magnetite  267
  5.3.1.6.4  Discussion  268

5.3.1.7  Molybdenum Adsorption/Co-precipitation  269
  5.3.1.7.1  Molybdenum Removal with Goethite  269
  5.3.1.7.2  Molybdenum Removal with Hematite  270
  5.3.1.7.3  Molybdenum Removal with Magnetite  271
  5.3.1.7.4  Discussion  272

5.3.1.8  Comparison of Vales Point Ash Water Trace Metal Removal by Iron Oxides and Oxyhydroxides  273
  5.3.1.8.1  Removal with Goethite  273
5.4 KINETICS AND EFFICIENCY OF TRACE ELEMENT REMOVAL WITH SYNTHETIC IRON OXIDES AND OXYHYDROXIDES

5.4.1 Trace Element Removal Rates in Laboratory Trials with Synthetic Iron Oxides and Oxyhydroxides

5.4.1.1 Selenium
5.4.1.2 Arsenic
5.4.1.3 Vanadium
5.4.1.4 Chromium
5.4.1.5 Antimony
5.4.1.6 Aluminium
5.4.1.7 Molybdenum
5.4.1.8 Concluding Remarks on Reaction Kinetics

5.5 REFERENCES

CHAPTER SIX: SUMMARY AND CONCLUSIONS

6.1 REFERENCES

ATTACHMENT 1 – VALES POINT PILOT PLANT TEST RESULTS

ATTACHMENT 2 – VALES POINT PILOT PLANT CORROSION PRODUCT LEACHATE TEST RESULTS

ATTACHMENT 3 – UNIVERSITY OF NEWCASTLE LABORATORY TRIAL TEST RESULTS

*Note all attachments provided on CD as electronic copies
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To my son Kyle I dedicate this thesis to you love mum.

ABSTRACT

The environmental impact of trace elements, in particular selenium in the selenite form, from discharge of ash dam water from Vales Point Power Station into Wyee Bay on Lake Macquarie New South Wales Australia is of concern, and has been the subject of a number of scientific investigations. These include both control of discharge and studies of effects on aquatic flora and fauna including the biomagnification or bioaccumulation and biotransference of selenium in fish and benthic organisms. Cost-effective and efficient chemical control of trace elements discharged to the environment is at the core of this study.

Measures to control the quantity and quality of ash water discharges from Vales Point Power Station has been proactively managed by the electricity generation industry over the past decade in the form of plant modifications and reduction in catchment inflows. Studies have been undertaken looking at a range of treatment options inclusive of precipitation (coagulation/flocculation), bioreactors and oxidised metallic iron. The latter treatment and sole focus of this thesis has been found to be potentially the most viable treatment option owing to its high efficiency of removal of selenium and other trace elements including arsenic, vanadium, antimony, chromium and to a lesser extent aluminium and molybdenum. Metallic iron was found to be the most viable treatment option owing to its availability, low cost and minimum operating and maintenance requirements.

Pilot plant investigations undertaken at Vales Point Power Station from 2002 to 2008 exploring the use of a number of iron products including iron bars, steel plates and steel wool revealed that the iron oxides and oxyhydroxides formed on the surface of metallic iron and responsible for the core processes of adsorption and coprecipitation of selenium and targeted trace elements were goethite, lepidocrocite, hematite and magnetite. Characterisation of these iron oxides and oxyhydroxides formed by the pilot plant employed X-Ray Diffraction and Scanning Electron Microscope Imagery, involving comparisons with synthetic samples.
The efficiency of selenium and trace element removal was found to be influenced by a number of parameters inclusive of surface area of metallic iron, crystal structure and surface area of iron oxides and oxyhydroxides formed on the iron surface, pH, solution matrix and concentration of targeted trace elements in ash water. Pilot plant test results with loosely packed steel wool over a six month period yielded the highest efficiency of removal owing to its high surface area with selenium reduced by 85% (on average), arsenic by 87%, antimony by 87%, chromium by 80%, vanadium by 97%, aluminium by 21% and molybdenum by 48%.

Adsorbed ions are generally not leached under natural environmental conditions over extended periods of time. Leachate studies of oxidised material from pilot plant operations were performed during 2003-2004. Samples stored with ash water over extended periods exhibited very little redissolution in the case of selenium, arsenic, antimony and aluminium with some test results indicating only 1% redissolution back into solution. Molybdenum was the only trace element that did display limited leaching with final levels being two to three times that in the initial ash water. Further studies in 2007 and 2008 by the USEPA Method 1311 leaching procedure provided no detectable levels of selenium, arsenic, antimony, chromium, vanadium and molybdenum. The only element which had modest levels above the detection limit was aluminium.

The surface area measured for synthetic/commercial samples of iron oxides and oxyhydroxides of goethite, hematite, lepidocrocite and magnetite differed, and influenced removal efficiency. Test results of laboratory trials with solution matrices of demineralised water, sodium sulphate solution, sodium chloride solution and ash water yielded overall efficiency of removal of selenite with each oxide in the following order: lepidocrocite > goethite > hematite > magnetite.

During laboratory trials at pH 8 and above, all systems displayed the following efficiency of removal of selenite in terms of the matrix of the solution: ash water > sodium chloride solution > sodium sulphate solution > demineralised water. This is an important aspect as the pH of Vales Point Power Station ash water fluctuated between 7.5 and 8.5 in the pilot plant trials, whereby high efficiency of trace element removal was achievable.
The rate profiles during laboratory trials for selenium, arsenic, chromium, vanadium, antimony, aluminium and molybdenum revealed that, overall, these trace elements were very rapidly adsorbed with the observed half-life of the initial process being in the order of one to two minutes. This rapid uptake highlights the benefits of this process, which can successfully deal with large flowing volumes for extended periods without reaching uptake capacity.

Overall, this research has exposed mechanistic aspects of the chemistry involved in iron-based trace element removal, and highlighted the beneficial nature of the process as being a highly efficient low-cost option for the treatment of process water (ash water) in high salinity or estuarine waters for the removal of trace elements of concern to the receiving environment such as selenium and arsenic.
PUBLICATIONS


# GLOSSARY OF ABBREVIATIONS AND TERMS

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
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<tr>
<td>AF</td>
<td>Affectation Factor</td>
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<tr>
<td>AIP</td>
<td>Aqueous-ion activity product</td>
</tr>
<tr>
<td>ALS</td>
<td>Australian Laboratory Services</td>
</tr>
<tr>
<td>ANZECC</td>
<td>Australian and New Zealand Environment Conservation Council</td>
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<tr>
<td>BC</td>
<td>Brine Concentrator</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller method</td>
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<tr>
<td>ccp</td>
<td>Cubic close packing</td>
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<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific Industrial Research Organisation</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DL</td>
<td>Detection Limit</td>
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<td>DLM</td>
<td>Double Layer Model</td>
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<td>ECL</td>
<td>Environmental Concern Level</td>
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<td>EGME</td>
<td>Ethylene Glycol Monoethylether Technique</td>
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<tr>
<td>EPRI</td>
<td>Electric Power Research Institute of the United States of America</td>
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<tr>
<td>EXAFS</td>
<td>X-ray Absorption Fine Structure</td>
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<td>hcp</td>
<td>Hexagonal close packing</td>
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<td>HDPE</td>
<td>High Density Polyethylene</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma-Atomic Emission Spectroscopy</td>
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<tr>
<td>iep</td>
<td>Ion Exchange Potential</td>
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<tr>
<td>LC50</td>
<td>Lowest concentration of a toxicant that kills all the test organisms</td>
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<tr>
<td>m²/g</td>
<td>Meter Square per Gram</td>
</tr>
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<td>mg/kg</td>
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</tr>
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<td>µg/L</td>
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</tr>
<tr>
<td>NZVI</td>
<td>Nano Zero-Valent Iron</td>
</tr>
<tr>
<td>NHMRC</td>
<td>National Health and Medical Research Council</td>
</tr>
<tr>
<td>NIPDWS</td>
<td>National Interim Primary Drinking Water Standards</td>
</tr>
<tr>
<td>ORC-ICPMS</td>
<td>Octopole Reactive Cell Inductively Coupled Plasma Mass Spectrometer</td>
</tr>
<tr>
<td>pcz</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>PQL</td>
<td>Practical Quantitation Limit</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SeO₃²⁻</td>
<td>Selenite</td>
</tr>
<tr>
<td>SeO₄²⁻</td>
<td>Selenate</td>
</tr>
<tr>
<td>SRB</td>
<td>Sulfate reducing bacteria</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TCLP</td>
<td>Toxicity Character Leaching Procedure</td>
</tr>
<tr>
<td>TLM</td>
<td>Triple Layer Model</td>
</tr>
</tbody>
</table>

**Trigger Values**

These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>Introduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Analysis of fly ash samples from five USA power plants.</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Vales Point Power Station fly ash analytical data.</td>
</tr>
<tr>
<td>Table 1.3</td>
<td>Ash pond water chemistry characterisation.</td>
</tr>
<tr>
<td>Table 1.4</td>
<td>Vales Point Power Station ash water analysis 24&lt;sup&gt;th&lt;/sup&gt; July 2008.</td>
</tr>
<tr>
<td>Table 1.5</td>
<td>Selenium reduction efficiencies with metallic iron powder as reported by Baldwin and co-workers. (Initial Se concentration was 0.440 mg/L).</td>
</tr>
<tr>
<td>Table 1.6</td>
<td>Reduction of selenate by elemental iron; time and pH dependence.</td>
</tr>
<tr>
<td>Table 1.7</td>
<td>Change in pH during oxidation of iron metal.</td>
</tr>
<tr>
<td>Table 1.8</td>
<td>Analysis of feed and exit solutions from a steel wool-packed column.</td>
</tr>
<tr>
<td>Table 1.9</td>
<td>The Iron Oxides and their General Properties.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Iron Oxides: A Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>The major iron oxides and oxyhydroxides.</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Conditions for the predominance of one compound in various competing pairs of oxides formed via oxidation of Fe&lt;sup&gt;2+&lt;/sup&gt; salts at pH 4 to 9.</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Typical ranges of surface areas of synthetic iron oxides.</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Surface area of cubic and spherical hematites.</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>X-ray powder diffraction data for iron oxides and oxyhydroxides.</td>
</tr>
<tr>
<td>Table 2.6</td>
<td>Parameters of the Langmuir isotherm obtained for Se(VI) and Se(IV) sorption on hematite and goethite at pH 4.</td>
</tr>
<tr>
<td>Table 2.7</td>
<td>Parameters of the Langmuir isotherm obtained for Se(VI) and Se(IV) sorption on magnetite at pH 4.</td>
</tr>
<tr>
<td>Table 2.8</td>
<td>Speciation of As(III) and As(V) and treated with iron oxides.</td>
</tr>
<tr>
<td>Table 2.9</td>
<td>Parameters of the Langmuir isotherm determined for antimony adsorption on goethite by Martinez-Lladó &lt;i&gt;et al.&lt;/i&gt; (2008).</td>
</tr>
<tr>
<td>Table 2.10</td>
<td>Initial and final solute concentrations and pH for 5mM Al(III) and 3 mM Fe(III); final concentration corresponds to 450 h reaction time.</td>
</tr>
<tr>
<td>Table 2.11</td>
<td>Recovery of molybdenum from sea water (for 6 µg Mo added to 300 mL of sea water; ambient temperature).</td>
</tr>
<tr>
<td>Table 2.12</td>
<td>Kinetics of selenite/selenate adsorption onto iron oxides, fitted to a pseudo-second order rate equation.</td>
</tr>
<tr>
<td>Table 2.13</td>
<td>Pseudo-first-order rate constant (k) and half-life (t&lt;sub&gt;1/2&lt;/sub&gt;) for arsenic adsorption on iron.</td>
</tr>
</tbody>
</table>
Chapter 3  Vales Point Power Station: Selenium and Trace Metal Reduction Pilot Plant Trials

Table 3.1  Total selenium test results in $\mu$g/L at the inlet and outlet of the pilot plant.  
Table 3.2  Pilot Plant 2004/05 measured operating conditions.  
Table 3.3  Weights of pilot plant steel plates at commencement and during trials.  
Table 3.4  Pilot plant trace metal analysis for samples from the inlet and outlet. Independent duplicate determinations, designated as (a) and (b), are shown.  
Table 3.5  Selenium and arsenic analytical test results at various pilot plant sites. The surface area of steel passed up to the various sites is also given in the final column.  
Table 3.6  Trace element removal levels with solid steel in the pilot plant.  
Table 3.7  Trace metal analysis of samples taken at points throughout the pilot plant.  
Table 3.8  Trace element depletion in the pilot plant containing steel wool.  
Table 3.9  Iron oxides and oxyhydroxides detected in corroded steel plate and hanger bar surfaces with XRD.  

Chapter 4  Leachability Studies

Table 4.1  Pilot plant corrosion products collected on 11/3/2004.  
Table 4.2  The pH values and conductivities of sludge storage solutions sampled after one year of storage.  
Table 4.3  The pH values and conductivities of sludge storage solutions sampled after one year of storage.  
Table 4.4  Analytical results for leachate samples collected after one year from jar experiments on sludge corrosion products. Results for both initial still solution samples and shaken solution samples are reported. Ash water used as a solution for half the studies carried low levels of elements targeted, and these values are reported at the top of the table below.  
Table 4.5  Percentage reduction/increase of trace elements in the added water over the storage period, for samples stored in ash water.  
Table 4.6  Final concentrations of trace elements leached from oxide sludge into demineralised water over a 12 month period.  
Table 4.7  Concentration of trace elements leached from the sludge/corrosion product into domestic (tap) water.  
Table 4.8  Trace element (Se, As, Sb, Cr, V, Al and Mo) analytical test results in mg/L from Vales Point Pilot Plant sludge samples obtained on 15/12/2007.  
Table 4.9  Trace element (Se, As, Sb, Cr, V, Al and Mo) analytical test results in mg/L from Vales Point Pilot Plant sludge samples obtained on 1/8/2008.
Chapter 5  Characterisation of Synthetic Iron Oxides and Oxyhydroxides and Application in Trace Element Removal

Table 5.1   XRD qualitative analysis of Sample 1. 219
Table 5.2   XRD qualitative analysis of Sample 2. 222
Table 5.3   XRD qualitative analysis of Sample 3. 223
Table 5.4   XRD qualitative analysis of Sample 4. 226
Table 5.5   XRD qualitative analysis of laboratory synthesised goethite. 227
Table 5.6   XRD qualitative analysis of laboratory-synthesised lepidocrocite. 229
Table 5.7   XRD qualitative analysis of commercial grade hematite. 231
Table 5.8   XRD qualitative analysis of commercial grade magnetite. 232
Table 5.9   Surface areas of synthetic goethite, magnetite, hematite and lepidocrocite. 238
Table 5.10  Laboratory trial matrices employed for studies of the removal of trace elements Se, As, V, Cr, Sb, Al and Mo. 241
Table 5.11  Trace Metal Standard Solution Specifications and Ash Water Trace Metal Analysis. 242
Table 5.12  Trace metal limits of reporting for analysis by ALS with ORC-ICPMS. 243

Chapter 6  Summary and Conclusion

Table 6.1   Characteristics of dominant iron oxides and oxyhydroxides formed on metallic iron in ash water. 292
Table 6.2   Summary of sorption data for Se, As, Cr, V, Sb, Al and Mo on goethite, hematite, lepidocrocite and magnetite. 293
Table 6.3   Reaction kinetic studies for Se, As, Cr, V, Sb, Al and Mo on goethite, hematite, lepidocrocite and magnetite. 294
Table 6.4   Surface areas of goethite, hematite, lepidocrocite and magnetite (m²/g). 297

LIST OF FIGURES

Chapter 1  Introduction

Figure 1.1  Lake Macquarie, New South Wales. [Numbers refer to sampling sites used in the CSIRO study [1] Wyee Bay and Mannering Bay, [2] Bonnells Bay, [3] Pipers Point [4], Myuna Bay [5], Marks Point [6], Crangan Bay [7] and Chain Valley Bay.] 18
Chapter 2  Iron Oxides: A Background

Figure 2.1  Schematic representation of formation and transformation pathways of common iron oxides together with the approximate transformation conditions.  

Figure 2.2  Structure of Goethite.  

Figure 2.3  Crystal forms of goethite.  

Figure 2.4  Structure of Lepidocrocite.  

Figure 2.5  Predominant crystal form of lepidocrocite.  

Figure 2.6  A view of the structure of hematite.  

Figure 2.7  Crystal forms of platy (left) and rhombohedral (right) hematite.  

Figure 2.8  Structure of magnetite, as a polyhedral model with alternating octahedra and tetrahedra-octahedra layers.  

Figure 2.9  Crystal forms of magnetite a) and c) octahedron, b) rhombodecahedron and d) twin.  

Figure 2.10  N₂ adsorption isotherms of several goethite synthesised at various temperatures (left) and the resultant BET plots (right).  

Figure 2.11  Standard gas adsorption isotherms, with type IV and V possessing a hysteresis loop with the lower representing adsorption and upper desorption.  

Figure 2.12  Comparison of four different methods for surface area determination using 30 synthetic hematites.  

Figure 2.13  Example X-ray powder diffraction patterns of Fe²⁺ oxides.  

Figure 2.14  Mobility isotherms of various retention modes.  

Figure 2.15  The effect of pH on the adsorption of some heavy metal cations on goethite and hematite, showing the typical adsorption edge for heavy metals.  

Figure 2.16  Modes of ligand coordination to the iron oxide surface and modes of coordination through COOH groups.  

Figure 2.17  Surface complex of octahedrally coordinated Cd on a) goethite and; b) lepidocrocite.  

Figure 2.18  Sorption isotherms for goethite and hematite for (a) Selenite and (b) Selenate 0.1 g of solid and pH 4.  

Figure 2.19  Sorption of selenium on (■) goethite, and (▲) hematite as a function of equilibrium pH with 5 g dm⁻³ of solid and \{Se\}_0 = 10^{-5} \text{ mol dm}^{-3} \text{ (a) selenite, (b) selenate.}  

Figure 2.20  Sorbed amount of selenite versus pH (\{Se\} = 4 \times 10^{-4} \text{ M}) for two ionic strengths: NaNO₃ 0.01 M (hollow squares) and 0.1 M (filled squares).
Figure 2.21 Isotherm for the sorption of selenite ions onto hematite: experimental values at pH 3 (○) and pH 4 (□) fitted by Tempkin equation.

Figure 2.22 Model of Se(IV) surface complexes on the hematite [100] face.

Figure 2.23 Adsorption of selenite as a function of equilibrium pH.
Selenite = 3.79 µmol and adsorbent = 250 mg/L. 1, 2, 3, 4 and 5 are the α-FeOOH (goethite), β-FeOOH (akaganeite), γ-FeOOH (lepidocrocite), δ-FeOOH (feroxyhyte) and ferricydrate respectively.

Figure 2.24 Adsorption of selenite as a function adsorbent concentration.
1, 2, 3, 4 and 5 are the α-FeOOH (goethite), β-FeOOH (akaganeite), γ-FeOOH (lepidocrocite), δ-FeOOH (feroxyhyte) and ferricydrate respectively.

Figure 2.25 Sorption isotherm for Se(IV) and Se(VI) 0.1g of magnetite at pH 4.

Figure 2.26 Sorption of selenium on magnetite as a function of pH. The experiment used 0.1g of magnetite and [Se]₀ = 2 x 10⁻⁵ mol dm⁻³.

Figure 2.27 Adsorption of As(III) on NZVI Fe as a function of pH. Reaction conditions: 1.0 mg L⁻¹ As(III) adsorbed on 1.0 g L⁻¹ NZVI in 0.01 M NaCl; reaction time 12 h; ambient pH 6.5 with adjustment with 1 M HCl or NaOH.

Figure 2.28 Removal ratios of arsenic compounds in 4 h as a function of initial pH value in unsealed and sealed systems. Reactors contained 25 g/L ZVI with [As] = 500 µg/L.

Figure 2.29 Eh-pH diagram for aqueous vanadium species in the system V-O-H [V]total = 5 x 10⁻⁵ m (~2.5ppm), where no polymer species are stable.

Figure 2.30 Adsorption of vanadium ions on goethite at I = 0.1 NaNO₃ at 25°C and 144 hours equilibrium time.

Figure 2.31 Multiple scattering configuration model used in EXAFS fits for vanadium(V) sorbed to goethite.

Figure 2.32 Models of O adsorption on V/Fe-hematite (a) 1/3 ML O on 0.5 ML V, (b) 1 ML O on 0.5 ML V, (c) 1/3 ML O on 1 ML (Vₓ, Vᵧ), (d) 1 ML O on 1 ML (Vₓ, Vᵧ).

Figure 2.33 Models of O adsorption on V/O₃-hematite (a) 1/3 ML O on 0.5 ML V, (b) 1/3 ML O on 1 ML V, (c) 1 ML O on 1 ML V.

Figure 2.34 Adsorption of Cr(III) (50 ppm) with amorphous iron(III) oxide (250 ppm) alone and with either 50 ppm Ni(II), 50 ppm Zn(II), or both 50 ppm Ni(II) and 50 ppm Zn(II) in combination.

Figure 2.35 Coprecipitation of Cr(III) (50 ppm) with amorphous iron (III) oxide (250 ppm) alone and with either 50 ppm nickel(II), 50 ppm zinc(II), or both 50 ppm nickel(II) and 50 ppm zinc(II).

Figure 2.36 The pE-pH diagram for chromium, based on equilibrium constants.

Figure 2.37 Solution concentrations of Al, Cu and Zn as a function of pH following adsorption onto iron.

Figure 2.38 Molybdenum adsorption with iron(III) hydroxide as a function
Figure 2.39  Molybdenum adsorption isotherms for kaolinite, showing a better fit to the Freundlich equation.

Figure 2.40  Adsorption of selenite with time on α-FeOOH (goethite) and δ-FeOOH (feroxyhyte) (1) [selenite] = 6.8 µmol, δ-FeOOH = 500 mg/L; (2) and (3) [selenite] = 2.53 µmol, α-FeOOH = 250 mg/L.

Figure 2.41  Variation of selenium sorbed onto magnetite with contact time.

Figure 2.42  Effect of dissolved oxygen on arsenic removal by Fe (0). {As(III) and As(V) = 100 mg/L; Fe (0) content = 1 g/L (100 mesh); pH 6}.

Figure 2.43  Removal of As(V) by Fe(0) at various pH: As(V) = 100 mg/L; Fe(0) content = 1 g/L (100 mesh); pH 4 for Se(IV) and pH 6 for Se(VI).

Figure 2.44  Removal of arsenic compounds by zero valent iron ZVI as a function of time. Reactions carried out with 0.1 g of magnetite and [Se]₀ = 3 x 10⁻⁵ M at pH 4 for Se(IV) and pH 6 for Se(VI).

Figure 2.45  Effect of contact time on the uptake of vanadium on metal sludge adsorbent temperature 25°C.

Figure 2.46  Metal profiles over time on a test column containing zero-valent iron.

Figure 2.47  The time-dependent profile for the oxidation of Cr(III) to Cr(VI) and adsorption on Mn-goethite as a function of time.

Figure 2.48  SV(V) sorption on goethite as a function of time.

Figure 2.49  Pseudo-second order kinetic rate equation for SV(V)-goethite data shown in the above figure, calculated at three temperatures.

Figure 2.50  Changes in metal concentration with time for adsorption on Peerless iron at (a) initial pH 2.3 and (b) initial pH 4.5.

Figure 2.51  Metal profiles over time on a test column containing zero-valent iron.

Chapter 3 Vales Point Power Station: Selenium and Trace Metal Reduction Pilot Plant Trials

Figure 3.1   Top down schematic of pilot plant fabric filter hanger bars.

Figure 3.2   Trial 1 selenium removed (µg/L) versus flow rate (L/sec); 98 m² iron surface was employed.

Figure 3.3 Trial 1 selenium inlet and outlet concentration trends; 98 m² iron surface.

Figure 3.4 Trial 2 selenium removed (µg/L) versus flow rate (L/sec); 140 m² iron surface was employed.

Figure 3.5 Trial 2 selenium inlet and outlet concentration trends; 140 m² iron surface.

Figure 3.6 Top down schematic of pilot plant fabric filter hanger bars.

Figure 3.7 Trial 3 selenium removed (µg/L) versus flow rate (L/sec); 98 m² iron surface was employed.

Table 3.1  Sorption capacity of different adsorbents for different elements.

Table 3.2  Properties of different adsorbents.

Table 3.3  Comparison of sorption capacity of different adsorbents for different elements.

Table 3.4  Comparison of properties of different adsorbents.
Figure 3.6  Top down schematic of pilot plant steel plates and ash water flow.

Figure 3.7  Percentage of total selenium removed versus flow rate.
Figure 3.8  Variation in the Pilot Plant 2004/05 measured operating conditions.
Figure 3.9  Percentage of selenium and arsenic removed versus area of steel (iron oxide) accessed during passage through the pilot plant.
Figure 3.10 Pilot plant total selenium inlet and outlet analysis (µg/L).
Figure 3.11 Percentage of selenium removed and variation in pH in the pilot plant plotted versus sampling date.
Figure 3.12 Total arsenic analysis (µg/L) for inlet (blue) and outlet (red) of the pilot plant determined at various dates throughout the study. Further, average % reduction in arsenic is shown in yellow.
Figure 3.13 The average percentage reduction in arsenic (green) and variation in ash water pH (orange) throughout the pilot plant trial.
Figure 3.14 Analysis (µg/L) of total antimony at inlet (dark blue) and outlet (pale blue) in the pilot plant across the test period, as well as average percentage antimony reduction (red).
Figure 3.15 Analysis results of total aluminium (µg/L) at the pilot plant inlet and outlet. The dark blue line represents the concentration of aluminium for the average of duplicate samples from the inlet and the red line for the average of duplicate samples from the discharge outlet. Average percentage reduction (in red) and the trend line (in black) are also shown.
Figure 3.16 Analysis results of total molybdenum (µg/L) at the pilot plant inlet and outlet. The dark blue line represents the concentration of molybdenum for the average of duplicate samples from the inlet and the red line for the average of duplicate samples from the discharge outlet. Average percentage reduction (in red) and the trend line (in black) are also shown.
Figure 3.17 Top-down schematic of a pilot plant trough fitted with steel plates and steel wool. The enforced flow path is also depicted.
Figure 3.18 Top-down schematic of third pilot plant trough containing ‘porous’ stainless steel plates and steel wool.
Figure 3.19 Selenium inlet and outlet analyses (µg/L) over time for the pilot plant containing oxidised steel wool.
Figure 3.20 Arsenic inlet and outlet analyses (µg/L) over time for the pilot plant containing oxidised steel wool.
Figure 3.21 Vanadium (red), antimony (green) and chromium (blue) inlet (solid lines) and outlet (dashed lines) analyses (µg/L) over time for the pilot plant containing oxidised steel wool.
Figure 3.22 Molybdenum (black), and aluminium (blue) inlet (solid lines) and outlet (dashed lines) analyses (µg/L) over time for the pilot plant containing oxidised steel wool.
Chapter 4  Leachability Studies

Figure 4.1  Final selenium concentrations (µg/L) in jar ash water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.2  Final arsenic concentrations (µg/L) in jar ash water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.3  Final antimony concentrations (µg/L) in jar ash water. Results for still and shaken, the later indicated by (S), samples are given.  

Figure 4.4  Final molybdenum concentrations (µg/L) in jar ash water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.5  Final aluminium concentrations (µg/L) in jar ash water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.6  Final selenium concentrations (µg/L) in jar demineralised water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.7  Final arsenic concentrations (µg/L) in jar demineralised water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.8  Final antimony concentrations (µg/L) in jar demineralised water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.9  Final molybdenum concentrations (µg/L) in jar demineralised water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.10  Final aluminium concentrations (µg/L) in jar demineralised water. Results for still and shaken samples, the later indicated by (S), are given.  

Figure 4.11  Total selenium, arsenic, antimony and aluminium concentrations (µg/L) in jar domestic water.

Chapter 5  Characterisation of Synthetic Iron Oxides and Oxyhydroxides and Application in Trace Element Removal

Figure 5.1  Equipment for lepidocrocite synthesis: (1) inlet for base addition; (2) glass electrode attached to a pH meter; (3) reaction beaker; (4) magnetic stirrer; (5) magnetic stirrer bar; (6) porous ceramic block for air entry and diffusion; (7) thermometer.  

Figure 5.2  XRD scan for Sample 1, which contains dominantly magnetite.  

Figure 5.3  XRD scan for Sample 2, containing magnetite as dominant the species. In this case, semi-dominant species are apparent, compared with the result for Sample 1.
Figure 5.4  XRD scan for Sample 3, containing goethite, magnetite and lepidocrocite.

Figure 5.5  XRD scan for Sample 4, containing lepidocrocite as the major constituent.

Figure 5.6  XRD scan for a sample of the laboratory-synthesised goethite.

Figure 5.7  XRD scan for a sample of laboratory-synthesised lepidocrocite.

Figure 5.8  XRD scan for a sample of commercial synthetic hematite.

Figure 5.9  XRD scan for a sample containing commercial synthetic magnetite.

Figure 5.10  Linear adsorption isotherms for nitrogen gas adsorption on goethite, hematite, magnetite and lepidocrocite.

Figure 5.11  Logarithmic adsorption isotherms of goethite, hematite, magnetite and lepidocrocite.

Figure 5.12  Cumulative volume (g/m³) as a function of pore size (Å) for goethite, hematite, magnetite and lepidocrocite.

Figure 5.13  Incremental volume (g/m³) as a function of pore size (Å) for goethite, hematite, magnetite and lepidocrocite.

Figure 5.14  Cumulative area (m²/g) as a function of pore size (Å) for goethite, hematite, magnetite and lepidocrocite.

Figure 5.15  Incremental area (m²/g) as a function of pore size (Å) for goethite, hematite, magnetite and lepidocrocite.

Figure 5.16  Selenite removal trends with 1 g of goethite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.17  Selenite removal trends with 5 g of goethite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.18  Selenite removal trends with 1 g of hematite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.19  Selenite removal trends with 5 g of hematite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.20  Selenite removal trends with 1 g of lepidocrocite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.21  Selenite removal trends with 1 g of lepidocrocite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown. In this figure, the highest selenite concentration in
demineralised water at pH 9 of 56 µg/L has been removed to enhance trends below 4 µg/L.

Figure 5.22  Selenite removal trends with 1 g of magnetite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.23  Selenite removal trends with 5 g of magnetite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.24  Arsenic removal trends with 5 g of goethite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.25  Arsenic removal trends with 5 g of hematite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.26  Arsenic removal trends with 5 g of magnetite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual concentrations are shown.

Figure 5.27  Vanadium removal trends with 5 g of goethite in solutions of demineralised water, sodium sulfate, sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.28  Vanadium removal trends with 5 g of hematite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.29  Vanadium removal trends with 5 g of magnetite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.30  Chromium(III) removal trends with 5 g of goethite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.31  Chromium(III) removal trends with 5 g of hematite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.

Figure 5.32  Chromium(III) removal trends with 5 g of magnetite in solutions of demineralised water, aqueous sodium sulfate, aqueous sodium chloride and Vales Point ash water. Residual solution concentrations are shown.
Figure 5.33  Antimony removal trends with 5 g of goethite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.34  Antimony removal trends with 5 g of hematite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.35  Antimony removal trends with 5 g of magnetite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.36  Aluminium removal trends with 5 g of goethite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.37  Aluminium removal trends with 5 g of hematite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.38  Aluminium removal trends with 5 g of magnetite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.39  Molybdenum removal trends with 5 g of goethite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.40  Molybdenum removal trends with 5 g of hematite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.41  Molybdenum removal trends with 5 g of magnetite in solutions of
demineralised water, aqueous sodium sulfate, aqueous sodium
chloride and Vales Point ash water. Residual solution
concentrations are shown.

Figure 5.42  Summary of trace element (Se, As, V, Cr, Sb, Al and Mo)
adsorption from ash water with goethite across the pH range
3 to 9. Residual solution concentrations are shown.

Figure 5.43  Summary of trace element (Se, As, V, Cr, Sb, Al and Mo)
adsorption from ash water with hematite across the pH range
3 to 9. Residual solution concentrations are shown.

Figure 5.44  Summary of trace element (Se, As, V, Cr, Sb, Al and Mo)
adsorption from ash water with magnetite across the pH range
3 to 9. Residual solution concentrations are shown.

Figure 5.45  Residual solution selenium concentration (µg/L) in time trials
of removal with goethite, hematite and magnetite.
Figure 5.46  Percentage of selenium adsorbed onto goethite, hematite and magnetite from ash water with time.  

Figure 5.47  Residual solution arsenic concentration (µg/L) in time trials for removal with goethite, hematite and magnetite.  

Figure 5.48  Residual solution vanadium concentration (µg/L) in time trials for removal with goethite, hematite and magnetite.  

Figure 5.49  Residual solution chromium concentration (µg/L) in time trials for removal with goethite, hematite and magnetite.  

Figure 5.50  Percentage of chromium adsorbed from ash water onto goethite, hematite and magnetite with time.  

Figure 5.51  Residual solution antimony concentration (µg/L) in time trials for removal with goethite, hematite and magnetite.  

Figure 5.52  Percentage of antimony adsorbed from ash water onto goethite, hematite and magnetite with time.  

Figure 5.53  Residual solution aluminium concentration (µg/L) in time trials for removal with goethite, hematite and magnetite. Results for this element are seriously impaired by separation and analysis problems.  

Figure 5.54  Residual solution molybdenum concentration (µg/L) in time trials for removal with goethite, hematite and magnetite.  

Figure 5.55  Percentage of molybdenum adsorbed onto goethite, hematite and magnetite with time.  

LIST OF IMAGES

Chapter 1  Introduction

Image 1.1  Trial laboratory equipment employed to probe selenite removal from Vales Point Power Station ash water.  

Chapter 2  Iron Oxides: A Background

Image 2.1  Large goethite crystals formed hydrothermally in a quartz geode 10 µm.  
Image 2.2  Common acicular goethite crystals terminated by [021] 0.1 µm.  
Image 2.3  TEM image of goethite twins with well developed [110] and [021] faces.  
Image 2.4  Lepidocrocite laths shadowed with 50 Å chromium at 45°.  
Image 2.5  Electron micrograph image of lepidocrocite; 0.1 µm.  
Image 2.6  Hematite (0.2 µm image) grown from ferrihydrite at pH 7 and room temperature; the acicular crystals also present are goethite.  
Image 2.7  Octahedral magnetite crystals produced hydrothermally at 250°C from 0.01 M Fe₂(SO₄)₃ solution in the presence of 0.4 M triethanolamine, 2.4 M NaOH and 0.05 M N₂H₄.  
Image 2.8  Magnetite octahedra produced by oxidation of a 0.5 M FeSO₄
solution with KNO₃ in 1.45 M KOH at 90°C.

Chapter 3  Vales Point Power Station: Selenium and Trace Metal Reduction Pilot Plant Trials

| Image 3.1  | Vales Point Power Station and ash dam ash water circulating system. | 133 |
| Image 3.2  | Vales Point Power Station ash return water pipeline. | 135 |
| Image 3.3  | Vales Point Power Station 2002 Selenium Removal Pilot Plant. | 137 |
| Image 3.4  | Inlet to the pilot plant with fabric filter hanger bars also displayed. | 138 |
| Image 3.5  | Top view of pilot plant fabric filter bars suspended from iron rods. | 139 |
| Image 3.6  | Inlet to pilot plant depicting formation of oxides and algal growth. | 140 |
| Image 3.7  | Modified Vales Point Power Station 2003 selenium and trace metal removal pilot plant. | 146 |
| Image 3.8  | Steel plates with iron oxide coating and timber support beams. | 150 |
| Image 3.9  | Steel plate with varying iron oxide formation evident. | 152 |
| Image 3.10 | Pilot plant Trough 1 with steel basket containing steel wool in the base. | 167 |
| Image 3.11 | Vales Point Pilot Plant with steel wool in baskets (left) and a bale of steel wool utilised in the final trial as supplied (right). | 169 |
| Image 3.12 | Crushed iron oxides and oxyhydroxides obtained from steel plates (left), along with a picture of the steel plate showing the oxide coating (right). | 178 |

Chapter 4  Leachability Studies

| Image 4.1  | Jar experiments for some samples from Troughs 1 to 3 Containing ash water and demineralised water. | 183 |
| Image 4.2  | Jar experiment (Trough 2 sample), with a close-up of the corrosion product. | 184 |
| Image 4.3  | Further jar experiments for samples from Troughs 1 and 3 containing ash water and demineralised water. | 184 |
| Image 4.4  | Sealed jar for a sample from Trough 1 containing ash water and corrosion product. This sealing proved sufficient to prevent any water loss during storage. | 185 |

Chapter 5  Characterisation of Synthetic Iron Oxides and Oxyhydroxides and Application in Trace Element Removal

| Image 5.1  | Laboratory synthesised goethite crystals. | 213 |
| Image 5.2  | Laboratory synthesised lepidocrocite crystals. | 214 |
| Image 5.3  | Laboratory synthesised hematite crystals. | 215 |
| Image 5.4  | Laboratory synthesised magnetite crystals. | 216 |
| Image 5.5  | Pilot plant iron oxide Sample 1. | 216 |
| Image 5.6  | Pilot plant iron oxide Sample 2. | 216 |
| Image 5.7  | Pilot plant iron oxide Sample 3. | 217 |
| Image 5.8  | Pilot plant iron oxide Sample 4. | 217 |
Image 5.9    An image of pilot plant oxide Sample 1 crystallites (major constituent magnetite) from SEM at 5 μm.  
Image 5.10  Another view of pilot plant oxide Sample 1 crystallites (major constituents magnetite) from SEM at 5 μm.  

Page

Image 5.11   A view of pilot plant oxide Sample 2 crystallites (major constituent magnetite) from SEM at 5 μm.  
Image 5.12   Another view of pilot plant oxide Sample 2 crystallites (major constituent magnetite) from SEM at 5 μm.  
Image 5.13   Pilot plant oxide Sample 3 (major constituents goethite, magnetite and lepidocrocite) crystals from SEM at 5 μm.  
Image 5.14   Pilot plant oxide Sample 3 (major constituents goethite, magnetite and lepidocrocite) crystals from SEM at 5 μm.  
Image 5.15   Pilot plant oxide Sample 4 (major constituent lepidocrocite, with semi-dominant goethite and magnetite) crystals from SEM at 5 μm.  
Image 5.16   Pilot plant oxide Sample 4 (major constituent lepidocrocite, with semi-dominant goethite and magnetite) crystals from SEM at 5 μm.  
Image 5.17   Laboratory-synthesised goethite crystals at a magnification of 10 μm.  
Image 5.18   SEM of laboratory-synthesised lepidocrocite (10 μm magnification).  
Image 5.19   SEM of laboratory synthesised lepidocrocite at a magnification of 10 μm.  
Image 5.20   SEM of synthetic hematite crystals at a magnification of 20 μm.  
Image 5.21   SEM of synthetic hematite crystals at a magnification of 10 μm.  
Image 5.22   SEM of synthetic magnetite crystals at a magnification of 20 μm.  

LIST OF PLATES

Chapter 2  Iron Oxides: A Background

Plate 2.1  Colours of the common iron oxides.  
Plate 2.2  Examples of the influence of particle size and other cations on oxide colour. Colours of goethite, lepidocrocite and hematite with large (left column) and small (middle column) crystals. The right-hand column shows a goethite with 6 mole % Mn-for-Fe substitution and with 10 mole % Cr-for-Fe substitution.  

Chapter 5  Characterisation of Synthetic Iron Oxides and Oxyhydroxides and Application in Trace Element Removal

Plate 5.1  Common colour of goethite.  
Plate 5.2  Colours of goethite crystals.
| Plate 5.3 | Common colour of lepidocrocite. | 214 |
| Plate 5.4 | Common colours of lepidocrocite. | 214 |
| Plate 5.5 | Common colour of hematite. | 214 |
| Plate 5.6 | Colours of hematite crystals. | 214 |
| Plate 5.7 | Common colour of magnetite. | 215 |