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
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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 minium 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

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<td>Å</td>
<td>Angstroms</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>
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<tr>
<td>ALS</td>
<td>Australian Laboratory Services</td>
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<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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<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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<td>DFT</td>
<td>Density functional theory</td>
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<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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<td>EPRI</td>
<td>Electric Power Research Institute of the United States of America</td>
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<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>
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<td>mg/kg</td>
<td>Milligrams Per Kilogram</td>
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<tr>
<td>mg/L</td>
<td>Milligrams Per Litre</td>
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<tr>
<td>µg/L</td>
<td>Micrograms Per Litre</td>
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<td>NZVI</td>
<td>Nano Zero-Valent Iron</td>
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<td>ORC-ICPMS</td>
<td>Octopole Reactive Cell Inductively Coupled Plasma Mass Spectrometer</td>
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<td>ppm</td>
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<td>PQL</td>
<td>Practical Quantitation Limit</td>
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<td>SeO₃²⁻</td>
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<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>
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<tr>
<td>TCLP</td>
<td>Toxicity Character Leaching Procedure</td>
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<td>TLM</td>
<td>Triple Layer Model</td>
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## 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.

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<td>X-Ray Diffraction</td>
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CHAPTER ONE
INTRODUCTION

1.1 ASH WASTE WATER STORAGE AND FLY ASH CONSTITUENTS

Fly ash and bottom ash are both by-products of the combustion of coal in an electricity generation plant. The type of coal being utilised and the handling and storage of ash will affect the interaction of this material with the environment. Traditionally, black coal-fired electricity generation plants built in New South Wales, Australia, have been constructed with wet ash (lean phase) disposal systems. A lean phase ash water system comprises nominally 70% water to 30% ash as opposed to a dense phase system, which comprises 30% water to 70% ash.

By transporting ash in a lean phase system, trace elements contained within the ash are released into the water transporting the ash. For inland power plants the medium for transporting ash can be fresh water and on coastal power plants saline water. The chemistry of these systems will depend on the quality of the water utilised in the system.

Interaction of ash water with the environment will be dependent on whether the system is circulating or single pass, and the amount of infiltration of other sources of water such as rain water and ground water [1]. In an effort to reduce the amount of rain water infiltration and release into the environment, some power stations, like the Vales Point Power Station in New South Wales, will have rain water diversion systems installed around the perimeter of the ash dam [1].

Fly ash may be found to contain higher concentrations of major and trace elements relative to normal geological materials [2]. The concentration of elements in fly ash leachates can be related to a number of chemical processes, including precipitation-dissolution and adsorption-desorption, along with varying rates of dissolution from the fly ash matrix [2]. Fly ash leachate can be acid or alkaline depending on the type of coal utilised. As such, the chemical processes in ash water systems can vary depending on a number of factors including the chemistry of coal
utilised, the type of combustion process employed to generate electricity, the medium used to transport ash in wet systems, and the environmental conditions of the storage system. The pH of fly ash can vary from 4.5 to 12, depending largely on the content of sulfur in the coal used, the type of coal used for combustion and the content of sulfur in the fly ash [3].

Fly ash produced through combustion of coal develops as very fine glass-like particles which range in particle size from 0.01 to 100 $\mu$m (average diameter <10 $\mu$m) [4]. Chemically, 90-99% of fly ash comprises Si, Al, Fe, Ca, Mg, Na and K, with Si and Al being a major component of the matrix [5]. The crystalline phases present in fly ash consist of compounds including quartz (SiO$_2$), mica, chlorite, feldspars, mullite (3Al$_2$O$_3$·2SiO$_2$), spinel (FeAl$_2$O$_4$), hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$), depending on the mineralogy of the coal being combusted [6-8].

Air-dried ashes taken from the lowest depth of test holes at the ash placement area of Vales Point Power Station (which is located on the southern shores of Lake Macquarie) were analysed by quantitative X-ray diffraction to determine crystalline and non-crystalline components [9]. XRD analysis showed the ashes to contain around 10% quartz, 15-20% mullite and around 70% amorphous material (glass) [9]. Small proportions of halite (NaCl) and gypsum (CaSO$_4$·2H$_2$O) were also present in the air-dried samples, presumably representing precipitates from evaporation of the saline water with which the samples had been saturated [9].

The Electric Power Research Institute (EPRI) of the United States of America completed a report in 1985 which included the analysis of fly ash taken from electrostatic precipitators of five USA electricity generator plants with a generating capacity greater than 350 megawatts. The study was undertaken to determine what chemical constituents were present in fly ash and ash pond effluent and thus to determine which substances required chemical treatment utilising a cost-effective process.

Table 1.1, which summarises an analysis of fly ash from five power plants in the USA, has been sourced from an EPRI report (CS-4087). This project (910-2), entitled “Trace Element Removal by Coprecipitation with Amorphous Iron Oxyhydroxide: Engineering Evaluation”, appeared some decades ago in 1985 [10]. The elemental composition at each power plant showed only limited variation for most major elements and trace elements. Some trace elements display significant variation, however; for
example, selenium concentrations in ash varied significantly with some as low as \(<5\) ppm whereas the highest was near 200 ppm.

Table 1.1 Analysis of fly ash samples from five USA power plants [10].

<table>
<thead>
<tr>
<th>Elemental composition (dry, whole-ash basis)</th>
<th>Plant A</th>
<th>Plant B</th>
<th>Plant C</th>
<th>Plant D</th>
<th>Plant E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Elements, % weight&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Unit 1</td>
<td>Unit 2</td>
<td>Unit 1</td>
<td>Unit 2</td>
<td>Unit 1</td>
</tr>
<tr>
<td>Silicon</td>
<td>19</td>
<td>16</td>
<td>28</td>
<td>29</td>
<td>20</td>
</tr>
<tr>
<td>Aluminium</td>
<td>5.8</td>
<td>5.7</td>
<td>&gt;12</td>
<td>&gt;12</td>
<td>9.5</td>
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<tr>
<td>Iron</td>
<td>5.1</td>
<td>5.1</td>
<td>4.1</td>
<td>4.5</td>
<td>3.1</td>
</tr>
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<td>Calcium</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>0.95</td>
<td>0.98</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Magnesium</td>
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<td>2.3</td>
<td>0.47</td>
<td>0.48</td>
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<tr>
<td>Sodium</td>
<td>4.7</td>
<td>5.0</td>
<td>0.23</td>
<td>0.29</td>
<td>0.44</td>
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<td>Potassium</td>
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<td>1.6</td>
<td>1.7</td>
<td>2.2</td>
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<tr>
<td>Titanium</td>
<td>0.25</td>
<td>0.27</td>
<td>0.95</td>
<td>0.81</td>
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<td>Phosphorus</td>
<td>0.05</td>
<td>0.04</td>
<td>0.6</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>Minor/Trace Elements, ppm&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Arsenic</td>
<td>150</td>
<td>500</td>
<td>200</td>
<td>150</td>
<td>20</td>
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<tr>
<td>Gold</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Boron</td>
<td>&gt;1,000</td>
<td>&gt;1,000</td>
<td>240</td>
<td>230</td>
<td>&gt;1,000</td>
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<tr>
<td>Barium</td>
<td>&gt;5,000</td>
<td>5,000</td>
<td>700</td>
<td>690</td>
<td>&gt;5,000</td>
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<tr>
<td>Beryllium</td>
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<td>6.3</td>
<td>21</td>
<td>21</td>
<td>4.0</td>
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<tr>
<td>Bismuth</td>
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<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Cadmium</td>
<td>c</td>
<td>c</td>
<td>190</td>
<td>90</td>
<td>c</td>
</tr>
<tr>
<td>Cobalt</td>
<td>14</td>
<td>16</td>
<td>110</td>
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<tr>
<td>Chromium</td>
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<td>89</td>
<td>210</td>
<td>180</td>
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<td>Copper</td>
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<tr>
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<td>17</td>
<td>37</td>
<td>85</td>
<td>83</td>
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<tr>
<td>Mercury</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>c</td>
<td>c</td>
<td>100</td>
<td>70</td>
<td>c</td>
</tr>
<tr>
<td>Lithium</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Manganese</td>
<td>410</td>
<td>680</td>
<td>244</td>
<td>240</td>
<td>1,200</td>
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<tr>
<td>Molybdenum</td>
<td>c</td>
<td>c</td>
<td>35</td>
<td>24</td>
<td>c</td>
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<tr>
<td>Niobium</td>
<td>c</td>
<td>c</td>
<td>110</td>
<td>71</td>
<td>c</td>
</tr>
<tr>
<td>Nickel</td>
<td>38</td>
<td>49</td>
<td>200</td>
<td>160</td>
<td>30</td>
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<tr>
<td>Lead</td>
<td>c</td>
<td>c</td>
<td>100</td>
<td>70</td>
<td>c</td>
</tr>
<tr>
<td>Rhenium</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Antimony</td>
<td>20</td>
<td>70</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Scandium</td>
<td>19</td>
<td>24</td>
<td>60</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>70</td>
<td>100</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Tin</td>
<td>3,400</td>
<td>6,700</td>
<td>850</td>
<td>800</td>
<td>NM</td>
</tr>
<tr>
<td>Tellurium</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Thallium</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>100</td>
<td>170</td>
<td>680</td>
<td>290</td>
<td>100</td>
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<tr>
<td>Tungsten</td>
<td>c</td>
<td>c</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>c</td>
</tr>
<tr>
<td>Yttrium</td>
<td>45</td>
<td>53</td>
<td>90</td>
<td>74</td>
<td>36</td>
</tr>
<tr>
<td>Zinc</td>
<td>c</td>
<td>c</td>
<td>150</td>
<td>120</td>
<td>c</td>
</tr>
<tr>
<td>Zirconium</td>
<td>380</td>
<td>380</td>
<td>500</td>
<td>450</td>
<td>580</td>
</tr>
</tbody>
</table>

<sup>a</sup> Relative error ± 15%.
<sup>b</sup> Relative error ± 1 to 15% for all but Zn which is ± 30%.
<sup>c</sup> Not measurable because of interferences (NM refers to elements simply not measured).
Table 1.2 below provides the chemical analysis data of fly ash samples taken from Vales Point Power Station plant in 2007, determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). On comparison of these results with those from the EPRI study in 1985, it is evident that the elemental composition and trace elements of ash are not that dissimilar.

Table 1.2  Vales Point Power Station fly ash analytical data.

<table>
<thead>
<tr>
<th>Major Elements</th>
<th>Fly Ash Elemental Composition %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Si 28.4</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al 11.3</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe 2.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca 1.33</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg 0.31</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na 0.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>K 1</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti 0.49</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P 0.3</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba 0.049</td>
</tr>
<tr>
<td>Sulphur</td>
<td>S 0.035</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr 0.035</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Minor Elements</th>
<th>Trace Element</th>
<th>mg/kg</th>
<th>Trace Element</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>Ag 0.29</td>
<td></td>
<td>Lithium</td>
<td>Li 56</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As 6.6</td>
<td></td>
<td>Manganese</td>
<td>Mn 431</td>
</tr>
<tr>
<td>Boron</td>
<td>B 94</td>
<td></td>
<td>Molybdenium</td>
<td>Mo 4.4</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba 457</td>
<td></td>
<td>Nickel</td>
<td>Ni 10</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be 6.1</td>
<td></td>
<td>Lead</td>
<td>Pb 48</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi 1.1</td>
<td></td>
<td>Rubidium</td>
<td>Rb 43</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd 0.45</td>
<td></td>
<td>Antimony</td>
<td>Sb 2.9</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co 9</td>
<td></td>
<td>Tin</td>
<td>Sn 6</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr 20</td>
<td></td>
<td>Strontium</td>
<td>Sr 364</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs 5</td>
<td></td>
<td>Selenium#</td>
<td>Se 4.44</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu 41</td>
<td></td>
<td>Vanadium</td>
<td>V 110</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga 21</td>
<td></td>
<td>Tungsten</td>
<td>W 6</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge 7</td>
<td></td>
<td>Zinc</td>
<td>Zn 69</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>La 42</td>
<td></td>
<td>Zirconium</td>
<td>Zr 301</td>
</tr>
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</table>

# Selenium alone was analysed by Hydride/Atomic Fluorescence Spectroscopy (others employed ICP-AES and ICP-MS).

Both Table 1.1 and Table 1.2 above demonstrate that, whilst fly ash constituents can be similar in nature for differing sources, the concentration of chemical constituents can vary depending on the source material from which the fly ash was produced. The
concentration of fly ash leachate will also vary due to a number of factors including the type of medium transporting the ash (fresh or saline water), the efficiency of the containment system itself, and the solubility of trace elements. The impact on the surrounding environment from fly ash leachate discharges will be dependent on site-specific conditions resulting in the release of certain trace elements, the concentration of these elements and of course the receiving environment itself.

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

In addition to the study of fly ash properties noted in Section 1.1, the EPRI in 1985 had undertaken an investigation into trace element removal from fly ash effluent by coprecipitation with amorphous iron oxyhydroxide [10]. The electric power industry has come under increasing regulatory pressure to limit the quantities of trace elements its plants discharge to the environment, leading to an examination of ways to control release of these elements. The objective of this research was to examine the technical and economic feasibility of removing inorganic trace elements such as arsenic (As), selenium (Se), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), silver (Ag), vanadium (V) and zinc (Zn) from power plant waste streams by coprecipitation with iron oxyhydroxide. Selenium and arsenic removal was emphasized [10].

From the five power plants investigated by the EPRI in 1985, both arsenic and selenium were of particular interest due to high levels of these trace elements in the ash pond water. Because the waste characterisation survey had indicated that arsenic and selenium concentrations in ash pond effluents exceeded the National Interim Primary Drinking Water Standards (NIPDWS) far more often than any other trace element [10], in the present study it was decided to concentrate on arsenic and selenium removal, whilst also examining the fate of some other elements.

Ash ponds are successful in trapping significant levels of trace elements, as is evident from influent and effluent levels. This is apparent in the following Table 1.3 on ash pond water chemistry characterisation, sourced from a recent EPRI report (1005365) entitled “Arsenic and Selenium Treatment Technology Summary for Power Plant Wastewaters - Technical Update” [11]. However, despite capture techniques applied, the released levels of several elements are still inappropriate.
Table 1.3 Ash pond water chemistry characterisation* [11].

<table>
<thead>
<tr>
<th>Element</th>
<th>Influent $^a$ (µg/L)</th>
<th>Effluent $^b$ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>Range $^c$</td>
</tr>
<tr>
<td>Aluminium</td>
<td>78,000</td>
<td>2,900 to 290,000</td>
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<tr>
<td>Antimony</td>
<td>8</td>
<td>&lt;D.L. (&lt;1) to 30</td>
</tr>
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<td>340</td>
<td>25 to 1,500</td>
</tr>
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<td>Barium</td>
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<td>93 to 7,800</td>
</tr>
<tr>
<td>Beryllium</td>
<td>15</td>
<td>1 to 49</td>
</tr>
<tr>
<td>Boron</td>
<td>1,200</td>
<td>430 to 5,500</td>
</tr>
<tr>
<td>Cadmium</td>
<td>6</td>
<td>1.5 to 23</td>
</tr>
<tr>
<td>Chromium</td>
<td>180</td>
<td>&lt;D.L. (&lt;10) to 380</td>
</tr>
<tr>
<td>Chromium(V)</td>
<td>10</td>
<td>&lt;D.L. (&lt;10) to 55</td>
</tr>
<tr>
<td>Copper</td>
<td>310</td>
<td>&lt;D.L. (&lt;10) to 780</td>
</tr>
<tr>
<td>Iron</td>
<td>35,000</td>
<td>4,000 to 170,000</td>
</tr>
<tr>
<td>Lead</td>
<td>120</td>
<td>5 to 250</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.3</td>
<td>0.05 to 4.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>110</td>
<td>15 to 350</td>
</tr>
<tr>
<td>Selenium</td>
<td>51</td>
<td>6 to 210</td>
</tr>
<tr>
<td>Thallium</td>
<td>5</td>
<td>&lt;D.L. (&lt;2) to 33</td>
</tr>
<tr>
<td>Vanadium</td>
<td>600</td>
<td>30 to 1,400</td>
</tr>
<tr>
<td>Zinc</td>
<td>380</td>
<td>&lt;D.L. (&lt;100) to 890</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
<td>4.0 to 9.6</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg/L)</td>
<td>270</td>
<td>91 to 860</td>
</tr>
<tr>
<td>Total Suspended Solids (mg/L)</td>
<td>3,900</td>
<td>41 to 20,000</td>
</tr>
</tbody>
</table>

* This data is taken from Table 5-2 of the Report “Metals Removal in Ash Ponds at PISCES Sites”.

$^a$ Influent samples are 24 hour composite samples taken from water flowing through the ash deltas.

$^b$ Effluent samples were collected outside discharge structures so do not represent permitted outfalls or reflect pH adjustment of some systems.

$^c$ Range is 5$^{th}$ to 95$^{th}$ percentile.

$^d$ The apparent increase in antimony concentrations from influent to effluent is likely due to the quality of data in the high-solids influent samples.

$^e$ <D.L. = The result was below the method of detection limit (MDL) for a conventional method achieved by the conventional laboratory.
The low levels of sodium, chloride and sulphate obvious in ash pond effluent from the five power plants in the EPRI investigation indicates the systems of containment of the ash effluent is based on fresh water and not saline water. The ash water effluent of Vales Point Power Station that is discharged via licensed discharge points into Mannering Bay and Wyee Bay located on the southern shores of Lake Macquarie in New South Wales is saline, due to the source of the transport medium being estuarine water extracted from the lake. Table 1.4 below provides the analysis of the Vales Point Power Station ash dam discharge into Wyee Bay in July 2008.

Table 1.4  Vales Point Power Station ash water analysis, 24th July 2008.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Reporting</th>
<th>Unit of Measure</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended Solids</td>
<td>1</td>
<td>mg/L</td>
<td>2</td>
</tr>
<tr>
<td>Sulfate as SO₄²⁻</td>
<td>1</td>
<td>mg/L</td>
<td>1360</td>
</tr>
<tr>
<td>Chloride</td>
<td>1</td>
<td>mg/L</td>
<td>9240</td>
</tr>
<tr>
<td>Sodium</td>
<td>1</td>
<td>mg/L</td>
<td>5770</td>
</tr>
<tr>
<td>Mercury (Dissolved)</td>
<td>0.0001</td>
<td>mg/L</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Dissolved Elements in Saline Water by ORC-ICPMS *

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Reporting</th>
<th>Unit of Measure</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>10</td>
<td>µg/L</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Selenium</td>
<td>2</td>
<td>µg/L</td>
<td>37</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.5</td>
<td>µg/L</td>
<td>21.9</td>
</tr>
<tr>
<td>Iron</td>
<td>5</td>
<td>µg/L</td>
<td>10</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.5</td>
<td>µg/L</td>
<td>5.2</td>
</tr>
<tr>
<td>Boron</td>
<td>100</td>
<td>µg/L</td>
<td>2800</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.2</td>
<td>µg/L</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.5</td>
<td>µg/L</td>
<td>9.0</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.2</td>
<td>µg/L</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Lead</td>
<td>0.2</td>
<td>µg/L</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.5</td>
<td>µg/L</td>
<td>10.2</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.1</td>
<td>µg/L</td>
<td>78.3</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.5</td>
<td>µg/L</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.5</td>
<td>µg/L</td>
<td>28.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>5</td>
<td>µg/L</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

* ORC-ICPMS – Octopole Reactive Cell Inductively Coupled Plasma Mass Spectrometer
Table 1.4 is representative of the quality of ash water being discharged from Vales Point Power Station. The abundances of the dissolved elements are not that dissimilar to those published by EPRI in 1985, although fresh water rather than salt water was employed in that earlier study.

The selenium level in Vales Point ash water is of a level that is considered as significant, whereas the arsenic level compared to the EPRI fly ash samples is low. Antimony and aluminium are of a similar magnitude, but are of less a concern to the environment, as are chromium and vanadium, which are also lower in concentration.

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

The toxicity of selenium and trace elements including vanadium, molybdenum, arsenic, aluminium, antimony and chromium leached from flyash and their impact on estuarine aquatic ecosystems will depend on the abundance of these trace elements being released, that is the mass load being discharged, and how these trace elements interact with the environment of the receiving waters. Water quality guidelines and trigger levels for estuarine receiving waters have been established over time from extensive research. The following sections provide a brief background of the environmental effect and guideline levels of selenium, arsenic, vanadium, chromium, antimony, aluminium and molybdenum, which are the subject of examination in this thesis.

1.3.1 Selenium

Selenium is present in the Earth’s crust and often accompanies sulfate-containing minerals [12]. This element is also present in almost all rocks and soils [13]. Estimates of the average selenium concentration in the Earth’s crust range from 0.03-0.8 mg Se/kg [14]. It can assume the four oxidation states (-2, 0, +4, +6) [12].

In soils, selenium is present as elemental selenium (Se), selenide (Se\(^{2-}\)), selenite (SeO\(_3^{2-}\)) and selenate (SeO\(_4^{2-}\)) at concentrations ranging from less than 0.1 µg/g to over 10,000 µg/g [15]. In turn, plants reflect these levels and range in tissue concentrations
of selenium from 0.01 µg/g to as high as 10,000 µg/g in selenium-accumulating species [15].

Acidic and reducing conditions reduce inorganic selenites to elemental selenium, whereas alkaline and oxidising conditions favour the formation of selenates [16]. Selenites and selenates are usually soluble in water, but elemental selenium is insoluble in water and not rapidly reduced or oxidised in nature. In alkaline soils, selenium is usually found as selenite bound to iron and aluminium oxides in compounds of very low solubility [16].

Selenium has not so far been found to be essential for plant growth [13]. However, selenium is a trace mineral essential for the health of mammals [17]. Selenium is essential for the liver, heart, spleen, pancreas, kidneys, male sperm cells and skin [17]. It is required for the production of prostaglandins and for the maintenance of good mitochondrial function [18]. Selenium is now known to be an essential component of the active sites of a number of enzymes, including the selenoenzyme species glutathione peroxidase, which scavenge hydroperoxides to prevent cellular damage and metabolise various substances in the liver [17]. Selenium deficiency has been associated with atherosclerosis [19], cancer [20], coronary artery disease [21], coeliac disease [22], cervical dysplasia [23], Crohn’s disease [24], dermatitis, psoriasis and vasculitis [25], and rheumatoid arthritis [26].

Although selenium itself is relatively non-toxic, certain selenium compounds are toxic towards humans, with one of the most acutely toxic substances being hydrogen selenide [27]. The adsorption of selenium compounds by the human body usually occurs through the lungs by dust or fumes and through the skin [27]. In the case of intoxication arising in seleniferous areas, the selenium is ingested generally from foods grown in such locations [27]. The most common symptom of intoxication appears to be gastrointestinal disturbances [27].

Although the major source of selenium in the environment is weathering of rocks and soils [28], anthropogenic sources such as emissions from burning fossil fuels may also contribute to selenium in natural waters [29]. Selenium in natural waters is usually present in concentrations of <500 ng/L but can be considerably elevated by waste discharges such as those from coal-fired power stations or drainage from seleniferous soils [30]. The difference between levels that cause toxicity and those that
are required for nutrients is small; it can be beneficial in food with concentrations below approximately 1 mg/kg but toxic above 5 mg/kg [31].

Selenium toxicity is dependent on its valency state. Selenium(IV) is generally more toxic than selenium(VI) [32]. These predominant forms in natural waters exist as the oxyanions selenite and selenate, respectively [32]. Selenites are readily removed from the water column but selenates can be readily bioaccumulated [32]. Food chain uptake, leading to secondary poisoning, is more significant than water uptake [32]. Sediments can be a significant source of selenium in fish and invertebrates [33]. Toxic effect threshold levels for selenium in freshwater, food chain organisms and fish have been reported as 2 \( \mu \text{g/L} \), 3 mg/kg and 4 mg/kg (for whole fish), respectively [33]. Natural freshwater plankton communities have been found to accumulate selenite 4-5 times faster than selenate over a 24 h period [34]. Factors affecting the uptake of selenium such as pH, hardness, sulfur and phosphate levels consequently affect toxicity [32]. Elements such as mercury and copper both ameliorate selenium toxicity [32]. Most toxicity values have been based on the uptake of selenium from the water column, but in natural populations this is significant compared to uptake through the food chain [33]. In general, the toxicity of selenium compounds follows the order: selenomethionine > selenite > selenate.

In very strongly reducing environments, for example pond bottom mud, hydrogen sulfide (H\(_2\)S) and polysulfide ions (S\(_n\)\(^2\)) are present [35]. Both H\(_2\)S and polysulfides react with Se\(^0\) to produce Se-substituted polysulfide anions (S\(_n\)Se\(^2\)), thereby greatly increasing the solubility of selenium in water [35]. Some S-containing organic compounds increase the solubility of Se\(^0\) and hence increase its biological availability [35].

Concentrations of selenium can build up to toxic levels in higher organisms even when selenium concentrations in the water column are low [33]. Sediments were found to be a significant source of selenium contamination in benthic infauna and in fish predators in Lake Macquarie, NSW [36]. Selenium in water can be bioconcentrated by between 100 and 30,000 times in food organisms eaten by fish and wildlife [33], sometimes causing reproductive failure without affecting the parents.

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000* provides a marine low reliability trigger value of 3 \( \mu \text{g/L} \) for Se (total) using an Affectation Factor (AF) of 100 [32]. An Environmental Concern Level
(ECL) of 6 µg/L for selenate, Se(VI), was derived from USEPA data. No figure could be derived for selenite Se(IV) in marine systems.

1.3.2 Arsenic

Arsenic is a widespread contaminant in the environment. Arsenic is released into the environment naturally by weathering of arsenic-containing rocks and volcanic activity. The estimated amount of arsenic released from human activities is about twice that from weathering [37]. Anthropogenic sources of arsenic, together with natural sources, have led to extensive leaching of arsenic into surface, ground and drinking waters [38].

Several oxidation states of arsenic occur in natural waters, depending upon the redox potential and pH. The two most common forms are arsenic(III) and arsenic(V) [32]. Both arsenic(III) and arsenic(V) form stable bonds with carbon, resulting in numerous organo-arsenical compounds, some of which are very toxic (e.g. methylarsine) [32]. Arsenic(III) is the more toxic but is less common in seawater [32]. Arsenic(V) toxicity is not affected by salinity [32]. Arsenic can bioaccumulate to some extent in marine organisms, but secondary poisoning is unlikely. Formation of organo-arsenical compounds complicates the assessment of bioaccumulation [32].

Marine organisms have been found to contain much higher levels of arsenic than terrestrial organisms; this is because of the high arsenate/phosphate ratio in oceans, which is a consequence of very low phosphate concentrations [38]. Marine organisms from Australian waters have been shown to accumulate high concentrations of arsenic [39-43]. Most studies investigating biotransformation have focused on marine environments [43], due to the formation of arsenoribosides and arsenobetaine in marine invertebrates and macroalgae [41].

Concentrations of arsenic found in open ocean seawaters are typically 1-2 µg/L. Arsenic is widely distributed in surface freshwaters. The concentrations in rivers and lakes are generally below 10 µg/L, although individual samples may range up to 5 µg/L near anthropogenic sources [38].

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000 provides an Environmental Concern Level (ECL) of 2.3 µg/L for arsenic(III) which could be adopted as a marine low reliability trigger value [32]. The
**Guidelines** does not provide a trigger value for marine data, but has derived a marine low reliability arsenic(V) trigger value of 4.5 µg/L [32].

### 1.3.3 Vanadium

Vanadium does not occur in the environment as the free metal, but rather as insoluble minerals and organometallic complexes [44]. Consequently, the concentration of vanadium in natural freshwaters is relatively low and is usually less than 20 µg/L [44]. Vanadium is a soft, silvery-grey metal that exists in a number of different oxidation states: -1, 0, +2, +3, +4 and +5 [45]. The environmental chemistry of vanadium is complex. In minerals, the oxidation state of vanadium may be +3, +4 or +5. Dissolution in water rapidly oxidises V(III) and V(IV) to the pentavalent state, which is the most usual form of the metal in the environment [45].

A large fraction of vanadium released into the aquatic environment from natural sources originates from erosion of land surfaces by water through rainfall runoff [46]. However, anthropogenic input has led to a significant enrichment of vanadium in the environment [46]. Studies have shown that vanadium is being introduced into the marine environment in quantities sufficient to allow for a significant bioaccumulation of the metal in the bodies of shellfish [47].

Vanadium is thought to be essential to enzyme systems that fix nitrogen from the atmosphere (bacteria) and is concentrated by some organisms (tunicates, some polychaete annelids, some microalgae), but its function in these organisms is uncertain [45]. Whether vanadium is essential to other organisms is unknown [45]. There is no evidence of accumulation or biomagnification in food chains in marine organisms, the most studied group [45]. Seawater concentrations in the open ocean range from 1 to 3 µg/L and sediment concentrations range from 20 to 200 µg/g with the highest levels in coastal sediments [45]. Acute LC50 values for aquatic organisms were found to range from 0.2 – 120 mg/L, with the majority lying between 1 and 12 mg/L [45]. Reports of sublethal effects were determined to be around 10 µg/L for algal photosynthesis, 50 µg/litre for oyster larval development, and 1130 µg/L for Daphnia reproduction [45].

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000* provides a trigger value for marine data for vanadium at a 95% level of protection of 100 µg/L [32].
1.3.4 Chromium

Chromium has been found to be widely distributed in the Earth’s crust [48]. It can exist in oxidation states from +2 to +6 [48]. Soils and rocks may contain small amounts of chromium, predominantly in the trivalent state [48]. In natural waters, chromium is present mainly in the trivalent chromium(III), but also hexavalent chromium(VI) forms [29]. The distribution of compounds containing chromium(III) and chromium(VI) depends on a number of influences such as, the redox potential, the pH, the presence of oxidising or reducing compounds, the kinetics of redox reactions, the formation of chromium(III) complexes or insoluble chromium(III) salts, and the total chromium concentration [48]. In the environment, chromium(VI) occurs mostly as CrO$_4^{2-}$ or HCrO$_4^-$ and chromium(III) as hydrated Cr(OH)$_{(3-n)}^+$ [48].

The form of chromium present appears to significantly affect the toxicity to aquatic organisms and the behaviour of chromium in the aquatic environment [32]. Precipitation of chromium(III) hydroxide is thought to be the governing removal mechanism for chromium(III) in natural waters [32].

Studies of lake waters show the ratio of chromium(III) to chromium(VI) is affected by the amount of organic matter and dissolved oxygen [49]. Chromium(VI) is quite soluble, existing in solution as a complex anion [32]. Chromium toxicity is affected by the valency state, with chromium(III) being generally much less toxic than chromium(VI). There is an equilibrium between the two chromium forms under different conditions [32]. The predominant form of chromium found in analysis of ash water from Vales Point power station in 2008 was the less toxic form chromium(III). Several studies have shown that the toxicity of both chromium(III) and chromium(VI) to freshwater organisms decreases with increasing water hardness and/or alkalinity [32].

There is limited Australasian data on the toxicity of Cr(VI) to marine organisms, although in general Cr(VI) is much more toxic to marine organisms than Cr(III) [32]. Under marine and estuarine conditions, the high sulfate concentrations leading to complexation make chromium toxicity unlikely, except where sampling sites are much polluted [32].

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000* provides a trigger value for marine data for chromium(III) at a 95% level of protection of 10 µg/L and for chromium(VI) at a 95% level of protection of 4.4 µg/L [32].
1.3.5 Antimony

Natural sources of antimony in the environment result from rock weathering and soil run off processes whilst anthropogenic sources include combustion of fossil fuels, mining and smelting activities, and the application of ‘superphosphate’ fertilisers to agricultural soils [50]. The release of antimony from these sources has led to widespread concentrations throughout environmental systems, and global soil concentrations are estimated at 1 mg/kg, whereas fresh and saline waters exhibit concentrations between 0.01-5.6 ng/mL [50].

Antimony is a relatively toxic element [51]. The toxicity profile of antimony compounds is similar to those of arsenic in that trivalent compounds are more toxic than pentavalent ones [51]. Knowledge of the chemical forms of antimony is essential when evaluating the environmental hazards connected with pollution from antimonials [51].

Two forms of antimony are found in natural waters [52]. Antimony(III) occurs under moderately oxidising conditions, whereas antimony(V) predominates in highly oxidising environments [52]. Concentrations of antimony in groundwater and surface water normally range from 0.1 to 0.2 µg/L [53]. Marine antimony concentrations are approximately 0.15 µg/L [54]. Antimony has been discovered not to be an essential element in plants or animals [55].

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000 does not provide a trigger value for marine data but has derived a marine low reliability antimony(III) trigger value of 270 µg/L [32].

1.3.6 Aluminium

Aluminium is the most abundant metallic element in the liposphere, but has been considered to have little or no known biological function [56]. Aluminium metal is used by a number of industries, such as the automotive, aircraft, electricity generation industries, in food packaging and as a structural material used in construction and in the production of metal alloys [57]. Aluminium salts are also widely used in water treatment processes as coagulants to reduce organic matter, colour, turbidity and microorganism levels [58]. The water treatment process usually adopted consists of the
addition of an aluminium salt (often the sulfate) at an optimum pH and dosage, followed by flocculation, sedimentation and filtration [58].

Aluminium is released to the environment mainly by natural processes and it exists solely in the +3 oxidation state [57]. There are several factors influencing aluminium mobility and subsequent transport within the environment. These include hydrological flow paths, soil-water interactions, chemical speciation and the composition of underlying geological material [57].

Aluminium can be present in a number of different forms in water [58] all in the +3 oxidation state. As a small, highly-charged hydrated cation, coordinated water molecules bonded to aluminium are very acidic and readily undergo deprotonation to form monomeric and polymeric hydroxy species [58]. These species then lead to colloidal polymeric solutions and gels, as well as precipitates, which are all based on aquated positive ions or hydroxylated aluminates [58]. In addition, aluminium can form complexes with various organic compounds (e.g. humic or fulvic acids) and inorganic ligands (e.g. fluoride, chloride, and sulfate) with most complexes being soluble [58]. The chemistry of aluminium in water is complex, and many chemical parameters, including pH, determine which aluminium species are present in aqueous solutions [58]. In pure water, aluminium has a minimum solubility in the pH range 6.0 – 6.5; concentrations of total dissolved aluminium increase at higher and lower pH values [58].

The bioavailability and toxicity of aluminium is usually greatest in acid solutions [59]. Toxicity to fish and invertebrates is increased at low (e.g. <5.5) and high (e.g. >9) pH levels [32]. Aluminium in acid habitats has been observed to be toxic to fish [60], amphibians [61] and phytoplankton [62,71]. The simple monomeric species [Al(OH)₂(aq)]⁺ is thought to be the most toxic [63].

There was insufficient spread of data to calculate a reliable guideline trigger value for aluminium in seawater [32], and as such the Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000 does not provide a trigger value for marine data, but has derived a marine low reliability aluminium trigger value of 0.5 µg/L [32]. This figure should only be used as an indicative interim working level, but could be revisited as more data become available [32].
1.3.7 Molybdenum

Molybdenum is used in the manufacture of a number of products including special steels, X-ray tubes, in electrical contacts, spark plugs, filaments, screens, and in the production of tungsten, glass-to-metal seals, nonferrous alloys, and pigments [64]. Molybdenum compounds are used in the agriculture industry for the direct treatment of seeds or in the formulation of fertilisers to prevent molybdenum deficiency in plants [65]. It occurs as molybdenite (MoS$_2$) and molybdates (MoO$_4^{2-}$) in igneous or sedimentary rocks [66]. The most common oxidation states are +4 and +6 [66].

Molybdenum is essential to all life, and it has been recommended that humans should consume a minimum of 0.2 mg per day [67]. It is also an essential trace element for aquatic organisms [68]. Molybdenum has been reported to occur naturally in seawater at around 10 µg/L [69]. Molybdenum in rivers and lakes appears to be evenly partitioned between dissolved and particulate phases, whereas in marine water there is usually 10,000 times more dissolved Mo than particulate Mo [70,71]. However, despite this, phytoplankton in the open ocean were observed to contain very low Mo residuals, suggesting that Mo may be less available in phytoplankton in seawater compared to freshwater due to competition with high sulfate concentrations in seawater [70,71].

There was insufficient spread of data to calculate a reliable guideline trigger value for molybdenum in seawater [32], and as such the Australian and New Zealand Guidelines for Fresh and Marine Water Quality October 2000 does not provide a trigger value for marine data but has derived an Environmental Concern Level (ECL) of 23 µg/L (as Mo is an essential element) as a low reliability trigger value [32].

1.4 BACKGROUND STUDIES OF TRACE ELEMENT (SELENIUM) INPUT INTO LAKE MACQUARIE NSW AND EFFECT ON AQUATIC FAUNA AND FLORA

Release of trace elements, in particular selenium, into the receiving environment through ash dam discharges has been of growing concern to communities, government authorities and electricity generation corporations [1]. As a result, a great deal of research has been undertaken on the effects to aquatic flora and fauna and mechanisms for reducing the level of trace elements [1].
Studies in the past of the effects of trace elements were performed with an emphasis on the protection of humans; however, just as important an issue is the effect that elevated trace metal concentrations have on other species such as fish growth, reproduction and survival. Elevated trace metal concentrations in fish have been found to affect reproductive success, with trace metals accumulating in adult female ovaries then being transferred to offspring via the egg yolk [72]. This early exposure can be detrimental to egg and larvae development and survival, and may cause physical deformities in larva [73,74]. This in turn may increase rates of mortality through their inability to feed effectively and avoid predators [73,74].

Selenium has been identified as a trace element of most concern from discharges of wet ash disposal systems from coal-fired power stations in New South Wales [75]. Elevated concentrations of this element have been found in biota (especially fish) in the rivers and lakes which have historically received discharges of supernatant water from power station fly ash ponds [76].

Vales Point Power Station is at the southern end of Lake Macquarie in New South Wales, a large estuarine barrier lake near the city of Newcastle [77]. The lake extends approximately 22 kilometres in a north-south direction from Cockle Creek to Chain Valley Bay. Lake Macquarie has a maximum width of about 10 kilometres and a maximum depth of approximately 11 metres, with an average depth of 8 metres [77]. The tidal range in Lake Macquarie is small [78]; however, despite this poor tidal exchange, the lake is estuarine in nature or marine dominated because of minimal freshwater dilution from the two main catchment inputs [79].

A study undertaken by the CSIRO Division of Coal and Energy Technology in 1993 on species of fish including luderick (Girella tricuspidate), yellow bream (Acanthopagus australis), dusky flathead (Platycephalus fuscus) and sea mullet (Mugil cephalus) sampled from Wyee Creek and Mannering Bay on Lake Macquarie (Figure 1.1) found trace elements analysed in fish tissue including chromium, zinc, arsenic, selenium, cadmium, antimony and lead were only elevated for selenium and arsenic against concentrations at a control site, Cams Wharf [80]. The concentrations of elements other than arsenic and selenium did not vary over a wide range and were not species dependent. Selenium concentrations were found to be high in all fish sampled upstream of Wyee Bay, although at two sites concentrations in luderick were lower [80]. Arsenic concentrations were found to be highest in bream, but there was no apparent site or size dependency, nor was there any correlation with selenium [80]. In
all cases concentrations were close to the National Health and Medical Research Council limit of 1 mg/kg, with the exception of bream where a mean concentration of 3 mg/kg was observed. However, the likelihood that this is all inorganic arsenic is remote, based on previous findings, with most being present as non-toxic arsenobetaine [80].

Factors that affect the accumulation of trace metals in general also appear to influence the accumulation of selenium. These include diet, age, the accumulation of other metals and physico-chemical factors [81]. Selenium may accumulate in fish by absorption or from dietary intake [82]. A number of studies have been performed on terrestrial animals and generally the liver and kidneys seem to accumulate the most selenium [83]. A study undertaken by Kleinow and Brooks in 1986 found urinary excretion was the primary route of selenium elimination followed by the gills [84]. Figure 1.2 below provides the possible biological pathways of selenium in fish [84].

![Biological pathways of selenium](image)

Figure 1.2 Biological pathways of selenium [84].

A 1994 study of fish including sea mullet (*Mugal cephalus*), tarwhine (*Rhabdosargus sarba*) and silverbiddy (*Gerres ovatus*) undertaken by Boyd on the accumulation of selenium, cadmium, zinc and copper, found fish contained high levels of selenium, although only at the higher lengths/weights [81]. The concentrations of cadmium, zinc and copper were below the National Health and Medical Research Council recommended levels [81]. The liver accumulated significantly greater levels of selenium in mullet, indicating that mullet in Lake Macquarie are chronically exposed to selenium [81].

Selenium concentrated in organic detritus in sediments is thought to be more important than that dissolved in water in contaminating food systems [85].
Measurements of selenium in sediments and benthic infauna of Lake Macquarie indicate that sediments are a significant source of selenium in the lake’s food network [36]. Sediment cores taken from sediments in Mannering Bay, near a power station at Vales Point, contained an average of 12 times more selenium in surficial sections than sediment cores from Nord’s Wharf, a part of the lake remote from direct input of selenium [36]. In the late 1990s the highest selenium concentration found in Mannering Bay sediments (17.2 µg/g) was ~70 times the apparent background concentration at Nord’s Wharf (0.25 µg/g) [36]. Pore water concentrations in Mannering Bay were also high – up to 5 µg/L compared to those at Nord’s Wharf, which were below detection limits (0.2 µg/L) [36].

A study of trace elements, in particular selenium, measured in mullet (Mugal cephalus), luderick (Girella tricuspidate), trumpeter whiting (Sillago maculata), yellow bream (Acanthopagrus australis) and dusky flathead (Platatycephalus fuscus) caught from most parts of Lake Macquarie [86] was compared to the selenium concentrations of Australian fish from unpolluted waters [87]. The comparison of selenium in fish showed that, on average, fish from Lake Macquarie contained six times the selenium concentration of those taken from unpolluted areas. In the case of mullet, the average selenium concentrations in fish from Lake Macquarie were found to be fourteen times higher than the national average [87].

In the 1998 study undertaken by Peters and co-workers, it was demonstrated that molluscs and polychaetes were accumulating more selenium at Mannering Bay than at Nord’s Wharf [36]. This is consistent with findings of studies showing that if an area of sediment is contaminated with selenium, benthos will have higher selenium concentrations than those considered to be background or unpolluted [88].

The bioaccumulation of selenium by Spisula trigonella, a filter feeder, in a study by Luoma et al. in the early 1990s found it is likely to have occurred via a number of pathways involving the ingestion of water, algae, microorganisms and sediment particles [89]. They found that benthic bivalves can directly accumulate selenium from sediment particles [89]. Two benthic organisms, the eunicid polychaete Marphysa sanguinea and the bivalve mollusc Spisula trigonella in the study undertaken by Peters and co-workers were maintained at different densities in selenium-spiked sediments. Both animals accumulated selenium from the spiked sediment, confirming bioaccumulation from contaminated sediments occurs [36].
The analysis of selenium concentrations in surficial sediments from around Lake Macquarie by Peters and co-workers showed that sediments in close proximity to Vales Point Power Station (Mannering Bay, Wyee Bay and Chain Valley Bay) have higher sediment selenium concentrations [36]. Higher selenium concentrations were found in pore waters from sediment samples, benthic invertebrates and fish associated with highly contaminated sediments [36]. Bioaccumulation experiments confirm that sediment-dwelling organisms accumulate selenium from contaminated sediments [36]. Collectively, these data suggest that the benthic fauna from certain areas of the lake system are important sources of selenium to the fish of Lake Macquarie [36].

In 2003, Barwick and Maher investigated the biotransference and biomagnification of selenium, copper, cadmium, zinc, lead and arsenic in a temperate seagrass ecosystem from the Lake Macquarie estuary. Biotransference is the transfer of trace metals from a food source to consumer, and biomagnification is when an increase in trace metal concentration occurs through at least two trophic levels in a food chain [90]. This study concluded that selenium biomagnification was found in the contaminated seagrass ecosystems, resulting in selenium concentrations above the maximum permitted concentrations for human consumption in three of the four carnivorous fish species examined, all of which are consumed by humans. Selenium concentrations were also above those that have been generally shown to cause adverse effects in aquatic organisms [90].

There was no evidence of biomagnification of copper, cadmium, zinc, or lead as concentrations were below levels shown to elude adverse responses to aquatic biota [90]. Arsenic showed some evidence of biomagnification [90]. Total arsenic concentrations were found to be similar to those found in other uncontaminated marine organisms and inorganic arsenic concentrations were below the maximum permitted concentrations for human consumption [90].

It is evident from the extensive research undertaken on trace element input from industrial sources such as Vales Point Power Station on Lake Macquarie over the past 20 years that the element of real concern impacting on the lake is selenium. As such, any ash dam water treatment process should be designed to maximise the reduction of this trace element above any other trace element present in the discharge water.
1.5 SUMMARY OF SELENIUM AND TRACE ELEMENT TREATMENT PROCESSES

The treatment of ash water for the removal of trace elements, in particular selenium, for electricity generation industries utilising coal in Australia and throughout the world has been the subject of ongoing investigations over the past 30 years. A number of different treatment processes have been investigated, in particular adsorption and coprecipitation with hydrous metal oxides. There are many factors which affect the efficiency of removal of a trace substance from solution, such as speciation of the trace element, oxidation state, pH, competing ligands and cations, type and characteristics of the solid substrate, general composition of the solution, temperature, competition for adsorption sites, time of contact, etc. [91]. The type of treatment process utilised for a source of contaminant such as ash water must be developed site-specifically to cater for the chemical characteristics of the water being treated.

Additional to a treatment process requiring a high efficiency of removal for targeted trace elements of environmental concern, the process also needs to be economically viable, low in complexity for operational control and maintenance, and must produce a waste product that is inert and capable of long term storage. A number of treatment options for the removal of trace elements, in particular selenium, from ash water which have been investigated in the past are briefly outlined in the following sections, including efficiencies of removal and a discussion of the technical feasibility of these processes in terms of the complexity of the process, cost and management of waste by-product(s).

1.5.1 Precipitation – Coagulation / Flocculation

Commercial iron salts such as ferrous chloride (FeCl₂) and ferrous sulfate (FeSO₄) in a coagulation/flocculation treatment process will achieve high efficiency of removal of both selenium and arsenic. In the case of selenium, the removal efficiency can be in the order of 90%, providing the selenium is predominantly in the selenite (SeO₃²⁻) form and at a pH range from 4 to 6. This technology works well for As(V), but is only marginally effective for As(III) [11].
Chapter 1 Introduction

The chemical reaction for the coagulation/flocculation of ferrihydrite (represented as the hydroxide Fe(OH)₃) adsorption process is as follows [11]:

\[
\begin{align*}
\text{Fe}^{3+} + 3 \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3^{\text{(solid)}} + 3 \text{H}^+ \quad (1) \\
\text{SeO}_4^{2-} + \text{Fe(OH)}_3^{\text{(solid)}} & \rightarrow \text{Fe(OH)}_3\cdot\text{SeO}_4^{2-}^{\text{(solid)}} \quad (2)
\end{align*}
\]

A key impediment to this process for the treatment of numerous trace elements is its inability to operate as a simple staged process not requiring pH adjustment. The optimal removal pH for selenium differs from that best suited for arsenic [11]. If both components are to be treated in a single process step, compromises have to be made that will affect the effluent quality. In order to achieve the lowest levels of both arsenic and selenium, a two-step process, operating at different pH levels, may be needed [11].

While coagulation/flocculation can be an effective process for removing arsenic and selenium, it has the major drawback of producing a residual sludge requiring appropriate disposal [11]. The dried sludge may be a hazardous waste, requiring further treatment which would result in high disposal costs [11]. Compared to other processes, coagulation/flocculation is a complicated, operator-intensive operation requiring handling of dangerous chemicals [11]. Moreover, the coagulation/flocculation process is a high cost process requiring a large mixing vessel, use of expensive chemical reagents and pH adjustment, implementation of a control system, operations personnel and management of waste disposal.

1.5.2 Reverse Osmosis

The reverse osmosis (RO) process can make use of either a cellulose acetate membrane or thin-film polyamide membrane [92]. These membranes operate as molecular filters to remove up to 95–99% of all dissolved minerals, 95–97% of most dissolved organic material and more than 98% of biological and colloidal matter from water [92].

Reverse osmosis membranes have shown the capacity to remove both arsenic and selenium to a relatively high degree [11]. Other than the standard RO pre-treatment, no special preconditioning is required [11]. Arsenic is rejected mostly in its
As(V) form, with rejections of greater than 90% [11]. However, As(III) is rejected to a lesser degree, with results showing 51 to 80% reductions [11].

An impediment to utilising RO for treatment of ash water is the need for pre-treatment and anti-scaling or anti-fouling agents. Scale or precipitous fouling is one of the major causes of inefficiencies of RO systems [94]. If membrane fouling occurs, the quality and quantity of the water produced will be affected. Contaminants such as calcium, magnesium, aluminium, manganese, iron, silica and sulfates can cause fouling of RO membranes [93].

Whereas RO treatment yields high reductions in selenium, arsenic and other trace elements, the cost of installation is high (in the millions of dollars) and requires ongoing expenditure for operation and maintenance. The amount of brine reject from an RO system could be as high as 20% [92]. For a plant treating 5 ML/day the amount of reject generated would be 1 ML/day [92]. The volume of an RO reject can be reduced by placement in evaporation ponds, but the concentrate would still require appropriate disposal [92].

Moreover, operation and maintenance of RO plant requires skilled personnel [92]. Incorrect operation of an RO plant could lead to destruction of membranes, for example by applying the wrong type of scale inhibitor [92], with significant cost implications.

1.5.3 Brine Concentrator

The Brine Concentrator (BC) system is essentially a process whereby wastewaters are purified through distillation [92]. From this process, approximately 95% of the waste stream is recovered as high-purity distilled water [92]. The BC units have the capacity to treat 3.4 ML/day of wastewater, producing 3.3 ML/day of distillate and approximately 0.1 ML/day of brine [92].

Evaporation would be an effective means of separating arsenic and selenium from bulk water [11]. Whereas many power plants have vapour compression or other evaporators as part of their wastewater management, these units are typically specifically sized for a final volume reduction stage prior to discharge to evaporation ponds or crystallisers and as such are suited to processes where the volume to be treated is not variable but known [11].
Like RO treatment, BC units require high capital and operating costs with the plant installation costing in the millions of dollars. The main advantage BC treatment has over RO is the volume of reject produced is much smaller, thus requiring less cost of disposal.

1.5.4 Ion Exchange

Ion exchange resins, both cationic and anionic, have been employed in the electricity generation industry primarily for the purification of water utilised in the generation of saturated steam by a process known as demineralisation. This process has not been generally used in the electricity industry in Australia for treatment of wastewater; however, it is an effective means of removing selenium, arsenic and other trace elements, although at a high capital and operating cost.

Strong base (anion) ion exchange resins are typically used for this application [11]. The order of ion exchange preference for the strong base resins as presented by the Electricity Power Research Institute 2004 report entitled “Arsenic and Selenium Treatment Technology Summary for Power Plant Wastewaters” is as follows:

\[
\text{HCrO}_4^- > \text{CrO}_4^{2-} > \text{ClO}_4^- > \text{SeO}_4^{2-} > \text{SO}_4^{2-} > \text{Br}^- > (\text{HPO}_4^{2-}, \text{HAsO}_4^{2-}, \text{SeO}_3^{2-}, \text{CO}_3^{2-}) > \text{CN}^- , \text{NO}_2^- > \text{Cl}^- > (\text{H}_2\text{PO}_4^-, \text{H}_2\text{AsO}_4^-, \text{HCO}_3^-) > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{F}^- \]

Selective selenium removal has been described using a metal hydroxide loaded ion exchange resin, an approach that is particularly valuable in high salt streams like brines but not in the treatment of ash water [11]. Selenium can also be selectively removed with chelating resins loaded with oxyanions, but this is a specialised treatment option [11].

There are several drawbacks to the use of ion exchange in this application. Since sulfate is a competing component, ion exchange is typically only useful if employed on waters of low total dissolved solids and low sulfate concentration [11]. Resin fouling or scaling is another potential problem. Although the spent regenerant in this application may be used several times before discharge, it contains the removed pollutants making it a hazardous waste as a solution [11]. Unless there is an on-site opportunity to co-treat this waste stream with other wastewaters, such as in an evaporator or membrane separation system or by chemical precipitation, disposal of the regenerant may be problematic and expensive with the volume created also a consideration [11].


1.5.5 Constructed Wetlands

Constructed wetlands have been used as a process to remove pollutants, including arsenic and selenium from wastewaters [11]. While viable and reasonably effective, this technology is not considered to be cost effective as a stand-alone process for selenium and arsenic, considering the scale and volume that can be treated [11].

In the late 1990s, Delta Electricity trialled the use of wetlands for the removal of selenium, in particular selenate, from the Kerosene Vale ash dam. Two wetlands were established near the ash dam to treat ash water from Wallerawang Power Station’s operations. The process was not deemed to be economically viable due to the large area required to treat ash water for the reduction in selenium that was achieved by this process.

A negative implication for using constructed wetlands to remove arsenic and selenium is the potential for creating a toxic hazard for fish and wildlife within the plants and sediment that takes up these substances [11]. Removed and retained arsenic and selenium can eventually lead to bioaccumulation, increasing its concentration in the aquatic food chain many times over [11].

1.5.6 Bioreactors

Studies have found biofilm reactors can be an effective and economical means for treating selenium and arsenic as well as other metals and pollutants in wastewater [11]. Bioreactors are typically anaerobic processes that are designed using specialised microbes which are controlled by the controlled addition of nutrients to sustain the biomass material within the reactor [11]. The biofilm is formed on a substrate within the reactor vessel where a stable biomass product is established [11]. The nutrient supplements added to maintain the process consist of organics such as ethanol, acetic acid and biosolids [11]. Due to the variable nature of feed waters, site specific selections of microbes, nutrient blended supplements and biomass configurations are required to optimise a treatment system [11].

Researchers have found there are problems in utilising bioreactors of mixed populations of bacteria [95]. Variations in the relative populations of the different organisms with changes in conditions (e.g. temperature and nutrient level) can have an
affect on the bioreactors ability to remove selenium [95]. Difficulties have also been found in optimising the reactors to minimise the release of excess nutrient to prevent any excess release of H$_2$S produced by the SRB [95].

1.5.7 Sirfloc

Sirfloc is a waste water treatment process licensed by the CSIRO which uses magnetite for the removal of some impurities. The process using magnetic powders or magnetite has been used in the application of treating sewage water and for the removal of colour and turbidity from surface and groundwaters.

The Sirfloc process has been adopted in Australia has been employed as large scale plant for treatment of sewage. The cost of development of such plant for treatment of ash water would be high for the volume to be treated.

1.5.7 Metallic Iron

The treatment process for reducing the concentration of selenium utilising metallic iron was patented in the USA in 1983 under patent number US4405464-A [96]. The treatment process in particular is for the removal of selenium, present mainly in the selenium(VI) oxidation state as selenate, from aqueous solutions derived from process effluent streams such as mine seepage or drainage waters [92]. For successful operation, the treatment process relies on the waste solution, containing selenium as either selenite or selenate (i.e. oxidation states (IV) and (VI) respectively), being reduced when contacted with metallic iron [92]. Selenium in the Se(VI) oxidation state is reduced by metallic iron to Se(IV) [92]. Concurrently, the metallic iron is oxidised to a higher valence state forming an iron oxyhydroxide, which can precipitate from the solution [92].

Baldwin and co-workers in 1983 found that a possible mechanism for the reduction process is that selenium is either precipitated on the iron by a cementation process or precipitated on the ferric hydroxide (i.e. ferrihydrite) by adsorption upon the surface of the precipitate to form an insoluble iron selenite [96]. The preference for the form of metallic iron were either particulate or shredded iron; these forms provided a greater surface area for contact with the aqueous solution [96].
A laboratory trial undertaken by Baldwin and co-workers utilising metallic iron powder with trials ranging from pH 2.5 to 5.6 demonstrated that selenium removal (both selenate and selenite) had an efficiency of removal ranging from 97% up to 99%. The percentage of selenium in the selenate form for these trials was 90%, with only 10% as selenite. The iron-filled column utilised in the trials was operated at laboratory ambient temperature of 21 to 23 °C. The concentration of selenium which was fed continuously in the reduction column containing metallic iron powder had a linear feed rate through a column of 18 mm/min and a concentration of 0.440 mg/L. The column was operated for eight hours after each pH adjustment. Table 1.5 provides the selenium reduction efficiencies obtained during the laboratory trials reported by Baldwin and co-workers.

Table 1.5  Selenium reduction efficiencies with metallic iron powder as reported by Baldwin and co-workers [96]. (Initial Se concentration was 0.440 mg/L.)

<table>
<thead>
<tr>
<th>Test Number</th>
<th>pH</th>
<th>Effluent Selenium Concentration in Reduction Column (mg/L)</th>
<th>Selenium Removed in Reduction Column (mg/L)</th>
<th>Reduction Column Extraction Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.6</td>
<td>0.014</td>
<td>0.426</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>5.3</td>
<td>0.013</td>
<td>0.427</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>4.6</td>
<td>0.003</td>
<td>0.437</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>4.2</td>
<td>0.006</td>
<td>0.434</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>3.7</td>
<td>0.005</td>
<td>0.435</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>0.012</td>
<td>0.428</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>0.012</td>
<td>0.428</td>
<td>97</td>
</tr>
</tbody>
</table>

Limited, though encouraging experimental studies completed by Riley and co-workers in 2001 assessed the feasibility of utilising elemental iron to remove selenium in both selenate and selenite forms by coupling the reduction of these compounds to the oxidation of iron metal [95]. One of the experiments conducted in their study was to utilise iron “wool” for the removal of selenate (SeO₄²⁻) over a period of a few hours at different pH levels. The results of these experimental trials found that selenate was reduced and removed from solution in a few hours. The rate of removal appeared to
have some dependence on pH. It is to be expected that the surface area is a major factor in the reaction [95]. Table 1.6 provides the experimental results of selenate removal trials performed using solutions which contained starting concentrations of 73 µg/L selenate. The amount of steel wool utilised in these trials was 4 g in 400 mL solutions. The 500 mL containers employed were mixed for a total of 22 hours, with 10 mL samples taken at intervals for analysis.

Table 1.6  Reduction of selenate by elemental iron; time and pH dependence [95].

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Initial pH</th>
<th>Se (total) µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.96</td>
<td>3.99</td>
</tr>
<tr>
<td>0</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>1</td>
<td>3.2</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>&lt;0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>22</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The results from this experimental trial demonstrates that the removal of selenate is most efficient at lower pH levels; moreover, over time this process will remove greater than 99% of selenium even in the selenate form [96]. The initial pH values were varied from pH 3 to 8. However, it should be noted that the pH changed during the course of the experiment [95]. Table 1.7 provides the pH values determined at the start of the experiments and after periods of 5 and 22 hours.

Table 1.7  Change in pH during oxidation of iron metal [95].

<table>
<thead>
<tr>
<th>Nominal pH</th>
<th>Time</th>
<th>Measured pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h</td>
<td>5 h</td>
</tr>
<tr>
<td>3</td>
<td>2.96</td>
<td>4.98</td>
</tr>
<tr>
<td>4</td>
<td>3.99</td>
<td>5.90</td>
</tr>
<tr>
<td>5</td>
<td>4.99</td>
<td>6.28</td>
</tr>
<tr>
<td>6</td>
<td>6.00</td>
<td>7.76</td>
</tr>
<tr>
<td>7</td>
<td>6.80</td>
<td>7.80</td>
</tr>
<tr>
<td>8</td>
<td>7.95</td>
<td>9.64</td>
</tr>
</tbody>
</table>
The continuous removal of selenium as selenate was also probed in the experiments undertaken by Riley and co-workers. They employed a column packed with steel wool and a solution of ‘artificial’ ash water, pumped via a peristatic pump into the base of the column at constant flow rates of 15 mL/h or 150 mL/h. The results of this experiment are provided in Table 1.8 below.

Table 1.8 Analysis of feed and exit solutions from a steel wool-packed column [95].

<table>
<thead>
<tr>
<th>Solution</th>
<th>Flow rate</th>
<th>Se µg/L</th>
<th>Fe mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td></td>
<td>204</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Exit day</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>15 mL/h</td>
<td>&lt;0.1</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.1</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>&lt;0.1</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.2</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>0.2</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.4</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>0.3</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.5</td>
<td>37</td>
</tr>
<tr>
<td>16</td>
<td>150 mL/h</td>
<td>31</td>
<td>36</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>&lt;0.1</td>
<td>41</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>0.4</td>
<td>39</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>2.5</td>
<td>46</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>4.3</td>
<td>44</td>
</tr>
</tbody>
</table>

As demonstrated in this experiment, selenate is effectively removed when the water is in contact with oxidising iron for only a few hours [95]. The pH of the ‘artificial ash dam water’ introduced into the column was 4.5. After passing through the
column, the pH had risen to approximately 5.5 [95]. The iron concentration had also increased, consistent with oxidation during the process [95].

The use of iron metal has a number of advantages [95]. Although no comprehensive study was completed on the effect of pH, it appears that the reaction may work at a higher pH range when employing direct adsorption onto iron oxyhydroxide [95]. Selenium was removed from water at pH 9, although the rate of removal was pH dependent [95]. A clear advantage of this process is its simplicity, in that the process only requires the ash water to have a sufficient amount of contact with the iron metal even at elevated pH levels to remove selenium at efficiencies of up to 99%. The cost of utilising a process of this nature would be low in terms of capital and operating cost. For these reasons, this process has been further investigated and is the subject of this thesis.

1.6 INVESTIGATION OF ASH WATER TREATMENT PROCESSES FOR VALES POINT POWER STATION

In 2000 a preliminary investigation was undertaken at Vales Point Power Station to determine the amount of removal of selenium from ash dam water, focusing mainly on selenate removal from Wallerawang Power Station ash dam water, utilising surface oxidised iron or metallic iron. Prior to the experiments being undertaken, the iron was placed in ash dam water to allow an initial coating of rust to form. As a result of achieving success in the removal of selenate from Wallerawang ash dam water, an experimental trial was conducted utilising Vales Point Power Station ash dam water, which contains selenium predominantly as selenite, SeO$_3^{2-}$. A laboratory testing apparatus was set up involving a Perspex column with an internal diameter of 38 mm and length of 550 mm. The column was filled with rusty iron bars. Vales Point Power Station ash water was pumped through the column by a Masterflex Easy-Load 11 peristatic pump at a rate of 100 mL/minute. A picture of this trial laboratory equipment conducted at Vales Point Power Station appears as Image 1.1, and outcome in terms of the reduction in selenium concentration over time in Figure 1.4.
Image 1.1 Trial laboratory equipment employed to probe selenite remove from Vales Point Power Station ash water.

Selenium reduction in this basic experiment utilising steel bars as a single-pass system occurred with an encouraging efficiency of removal of 70%. The following Figure 1.3 illustrates this trend, with total selenium concentration (µg/L) versus time in minutes for the single-pass system.

![Selenium Reduction with Rusty Steel Bars](image)

Figure 1.3 Selenium reduction using rusty steel bars in a single-pass system.

The laboratory apparatus used in the above experiment with steel bars was also employed with these replaced by steel wool, which has a much higher surface area. The result of this preliminary trial was a removal of 99% selenite from the ash dam water in less than 20 minutes. Clearly, the process has promise.
1.7 REMOVAL OF TRACE ELEMENTS WITH IRON OXIDES

Iron oxides are common compounds which are present everywhere in nature [97,98]. They are found in soils and rocks, lakes and rivers, on the seafloor, in the air and in organisms [98]. Iron oxides are of great significance for many of the processes taking place in ecosystems [98]. They are important regulators of the concentration and distribution of plant nutrients and pollutants such as heavy metals [98]. Iron oxides are, in general, compounds with low to very low solubility. In natural systems, where most iron is in the form of Fe(III) oxides or oxyhydroxides, the iron should be present in an immobile form [98].

There are sixteen iron oxide species known, and consist of oxides, hydroxides or oxyhydroxides [98]. They are composed of iron together with $O^{2-}$ and/or $OH^-$, and in most compounds iron is in the trivalent state. Table 1.9 reports general properties of major iron oxides, and is taken from Schwertmann and Cornell [97]. It lists the properties of eight iron oxides. Four oxides that form the subject of this thesis are included, being goethite, hematite, lepidocrocite and magnetite; these are outlined further below.

Precipitation, dissolution and reprecipitation of iron oxides in the environment depend very much on factors such as pH, Eh, temperature and water activity [97]. Goethite, $\alpha$-FeOOH, and hematite, $\alpha$-Fe$_2$O$_3$, are thermodynamically the most stable at ambient temperatures. These iron oxides form under aerobic surface conditions and are the most widespread Fe oxides in soils and sediments [97].

Goethite has the diaspore structure which is based on a hexagonal close packing (hcp) arrangement of anions and, being one of the most thermodynamically stable, it is the first oxide to form and also the end member of many transformations [98]. In massive crystal aggregates, the oxyhydroxide goethite is dark brown or black, whereas the powder is yellow and is responsible for the colour of many rocks, soils and ochre deposits [98].

Hematite is the oldest known iron oxide mineral in the world and is widespread in soils and rocks, with the corundum structure which is based on an hcp anion packing structure [98]. The colour of hematite is red if finely divided, and black or sparkling grey if coarsely crystalline [98]. Like goethite, hematite is extremely stable and is often the end member of transformations of other iron oxides [98].
Lepidocrocite, $\gamma$-FeOOH, is generally less widespread [97]. It does occur frequently as orange accumulations in certain environments which are characterised by the presence of Fe(II) from which lepidocrocite forms as a result of oxidation [97]. The presence of this mineral, therefore, indicates a deficiency of oxygen; in soils this is due mainly to excessive moisture [97]. The colour of lepidocrocite is orange and it has the boehmite structure which is based on a cubic close packing (ccp) arrangement of anions [98].

Magnetite, Fe$_3$O$_4$, in soils is often lithogenic in origin, but can be formed in surface environments by biological processes. It has been detected in various biota including bacteria, bees and pigeons [97] and in the electricity generating industry magnetite formation in boiler wall tubes has been promoted to prevent corrosion. It is a black, ferrimagnetic mineral containing both Fe(II) and Fe(III) and it’s structure is that of an inverse spinel [98].

The adsorption of ions on iron oxides regulates the mobility of species in various parts of ecosystems, including uptake of plant nutrients from soil and the movement of pesticides or other pollutants from soils to aquatic systems [98]. In such environments various ions often compete with each other for adsorption sites [98]. Adsorption is the essential precursor of metal substitution, dissolution reactions and many interconversions [98]. In industry, adsorption on iron oxides is of relevance to flotation processes, pollution control, and waste and anti-corrosion treatments [98].

The abundance and availability of inexpensive iron materials to form iron oxides such as goethite, hematite, lepidocrocite and magnetite is high. Consequently, the ability of the oxides to remove trace elements present in industrial waste water such as ash dam water (including selenium, arsenic, vanadium, chromium, aluminium and molybdenum) is industrially attractive, and warrants more definitive research. In particular, research to determine the efficiency of removal of targeted trace elements such as selenium utilising goethite, hematite, lepidocrocite and magnetite across various pH values and reaction times is required; this is to not just to seek a better understanding of the chemical and physical processes involved, but to be able to optimise the efficiency of the process for industrial scale water treatment.

The following Figure 1.4 provides the pH-potential diagram or Eh-pH (Pourbaix) diagram of iron oxides which highlights at specific pH levels the iron species present.
Figure 1.4 Pourbaix diagram of Iron

Table 1.9 on the following page provides general properties of a number of iron oxides and oxyhydroxides.
### Table 1.9 The Iron Oxides and their General Properties [97].

<table>
<thead>
<tr>
<th></th>
<th>Goethite</th>
<th>Hematite</th>
<th>Lepidocrocite</th>
<th>Magnetite</th>
<th>Maghemite</th>
<th>Ferrihydrite</th>
<th>Akaganeite</th>
<th>Feroxyhyte</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>α-FeOOH</td>
<td>α-Fe₂O₃</td>
<td>γ-FeOOH</td>
<td>Fe₃O₄</td>
<td>γ-Fe₂O₃</td>
<td>Fe₅HO₈.4H₂O</td>
<td>β-FeOOH</td>
<td>δ-FeOOH</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>orthorhombic</td>
<td>Trigonal</td>
<td>orthorhombic</td>
<td>cubic</td>
<td>cubic (or tetragonal)</td>
<td>hexagonal</td>
<td>tetragonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td><strong>Cell dimension (nm)</strong></td>
<td>a=0.4609 b=0.9956 c=0.30215</td>
<td>a=0.5034 b=1.3752</td>
<td>a=0.388 b=1.254 c=0.307</td>
<td>a=0.839</td>
<td>a=0.834 a=0.508 c=0.94</td>
<td>a=1.000 b=0.3023 c=1.0513</td>
<td>a=0.293 c=0.460</td>
<td></td>
</tr>
<tr>
<td><strong>Formula units per unit cell, Z</strong></td>
<td>4</td>
<td>6</td>
<td>4</td>
<td>8</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>yellow-brown</td>
<td>red</td>
<td>orange</td>
<td>black</td>
<td>reddish-brown</td>
<td>red-brown</td>
<td>yellow-brown</td>
<td>red-brown</td>
</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>4.26</td>
<td>5.26</td>
<td>4.09</td>
<td>5.18</td>
<td>4.87</td>
<td>3.96</td>
<td>3.56</td>
<td>4.20</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>5-5.5</td>
<td>6.5</td>
<td>6</td>
<td>5</td>
<td>5.5</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Octahedral site occupancy</strong></td>
<td>1/2</td>
<td>2/3</td>
<td>1/2</td>
<td>-</td>
<td>-</td>
<td>&lt;2/3</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td><strong>Type of magnetism</strong></td>
<td>antiferromag.</td>
<td>weakly ferromag. or antiferromag.</td>
<td>antiferromag.</td>
<td>ferrimag.</td>
<td>ferrimag.</td>
<td>speromag.</td>
<td>antiferromag.</td>
<td>ferrimag.</td>
</tr>
<tr>
<td><strong>Neel (Curie) temperature (K)</strong></td>
<td>400</td>
<td>(956)</td>
<td>77</td>
<td>(850)</td>
<td>(820-986)</td>
<td>25-115*</td>
<td>290</td>
<td>440-450</td>
</tr>
<tr>
<td><strong>Standard free energy of formation ΔG°(kJ/mol)</strong></td>
<td>-488.6</td>
<td>-742.7</td>
<td>-477.7</td>
<td>-1012.6</td>
<td>-711.1</td>
<td>-699</td>
<td>-752.7</td>
<td>-</td>
</tr>
<tr>
<td><strong>Solubility product (pFe³⁺pOH)</strong></td>
<td>40-44</td>
<td>42.2-43.3</td>
<td>~42</td>
<td>35.7**</td>
<td>40.4</td>
<td>38.0-39.5</td>
<td>34.8***</td>
<td>-</td>
</tr>
</tbody>
</table>

* blocking temperature
**log(Fe³⁺)³/(H)₈(e⁻)²
***pFe + 2.7pOH
1.8 AIMS AND RESEARCH OUTLINE

The objectives of this research are divided into five main areas as outlined below:

1. To determine, during a field investigation utilising a pilot plant, the process of coprecipitation and/or adsorption of trace elements, in particular selenium, and the efficiency of removal of trace elements from power station ash water with the use of iron oxyhydroxide formed from the rusting of solid iron materials.

2. To determine, through field investigations in an industrial chemical process environment, the abundances and types of iron oxide forms generated by the use of oxidising iron materials which cause removal of selenium and other trace elements from ash waste water to occur.

3. To examine, through laboratory trials using pure synthetic iron oxides that are components of the oxidised iron surface in the pilot plant, the efficiency of removal of trace elements such as environmentally sensitive selenium and arsenic, and to examine to a lesser extent chromium, vanadium, aluminium, antimony and molybdenum removal; this will employ a range of pH values and solution matrices such as demineralised water, sodium chloride and sodium sulphate solutions, and power station ash water.

4. To determine the rate of removal of trace elements including selenium, arsenic, chromium, aluminium, vanadium, antimony and molybdenum from power station ash water with iron oxide material identical to that formed by the pilot plant at Vales Point Power Station.

5. To investigate the leachability of precipitated oxyhydroxide sludge formed during the pilot plant field investigation to determine the viability of the process in terms of long term storage of the product material.
1.9 REFERENCES


CHAPTER TWO
IRON OXIDES: A BACKGROUND

2.1 INTRODUCTION

As proposed in Chapter One, the treatment for removal of trace elements such as selenium in ash water can be costly and complex in design, ongoing operation and maintenance. However, the use of iron oxides (in particular goethite, hematite, lepidocrocite and magnetite formed through the surface oxidation or rusting of solid iron in the presence of waste ash water) has been proposed as an inexpensive and simple process requiring minimal operator and process control.

To minimise environmental impacts by adjusting trace pollutants to below guideline trigger levels, it is important to optimise the rate and/or efficiency of removal by iron oxides of targeted trace elements such as selenium, arsenic, chromium, vanadium, molybdenum and aluminium. For this to occur, an understanding of chemical characteristics, crystalline structures, the formation of oxides and the adsorption/co-precipitation process or processes is required, both under controlled laboratory conditions and in the field utilising pilot plant trails. The background that provides the basis for this understanding is developed below.

2.2 CHARACTERISATION OF IRON OXIDES

Iron oxides produced in nature and under both controlled and uncontrolled environments can be characterised by a number of parameters including: chemical composition and formula; colour; crystalline dimensions and structure; and surface area and porosity. There is an array of methods available to determine these parameters both qualitatively and quantitatively [1, 2]. These include visual colour observations by colour comparisons involving charts, submicroscopic particle characterisation utilising X-ray diffraction and electron microscopy, and surface area determination using methodologies such as the Brunauer-Emmett-Teller (BET) or Ethylene Glycol Mono Ethylether (EGME) techniques.
Iron oxides form readily in both natural and manipulated environments. The characteristics of iron oxides developed in an environment such as a laboratory or manufacturing process whereby the temperature, type and mass of chemical reagents, volume of solution, rate of mixing, pH and dissolved oxygen concentration are controlled will differ from that in an uncontrolled environment such as a field plant process. This relates to the low level of control in the latter situation, where variation in conditions over time can lead to a complex suite of oxide materials.

The formation of the iron oxides may not be just due to precipitation from iron containing solutions, but can be the result of oxidation of metallic iron or steel in naturally aerated water flowing over the surface. In this type of environment the size of the iron oxide crystals and their chemical composition may be governed by factors including pH, conductivity, dissolved oxygen concentration, solution matrix or purity of water, purity of carbon steel and surface area, and rate of flow across the solid surface. Transformations from an initially formed iron oxide or oxyhydroxide to other structures along with interconversions can also occur over time, complicating the system under study. Interconversions between the different compounds listed in Table 2.1 are possible and often occur readily [1]. At lower temperatures and in the presence of solutions, interconversions often involve dissolution followed by reprecipitation of the new phase, although oxidation or reduction reactions are also possible [1].

Table 2.1  The major iron oxides and oxyhydroxides.

<table>
<thead>
<tr>
<th>Oxyhydroxides</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td><strong>Mineral</strong></td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>Goethite</td>
</tr>
<tr>
<td>$\beta$-FeOOH</td>
<td>Akaganeite</td>
</tr>
<tr>
<td>$\gamma$-FeOOH</td>
<td>Lepidocrocite</td>
</tr>
<tr>
<td>$\delta$-FeOOH</td>
<td>Feroxyhyte</td>
</tr>
<tr>
<td>Fe$_5$HO$_8$.4H$_2$O</td>
<td>Ferrihydrite</td>
</tr>
</tbody>
</table>

In this work, the characterisation of iron oxides employs an array of methods. These involve visual comparison to colour plates, particle sizing, scanning electron microscopy and X-ray diffraction. These are applied both to samples generated by field trials, which have uncontrolled parameters such as flow, temperature, pH, conductivity,
dissolved oxygen and trace element concentrations, and to those prepared in a controlled laboratory environment.

### 2.2.1 Iron Oxide Formation and Transformation Pathways

During field investigations, the formation of goethite, hematite, lepidocrocite and magnetite on carbon steel plates occurred. This process most likely developed through oxidative dissolution of the parent material, via the formation and transformation pathways (Figure 2.1) defined by Schwertmann and Cornell [1].

![Figure 2.1 Schematic representation of formation and transformation pathways of common iron oxides, together with the approximate transformation conditions [1].](image)
The formation of oxyhydroxides and oxides in the field investigation of the treatment of ash water by solid iron reported in the following chapters should be governed in large part by the chemical characteristics of the ash water that is being treated by the process. The formation of the four oxyhydroxides/oxides observed are likely to be influenced by the solution matrix, where chloride and sodium concentrations in the order of 9,000 mg/L and 7,000 mg/L and sulfate concentrations of 1,300 mg/L exist. The pH of the ash water, which was observed to be in the range 8.0 to 8.8, would also be a contributing factor, along with the concentration of dissolved oxygen. Further, there are a wide range of trace elements present in the ash water, which include aluminium, selenium, antimony, iron, arsenic, boron, cadmium, chromium, cobalt, lead, manganese, molybdenum, nickel, vanadium, zinc and fluoride, and these can influence speciation, as reported in earlier studies.

The synthesis of thermodynamically stable iron oxides from initially formed green rusts or from ferrihydrite involves phase transformation or the conversion of one crystalline iron oxide or oxyhydroxide into another [1]. Ferrihydrite is the initial product that results from the fast hydrolysis of a Fe$^{3+}$ salt solution formed with mixing of an alkali [1]. This thermodynamically unstable product will over time transform into goethite or hematite, which are formed by different pathways, or else a mixture of the two [1]. Goethite precipitates directly in solution via a nucleation-crystal growth process, whereas formation of hematite requires the presence of ferrihydrite as a precursor [1]. Hematite forms within the ferrihydrite particles by a dehydration/rearrangement mechanism, whereas formation of goethite can proceed via dissolution of ferrihydrite followed by nucleation and growth of the crystalline phase [1]. The formation of hematite and goethite is found to be competitive. The conditions that favour the formation of hematite can inhibit the formation of goethite and vice versa [3]. Conditions affecting transformation reactions include those that affect the kinetics of transformation and the composition and morphology of the transformation products [3]. The formation of goethite is favoured under pH conditions whereby ferrihydrite dissolution is promoted between pH <4 and pH >11 [4]. The formation of hematite is preferred under pH conditions which promote internal aggregation [pH values close to the p.z.c. of ferrihydrite (pH 7-8)] [4]. Thus, pH values which favour the formation of goethite inhibit the formation of hematite. Soluble ions will influence the composition of the transformation products of ferrihydrite through the alteration of the relative rates at which hematite and goethite form [5]. The presence of foreign ions
generally inhibits the formation of goethite, resulting in the indirect formation of hematite [3].

Green rusts have been described as a group of blueish-green Fe$^{2+}$ and Fe$^{3+}$ hydroxy salts formed during the corrosion of steel under oxygen deficient conditions [2]. Green rusts are not simple iron oxides or oxyhydroxides as they contain anions as essential structural components [1], and consist of hexagonally close-packed layers of OH$^{-}$ and O$_2^-$ of the Fe(OH)$_2$ type with Fe$^{2+}$ and Fe$^{3+}$ in the interstices [6,7]. The Fe$^{3+}$ ions give the structural layers a positive charge which is balanced by intercalation of anions between the layers [1]. Structures with chloride, sulfate and carbonate between the layers have been found [1]. The formation of intermediate, green rust mixed with Fe$^{2+}$ and Fe$^{3+}$ phases will predominate if oxidation takes place under slightly acid to slightly alkaline conditions [2]. This is because the solubility product of Fe(OH)$_2$ is then no longer exceeded [2].

Lepidocrocite has been found to form through oxidation of aqueous Fe$^{2+}$ solutions via a green rust intermediate with a direct precipitation from low molecular weight Fe$^{3+}$ species also taking place [2]. Magnetite can be formed from weakly alkaline aqueous systems with pH levels greater than 8 via precipitation from a mixed Fe$^{2+}$ and Fe$^{3+}$ solution through the oxidation of Fe$^{+2}$ solution from green rust or Fe(OH)$_2$, and by interaction of Fe$^{2+}$ with ferrihydrite [2].

Iron oxides and oxyhydroxides including goethite, lepidocrocite, magnetite and hematite can be produced from Fe$^{2+}$ solutions by oxidation followed by hydrolysis [2]. The formation of these oxides and oxyhydroxides is governed by parameters such as pH, temperature, concentration of Fe$^{2+}$, other ions or compounds in the system, and the rate of oxidation. Unless the reaction conditions of the formation process are carefully controlled, mixtures, rather than a monophasic product can result [2]. This may result in the formation of pairs of products or even more admixed species of iron oxides and oxyhydroxides forming.

The conditions for the predominance of one iron oxide or oxyhydroxide in various pairs of oxides formed via oxidation of Fe$^{2+}$ salts at pH 4 to 9 is illustrated in Table 2.2, as developed by Cornell and Schwertmann [2]. The predominance of one iron oxide and oxide-hydroxide pair formed in an uncontrolled system such as that operating in a field investigation, such as where waste ash water passes over solid iron, will be affected by parameters such as the concentration of dissolved oxygen, conductivity, pH, temperature, flow rate and cation and anion concentrations.
Table 2.2 Conditions for the predominance of one compound in various competing pairs of oxides formed via oxidation of Fe$^{2+}$ salts at pH 4 to 9 [2].

<table>
<thead>
<tr>
<th>Goethite</th>
<th>Lepidocrocite</th>
<th>Lepidocrocite</th>
<th>Ferrihydrite</th>
<th>Lepidocrocite</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ present</td>
<td>CO$_2$ absent</td>
<td>slow oxidation</td>
<td>fast oxidation</td>
<td>slow oxidation</td>
<td>fast oxidation</td>
</tr>
<tr>
<td>sulfate present</td>
<td>chloride present</td>
<td>lower pH</td>
<td>higher pH</td>
<td>pH &gt;5</td>
<td>pH &lt;5</td>
</tr>
<tr>
<td>slow oxidation</td>
<td>fast oxidation</td>
<td>Al, Mn, Co ions present</td>
<td>-</td>
<td>Si present</td>
<td></td>
</tr>
<tr>
<td>lower pH</td>
<td>higher pH</td>
<td>Lepidocrocite</td>
<td>Lepidocrocite</td>
<td>Lepidocrocite</td>
<td>Magnetite</td>
</tr>
<tr>
<td>slow oxidation</td>
<td>fast oxidation</td>
<td>pH &gt;5</td>
<td>pH &lt;5</td>
<td>Si present</td>
<td></td>
</tr>
<tr>
<td>fast oxidation</td>
<td>slow oxidation</td>
<td>low temperature</td>
<td>high temperature</td>
<td>low temperature</td>
<td>high [Fe$^{2+}$]</td>
</tr>
<tr>
<td>lower pH</td>
<td>higher pH</td>
<td>chloride present</td>
<td>-</td>
<td>high [Fe$^{2+}$]</td>
<td></td>
</tr>
<tr>
<td>low [Fe$^{2+}$]</td>
<td>-</td>
<td>Lepidocrocite</td>
<td>Magnetite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In an uncontrolled environment or field investigation where the aqueous system is saline ash water which passes over the surface of oxidising iron, the concentrations of anions such as chlorides, sulfates and silicates vary along with cations, pH, temperature and dissolved oxygen levels. Hence it can be expected that a number of mixed iron oxides and oxyhydroxides will form as local conditions vary. The abundances or growth of iron oxide and oxyhydroxide substances such as goethite, hematite, lepidocrocite and magnetite in an uncontrolled system could be constantly changing depending on the conditions at the time of formation.

### 2.2.2 Colour of Iron Oxides

Colour provides a simple and effective guide to the type of iron oxide. In the present study, the iron oxides which had formed on the surface of carbon or mild steel plates during field trials were separated and subjected to preliminary characterisation in accordance with the colour of the oxide formed and the definitive colours of the
Schwertmann and Cornell plate, reproduced as Plate 2.1 below [1]. Samples were collected by taking solid pieces of oxide material flaking off the surface of the plates. This is a standard methodology that is quite effective because of the colour diversity of iron oxides.

Plate 2.1 Colours of the common iron oxides [1].

The colour of an iron oxide in a powdered form depends mainly on its mineral-specific crystal structure [1]. Each oxide has, therefore, a typical colour, as defined in Plate 2.1. For example, goethite and akaganeite usually exhibit yellow-brown colours whereas hematite’s are mostly red. However, colour does vary with particulate size and the presence of other metal ions, as clearly illustrated in Plate 2.2. This behaviour, which is typical of inorganic solids generally, can complicate making an assignment from visual inspection alone, so additional characterisation is required. By separating
the oxide material by its colour and crushing the separated solid pieces into a powder, the types of oxides formed on the solid steel plates identified initially by their colour could be subjected to deeper analysis. Structural type was later confirmed through sample examination by X-ray diffraction and by the crystalline form and chemical composition determined by electron microscope imagery.

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 are shown. The right-hand column shows a goethite made with 6 mole% Mn-for-Fe substitution and with 10 mole % Cr-for-Fe substitution [1].
2.2.3 Crystal Structures of Iron Oxides

“Crystal growth may be controlled either by transport processes or by the rate of the surface chemical reaction.” Schwertmann and Cornell [1], although the mechanisms by which a crystal grows may also depend upon solution conditions [1]. Changes in the degree of supersaturation or other solution variables may even lead to a change in mechanism during growth [1]. The habit of a crystal is governed by the rate of growth of its different faces [1]. Those faces which grow slowly tend to persist in the crystal’s structure, whereas fast growing faces are eliminated [1]. Adsorbing foreign ions may alter the rates at which different crystal faces grow and thus modify the habit of the crystal [1]. The growth of crystals in the formation of oxides and oxyhydroxides on solid iron surfaces in an uncontrolled environment where the chemical constituents of the solution vary along with flow rate would be governed by both surface chemical reactions and transport processes.

Structural studies of iron oxides including X-ray structures are extensive, so the crystalline character is well understood. The structures of the dominant forms of iron oxides are described below.

2.2.3.1 Goethite

Goethite has an orthorhombic unit cell structure with \( a = 0.4608 \, \text{nm} \), \( b = 0.9956 \, \text{nm} \) and \( c = 0.3021 \, \text{nm} \) [8,12]. The goethite structure has been found to consist of an \( \text{hcp} \) array of anions (\( \text{O}^2- \) and \( \text{OH}^- \)) stacked along the [100] direction with \( \text{Fe}^{3+} \) ions occupying half the octahedral interstices within a layer of the crystal [2]. The Fe ions are arranged in double rows separated by double rows of empty sites; at the crystal surfaces the empty sites appear as grooves [2]. “Each Fe ion is surrounded by three \( \text{O}^2- \) and three \( \text{OH}^- \) to give \( \text{FeO}_3(\text{OH})_3 \) octahedra, and the structure is usually described in terms of these octahedra). Double chains of octahedra formed by edge-sharing run parallel to the [001] direction. These chains are linked to adjacent double chains by corner-sharing with one chain ultimately leading to the orthorhombic symmetry.” Cornell and Schwertmann [2]. The 2 × 1 octahedra “tunnels” are crossed by hydrogen bridges as depicted in Figure 2.2 where the double lines represent H bonds [1]. The basic morphology or external shape of goethite has been found to be acicular, as
depicted in Figure 2.3. Acicular goethite crystals can range in length from a few tens of nm to several microns in size [2]. Macroscopic crystals of natural goethite have been found to be several mm in length [2].

Figure 2.2 Structure of Goethite [1].

Figure 2.3 Crystal forms of goethite [11].

The better developed the crystal, the more forms may be present in a sample [2]. A sample composed of prismatic macrocrystals is shown in Image 2.1 below.
The basic morphology of goethite is acicular and for the synthetic goethite crystals shown by Image 2.2 tend to be elongated along the [001] direction (c-axis) and terminate in [021] faces [2]. “This type of morphology appears to have been adopted in response to the double chains of corner-shared octahedra which run parallel to the [001] direction and dominate the goethite structure.” Cornell and Schwertmann [2]. When the conditions for crystal formation is very rapid growth and/or in the presence of impurities the crystal structures form as long thin needles with a high aspect ratio [2].

The transmission electron microscope (TEM) image (Image 2.3) shows large well-developed [110] and [021] faces at the end of the goethite twinned crystal and a diamond-like cross section; it has been demonstrated that both natural and synthetic goethite crystals have a tendency to form this shape [2]. Whilst other forms of crystals cannot be excluded, it appears the [110] and [021] forms are the most important for synthetic goethite in determining the configuration and density of surface functional Fe-
OH groups which participate in adsorption reactions [2]. Larger crystals have been observed to develop more variety of faces [2].

Image 2.3  TEM image of goethite twins with well developed [110] and [021] faces [13].

“Goethite crystals produced by oxidation of Fe^{2+} solutions at ambient temperature in neutral solution – a process likely to occur in nature – are usually much less developed and the crystals are smaller than those obtained in alkaline Fe^{3+} solutions.” Cornell and Schwertmann [2]. If Al^{3+} forms part of the crystalline structure, then the crystals become exceedingly small and exhibit almost no particular habit. Although at higher pH levels around 12 the structure becomes acicular again despite Al being present in the structure (Al/(Fe+Al)~0.3) [2]. These crystals do however, show internal disorder with star shapes frequently observed [2].

“Conditions which promote multidomainic goethite are high ionic strength (either [KOH] or salt) and also low synthesis temperature (<40 °C).” Cornell and Schwertmann [2]. Such conditions apply in saline ash water treated at ambient temperatures. What has also been found is that in alkaline solutions the multidomainic character decreases whilst the domain width increases as Al substitution increases to an Al/(Fe+Al) of 0.15; at an Al/(Fe+Al) > 0.15 causing single domain crystals to form [14,15].

2.2.3.2 Lepidocrocite

Lepidocrocite has been reported as being a layered compound [2]. The orthorhombic unit cell contains four formula units with edge lengths of \( a = 0.388 \) nm, \( b = 1.254 \) nm and \( c = 0.307 \) nm [16–18]. “The crystal structure of lepidocrocite consists of
arrays of ccp anions (O\(^2-\)/OH\(^-\)) stacked along the [051] direction, with Fe\(^{3+}\) ions occupying the octahedral interstices.” Fasiska [19]. “The [051] direction of the orthorhombic unit cell corresponds to the [111] direction of a distorted cubic cell and this relationship facilitates dehydroxylation to a spinel phase.” Cornell and Schwertmann [2].

Lepidocrocite crystals are reported by Cornell and Schwertmann [2] as being like goethite and consisting of double chains of Fe(O,OH)\(_6\) octahedra running parallel to the c-axis [2]. “The double chains share edges with adjacent double chains and each chain is displaced by half, with respect to its neighbour, thus forming corrugated sheets of octahedra. The sheets are stacked perpendicular to the [010] direction and are separated by double rows of empty octahedral sites.” Cornell and Schwertmann [2]. Figure 2.4 illustrates how the sheets are held together by the hydrogen bonds [1].

Lepidocrocite crystals have been reported as being lath-like or tabular in form [2]. Ramdohr and Strunz [11] illustrate macrocrystalline lepidocrocite as being in the form of tabular crystals with [010] faces being the most predominant, as depicted in Figure 2.5. The other varieties of lepidocrocite crystals reported by Cornell and Schwertmann include micaceous and fibrous textures and aggregated scales [2].

![Figure 2.4 Structure of lepidocrocite](image)

Figure 2.4 Structure of lepidocrocite [1].
“Synthetic crystals of lepidocrocite are usually platy or lath-like, elongated in the c-direction, and terminate in [101] faces. The predominant face is [010], and crystals often lie on this face.” Cornell and Schwertmann [2]. An example of the lepidocrocite crystal formation of flat laths is demonstrated in Image 2.4, where the sample was synthesised by oxidising a FeCl₂ solution with air (100 mL/min) at 50 °C [21].

The most common process from which lepidocrocite is formed is through oxidation of Fe²⁺ systems where the crystal pattern varies with the conditions under which oxidation takes place [2]. Schwertmann and Thalmann [22] note that if the lepidocrocite crystals are formed at a faster rate, the crystals are thinner and multidomainic with domains that are ~10–20 nm wide and terminate in [101] faces [2], as depicted in Image 2.4 [1].
Additional forms are also known. “Under conditions of very rapid oxidation at low pH and/or in the presence of crystallisation inhibitors, grassy type or ‘hedgehog-like’ spherulites form.” Cornell and Schwertmann [2]. Examples of inhibitors that promote this behaviour include silicates, organics [22] and the aluminium ion [23]. Lepidocrocite precipitated rapidly from solution can also grow as thin, crumpled sheets as depicted in Image 2.5 [24,25].

2.2.3.3 Hematite

Hematite has been described by Cornell and Schwertmann as being isostructural with corundum [2]. They give the unit cell as hexagonal with \( a = 0.5034 \) nm and \( c = 1.3752 \) nm [26-28] with six formula units per unit cell [2]. Hematite may also be categorised in the rhombohedral system owing to its unit cells and formula [2]. “The structure of hematite can be described as consisting of \( hcp \) arrays of \( O^2- \) stacked along the [001] direction; that is, planes of anions are parallel to the [001] plane, thereby forming six-fold rings with the arrangement of cations produces pairs of \( \text{Fe(O}_6 \) octahedra.” Cornell and Schwertmann [2]. Each octahedron of the crystal structure shares edges with three neighbouring octahedra in the same plane and one face with an octahedron in an adjacent plane [2], as depicted in Figure 2.6.
Figure 2.6 A view of the structure of hematite [1].

Face-sharing as illustrated by Figure 2.6 occurs along the $c$-axis [2], and is reported by Cornell and Schwertmann [2] as being responsible for the distortion of the cation sub-lattice from ideal packing with Fe ions in the octahedra being repelled along the direction normal to [001], causing the cations to shift closer to the unshared faces [2]. “The O-O distances along the shared face of an octahedron are shorter (1.2669 nm) than the distance along the unshared edge (0.3035 nm), and hence the octahedron is trigonally distorted.” Cornell and Schwertmann [2]. They also assert that structural relationships exist between certain planes in the hematite structure and in iron oxides like magnetite and goethite causing growth on planes of hematite [2]. A charge balance in hematite occurs with $O^{2-}$ being partly replaced by $OH^{-}$ and accompanied by $Fe^{3+}$ vacancies [2]. “These anion-substituted hematites are sometimes called hydrohematite or protohematite.” Cornell and Schwertmann [2].

The synthesis temperature has been found by Cornell and Schwertmann [2] to also affect the unit cell parameters of hematite by increases in $a$ from 0.5033 to 0.5042 nm as temperatures decrease from 100 °C to 25 °C [2]. As a consequence structural disorders and incorporation of $OH^{-}$ is thought to be the cause. The most common habits
found for hematite crystals are rhombohedral, platy and rounded [2], as depicted by Figure 2.7.

![Figure 2.7 Crystal forms of platy (left) and rhombohedral (right) hematite [2].](image)

The plates of the hematite crystals have been found to vary in thickness and form different shapes which are round, hexagonal or irregular [2]. Rosler [29] found that under hydrothermal conditions, these three crystalline structures predominate successively as the temperature decreases during formation. “The crystal structure of hematite has a less directional effect on crystal habit than that of goethite and for this reason the habit of hematite is readily modified.” Cornell and Schwertmann [2]. The forms of macrocrystalline hematite are reported by Cornell and Schwertmann [2] to be rhombohedral, platy or fibrous with crystals that are formed from solution resulting in thick plates or rhombohedral shapes. Crystals formed grown from the vapour phase produce thin plates [30]. “Maritic hematite appears as octahedra or dodecahedra formed by pseudomorphic transitions from magnetite and pyrite respectively.” Cornell and Schwertmann [2].

Hematite structures have been found to include crystal shapes such as plates and discs, rods, spindles, spheres, ellipsoids, double ellipsoids, rhombohedra, stars and cubes [2]. Cornell and Schwertmann [2] propose there are two regular ways of producing idiomorphic hematite crystals including formation with ferrihydrite in neutral to alkaline media and by forcing the hydrolysis of a Fe³⁺ salt solution at low pH levels. Image 2.6 on the following page provides the formation of hematite which has grown from a suspension of ferrihydrite at temperatures <100 °C. The crystal structure depicted displays the dominant form as hexagonal or subrounded plates with [001] [2].
Image 2.6  Hematite (0.2 μm image) grown from ferrihydrite at pH 7 and room temperature; the acicular crystals also present are goethite [2].

The structure of naturally occurring hematite rarely forms in high temperatures above 500 °C and usually consists of single idiomorphic crystals [1]. Most hematites produced in aqueous systems contain some OH⁻ or H₂O molecules in the crystalline structure [1]. “When hematite is produced below 100 °C, up to 1/6 of the Fe positions can be replaced by Al, and the relationship between unit cell parameters and incorporation of Al is usually linear and significant for the \( a \) edge lengths, but not for the \( c \) edge length, probably because of stacking faults which occur along the \( c \)-axis.” Cornell and Schwertmann [2].

2.2.3.4 Magnetite

The magnetite structure has been described by Hill et al. as that of an inverse spinel [31]. “Magnetite has a face-centred cubic unit cell based on 32 O²⁻ ions which are regularly cubic close packed along [111]. The unit cell edge length \( a = 0.839 \) nm. There are eight formula units per unit cell.” Cornell and Schwertmann [2].

The structure of magnetite crystals differs from other iron oxides owing to it containing both divalent and trivalent iron [2]. The formula has been expressed by Cornell and Schwertmann [2] as \( \text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4 \), where the brackets denote octahedral sites. The eight octahedral sites have been found to distribute between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \). The structure depicted in Figure 2.8 displays the octahedral and mixed tetrahedral/octahedral layers stacked along the [111] plane [2].
Magnetite has been described by Cornell and Schwertmann as frequently being non-stoichiometric and having a cation deficient Fe$^{3+}$ sub-lattice [2]. “In stoichiometric magnetite, Fe$^{2+}$/Fe$^{3+} = 0.5$. The divalent ions may also be partly or fully replaced by other divalent ions (e.g. Mn$^{2+}$ and Zn$^{2+}$); fitting of guest ions into the structure is assisted by the flexibility of the oxygen framework, which can expand or contract to accommodate cations that differ in size from Fe$^{2+}$. Cation substitution is accompanied by changes in the unit cell edges.” Cornell and Schwertmann [2].

The crystal structures of natural and synthetic magnetite depicted in Figure 2.9 occurs mostly as octahedral crystals rounded by [111] planes and as rhombodecahedron [110] [2].

Figure 2.9 Crystal forms of magnetite: (a) and (c) octahedron; (b) rhombodecahedron, and; (d) twin [2].
The syntheses of magnetite produced by hydrothermal process will produce single octahedral crystals as large as 10 mm [2]. The octahedral magnetite crystals in Image 2.7, produced hydrothermally at 250 °C, displays how these crystals are intergrown with sizes several microns across [2].

Image 2.7 Octahedral magnetite crystals produced hydrothermally at 250 °C from 0.01 M Fe$_2$(SO$_4$)$_3$ solution in the presence of 0.4 M triethanolamine, 2.4 M NaOH and 0.05 M N$_2$H$_4$ [36].

Syntheses under aqueous conditions are common [32-39], and temperatures <100 °C produce fine-grained (<0.1 µm) rounded, cubic or octahedral crystals, as shown in Image 2.8 [2]. Magnetite crystals can be formed through the oxidation of Fe$^{2+}$ solutions at neutral pH via green rusts [32,33]. They can also be produced by direct precipitation from mixed Fe$^{2+}$/Fe$^{3+}$ solutions between pH values of 4 to 6 [2].

Image 2.8 Magnetite octahedra produced by oxidation of a 0.5 M FeSO$_4$ solution with KNO$_3$ in 1.45 M KOH at 90 °C [1].
Larger magnetite crystals of uniform octahedra and spheres with sizes ranging from 0.03-1.1 µm have been synthesised when green rust is oxidised with KNO₃ at 90 °C and at pH levels between 6-10 [38,39]. Spherical magnetite is formed when Fe²⁺ is in excess of the concentration of the OH⁻ ion, however when the OH⁻ is greater in concentration then cubic crystals are formed [2].

“Magnetite obtained from Fe(OH)₂ in very basic solution forms large cubes whilst that obtained from green rust buffered at pH 8.5 occurs as thick little plates.” Feitknecht [34].

“Magnetite produced by dry reduction of hematite maintains the shape and size of the original hematite particles; both lath-shaped and spherical magnetite’s have been obtained in this way.” Cornell and Schwertmann [2].

Cubic crystals with sizes 10-50 nm across are formed from metal substituted magnetites with Mn, Co, Cu, Ni formed from metal substituted ferrihydrites at pH 12 [36,37]. “Magnetite grown by slow oxidation of green rust at pH 6 in the presence of 0.05-0.10 mol mol⁻¹ phosphate had a well defined octahedral habit with smooth [111] planes; this habit was attributed to stabilisation of the planes by absorbed phosphate, as in the absence of the additive rather irregular crystals formed.” Couling and Mann [35].

### 2.2.4 Iron Oxide Surface Area and Porosity

The structural and functional groups on the surface of iron oxides and oxyhydroxides known as sites interact with gaseous and soluble species with the number of available reactive sites per unit mass of the solid being dependent on the specific surface area of the sample [2]. This aspect is responsible for adsorption interactions, phase transformations, dissolution and dehydroxylation behaviour and the thermodynamic stability of the iron oxides and oxyhydroxides [2]. The measurement of the specific surface area of a solid is expressed as m²/g [2]. There is an inverse relationship between particle size and surface area meaning larger crystals will have a lower surface areas compared to smaller crystals or powders [2]. “As particle size and crystallinity is governed largely by the chemical environment experienced during crystal growth, the surface areas of synthetic iron oxides depend upon the method of synthesis and those of natural ones on the environment of their formation.” Cornell and Schwertmann [2].
Unlike synthetic growth of iron oxide crystals, where it can be expected the surface area of crystals to be of a uniform size and structure, in a field-based process controlled growth is not expected. Where the source of iron oxides formed is from mild steel and the flow rate, pH, temperature and solution matrix can vary, then it can be anticipated that the size of crystals formed, their surface areas and porosities will also be variable. It is likely at ambient temperatures that the iron oxide and oxyhydroxide crystals formed will be smaller in size and thus have a higher surface area than those synthesised under controlled conditions.

Surface areas of iron oxides are commonly measured by the Brunauer-Emmett-Teller (BET) method using \( \text{N}_2 \) as the adsorbate [2]. “This method proceeds when a gas such as \( \text{N}_2 \) is brought in contact with a powdered solid (adsorbent) at a temperature near the condensation temperature of the gas, whereby some gas (adsorbate) is physically adsorbed on the surface of the solid.” Cornell and Schwertmann [2]. “The BET isotherm is determined by the measuring the volume of gas absorbed at a series of known gas pressures with the surface area of a solid determined by the following equation:

\[
\frac{\rho}{V(\rho_o - \rho)} = \frac{1}{V_m \cdot C} + \frac{(C-1) \cdot \rho}{V_m \cdot C \cdot \rho_o}
\]  

(4)

where \( V \) is the volume of gas absorbed at a pressure \( \rho \). \( \rho_o \) is the saturation vapour pressure of the gas and \( V_m \) is the volume of the adsorbate required to cover the adsorbent with a monolayer with \( C \) the constant for any given system which is related to the heat of liquefication of the gas [1]. “The monolayer volume \( V_m \) is found from the slope and intercept of the linear part of the curve obtained by plotting \( \rho/V(\rho_o - \rho) \) versus \( \rho/\rho_o \)” Schwertmann and Cornell [1]. The BET method does have its limitations due to the \( \text{N}_2 \) molecule being large and not being able to enter small pores on the surface of the oxide and as such owing to its non-ideal gas behaviour, \( \text{N}_2 \) cannot be used for surface areas of \(<1 \text{ m}^2/\text{g} \) [2]. Utilising other substances such as water or argon can overcome this problem [2].

Iron oxides and oxyhydroxides do not have internal surface areas that are accessible, therefore the BET method can effectively measure the total surface area of
the solid [1]. Figure 2.10 provides an example of N$_2$ adsorption curves of five goethites synthesised at temperatures of 4, 15, 30, 50 and 70 °C, along with their BET plots [1].

Porosity has been described as the volume of pores in a solid which contributes to the “internal” surface area of the sample influencing the kinetics of adsorption with the sum of all the pores is called the pore volume (porosity) [2]. Cornell and Schwertmann [2] consider that diffusion into and out of pores as being responsible for slow adsorption and desorption processes. “Pores vary in size and shape and are classified according to widths as micropores (<2 nm), meso- or transitional pores (2-50 nm), and macropores (>50 nm).” Sing et al. [40].

![Figure 2.10 N$_2$ adsorption isotherms of several goethite samples synthesized at various temperatures (left) and the resultant BET plots (right) [1].](image)

Figure 2.10 N$_2$ adsorption isotherms of several goethite samples synthesized at various temperatures (left) and the resultant BET plots (right) [1].

Pores can be incorporated into iron oxides as a structural feature or resulting from aggregation, but they also could be the result of partial dehydroxlation (in the oxyhydroxides) or dissolution [2]. Pores can have different shapes but common shapes include slit shaped, ink bottle and cylindrical [2]. “Upon partial dissolution, pores bounded by well defined crystal faces (e.g. [021] in goethite) develop and each type of pore is associated with a characteristic type of adsorption isotherm.” Cornell and Schwertmann [2]. Characterising the porosity of an iron oxide is obtained from absolute adsorption/desorption isotherms. The standard gas adsorption isotherms appear in Figure 2.11. The different loop shapes in Figure 2.11 correspond to cylindrical, slit-shaped and ink bottle pores with the loops in isotherms IV and V corresponding to cylindrical pores [2]. The presence of wide loops is an indication of broad pore size distribution whilst it’s absence meaning the sample is either nonporous or microporous [2]. The six isotherms only provide a general guide to the porosity of a
sample. In fact, the adsorption/desorption isotherms are often more complicated than those in the figure owing to a mixture of pore types and/or a wide pore size distribution [2].

Another method that can be used to determine surface area is the Ethylene Glycol Mono-Ethylene (EGME) method [41]. In this method the surface area is determined by the amount of EGME adsorbed at a constant vapour pressure and the change in weight of iron oxides such as ferrihydrite [1]. This technique involves holding the sample in an evacuated desiccator over the solvent until a constant weight is obtained [1]. “One EGME molecule covers 0.52 nm$^2$, i.e. 1 m$^2$ of a monolayer amounts to $0.286 \times 10^{-3}$ g of EGME. The surface area determined is $S = \frac{W_a}{W_s \times 0.286 \times 10^{-3}}$, where $W_a$ and $W_s$ are the weights in g of the EGME retained by the sample and of the P$_2$O$_5$-dried sample, respectively.” Schwertmann and Cornell [1].

![Diagram of gas adsorption isotherms]

**Figure 2.11** Standard gas adsorption isotherms, with types IV and V possessing a hysteresis loop with the lower representing adsorption and upper desorption [2].
The variations found from using different methods may be a result of deviations from assumed monolayer saturation [1]. "The main problem with dipolar molecules (the EGME method) lies in their mutual association, which may lead to localised adsorption beyond a monolayer (capillary condensation), particularly on porous material." Cornell and Schwertmann [2].

In the study by Torrent et al. [42] surface areas of 31 synthetic goethite's of variable crystal size and morphology were measured using N₂ and H₂O adsorption with results of two methods averaged. The results obtained found that ten natural goethite-rich samples had higher values on average of 43% with the EGME technique than with N₂ [2]. Testing of 14 natural hematite’s found the method with N₂-surface area (10-36 m²/g) was lowest followed by H₂O surface area (20-90 m²/g) [42]. Figure 2.12 illustrates how surface area determinations can vary depending on the technique utilised to derive the value. This work by Colombo et al. [43] compared four surface area methods (N₂, H₂O, EGME and calculated) for 30 synthetic hematite’s. Such typical variances should be considered in interpretation of any published and experimental data [2].

![Comparison of four different methods for surface area determination using 30 synthetic hematomites](image)

Figure 2.12: Comparison of four different methods for surface area determination using 30 synthetic hematites [43].
Particle size, surface area, and porosity will be governed by the conditions under which crystal growth takes place [2]. An example of this provided by Cornell and Schwertmann includes high rates of crystal growth at low temperatures that lead to small and poorly-ordered crystals with surface areas of up to several hundred m$^2$/g [2]. Low surface area crystals, however, may grow at higher temperatures and at slow rates of formation [2]. “Numerous experiments have identified such factors as temperature, source of Fe (Fe$^{2+}$, Fe$^{3+}$, Fe complexes), pH, presence of interfering or substituting ions such as aluminium, manganese, silica and organics, and even stirring as against not stirring, as having a marked effect on growth.” Schwertmann and Cornell [2]. Predicting surface areas from a particular preparation is difficult due to various factors [2]; however, Table 2.3 provides typical ranges of surface areas for synthetic iron oxides.

Table 2.3  Typical ranges of surface areas of synthetic iron oxides [2].

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>8-200</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>15-200</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>spindles</td>
</tr>
<tr>
<td></td>
<td>22-60</td>
</tr>
<tr>
<td></td>
<td>rods</td>
</tr>
<tr>
<td></td>
<td>100-150</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>100-400</td>
</tr>
<tr>
<td>Hematite</td>
<td>2-90</td>
</tr>
<tr>
<td>Magnetite</td>
<td>4-100</td>
</tr>
</tbody>
</table>

2.2.4.1 The Goethite Surface

Surface areas of both natural and synthetic goethites have been observed to range from a few to several hundred m$^2$/g [2]. Goethites grown from ferrihydrite in solutions containing high hydroxide ions provided surface areas (tested by EGME) from 153 m$^2$/g at 4 °C to 9 m$^2$/g at temperatures between 60-90 °C [44]. The BET method however provided lower values in the order of 15-88 m$^2$/g [45]. Recrystallisation can lower higher surface areas, for example goethite developed at 4 °C from 153 to 34 m$^2$/g under hydrothermal conditions at the higher temperature of 180 °C, which has been given the term “healing” [2]. This recrystallisation process can eliminate serrated edges.
without affecting the overall crystal size [45]. At pH levels ~12 twinned goethites will
grow from Fe$^{3+}$ solutions with low surface areas (<40 m$^2$/g) and crystals that are
reasonably large and well developed in all crystallographic directions [44]. “Surface
areas of acicular samples range from 30-90 m$^2$/g.” Atkinson et al. [46] and Cornell et al.
[47]. Goethites crystals developed by Fe$^{3+}$ solution and acid hydrolysis results in
surface areas of ~100 m$^2$/g [48]. “High surface areas (80-150 m$^2$/g) are also reported
for goethites formed by oxidation of Fe$^{2+}$ systems at pH 6-7 and room temperature,
whereas those grown at pH 12 have a lower area of around 30 m$^2$/g.” Torrent et al. [42].

The effect on the surface area of goethite crystals by aluminium is dependent on
the amount of Al in the media and on the source of iron [2]. Aluminium can reduce
both the rate of growth and the crystal size which in turn can affect surface area
depending on what predominates [2]. “The surface area (EGME) of goethite grown
from ferrihydrite in 0.3 M KOH at 25 °C dropped from 52 to 26 m$^2$/g as the extent of Al
substitution rose from 0 to 0.16 mol mol$^{-1}$.” Schulze and Schwertmann [49]. Synthetic
goethites can show no sign of being porous as was found by Torrent et al. [42] with 15
synthetic goethites grown from Fe$^{2+}$ and Fe$^{3+}$ solutions between pH 6-12 having no
porosity being evident [2]. “The N$_2$ adsorption isotherms of a raft-like goethite grown
in acidic media were intermediate between type II and IV with desorption hysteresis at
high relative pressures indicating open ended, cylindrical macropores which are
considered to exist between the crystalline structure in the rafts.” Koch and Møller
[114].

### 2.2.4.2 The Lepidocrocite Surface

The surface areas of lepidocrocite crystals have been reported to range from 15-
260 m$^2$/g depending on the conditions of their synthesis [50]. Lower surface areas of
lepidocrocite crystals have been made by oxidation at pH 6-7, with the surface area
increasing as the pH of the solution falls to 5 [22,51,52]. The presence of compounds
such as silicates can have an effect on surface areas which has been reported in the case
of silicates to exceed 100 m$^2$/g [22,53,54]. “Lepidocrocite illustrates the effect of
crystal shape as well as size on surface area, with lath-shaped crystals elongated along
[100] and with smooth terminal [101] faces having surface areas of 20–30 m$^2$/g,
whereas crystals of similar size gain additional surface area from the highly serrated terminals.” Schwetmann and Thalmann [22].

Gomez-Villacieros et al. found a well crystallised lepidocrocite having smooth edges and a surface area of 32.5 m²/g was nonporous and displayed a reversible type II N₂ adsorption isotherm [55]. “Lepidocrocite crystals with highly serrated terminals had a surface area of 67 m²/g, of which 13% could be attributed to micropores calculated to be 1.5 nm across.” Weidler [45].

2.2.4.3 The Hematite Surface

The surface area of synthetic hematite depends on how the oxide is produced either by a process of treatment with heat such as roasting or calcination or grown in solution [2]. The surface areas of hematites grown from solution at temperatures less than or around 100 °C have been reported to range from 10-90 m²/g depending on the particle size and shape of the crystals [2]. Hematite crystals with uniform size of ~1 µm are grown from strongly alkaline solutions with surface areas reported as low as 2 m²/g [1,58]. Table 2.4 below provides the surface area of spherical crystals grown by forced hydrolysis of Fe³⁺ solutions at 100 °C [2]. The Figures in Table 2.4 are in reasonable agreement between the N₂, water absorption and calculated surface areas [59]. However, for the cubic particles Kandori et al. [59] found the water surface area was three times as great as the N₂ area due to capillary condensation.

Table 2.4 Surface area of cubic and spherical hematites [59].

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Particle diameter (µm)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td>Spherical</td>
<td>0.107</td>
<td>12.6</td>
</tr>
<tr>
<td>Cubic</td>
<td>1.100</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Information concerning the porosity of solution-grown hematite by Cornell and Schwertmann was found to be sparse [2]. The spherical particles size in Table 2.4 is nonporous, whereas the cubic crystals displayed a much higher particle size [59]. “A platy hematite had a surface area of 20 m²/g, of which 22% was determined to be pore surface with a pore diameter of 0.5 nm.” Weidler [45].
2.2.4.4 The Magnetite Surface

Magnetite surface areas can range from 10 m²/g for crystals formed through the reduction of hematite to 100 m²/g for particles made by precipitation and 50 nm across [2]. Cornell and Schwertmann [2] determined the surface area of cubic magnetite crystals are 194 nm across when made through reduction of hematite with surface areas analysed to range between 5.6-6.6 m²/g [2]. “Partly oxidised Al-magnetite crystals grown from aqueous solution at room temperature were between 20 and 70 nm in diameter and tended to become smaller as the structural Al increased.” Schwertmann and Murad [60]. Magnetite has been quoted by Cornell and Schwertmann [2] as being nonporous.

2.2.5 X-Ray Diffraction Patterns of Iron Oxides

X-ray diffraction is an analytical technique used for the identification of substances like iron oxides through the interaction of electromagnetic radiation (measured by wavelength (\(\lambda\)) at about 0.1 nm) with atoms in the solid lattice [2]. With the distances between atoms in a crystal structure being similar with the wavelength of radiation, crystals diffract X-rays [2]. “In certain directions (angles of incidence, \(\theta\)) the elastically scattered rays interfere constructively, thus leading to enhanced intensity.” Schwertmann and Cornell [2]. The following Bragg equation gives this relationship between the angles of incidence \(\theta\), wavelength of the rays (\(\lambda\)) and the lattice spacings (d_{hkl}), as:

\[ n\lambda = 2d_{hkl} \sin\theta \]  

(5)

The identification of substances using X-ray diffraction patterns is through a comparison of observed diffraction intensity against the Bragg angle, \(\theta\) with each atom plane producing its own series of n reflections [2]. From the XRD patterns interplanar spacings (d_{hkl} value) are calculated by the Bragg equation and because each compound has its own set of d values and corresponding intensities these patterns are used for identification [2]. Non-crystalline or amorphous materials do not diffract and as such cannot be detected by this analytical technique [2]. Table 2.5 provides the diffraction patterns for goethite, lepidocrocite, hematite and magnetite with their own unique set of interplanar spacing and intensities, sourced and summarised by Cornell and Schwertmann [2].
Table 2.5 X-ray powder diffraction data for iron oxides and oxyhydroxides [2].

<table>
<thead>
<tr>
<th>Goethite</th>
<th>Lepidocrocite</th>
<th>Hematite</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>d nm</td>
<td>I  hkl</td>
<td>d nm</td>
<td>I  hkl</td>
</tr>
<tr>
<td>0.498</td>
<td>12 200</td>
<td>0.627</td>
<td>61 200</td>
</tr>
<tr>
<td>0.183</td>
<td>100 101</td>
<td>0.3294</td>
<td>210 301</td>
</tr>
<tr>
<td>0.3383</td>
<td>10 201</td>
<td>0.2981</td>
<td>8 101</td>
</tr>
<tr>
<td>0.2693</td>
<td>35 301</td>
<td>0.2473</td>
<td>76 301</td>
</tr>
<tr>
<td>0.2583</td>
<td>12 210</td>
<td>0.2434</td>
<td>34 410</td>
</tr>
<tr>
<td>0.2527</td>
<td>4 011</td>
<td>0.2068</td>
<td>9 600</td>
</tr>
<tr>
<td>0.2489</td>
<td>10 400</td>
<td>0.19404</td>
<td>53 501</td>
</tr>
<tr>
<td>0.2450</td>
<td>50 111</td>
<td>0.19351</td>
<td>72 020</td>
</tr>
<tr>
<td>0.2303</td>
<td>1 002</td>
<td>0.18502</td>
<td>12 220</td>
</tr>
<tr>
<td>0.2253</td>
<td>14 211</td>
<td>0.18375</td>
<td>8 610</td>
</tr>
<tr>
<td>0.2190</td>
<td>18 401</td>
<td>0.1735</td>
<td>21 511</td>
</tr>
<tr>
<td>0.2089</td>
<td>1 202</td>
<td>0.16238</td>
<td>5 121</td>
</tr>
<tr>
<td>0.2011</td>
<td>2 311</td>
<td>0.1565</td>
<td>3 800</td>
</tr>
<tr>
<td>0.1920</td>
<td>5 410</td>
<td>0.15344</td>
<td>33 002</td>
</tr>
<tr>
<td>0.1802</td>
<td>6 112</td>
<td>0.15248</td>
<td>30 321</td>
</tr>
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<td>0.17728</td>
<td>1 411</td>
<td>0.14915</td>
<td>5 202</td>
</tr>
<tr>
<td>0.17192</td>
<td>20 212</td>
<td>0.1451</td>
<td>5 810</td>
</tr>
<tr>
<td>0.16906</td>
<td>6 402</td>
<td>0.14457</td>
<td>8 711</td>
</tr>
<tr>
<td>0.16593</td>
<td>3 600</td>
<td>0.14192</td>
<td>3 620</td>
</tr>
<tr>
<td>0.16037</td>
<td>4 312</td>
<td>0.13916</td>
<td>12 212</td>
</tr>
<tr>
<td>0.15637</td>
<td>10 511</td>
<td>0.13711</td>
<td>12 521</td>
</tr>
<tr>
<td>0.15614</td>
<td>8 601</td>
<td>0.12984</td>
<td>4 412</td>
</tr>
<tr>
<td>0.15091</td>
<td>8 020</td>
<td>0.12672</td>
<td>3 901</td>
</tr>
<tr>
<td>0.14675</td>
<td>2 203</td>
<td>0.12637</td>
<td>5 230</td>
</tr>
<tr>
<td>0.14541</td>
<td>5 610</td>
<td>0.12175</td>
<td>2 820</td>
</tr>
<tr>
<td>0.14207</td>
<td>2 121</td>
<td>0.12045</td>
<td>9 911</td>
</tr>
<tr>
<td>0.13936</td>
<td>3 303</td>
<td>0.1203</td>
<td>11 022</td>
</tr>
<tr>
<td>0.13694</td>
<td>2 013</td>
<td>0.11914</td>
<td>7 1010</td>
</tr>
<tr>
<td>0.13590</td>
<td>3 701</td>
<td>0.11845</td>
<td>7 131</td>
</tr>
<tr>
<td>0.13459</td>
<td>1 602</td>
<td>0.11814</td>
<td>7 222</td>
</tr>
<tr>
<td>0.13173</td>
<td>3 321</td>
<td>0.11781</td>
<td>4 612</td>
</tr>
<tr>
<td>0.12921</td>
<td>802</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-ray powder diffraction data such as those in the above table were utilised in this thesis for the identification of iron oxides and oxyhydroxides from the field pilot plant. This ensured that all crystalline or microcrystalline material collected on the surface of the parent metal, which will be a mixture of iron oxide crystals in either a solid or powder form, are identified.

X-ray powder diffraction patterns of Fe$^{2+}$ oxides shown in Figure 2.13 provide three parameters including line (angle) position, width and intensity from which the nature of the oxide, its quantity (in a mixture), its unit cell parameters and its crystallinity (crystal size and order) can be deduced [2]. XRD allows for the
identification and the quantification of unknown crystals, such as those formed during the field pilot plant investigation.

Crystals that are small or less than 100 nm or display structural disorder result in broadening of the reflection which is greater than instrumental broadening [2]. These differences in broadening of various reflections due to different degrees of development of small crystals provide information about the shape of the crystal [2]. An example of this is provided by the platyness of very small hematite crystals less than 100 nm with broad hkl and sharp hk0 lines [61,62]. The line intensities presented in Table 2.5 are only observed if the crystals are randomly oriented within the sample [2]. “An-isodimensional particles (plates, rods) tend to show preferred orientation and these changes the relative intensities of the peaks. From such changes, information about the shapes of Fe oxide crystals can also be obtained.” Schwertmann et al. [63].
2.3 COPRECIPITATION/ADSORPTION OF IONS ON IRON OXIDES AND OXYHYDROXIDES

The process by which contaminants, both anionic and cationic, in ash waste water including selenium (selenite, $\text{SeO}_3^{2-}$), arsenic, aluminium, vanadium, chromium and molybdenum react with iron oxides and oxyhydroxides formed on the surface of solid iron is likely to be complex. It is anticipated that it will occur via a number of mechanisms including adsorption, coprecipitation, or a combination of both absorption and coprecipitation. The processes for removal of ions would be dependent on the type of iron oxides or oxyhydroxides formed through corrosion of solid iron (including goethite, lepidocrocite, hematite and magnetite) along with their respective abundances in terms of surface area and contact with the ions in solution. Other factors influencing the mechanism by which ions react with surface iron oxides and oxyhydroxides include pH, temperature and the type of ions in solution and their concentrations.

The reactions taking place on the surface of the iron oxides and oxyhydroxides can be likened to that of the hydroxide precipitation process, with the exception of the addition of a precipitating agent to the influent stream of a flocculation reaction vessel. In this scenario the precipitating agent is the iron oxide and/or the oxyhydroxide formed on the surface of the parent metal, which interacts with ions in solution. Mechanisms involved in the removal of targeted ions reacting with iron oxides and/or oxyhydroxides can also play a role in the formation of iron oxides and oxyhydroxide crystals. Absorption provides the basis for metal substitution, dissolution reactions and numerous interconversions [2]. It plays an important role in the synthesis of iron oxides and oxyhydroxides along with their crystal growth [2].

2.3.1 Adsorption, Coprecipitation and Mobility Isotherms

“...The adsorption process involves interactions of the absorbing species, the adsorbate, with the surface hydroxyl groups on the iron oxide, the adsorbent. The oxygen donor atom of the surface hydroxyl group can interact with protons, whereas the underlying metal ion acts as a Lewis acid and exchanges the OH group for other ligands to form surface complexes.” Cornell and Schwertmann [2]. Adsorption is described as a process involving the two-dimensional accumulation of an ion at the interface between a preformed solid and the aqueous phase [79]. Coprecipitation,
however, involves the instantaneous removal of ions in solution during the formation of metal precipitates such as iron oxides. Coprecipitation has been described as including some or combinations of processes such as adsorption, homogeneous solid solution, heterogeneous solid solution, cluster formation [64,65]. Coprecipitation is pictured as a three-dimensional process, whereas absorption can only be a two-dimensional process [3]. The multiple-site adsorption model is described as having different groups of adsorption sites with different binding strengths which can exist within a single phase [66]. Coprecipitation is viewed as the adsorption of the adsorbate to binding sites thermodynamically preferred but kinetically inaccessible by the adsorption process [65], and as such would deliver greater efficiencies of ion removal to that of simple adsorption processes. The difference in treatment efficiencies of coprecipitation and adsorption systems noted by Laxen [67] is attributed to an increased available surface area compared to the adsorption process; availability of adsorption sites with a higher binding strength and formation of a mixed hydroxy species with a lower degree of solubility than pure metal hydroxides.

These conditions strengthen the concept of a number of processes occurring simultaneously in the removal of ions from surface developed iron oxides and oxyhydroxides. Other conditions may exist to aid in the precipitation process, such as surface-enhanced precipitation. “The presence of adsorptive phases in many systems can provide sites for heterogeneous nucleation of a secondary phase(s) for which the solid phases act to accumulate the secondary ions via surface coordination and exchange, enhancing and directing two-dimensional condensation.” Baltpurvin [3]. Baltpurvin [3] also notes that a nucleation surface provides the most effective means of inducing precipitation if its crystal structure is similar to that of the crystal being formed and that surface-enhanced hydroxide precipitation is generally observed for systems where adsorptive processes concentrate the secondary ion at the surface such that the aqueous-ion activity product (AIP) is exceeded at pH values below the single constituent equilibrium AIP [3]. A graphical representation of observed metal ion concentrations versus pH trends (mobility isotherms), as depicted by Baltpurvin [3], appear in Figure 2.14, and demonstrates the close relationship that exists between the four processes of adsorption, coprecipitation, surface-enhanced precipitation and bulk precipitation [3].
Competitive coprecipitation could be another scenario to consider amongst the reactive processes occurring in a system where mixed iron oxides or oxyhydroxides are forming and reacting with mixed ions in ash wastewater. Baltpurvins [3] interprets competitive coprecipitation isotherms by three separate pH intervals with the first interval being pH < 5 coagulation. The second interval 5 < pH < pH_ρ (pH_ρ = pH at which precipitation occurs) is termed adsorption, with the third interval at pH > pH_ρ being precipitation [3].

### 2.3.2 Anion Adsorption

Anions possess one or more lone pairs of electrons and as such can function as the donor in a coordinate bond [2]. Adsorption of anions on an oxide surface may be specific or non-specific depending on both the anion and the oxide [68]. In non-specific adsorption the adsorbing force is the electrostatic force between the absorbent and adsorbate [2]. It is influenced by the ionic strength of the system and is treated to some extent as a form of ion exchange [69]. Nitrate provides a good example of non-specific adsorption on iron oxides as well as chloride [69,70].
Schwertmann and Cornell [2] define specific absorption as the replacement of the surface hydroxyl groups by the adsorbing ion acting as a ligand, $L$, as provided in the following equations:

\[ \equiv \text{FeOH} + L^- \rightleftharpoons \equiv \text{FeL} + \text{OH}^- \quad (6) \]
\[ \equiv (\text{FeOH})_2 + L^- \rightleftharpoons \equiv \text{Fe}_2L^+ + 2\text{OH}^- \quad (7) \]

where

\[ K_1^s = \frac{[\equiv \text{FeL}]}{[\equiv \text{FeOH}][L^-]} \quad (8) \]
\[ \beta_2^s = \frac{[\equiv \text{Fe}_2L^+]^2}{[\equiv \text{FeOH}]^2[L^-]} \quad (9) \]

“The binding constants $K_1^s$ and $\beta_2^s$ for the surface complexes show the same stability trend as do the constants for the equivalent complexation reactions in solution.” Cornell and Schwertmann [2].

From the above equations, specific adsorption has been defined by Cornell and Schwertmann [2] as involving direct coordination of the adsorbing species to the surface metal atoms of the solid. As a consequence of this reaction there is no solvent molecule between the adsorbed species and the surface so the linkage will have a large proportion of covalent character. “The chemical component of the adsorption free energy predominates, and as a result adsorption may take place on a neutral surface or even one with the same charge as the adsorbing species. Specifically adsorbing ions modify the surface charge on the oxide and hence cause a shift in the pzc/iep. That is a surface charge is at its point of zero charge when the surface charge density is zero. Adsorbing ions can be tightly bound and as such will not be easily displaced. Anions that adsorb specifically on iron oxides include phosphate, silicate, selenite, arsenite, chloride, fluoride, citrate and oxalate.” Cornell and Schwertmann [2].

Adsorption of anions onto an oxide is usually accompanied by the uptake of protons (or the release of hydroxyl ions) [2]. The ratio between the number of protons that are coadsorbed and the level of anion adsorption is not typically stoichiometric [2]. “Anion adsorption at any pH increases with rising concentration of the adsorbing species. The adsorption isotherms frequently display Langmuirian behaviour, which is
considered to involve only one type of adsorption site and for iron oxide this is the singly coordinated surface hydroxyl group.” Cornell and Schwertmann [2].

The Langmuir equation is used to determine the adsorption of anions on iron oxides [2]. “The Langmuir equation is expressed as:

\[
\Gamma_x = \Gamma_{\text{max}} \left( \frac{K_{\text{ads}} \cdot X_{\text{aq}}}{1 + K_{\text{ads}} \cdot X_{\text{aq}}} \right)
\]  

(10)

where \(X_{\text{aq}}\) is the equilibrium concentration of the adsorbate, \(\Gamma_x\) is the ratio of mass of adsorbate to mass of adsorbent and \(\Gamma_{\text{max}}\) is the level of adsorbate required to saturate all available surface sites (at \(X_{\text{aq}} \gg 1\) and provide a monolayer coverage.” Cornell and Schwertmann [2]. Adsorption of anions is described as being normally a two-step process having an initial rapid stage with a duration of minutes to hours limited predominantly by diffusion of adsorbing species to readily accessible sites [2]. The second stage is attributed to diffusion into particle aggregates or crystal micropores and structural rearrangement of the surface complexes [71,72], which may take days for the reaction to be complete.

### 2.3.3 Cation Absorption

Cation adsorption on oxides surfaces behaves in a similar way to anion adsorption as it can be specific or non-specific in nature [5]. Non-specific adsorption has been differentiated by the formation of ion pairs [5] as denoted in the following equation:

\[
\equiv \text{FeO}^- + \text{M}^{2+} \rightleftharpoons \equiv \text{FeO}^- \cdot \text{M}^{2+}
\]  

(11)

With non-specific adsorption, there is at least one water molecule between the adsorbing species and the surface functional group [2], a component of the electrostricted solvent layer around the ion.

Heavy metal cation and alkaline earth cations are adsorbed specifically [73]. “Specific adsorption involves interaction with deprotonated surface hydroxyl groups to form mono- and bi-nuclear, inner sphere complexes.” Cornell and Schwertmann [2]. This is denoted by the following equations [2]:

\[
\equiv \text{FeOH} + \text{M}^{2+} \rightleftharpoons \equiv \text{FeOM}^{(x-1)+} + \text{H}^+
\]  

(12)

and

\[
\beta_2^s
\]
\[
(\text{FeOH})_2 + M^{2+} \rightleftharpoons (\text{Fe-O})_2M^{(z-1)+} + 2H^+ \tag{13}
\]

with

\[
K_1^s = \frac{[\equiv\text{FeOM}^{(z-1)+}][\equiv\text{FeOH}][H^+]^{-1}}{[\equiv\text{FeOH}][M^{2+}]} \tag{14}
\]

\[
\beta_2^s = \frac{[\equiv(\text{FeO})_2M^{(z-1)+}][H^+]^{2}}{[\equiv\text{FeOH}]^{2}[M^{2+}]} \tag{15}
\]

where \(K_1^s\) and \(\beta_2^s\) are the appropriate equilibrium constants \([2]\). The surface speciation is generally determined on the basis of the measured extent of adsorption or from modelling \([2]\). Trivalent cations seem to adsorb as surface hydroxo species, as depicted in the following equation \([2]\):

\[
\equiv\text{FeOH} + \text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{Fe-O-AlOH}^+ + 2H^+ \tag{16}
\]

The cation adsorption reaction releases protons as a product, with the number of protons being released per cation defined as \(z\) \([2]\). Ideally, \(z\) should be one for mononuclear complexes and two for binuclear complex, but, in fact, the value is often found to be between one and two, and increases as the pH of the system rises \([2]\).

Adsorption may not involve specifically one mechanism. Cation adsorption may be suppressed as the ionic strength increases indicating outer sphere (non-specific) adsorption, although it may also be the result of ion pairing in solution \([2]\). Increasing ionic strength has been reported to increase cation adsorption on an iron oxide due to more effective shielding of the highly charged surface complexes \([73,74]\).

Cations will initially occupy the small proportion of higher energy surface sites followed by the lower energy sites \([5]\). “This site heterogeneity may be the reason for the shift in the adsorption edge of metals to higher pH values when the molar ratio of aqueous metal ion to site concentration increases.” Lin, X. \([5]\). For most monovalent cations adsorption depends directly on the surface charge of the oxides and as such there is hardly any adsorption at or lower than the pzc of the oxide \([5]\). “Above the pzc, cations are adsorbed to counterbalance the net negative surface charge.” Lin, X \([5]\).

Figure 2.15 illustrates trends in cation adsorption versus pH. The typical behaviour is sigmoidal, and uptake increases over a narrow pH range \([2]\). Differentiation between cations is apparent. The adsorption edges of cations on Fe oxides shift to a higher pH
as the initial concentration of the ion in solution rises and as the solid/solution ratio falls [66,75]. Cation adsorption on Fe oxides is initially rapid, but adsorption of trace elements can continue over days with long reaction times being needed to reach equilibrium [2], and increasing the temperature appears to promote cation adsorption [76].

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 [2].

### 2.3.4 Surface Complexation Models

Investigations into the chemical reactions involved in the adsorption process of iron oxides and oxyhydroxides such as goethite, lepidocrocite, hematite and magnetite have not just adopted Langmuir and Freundlich equations, but also employed other models which define more explicitly the adsorption process, such as surface complexation modes, diffuse and double layer or triple layer models. "These models treat adsorption as an interaction of adsorbing species with well-defined coordination sites (the surface OH groups) in a manner analogous to complexation reactions in solution, with the chemical free energy predominating and electrostatic effects having a secondary role." Cornell and Schwertmann [2].

### 2.3.5 Modes of Coordination

Simple ligands such as selenite, sulphate, phosphate and halide ions can adsorb on iron oxides to form a variety of surface species [2]. These species include mononuclear monodentate, mononuclear didentate and binuclear mono- or didentate complexes which can also be protonated [2]. Figure 2.16 illustrates these modes of
coordination. How adsorbed ligands (and cations) are coordinated to the oxide surface can be deduced from adsorption data, particularly from the area per adsorbed species and from coadsorption of protons [2].

![Figure 2.16](image)

“A binuclear, didentate complex will bind to the surface hydroxyls located on the corners of two adjacent Fe(OH)$_6$ octahedra.” Cornell and Schwertmann [2]. This type of binding is dominant on the [101] planes on goethite [2]. The mononuclear didentate complex, however, binds to groups on the edge of an Fe(OH)$_6$ crystalline structure [2]. These edge sites of the crystalline structure are thought to be high energy sites that are preferentially occupied by low surface coverages [2]. This form of binding to the edge sites can also be found on lepidocrocite. Figure 2.17 illustrates both the double corner and binding to the edge of goethite and lepidocrocite.

![Figure 2.17](image)

Figure 2.17 Surface complex of octahedrally coordinated Cd on: a) goethite, and; b) lepidocrocite [2].
The ratio of edge sites to corner sites has been determined to be much greater for ferrihydrite and lepidocrocite than for goethite [77,78]. This difference in ratio has been thought to be the reason for differences in the types of surface complexes found on different Fe oxides [77,78].

### 2.4 SORPTION, ABSORPTION AND/OR COPRECIPITATION OF TRACE ELEMENTS FROM WASTEWATER UTILISING IRON OXIDES AND OXYHYDROXIDES

#### 2.4.1 Selenium

Selenium in ash water of Vales Point Power Station is predominantly selenite (SeO$_3^{2-}$), with a minor percentage being in the form of selenate (SeO$_4^{2-}$). Both are anions which adsorb specifically on iron oxides. Selenite and selenate ions demonstrate the effect of the oxidation state on adsorption. The selenite ion adsorbs strongly and specifically on goethite and shifts the iep of both goethite and ferrihydrite to lower pH values [79-82]. Adsorption of selenite and selenate is at a maximum in the acid region but decreases to negligible values above pH 10. The process is largely irreversible [2]. Selenate has a much lower capacity for adsorption onto Fe oxides than does selenite, and it does not adsorb above pH 7 [2]. Selenite therefore shows a greater ability to adsorb onto the iron oxide surface than does selenate [79].

The kinetics of adsorption of selenite on synthetic goethite (surface area 70.1 m$^2$/g) studied by Zang and Sparks [82] found the first step of the adsorption mechanism involved the formation of outer-sphere complexes in the initial phase which then transformed into inner-sphere complexes. In a study of adsorption of selenite and selenate onto natural iron oxide and oxyhydroxide (goethite and hematite) Rovira et al. [83] undertook a series of experiments with selenite and selenate concentrations of between $2\times10^{-6}$ and $5\times10^{-6}$ mol dm$^{-3}$ whereby the solutions were placed in contact with known quantities of these oxides. Data in Table 2.6 has been fitted to a non-competitive Langmuir isotherm. From this study, the plots of adsorption isotherms for goethite and hematite (Figure 2.18) shows for hematite a maximum adsorption is not
reached in the range of selenite and selenate concentrations in adsolution, and that adsorption is higher in natural hematite than in natural goethite [83].

Table 2.6 Parameters of the Langmuir isotherm obtained for Se(VI) and Se(IV) adsorption on hematite and goethite at pH 4 [83].

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma_{\text{max}}$ (mol m$^{-2}$)</th>
<th>$K_L$ (dm$^3$ mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(IV)-goethite</td>
<td>(3.3±0.1) $3 \times 10^{-6}$</td>
<td>(1.5±0.1) $3 \times 10^4$</td>
<td>0.994</td>
</tr>
<tr>
<td>Se(IV)-hematite</td>
<td>(1.3±0.8) $3 \times 10^{-5}$</td>
<td>(9±1) $3 \times 10^3$</td>
<td>0.96</td>
</tr>
<tr>
<td>Se(VI)-goethite</td>
<td>(1.1±0.4) $3 \times 10^{-6}$</td>
<td>(1.1±0.3) $3 \times 10^4$</td>
<td>0.96</td>
</tr>
<tr>
<td>Se(VI)-hematite</td>
<td>(8.0±0.5) $3 \times 10^{-6}$</td>
<td>(6±2) $3 \times 10^3$</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Rovira et al. [83] also investigated the influence on pH for selenite and selenate adsorption on goethite and hematite. The plots of selenite and selenate adsorbed versus pH, as shown in Figure 2.19, showed a decline at pH levels beyond six or in alkaline pH. This is due to the large surface charge and the dominance of the selenium species in solution [83]. For both goethite and hematite, maximum sorption is observed when the surface charge is positive [83]. For selenate, sorption was found to decrease at alkaline pH and is due to a decrease in the fraction of the aqueous species HSeO$_4^-$ [83]. The maximum sorption for selenite coincides with the predominance of HSeO$_3^-$ [83]. Although this study had insufficient data to model the sorption behaviour, the trends in Figure 2.19 had still been fitted with experimental data to represent the surface complexation model using the triple-layer model (TLM). The studies also concluded that sorption of selenite on ferric oxyhydroxides occurs by inner-sphere complexation; however the mechanism for selenate sorption on goethite and hematite is not so obvious [83].
As can be seen by both the sorption isotherms and plots against pH both hematite and goethite display similar behaviours. Rovira et al. [83] successfully applied similar models to those proposed for selenite and selenate into synthetic hematite and goethite to describe the sorption in the natural iron oxides. They assert that through the experimental data of selenite sorption on natural hematite was best explained by a monodentate inner sphere deprotonated surface complex; however for selenite on natural goethite it fitted a mixture of a monodentate inner-sphere deprotonated and protonated surface complexes [83]. “Selenate sorption data was modelled using a mixture of a monodenate inner-sphere complex and a bidentate outer-sphere complex.” Rovira et al. [83].

An investigation by Duc et al. [84] into the sorption of selenite ions on hematite as a function of pH (2-12), ionic strength (0.01-0.1 M) and selenite concentration of (10^{-7} - 10^{-2} M) was undertaken according to surface complexation and precipitation of ferric selenite. In this study in order to predict the competitive nature of other ions it was important to differentiate between inner-sphere and outer-sphere complexes, because weakly bound ions like chloride and nitrate can compete only with outer-sphere complexes [84]. The study determined the sorption mode of an ion, based on the effect of ionic strength on the sorbed amount [84]. The results of sorption of selenite on hematite at two ionic strengths are shown in Figure 2.20. As no effect of ionic strength was observed, it was concluded that selenite forms inner-sphere complexes [84].

Figure 2.20  Sorbed amount of selenite versus pH ([Se] = 4 3 10^{-4} M) for two ionic strengths: NaNO₃ 0.01 M (hollow squares) and 0.1 M (filled squares) [84].
The sorption isotherm of selenite on hematite which Duc et al. [84] fitted to the Tempkin equation as shown in Figure 2.20 shows hematite has a strong sorption ability for selenite, over a large pH range from acid solutions to pH 9. “The sorption of selenium on hematite proceeds according to two processes: a surface complexation process, followed by precipitation of ferric selenite starting at approximately \( \{\text{Se}\} = 4 \times 10^{-4} \text{ M} \) (surface coverage > ca. 2 atoms per nm\(^2\)).” Duc et al. [84]. From these processes Duc et al. concluded this precipitation may explain why the selenium sorption capacity largely exceeds the acid-base site density [84]. They also observed that goethite and hematite have similar sorption properties for selenite even though the iron oxide and oxyhydroxide exhibit different acid-base properties [84].

Figure 2.21 provides further confirmation of sorption of selenite on hematite at two ionic strengths and selenite forming inner-sphere complexes [84]. This discovery is important, as weakly bound ions such as chloride and nitrate can only compete with outer sphere complexes [84].

![Figure 2.21 Isotherm for the sorption of selenite ions onto hematite: experimental values at pH 3 (○) and pH 4 (□) fitted by the Tempkin equation [84].](image)

The inner-sphere adsorption geometry of selenite at the hematite (100) water interface has been investigated by Catalano et al. [85] using X-ray standing wave measurements. They identified the inner-sphere didentate surface complexes that bridge...
between adjacent singly-coordinated oxygen sites were the primary adsorption sites [85]. Selenite was found to adsorb in a bridging didentate geometry on adjacent singly coordinated oxygen groups [85]. “As doubly-coordinated oxygen groups were also exposed on the surface, exclusive binding to the slightly-coordinate groups was likely due to differences in the reactivity or kinetics of these groups.” Catalano et al. [85]. The following Figure 2.22 shows the position of Se above the pairs of singly-coordinated oxygens on the surface and demonstrates that the Se binds in a bridging bidentate geometry with Se-O_{\text{surface}} distances of 1.6-1.7 Å and Se-Fe distances of 2.9-3.0 Å [85].

Figure 2.22  Model of Se(IV) surface complexes on the hematite [100] face [85].

Earlier studies of adsorption of selenite on different forms of iron oxyhydroxides undertaken by Parida et al. [86] indicated that surfaces of all forms of oxyhydroxides and ferrihydrite are naturally heterogeneous with adsorption fitting into a heterogeneous site binding model. They found the adsorption capacity of oxyhydroxides for SeO_3^{2-} follows the order of β-FeOOH (akaganeite) > α-FeOOH (goethite) > γ-FeOOH (lepidocrocite) > δ-FeOOH (feroxyhyte) > ferrihydrite [86].

For the effect of pH on adsorption of iron oxyhydroxides Parida et al. found selenite adsorbed even at pH values greater than the pH_{PZC} of iron oxyhydroxides (~8.0) where the surface has a negative charge [86]. “The adsorption of an anion on a negatively charged surface can occur if the chemical (i.e. specific) compound dominates the electrostatic component.” Parida et al. [86]. Figure 2.23 illustrates the adsorption of
selenite at a particular concentration is higher at lower pH levels and that the iron oxide hydroxide with highest percentage adsorbed is ferrihydrite with lepidocrocite second and goethite third.

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 α-FeOOH (goethite), β-FeOOH (akaganeite), γ-FeOOH (lepidocrocite), δ-FeOOH (feroxyhyte) and ferrihydrite respectively [86].

The adsorption of selenite at a particular initial concentration in Figure 2.23 is seen to be higher at a lower pH but progressively decreases with increasing pH. This is represented by the following Parida et al. [86] equations, where $S$ represents the surface:

$$S-\text{OH} + H^+ + \text{SeO}_3^{2-} \leftrightarrow S-\text{SeO}_3^- + H_2O \quad (17)$$

$$S-\text{OH} + 2H^+ + \text{SeO}_3^{2-} \leftrightarrow S-\text{HSeO}_3 + H_2O \quad (18)$$

The $S-\text{OH}$ is the surface hydroxyl group and $S-\text{SeO}_3^-$ and $S-\text{HSeO}_3$ are the adsorbed selenite species. This process is characteristic of anion adsorption.
The effect of adsorbent concentrations at pH 3 on the removal of selenite illustrated in Figure 2.24 implies that the increase in adsorption through increase in particulate concentration is due to the greater amount of available binding sites for selenite [86].

Parida et al. [86] postulated that there are two-step mechanisms involved in the adsorption and desorption reactions, with the first step being the formation of outer-sphere surface complexes ($SOH_2^+\cdots HSeO_3^-$ and $SOH_2^+\cdots HSeO_3^{2-}$) through electrostatic attraction between the surface hydroxyl groups ($S-OH$) and HSeO$_3^-$, SeO$_3^{2-}$ and H$^+$. “In the second step, divalent and monovalent selenite anions replace a molecule of water from the active sites of iron oxyhydroxide to form the inner-sphere surface complexes $S-\text{SeO}_3^{-}$ and $S-\text{HSeO}_3^{0}$.” Parida et al., as illustrated in the following scheme from the literature [86].
The mechanism provided implies the removal of selenite from solution by adsorption on oxyhydroxides and oxide surfaces is influenced by a number of parameters including the surface hydroxyl group, pH, concentration of available binding sites and the equilibrium selenite concentration [86].

The sorption of selenite and selenate onto magnetite (Fe₃O₄) studied by Martinez et al. [87] is dissimilar to studies of sorption onto goethite and hematite, in that it forms inner-sphere complexes whereas selenate forms outer-sphere complexes. The sorption isotherms for selenite and selenate (Figure 2.25) of Martinez et al. [87] each display a good fit to a Langmuir isotherm, which strongly supports monolayer coverage on the iron mineral surface [87]. The parameters in Table 2.7 were obtained from the sorption isotherms in Figure 2.25.

Figure 2.25  Sorption isotherm for Se(IV) and Se(VI) on 0.1 g of magnetite at pH 4 [87].

Table 2.7  Parameters of the Langmuir isotherm obtained for Se(VI) and Se(IV) sorption on magnetite at pH 4 [87].

<table>
<thead>
<tr>
<th></th>
<th>Γₘₐₓ (mol m⁻²)</th>
<th>Kₐ (dm³ mol⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(VI)</td>
<td>(3.5±0.2) 3 10⁻⁶</td>
<td>(3.0±0.1) 3 10⁵</td>
<td>0.995</td>
</tr>
<tr>
<td>Se(IV)</td>
<td>(3.13±0.06) 3 10⁻⁶</td>
<td>(1.19±0.07) 3 10⁶</td>
<td>0.975</td>
</tr>
</tbody>
</table>

The values of the Langmuir constant Kₐ in Table 2.7 above are higher than the values in Table 2.6 for hematite and goethite for both Se(IV) and Se(VI). The maximum metal adsorption though for magnetite is similar to that of hematite and goethite [87].
Martinez et al. [87] studied the influence of pH on the sorption of both selenite and selenate, and as expected found the sorption of selenium presents anionic behaviour, decreasing at more alkaline pH values as has been observed with similar curves for sorption on hematite and goethite. Figure 2.26 illustrates the sorption behaviour of selenite and selenate onto magnetite as a function of pH.

![Figure 2.26 Sorption of selenium on magnetite as a function of pH. The experiment used 0.1 g of magnetite and [Se]₀ = 2.3 × 10⁻⁵ mol dm⁻³ [87].](image)

The triple-layer surface complexation model utilised by Martinez et al. [87] was found to be a best fit for selenite with two inner-sphere complexes, \(\text{\text{\text{\`FeOHSeO}_3}^{2-}}\) and \(\text{\text{\text{\`FeHSeO}_3}}\), whereas selenate was best fitted with the outer-sphere complex \(\text{\text{\text{\`FeOH}_2}^{+}\cdot\text{SeO}_4}^{2-}\).

### 2.4.2 Arsenic

In the arsenic study with zero valent iron by Manning et al. [88] of surface water and groundwater it was found that arsenic forms inorganic species arsenate [As(V)] and arsenite [As(III)] with As(V) existing as oxyanions (\(\text{H}_2\text{AsO}_4^-\) and \(\text{HAsO}_4^-\)) at a neutral pH [88]. For As(III), the species was determined to be \(\text{H}_3\text{AsO}_3^0\) at pH values below 9.2. In Vales Point ash water it can also be assumed that arsenic would also be present in the forms of both arsenate, As(V), and arsenite, As(III).
The Manning et al. [88] experiments with metallic iron (Fe⁰) for the treatment of arsenic through its active corrosion oxidation products lepidocrocite (γ-FeOOH), magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) indicates Fe(II) oxidation as an intermediate step in the corrosion of Fe⁰. In this study under aerobic conditions no reduction of As(V) to As(III) occurred, but it did cause the oxidation of As(III) to As(V) [88]. “Oxidation of As(III) was also caused by maghemite and hematite minerals, indicating that the formation of certain oxides during Fe⁰ corrosion favours the As(V) species.” Manning et al. [88]. It was also suggested that from water reduction and the release of OH⁻ ions in solution on the surface of the iron oxides during Fe⁰ corrosion As(III) oxidation could be promoted [88]. In a study undertaken by Melitas et al. [89], the electrochemical potential for the reduction of As(V) to As(III) was discovered to be lower than the potential produced at the surface of the corroding Fe⁰ in solution [89]. The following Table 2.8 provides data obtained from the Manning et al. [88] study, where As(V) and As(III) are treated with rust containing lepidocrocite and magnetite and/or maghemite.

Table 2.8 Speciation of As(III) and As(V) treated with iron oxides [88].

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution (t = 0 h)</th>
<th>Solution (t = 24 h)</th>
<th>Sorbed AsTotal (t = 24 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[As(III)]₀ (%)</td>
<td>[As(III)]₀ (%)</td>
<td>[As(V)]₀ (%)</td>
</tr>
<tr>
<td>Goethite</td>
<td>100</td>
<td>0.27</td>
<td>not detected</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>100</td>
<td>1.95</td>
<td>0.19</td>
</tr>
<tr>
<td>Maghemite</td>
<td>100</td>
<td>0.18</td>
<td>not detected</td>
</tr>
<tr>
<td>Magnetite</td>
<td>100</td>
<td>100</td>
<td>not detected</td>
</tr>
<tr>
<td>Hematite</td>
<td>100</td>
<td>100</td>
<td>not detected</td>
</tr>
</tbody>
</table>

Note: At t = 0, [As(III)]₀ = 0.2 mM; 1000 ± 0.009 g solid in 25 mL used.

It is evident from Table 2.8 that adsorption of As(III) to greater than 97% occurred for the iron oxyhydroxides goethite, lepidocrocite and maghemite, whereas no adsorption during the 24 hour testing period occurred for the iron oxides magnetite and hematite. X-ray adsorption data obtained during the study by Manning et al. [88] showed substantial adsorption of As(III) with goethite and lepidocrocite even though
As(III) was not oxidised. Maghemite, however, showed both strong As(III) adsorption and oxidation processes [88]. As(V) was not detected in the adsorption experiment except with lepidocrocite [88]. However, the adsorption was still greater than 99% with As(V) uptake during Fe⁰ corrosion [88].

In the Manning et al. [88] batch trials, the initial pH was 5, with no further pH adjustments made during the batch experiments. Post-reaction pH values were greater than 9.0 indicating As(III) may have been exposed to a high pH environment [88]. Previous work by Manning and Goldberg [90] found the pH dependence of the As(III) oxidation reaction shows As(III) auto-oxidises at pH values greater than the first pKₐ for As(III) at pH 9.2.

The zero valent iron experiments undertaken by Bang et al. [92] also found that, in the presence of dissolved oxygen, As(III) removal was slower than As(V) removal at pH 7, and that removal of arsenic under oxic conditions was attributed to the adsorption on ferric hydroxides formed rapidly through oxidation of Fe⁰ [92]. The adsorption envelopes have been found to cross in the pH region 6-7.5 and this has been found to be attributed to differences in the types of surface complexes formed by the two oxidation states [2].

The X-ray absorption fine structure spectroscopy undertaken by Manning et al. [88] found that the heterogenous reactions occurring at the corroding zero-valent iron surface are complex and that the products after reaction of As(III) and As(V) with zero-valent iron were inner-sphere didentate As(III) and As(V) complexes. The predominant As–Fe interatomic distance was determined by Manning et al. to be 3.30-3.36 Å [88].

The study of arsenite removal from groundwater with nanoscale zero-valent iron (NZVI) by Kanel et al. [91] discovered that high removal in the order of 88.6 to 99.9% was achieved in the pH range 4-10 and decreased sharply below pH 4 and above pH 10. “The pH-dependent behaviour can be explained by ionisation of both the adsorbate and the adsorbent causing repulsion at the surface and decreasing the net As(III) adsorption.” Kanel et al. [91]. Below pH 9.2 they found H₃AsO₃ is the predominant species being adsorbed but above 9.2, H₃AsO₃⁻ predominants [91]. The effect of pH on As(III) adsorption on NZVI by Kanel et al. [91] is presented in Figure 2.27 on the following page.
Kanel et al. found that the surface of untreated NZVI provided a net positive charge at pH levels lower than (pH_{pzc}) of 7.8 [91]. “The effect of increased As(III) adsorption causes a negative shift in the pH_{pzc} of NZVI to 7.6 and 7.0 for 0.1 and 1.0 mg/L As(III) respectively.” Kanel et al. [91]. They also determined that the shifts in pH_{pzc} to lower values were characteristic of inner-sphere complexation [91]. This is where H_3AsO_3 and H_2AsO_4^- species form complexes directly with the surface of octahedral Fe(III) and that in solution block Fe(III)-OH proton exchange [91]. Through As(III)/(V) desorption and speciation experiments, Kanel et al. (2005) found oxidation of As(III) to As(V) does form a part in the removal of arsenic with NZVI [91]. They proposed the formation of Fe^{2+} and H_2O_2 on the corroding Fe^0 surface that in turn forms OH^- radicals, with the resulting As(III) reaction proceeding as in the following equation [91]:

\[
2\text{OH}^- + \text{H}_3\text{AsO}_3 \rightarrow \text{H}_2\text{AsO}_4^- + \text{H}_2\text{O} + \text{H}^+ \quad (19)
\]

Sun et al. [93] utilised zero-valent iron in batch experiments in both aerobic and anaerobic conditions for the removal of arsenate and arsenite. From the trends observed (Figure 2.28), it is evident that arsenite can be removed more rapidly than arsenate in comparable anaerobic conditions, whereas results are contrary in aerobic conditions, which means different mechanisms are taking place [93]. They also found that arsenic is removed mainly through precipitation in anaerobic conditions; whilst adsorption of arsenic on iron and iron corrosion products takes place in aerobic conditions [93].
Sun et al. [93] also ascertained that oxidation of As(III) to As(V) could be the reason for the high removal rate of As(III) in an unsealed system with ample oxygen as illustrated in the above trends. The following equations used by Sun et al. explain these trends [93]:

\[
Fe(II) + O_2 \rightarrow Fe(III) \quad (20)
\]

and

\[
2 \ Fe(III) + As(III) \rightarrow 2 \ Fe(II) + As(V) \quad (21)
\]

The effect of anions including sulfate, nitrate and phosphate on the removal arsenate was also examined by Sun et al. [93]. These studies found that low concentration of the sulfate inhibits arsenate removal, but the opposite effect occurs when sulfate concentration increased above 600 mg Na₂SO₄/L [93]. The presence of high-level nitrate anion was found to accelerate arsenate removal, whereas phosphate provided a competitive effect [93].
2.4.3 Vanadium

Vanadium exists in a number of oxidation states, including +3, +4 and +5, under aqueous conditions, with the +5 oxidation state being stable in oxic seawater [94]. Vanadium substances found in aqueous solution are illustrated in the Eh-pH diagram presented by Peacock and Sherman [94], Figure 2.29.

![Eh-pH diagram](image)

Figure 2.29 The Eh-pH diagram for aqueous vanadium species in the system V-O-H. $[V]_{\text{total}} = 5 \times 10^{-5} m$ (~2.5 ppm), where no polymer species are stable [94].

The Eh-pH diagram shows that the conjugate acids of vanadate are the dominant species in the Eh-pH range of natural oxic waters [94]. In their study, they measured adsorption onto goethite from pH 1.5 to 12 at both 2.5 and 25 ppm $[V]_{\text{total}}$ [94]. Figure 2.30, developed from their experiments, shows the adsorption envelope at each $[V]_{\text{total}}$ for both the Double Layer Model (DLM) and Triple Layer Model (TLM) [94]. From the observed trends in adsorption of vanadium ions on goethite, it is evident that there is an effect of concentration of vanadium on adsorption at higher pH levels [94]. At the higher vanadium concentration of 25 ppm $[V]_{\text{total}}$, adsorption decreases from pH 6 to pH 10 [94]. However, with the lower vanadium concentration of 2.5 ppm, the reduction in adsorption does not occur until about pH 9 [94]. Peacock and Sherman (2004) tentatively attributed the decrease in adsorption between pH ~6 and 9 at 25 ppm $[V]_{\text{total}}$ to the formation of metavanadate species such as $V_5O_9^{3-}$ in solution [94]. They also report the pH$_{\text{pzc}}$ to be 8.5, which agrees with previous other experimental values of ~7.5 to 9.5 [94].
Figure 2.30 Adsorption of vanadium ions on goethite at I = 0.1 M NaNO₃ at 25 °C and 144 hours equilibrium time [94].

In the study of vanadium(V) adsorption onto goethite, Peacock and Sherman (2004) used analysis by the EXAFS technique, and found vanadium adsorbs by forming inner-sphere surface complexes such as “VO₂(OH)₂” and “VO₃(OH)” [94]. A model of the three dimensional structure of the vandium(V) environment shown in Figure 2.31 was used in multiple scattering calculations for the determination of bond angles and lengths [94].

Figure 2.31 Multiple scattering configuration model used in EXAFS fits for vanadium(V) sorbed to goethite [94].
Peacock and Sherman [94] furthermore attribute vanadium(V) surface adsorption to the formation of didentate corner-sharing Fe$_2$O$_2$V(OH)$_2^+$ and Fe$_2$O$_2$VO(OH)$^0$ surface complexes, with no evidence of monodentate complexes [94]. From the identification of these surface complexes, the experimental vanadium(V) adsorption data of Peacock and Sherman [94] was fitted to the following equations:

\[
2\text{FeOH}_2^+ + \text{VO}_2^+ \leftrightarrow \text{Fe}_2\text{O}_2\text{V(OH)}_2^+ + 2\text{H}^+ \quad (22)
\]

and

\[
2\text{FeOH} + \text{HVO}_4^{2-} \leftrightarrow \text{Fe}_2\text{O}_2\text{VO(OH)}^0 + 2\text{OH}^- \quad (23)
\]

Jin et al. [95] studied the adsorption of a monolayer of vanadium on idealised Fe and oxygen-terminated hematite [001] surfaces by density functional theory (DFT). Their research included the comparison of theoretical results with X-ray standing surface wave and X-ray photoelectron spectroscopic measurements, which were interpreted against data on sub-monolayer coverages [95]. The resultant models in Figures 2.32 and 2.33 represent oxygen adsorption on V/Fe-hematite and on V/O$_3$-hematite from the Jin et al. [95] study.

In the above study, Jin et al. [95] found for O-1 ML V/Fe-hematite, the O$_{\text{ads}}$–V bond length decreases as coverage goes up, suggesting a stronger bonding affinity for
the metallic overlayer. As the $O_{ads}$–$V$ bond becomes shorter, $O$–$Fe$ bond lengths become longer with increasing coverage [95]. “For 1 ML V/O$_3$-hematite, as $V_B$ sinks below the top-most O plane, at 1/3 ML O adsorption the most preferred adsorption site is on top of the higher V with formation of a vanadyl bond V=O. Here the anionic potential barrier prevents the adsorbed O from bonding with both V atoms and no stable $O_b$ sites were found.” Jin et al. [95]. They concluded that in near surface Fe reduction under V adsorption, the effects and subsequent response to oxidation are highly site specific [95].

2.4.4 Chromium

Chromium(III) is the only detectable form of chromium in Vales Point Power Station ash water. In the study of chromium(III) sorption with zeolite synthesised from coal fly ash, Sui et al. [96] found the mechanism by which Fe$_2$O$_3$ binds Cr$^{3+}$ can be explained by an adsorption process where the functional surface hydroxyl groups ≡FeOH of ferric oxide acts as Lewis bases in the deprotonated form (≡FeO$^-$) to bind the Lewis acid chromium(III) ions. These are expressed by the following Sui et al. [96] equations:

\[
\text{≡FeOH} + \text{Cr}^{3+} \leftrightarrow \text{FeOCr}^{2+} + \text{H}^+ \quad (24) \\
\text{≡FeOH} + \text{Cr(OH)}^{2+} \leftrightarrow \text{FeOCr(OH)}^+ + \text{H}^+ \quad (25) \\
\text{≡FeOH} + \text{Cr(OH)}_2^+ \leftrightarrow \text{FeOCr(OH)}_2 + \text{H}^+ \quad (26) 
\]

The inner-sphere complexes formed are in general stable, consistent with the inert nature of the d$^3$ Cr$^{3+}$ ion, and cause the adsorption to become irreversible [97]. Sui et al. [96] found the adsorption increases with increasing pH, associated with the speciation of Cr$^{3+}$ in solution as a function of pH [97].

Past investigations dealing with the removal of chromium from wastewaters through sorption type processes with metal oxyhydroxides are related more to the toxic chromium(VI) species. Not a great deal of research has been found to exist for the treatment and removal of chromium(III) with iron oxides and oxyhydroxides. However, Crawford et al. [98] investigated chromium(III) adsorption and coprecipitation onto hydrated oxides of iron. In their study of the removal of
chromium(III) by adsorption with amorphous iron(III) oxide (ferrihydrite) in the presence of the other metal ions Ni\textsuperscript{2+} and Zn\textsuperscript{2+}, the removal profiles were the same. They also concluded that the lack of influence other metals have on the removal of Cr\textsuperscript{3+} by amorphous iron(III) oxide was not surprising, since Cr\textsuperscript{3+} either adsorbs or coprecipitates at a significantly lower pH than the ions Zn\textsuperscript{2+} or Ni\textsuperscript{2+} [98]. The percentage adsorption versus pH curve in Figure 2.34 illustrates this point, with the maximum removal at 100% occurring at about pH 6 [98]. The chemical free energy used by Crawford et al. (1993) for modelling the chromium(III) adsorption onto amorphous iron oxide was -50 kJ mol\textsuperscript{-1}. Figure 2.34 displays the chromium(III) absorption with amorphous iron(III) oxide, and highlights the absence of any influence of added metal(II) ions.

Removal by coprecipitation of chromium(III) with amorphous iron(III) oxide (ferrihydrite) in the same metal ion environments as the adsorption experiment is provided in Figure 2.35 [98]. The four coprecipitation curves again follow the same removal profile, and can be modelled using a single theoretical isotherm. The presence of nickel(II) and/or zinc(II) has no influence over the coprecipitation profile of chromium(III) onto amorphous iron(III) oxide [98]. The extent of removal by coprecipitation is, at any given pH, greater than the extent of removal by adsorption [98].

![Figure 2.34](image.png)

Figure 2.34 Adsorption of chromium(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) in combination [98].
Chapter 2 Iron Oxides: A Background

Figure 2.35  Coprecipitation of chromium(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) in combination [98].

In the investigation of chromate (CrO$_4^{2-}$) reduction and immobilisation under high pH and ionic strength conditions by Yongtian He [99], the pH of the aqueous system affects both the amount of Cr(VI) reduced to Cr(III) and the partition of Cr(III) between aqueous and adsorbed species [99]. Reduction of Cr(VI) by organic matter and other electron donors including Fe(II) and sulphides is favoured at lower pH. Under both acid and alkaline pH conditions, a mixed Fe-Cr precipitate formed [99]. Figure 2.36 is a phase diagram (pE-pH plot) of the dominant chromium aqueous species based on equilibrium constants [100].

Figure 2.36  The pE–pH diagram for chromium, based on equilibrium constants [100].
Yongtian He (2003) found Cr(III) is strongly hydrolysed in aqueous solution [99]. The principal species in the pH range 6.5-10.5 is Cr(OH)$_3$, whereas at higher pH Cr(OH)$_6^{3-}$ is the dominant species [99]. What was also found in this study is, in the homogeneous system examined, the extent of Cr(VI) reduction increases with the amount of Fe(II) added [99]. Additionally all reduced Cr(III) precipitated out and was present in the solid phase, with Cr remaining in the aqueous phase being all in the form of Cr(VI) [99]. Even at a very high pH of 13.5, Cr(VI) was reduced by Fe(II) very quickly and formed red-brown precipitates which was found not to redissolve in highly alkaline solutions [99].

2.4.5 Antimony

Antimony is usually present in natural water in the two oxidation states of Sb(III) and Sb(V), with the Sb(V) being the dominant species [101]. The antimony species that is the dominant form in solutions at pH levels higher than 3 is Sb(OH)$_6^{3-}$ [101,102].

The study of sorption of both Sb(V) and Sb(III) on goethite as a function of pH by Leuz et al. determined the maximum sorption site density for Sb(V) was $4 \times 10^{-6}$ mol m$^{-2}$ [102]. They also observed, from sorption envelopes, high sorption at neutral to acidic pH in the range of 3 to 7 with a decreasing sorption in pH ranges of 7 to 12.

In the Martinez-Lladó et al. [101] study of sorption of Sb(V) on goethite in carbonate medium, the maximum sorption occurred at acidic pH, whereas at a pH higher than 8 the sorption decreased with increasing pH. The maximum sorption is obtained when the surface charge is positive because of the predominance of the Sb(OH)$_6^{3-}$ complex in solution at pH >3 [101]. Martinez-Lladó et al. [101] found the ionic strength does not seem to influence the sorption of antimony on goethite, with the isotherms very similar at both ionic strength values of 0.001 and 0.01 mol dm$^{-3}$ (see Table 2.9).

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Ionic Strength (mol dm$^{-3}$)</th>
<th>$\Gamma_{\text{max}}$ (mol m$^{-2}$)</th>
<th>$K_L$ (dm$^3$ mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.01</td>
<td>$(2.21\pm0.04) \times 10^{-6}$</td>
<td>$(5.6\pm0.8) \times 10^4$</td>
<td>0.9990</td>
</tr>
<tr>
<td>25</td>
<td>0.01</td>
<td>$(2.11\pm0.02) \times 10^{-6}$</td>
<td>$(1.6\pm0.02) \times 10^5$</td>
<td>0.99992</td>
</tr>
<tr>
<td>35</td>
<td>0.01</td>
<td>$(2.14\pm0.03) \times 10^{-6}$</td>
<td>$(8\pm7) \times 10^4$</td>
<td>0.991</td>
</tr>
<tr>
<td>25</td>
<td>0.001</td>
<td>$(1.98\pm0.01) \times 10^{-6}$</td>
<td>$(9\pm2) \times 10^4$</td>
<td>0.998</td>
</tr>
</tbody>
</table>
In considering the modelling of sorption behaviour of Sb(V) on goethite, Martinez-Lladó et al. [101] utilised the extended X-ray absorption fine structure (EXAFS) measured by Scheinost et al. (2006) (to model their own experimental data) [103]. Scheinost et al. (2006) found Sb(V) forms an inner-sphere edge-sharing complex with goethite. Martinez-Lladó et al. [101] described the complexation reaction as:

$$\text{Fe(OH)}_2 + \text{Sb(OH)}_6^- \leftrightarrow \text{FeO}_2\text{Sb(OH)}_4^- + 2\text{H}_2\text{O} \quad (27)$$

They also found that $\log K_{ab(Sb)} = 5.2 \pm 0.1$, with no improvement in the fitting of the experimental data achieved by including the formation of ion pairs between $\text{Na}^+$ and $\text{Sb(OH)}_6^-$ [101]. As a result of this, Martinez-Lladó et al. [101] concluded that the sorption edge experimental data was successfully modelled using a didentate edge-sharing surface complex and the thin layer.

### 2.4.6 Aluminium

There are few studies observed for the removal of aluminium(III) from wastewaters, and this is most likely due to amorphous aluminium hydroxides themselves being utilised as the agent for the adsorption or coprecipitation of trace metals.

Wilkin and McNeil [105] studied metal uptake, including aluminium(III), from acid mine drainage water with zero-valent iron. This was undertaken by batch experiments, where the initial pH values ranged from 2.3 to 4.5 to final values of 5.0 to 10.0. Table 2.10 provides the initial and final aluminium(III) concentrations with various types of zero-valent iron, as well as initial and final pH levels.

Table 2.10  Initial and final solute concentrations and pH for 5 mM Al(III) and 3 mM Fe(III); final concentration corresponds to 450 h reaction time [105].

<table>
<thead>
<tr>
<th>Batch Expt</th>
<th>Al (mg L$^{-1}$)</th>
<th>pH</th>
<th>Batch Expt</th>
<th>Al (mg L$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH 2.3</td>
<td>126</td>
<td>2.3</td>
<td>Initial pH 3.5</td>
<td>1.3</td>
<td>3.5</td>
</tr>
<tr>
<td>10 g Peerless</td>
<td>0.12</td>
<td>5.7</td>
<td>10 g Peerless</td>
<td>0.003</td>
<td>9.4</td>
</tr>
<tr>
<td>10 g Peerless</td>
<td>0.007</td>
<td>6.0</td>
<td>10 g Peerless</td>
<td>0.004</td>
<td>10.0</td>
</tr>
<tr>
<td>10 g Fisher</td>
<td>0.003</td>
<td>5.3</td>
<td>1 g Peerless</td>
<td>0.004</td>
<td>5.7</td>
</tr>
<tr>
<td>1 g Peerless</td>
<td>0.003</td>
<td>5.5</td>
<td>Initial pH 4.5</td>
<td>0.1</td>
<td>4.5</td>
</tr>
<tr>
<td>1 g Peerless</td>
<td>0.05</td>
<td>9.8</td>
<td>1 g Peerless</td>
<td>0.05</td>
<td>9.8</td>
</tr>
</tbody>
</table>
At an initial pH of 3.5 ($\rho_m = 0.23$), the concentration of aluminium(III) was reduced to below limits of detection [105]. Metal removal was independent of the initial presence or lack of aluminium(III) [105]. Removal rates for the metal ions examined in the Wilkin and McNeil (2003) study followed the order Al>Cu>As>Cd>Ni>Zn, with the aluminium(III) adsorption half-life being 1.5 hours [105]. The final metal ion concentration versus pH profiles are reported in Figure 2.37, which includes aluminium(III), were obtained in their study [105].

![Figure 2.37 Solution concentrations of Al, Cu and Zn as a function of pH following adsorption onto iron [105].](image)

From this study, Wilkin and McNeil [105] found the aluminium(III) solutions were observed to approach saturation with respect to gibbsite, Al(OH)$_3$, over the pH range of 4 to 7. At more alkaline pH values from 8 to 10.5, Al(III) is again undersaturated [105]. “This behaviour suggests that Al(III) may be present in a more stable form within the reactive material relative to aluminium hydroxide or that
dissolution rates of aluminous materials are retarded, perhaps due to armouring by iron corrosion products.” Wilkin and McNeil [105]. Their results indicate the rapid removal of metals from solution is due to adsorption onto the iron metal surface or onto iron corrosion products that had been present on the unreacted metal surface [105]. Wilkin and McNeil [105] also state that “continued adsorption onto iron corrosion products and co-precipitation with corrosion products, or both, are likely to be secondary and slower metal uptake processes.”.

2.4.7 Molybdenum

Like the aluminium ion, there are few sorption studies of molybdenum species by iron oxides and oxyhydroxides. Molybdenum differs to other metal ions by existing in solution only as oxyanion species and not as the free aquated cation [2]. Some studies have been undertaken utilising iron(III) hydroxide and goethite. These findings are briefly described for each material utilised in the study.

Kim and Zeitlin [106] studied of the use of iron(III) hydroxide to remove molybdenum species from sea water, where it exists as the molybdate anion (MoO₄²⁻) above a pH of 1. In their study, the yield of molybdenum was optimum at pH 4.0. The amount of molybdenum then decreased significantly as pH increased to a lowest amount at 8.5, where some detectable amounts of molybdenum were observed [106]. They also found that the iron colloid which forms at pH 4.0 has maximum positive charge density on its surface enabling absorption of the negatively charge molybdate anions [106]. By increasing the pH a decrease in the positive charge density occurs resulting in a decrease in the recovery of molybdenum [106]. Kim and Zeitlin [106] found that at pH 8.5 the positive-charge density is quite low and as a consequence the recovery of molybdenum is also low. In their experimental work Kim and Zeitlin (1969) found that above this pH the charge on the iron(III) hydroxide is reversed with the presumption that the colloid is able to capture only cations. Hence at pH 10.0, the negatively charged iron(III) hydroxide will not be capable of collecting anionic species such as the molybdate ion, but good recovery was achieved [106]. Kim and Zeitlin [106] found that the good molybdenum removal at pH levels higher than 9 could be attributed to coprecipitated calcium and magnesium molybdate salts. Table 2.11 summarises the recovery data for molybdenum in sea water.
Table 2.11 Recovery of molybdenum from sea water (for 6 µg Mo added to 300 mL of sea water; ambient temperature) [106].

<table>
<thead>
<tr>
<th>pH</th>
<th>Absorbance (averaged)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.372</td>
<td>96.5</td>
</tr>
<tr>
<td>5.5</td>
<td>0.344</td>
<td>89.4</td>
</tr>
<tr>
<td>7.5</td>
<td>0.236</td>
<td>61.4</td>
</tr>
<tr>
<td>8.5</td>
<td>0.090</td>
<td>23.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.340</td>
<td>88.5</td>
</tr>
</tbody>
</table>

The molybdenum reduction trend observed with iron(III) hydroxide at varying pH levels was also observed by Goldberg and Foster [107] utilising goethite as the adsorbing medium. They found that molybdenum adsorption on goethite is dependent on particulate concentration and that data showed pronounced pH dependence, revealing maximum adsorption at low pH levels [107]. As pH increased adsorption was found to be virtually zero above pH 8 [107]. Figure 2.38 illustrates molybdenum adsorption as a function of pH.

Figure 2.38  Molybdenum adsorption with iron(III) hydroxide as a function of pH and concentration [107].
Goldberg and Foster [107] also determined through their experimental work with molybdenum adsorption on kaolinite, that the fit to the Freundlich adsorption isotherm equation was better than that to the Langmuir equation. They found that this is because the experimental isotherm does not indicate an adsorption maximum and that molybdenum adsorption on kaolinite and goethite is dependent on the solution pH [107]. The Freundlich adsorption isotherm equation has an $R^2 = 0.99$, whereas the Langmuir adsorption isotherm equation was $R^2 = 0.94$; the fit of the data is illustrated in Figure 2.39.

![Figure 2.39](image)

Figure 2.39  Molybdenum adsorption isotherms on kaolinite, showing a better fit to the Freundlich equation [107].

The effect of solution ionic strength on molybdenum adsorption as a function of pH was also assessed by Goldberg and Foster [107], along with the affect of other anions in solution. They found that goethite shows very little ionic strength dependence [107]. The competitive effect of arsenate and phosphate showed that molybdenum adsorption was unaffected by both of these anions in solution [107]. Goldberg and Foster [107] attribute this effect to possibly lack of competition for adsorbing sites and also suggest for clay minerals the adsorbing sites are heterogenous allowing some preference for molybdenum.
2.5 KINETICS AND EFFICIENCY OF TRACE ELEMENT REMOVAL FROM WASTEWATER

2.5.1 Selenium

Studies of the kinetics of selenium oxyanion sorption/adsorption on iron oxides including goethite, hematite and magnetite has illustrated how most of the removal of selenate and selenite occurs within a short timeframe of under 30 minutes. It is expected that the reaction kinetics of lepidocrocite would behave in a similar manner. Trends of selenate and selenite removal all display a rapid and significant amount of sorption/adsorption within 30 minutes, and then a tapering off over a period of hours and days.

The adsorption experiment undertaken by Parida et al. [86] found that the adsorption of selenite on different forms of iron oxyhydroxides and ferrihydrite was quite rapid and reached equilibrium in about two hours. There was no further change in equilibrium concentration up to 24 hours [86]. Parida et al. [86] did, however, find for ferrihydrite and ferrihydrite tested under various pH levels, that the adsorption reaction was faster, with the equilibrium reached in less than two hours, as depicted in Figure 2.40.

Figure 2.40 Adsorption of selenite with time on α-FeOOH (goethite) and δ-FeOOH (ferrihydrite) (1) [selenite] = 6.8 μmol, δ-FeOOH = 500 mg/L; (2) and (3) [selenite] = 2.53 μmol, α-FeOOH = 250 mg/L [87].
Rovira et al. [83], in their study of selenium sorption with contact time for goethite and hematite, found that equilibrium was always reached in much less than 50 hours. Their plot of \( \{t/Se\}_s \) against \( t \) from their data resulted in linear relationships that demonstrate the sorption process followed pseudo-second order kinetics [83]. The resultant parameters are given in Table 2.12.

### Table 2.12 Kinetics of selenite/selenate adsorption onto iron oxides, fitted to a pseudo-second order rate equation [83].

<table>
<thead>
<tr>
<th></th>
<th>Rate constant, ( k ) (m² mol⁻¹ h⁻¹)</th>
<th>( {Se}_s\text{eq} ) (mol m⁻²)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(IV)-goethite</td>
<td>0.95 ±0.003</td>
<td>((4.2 ±0.1) \times 10^{-7})</td>
<td>0.9990</td>
</tr>
<tr>
<td>Se(IV)-hematite</td>
<td>1.12 ±0.002</td>
<td>((3.0 ±0.1) \times 10^{-6})</td>
<td>0.9997</td>
</tr>
<tr>
<td>Se(VI)-goethite</td>
<td>0.60 ±0.002</td>
<td>((2.8 ±0.1) \times 10^{-7})</td>
<td>0.9990</td>
</tr>
<tr>
<td>Se(VI)-hematite</td>
<td>0.64 ±0.002</td>
<td>((1.5 ±0.2) \times 10^{-6})</td>
<td>0.9990</td>
</tr>
</tbody>
</table>

The sorption of selenite and selenate onto magnetite as studied by Martinez et al. [87] followed a similar trend to that on goethite and hematite. Equilibrium was reached in less than 30 hours for both selenite and selenate, as illustrated in Figure 2.41.

![Figure 2.41](image_url)  
**Figure 2.41** Variation of selenium sorbed onto magnetite with contact time. Experiments carried out with 0.1 g of magnetite and \([Se]_0 = 3 \times 10^{-5}\) M at pH 4 for Se(IV) and pH 6 for Se(VI) [88].

Like the sorption experiments undertaken by Rovira et al. [83] onto goethite and hematite, sorption onto magnetite also appears to follow pseudo-second order kinetics. The trends for both selenate and selenite in Figure 2.41 are also closely similar; however,
the pH for which the experiments were undertaken were different, with the selenate experiment undertaken at pH 6 whilst for selenite the pH was 4 [88]. It is evident from the experimental data that a high percentage of Se in both selenite and selenate forms can be adsorbed rapidly, and almost completely over a duration of days, providing the conditions for the removal such as pH are at the optimum for the anion, along with the correct level of iron oxide and oxyhydroxide being utilised relative to the selenium concentration.

2.5.2 Arsenic

The rapid reduction displayed in trends for selenium removal with iron oxides and oxyhydroxides is not as evident in the trends observed for removal of arsenic oxides. In fact, studies of arsenate and arsenite under aerobic and anaerobic conditions by Bang et al. [92] have described the process as being a slow, pseudo-first order reaction. In their study of arsenic removal with zero-valent iron under oxic and anoxic conditions, Bang et al. [92] found arsenate removal under oxic conditions was faster than for arsenite. Under anoxic conditions, both As(III) and As(V) removal was substantially less than under oxic conditions due to the lack of ferric oxide formation and slow kinetics of electrochemical reduction of arsenate and As(V) to As(0) by Fe(0) [92]. The small amount of As(V) and As(III) removed under anoxic conditions, seen in Figure 2.42, was attributed to adsorption on the ferric hydroxide layer of the iron filings [92].

![Figure 2.42](image)

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} [92].
Bang et al. [92] defined the above reactions of As(V) and As(III) in terms of these species being mostly removed by the iron hydroxide precipitate through adsorption processes. Because iron hydroxide has a higher adsorption capacity for As(V) than for As(III) at neutral pH, As(V) removal was greater than As(III) [92]. In addition to this experiment, Bang et al. [92] also analysed the effect of pH on As(V) removal with zero-valent iron in solutions at controlled pH values of 6, 7 and 8. The removal of As(V) over a period of 9 hours was determined, with each trend displaying pseudo-first order kinetics, with the highest percentage of As(V) removal occurring at pH 6 [92]. The removal of As(V) after 9 hours at pH 6 was 99.8 %, with only 55.5 % removal at pH 7 and 2% for pH 8 (Figure 2.43) [92]. “The formation of iron hydroxides from Fe(0) filings decreased dramatically when the solution pH increased from 6 to 8.” Bang et al. [92]. It is apparent that As(V) removal is directly proportional to the amount of ferric hydroxide precipitate formed. “In addition to increased Fe(0) corrosion at low pH, the water pH directly influences the adsorption of arsenic by iron hydroxides and oxides.” Bang et al. [92].

![Image](image.jpg)

Figure 2.43 Removal of As(V) by Fe(0) at various pH values. As(V) = 100 mg/L; Fe(0) content = 1 g/L (100 mesh); mixing in ambient air [92].

Table 2.13 summarises the kinetic data obtained from analysis of the above trends for both arsenite and arsenate adsorption onto zero-valent iron in terms of a pseudo-first order rate reaction.
Table 2.13  Pseudo-first order rate constant (k) and half-life (t½) for arsenic adsorption on iron [92].

<table>
<thead>
<tr>
<th>Condition</th>
<th>pH</th>
<th>As Species</th>
<th>k (h⁻¹)</th>
<th>t½ (h)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxic</td>
<td>6</td>
<td>As(III)</td>
<td>1.75 ×10⁻¹</td>
<td>3.96</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>As(V)</td>
<td>3.24 ×10⁻¹</td>
<td>2.14</td>
<td>0.945</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>A(V)</td>
<td>7.95 ×10⁻²</td>
<td>8.72</td>
<td>0.980</td>
</tr>
<tr>
<td>anoxic</td>
<td>8</td>
<td>As(V)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>As(V)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>As(III)</td>
<td>1.78 ×10⁻²</td>
<td>38.93</td>
<td>0.830</td>
</tr>
</tbody>
</table>

The efficiency and kinetics of arsenic removal by zero-valent iron has also been studied by Sun et al. [93]. In their study of the kinetics of arsenite and arsenate removal, they too studied the effects under aerobic and anaerobic conditions, in this case at the two concentration levels of 100 and 500 µg As/L [93]. For the two arsenic concentration levels the removal process of both arsenate and arsenite fits the first-order kinetics in either the sealed or unsealed system [93]. The trends in Figure 2.44 provide a summary of the results of the two experiments, presenting arsenic removal in µg As/L with zero-valent iron as a function of time.

Figure 2.44 Removal of arsenic compounds by zero-valent iron (ZVI) as a function of time. {Reactors contained 2.5 g/L ZVI, with [As] = 100 µg/L (a) or [As] = 500 µg/L (b), at an initial pH of 8.28 in unsealed/sealed systems} [93].

In the Sun et al. [93] experiments with the unsealed system, arsenate was removed more efficiently from water than arsenite. The experiment showed that more
than 99% of arsenate was removed from the solution in 4 hours for both 100 and 500 µg/L, whereas only about 60% of arsenite was removed in the 4 hour period [93]. The reaction rate constants (k) of arsenate removal at 500 µg/L was 0.348 h⁻¹ and for 100 µg/L was 0.367 h⁻¹ [93]. These values are greater than those of arsenite, which for 500 µg/L was 0.223 h⁻¹ and for 100 µg/L was 0.224 h⁻¹ [93]. However, Sun et al. (2006) did observe that arsenite could be removed to a greater extent over an extended period of time, with 95% removal efficiency in 16 hours for the two initial levels [93]. What was also observed was that oxidation of arsenite to arsenate can be promoted by iron species in aerobic environments [93]. Sun et al. [93] also investigated the effect of competing species noting that concentrations of sulfate above 600 mg Na₂SO₄/L, as well as high nitrate anion levels, can accelerate arsenate removal.

2.5.3 Vanadium

There are limited scientific investigations on the kinetics of vanadium removal with iron oxides and oxyhydroxides extant. However, one study undertaken by Bhatnagar et al. [108] investigated the adsorption potential of metal sludge containing predominantly Ca, Fe and Zn. From the kinetics of adsorption, Bhatnagar et al. [108] found the equilibrium adsorption of vanadium on metal sludge was achieved within seven hours. The conclusion from their study of adsorption kinetics indicated that the adsorption process is pseudo-first order and intraparticle diffusion controlled [108]. Figure 2.45 provides the adsorption of vanadium on metal sludge as a function of contact time. It would be expected that adsorption of vanadium onto synthetic or natural iron oxides and oxyhydroxides would display the same adsorption process, being pseudo-first order, which has been the case for other trace elements discussed in this thesis.

Bhatnagar et al. [108], in order to understand the effect of temperature on the adsorption of vanadium, also conducted experiments at two temperatures, 25 °C and 45 °C. The plots of the adsorption isotherms show that adsorption slightly increases (24.8 - 27 mg/g) upon increasing the temperature [108]. The adsorption data and plots also conformed to the Langmuir model [108]. The plots were found to be linear having good correlation coefficients with R² values of 0.9992 and 0.9989 at 25 and 45 °C respectively [108].
Figure 2.45  Effect of contact time on the uptake of vanadium on metal sludge adsorbent at 25 °C [108].

### 2.5.4 Chromium

The behaviour shown in Figure 2.46 below for Ni, Cr, Cu and Al removal observed by Fiore and Zanetti [109] illustrates the rapid removal of chromium with zero-valent iron. In this study, chromium(III) was reduced from 100 mg/L within one hour of being in contact with zero-valent iron [109]. Chromium displays the same characteristics as aluminium ion, with a similar trend, and a removal efficiency of about 99%. As such, it is likely chromium(III) also demonstrates first-order reaction kinetics analogous to aluminium(III), with a first-order rate constant of $5.0 \times 10^{-3}$ s$^{-1}$.

Figure 2.46  Metal profiles over time on a test column containing zero-valent iron [109].
The rapid reduction of chromium observed in Figure 2.44 was also found in the study of Wu et al. [110], where the investigation involved the oxidation of cationic Cr(III) to anionic Cr(VI) on Mn-substituted goethite and subsequent adsorption. As can be seen in Figure 2.47, the bulk of the extraction occurs within the first hour.

![Figure 2.47](image) The time-dependent profile for the oxidation of Cr(III) to Cr(VI) and adsorption on Mn-goethite at pH 4 as a function of time [110].

### 2.5.5 Antimony

Antimony is found in oxidation states +3 or +5, and their chemistries differ. Consequently, it is not surprising that the sorption behaviour of Sb(V) and Sb(III) on iron oxides and oxyhydroxides are dissimilar. Some analogy to the behaviour of arsenic, also present in oxidation states +3 and +5, has been raised. Scott and Morgan (1996) suggest that, since the process of electron transfer and release of As(V) is fast compared to the adsorption of As(III), this may be also the case for Sb(III) [111]. The oxidation of Sb(III) with natural iron oxyhydroxide is relatively slow, with a study by Belzile et al. [104] providing a pseudo-first order rate constant of $0.574 \pm 0.093$ days$^{-1}$. However, Martinez-Lladó et al. [101] found that the sorption kinetics of Sb(V) on synthetic goethite is very fast (Figure 2.48), with kinetic data fitting a pseudo-second order kinetic rate equation, as illustrated in Figure 2.49 [101].
Figure 2.48 Sb(V) sorption on goethite as a function of time [101].

Figure 2.49 Pseudo-second order kinetic rate equation for Sb(V)-goethite data shown in the above figure, calculated at three temperatures [101].

2.5.6 Aluminium

Unlike many other metals, aluminium has only one common oxidation state, although it is given to hydrolysis and oligomerisation reactions at elevated pH values [2]. The time-dependent changes in metal concentration, including Al(III), studied by Wilkin and McNeil [105] utilising zero-valent iron demonstrated rapid removal at pH levels of 2.3 and 4.5 where the Al^{3+}_{aq} ion is dominant. The pseudo-first order rate constant determined for aluminium ion was $k_{obs} = 0.35 \pm 0.02$ h^{-1} and consequently the reaction half-life was $t_{1/2} = 1.5 \pm 0.09$ h [105]. Trends for several metal ions including Al(III) appear in Figure 2.50.
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 [105].

2.5.7 Molybdenum

Like vanadium, there are few investigations on the adsorption kinetics of molybdenum onto iron oxides and oxyhydroxides. Solution-based redox chemistry has been probed, however, and may point towards anticipated reactivity trends on surfaces where redox processes also apply. An investigation was undertaken by Diebler and Millan [112] into redox reactions between complexes of molybdenum in oxidation states III and VI and iron in aqueous solutions. Figure 2.51 summarises the behaviour for the reaction of Mo(VI) and Fe(II) in terms of the dependence of the apparent first-
order rate constant on the concentration of Fe(II). A simple first-order dependence on [Fe(II)] is apparent, with half-lives of 2.5 - 18 minutes [112]. The straight line passes through the origin and yields a second-order rate constant \( k = 3.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \) at 20 °C and 8 M HCl [112].

![Figure 2.51 Reduction of Mo(VI) by Fe(II). Dependence of the apparent first-order rate constant on \[\text{Fe(II)}\] (20 °C, 8 M HCl) [112].](image)

The kinetics of the reaction of \( \text{Fe}^{2+} \) and \( \text{Mo}_2\text{O}_4^{2+} \) in dilute HClO₄ and 25 °C was also investigated by Diebler and Millan [112]; the results showed the dependence of the pseudo-first order rate constant on \([\text{Fe}^{2+}\)]\) for various H⁺ concentrations. The rate constant for this reaction is \(\leq 0.2 \text{ M}^{-1} \text{ s}^{-1}\), and the apparent second-order rate constant depends on H⁺ concentration [112]. Few other studies of relevance have appeared. However, molybdate ion has a tendency to rapidly form polyoxometalates, which may include foreign ions in their lattice [112]. These polymeric ions may adsorb well under some circumstances, and offer a potential way for molybdenum to be removed from aqueous solution.

### 2.6 LEACHABILITY OF TRACE ELEMENTS ABSORBED/COPRECIPITATED WITH IRON OXIDES AND OXYHYDROXIDES

Surface-adsorbed ions may not be bound irreversibly, and may suffer release and redissolution under certain chemical circumstances. Understanding the leachability or release of trace elements adsorbed or coprecipitated onto iron oxides and oxyhydroxides that returns them back into the environment is an important aspect of the treatment.
process. Factors in the environment which can influence the stability of the corrosion product or iron oxide including the re-release of trace elements such as Se, As, V, Sb, Cr, Al and Mo include effects as simple as temperature and UV light. Other factors which may affect the leaching of these trace elements are the composition of the solution phase and properties of the form of the iron oxides involved in the process including any interconversions that occur with time. The process may include dissolution of the iron oxide itself, with concomitant dissolution of adsorbed ions. In particular, pH has a strong influence on the dissolution of iron oxides [2]. The high affinity of protons with structural $O^{2-}$ assists the release of iron, particularly at low pH levels [2]. It is the release of the cations, rather than the anions, which is likely to be rate limiting. The pH also influences the electrochemical surface potential and hence redox processes [2].

Cornell and Schwertmann [2] propose three mechanisms for the dissolution of iron oxides and oxyhydroxides, being protonation, complexation and reduction. Protonation involves the general reaction between protons and Fe(III) oxides by the formula:

$$\text{FeOOH}_{aq} + n\text{H}^+ \rightarrow [\text{Fe(OH)}_{(3-n)}]^n_{aq} + (n-1) \text{H}_2\text{O} \quad (28)$$

Proton adsorption weakens the Fe–O bond, probably by polarising it, and so promotes detachment of Fe from the solid and thereby returns it to the bulk solution [2]. Chloride ions and complexes of both organic and inorganic ligands with the surface functional groups can substantially increase the rate of dissolution [2]. These ligands may accelerate, retard, or even block dissolution. The ligand first adsorbed on the surface of the Fe oxide weakens the Fe–O bonds to neighbouring atoms and eventually leads to detachment of the Fe(III) complex. Ligands which promote dissolution are thought to form mononuclear surface complexes, whereas those that inhibit the process form binuclear or trinuclear surface complexes [2].

Reduction involves a mechanism by which the structural bonds between Fe atoms and oxygen atoms in iron oxides may be weakened by the reduction of structural Fe(III) to Fe(II) [2]. In natural environments, reductive dissolution is by far the most important and is mediated both biotically and abiotically. The most important electron donors, particularly near surface ecosystems, result from metabolic oxidation of organic compounds under $O_2$-deficient conditions [2]. Some reductants found in the environment include $H_2S$, $H_2$, Fe(II), ascorbic acid, fulvic acid, biomass and some bacteria [2].
There have been a number of key studies of adsorption that comment on the reversibility or irreversibility of the process. Cornell and Schwertmann [2] found selenite anion (SeO$_3^{2-}$) adsorbs strongly and specifically on goethite by a ligand exchange mechanism [2]. Adsorption is largely irreversible. It is at a maximum in the acid region, and decreased to negligible values at pH 10. It is likely the adsorption onto lepidocrocite, hematite and magnetite would result in the process being predominantly irreversible at lower pH levels. In Baltpurvin's study of the transformation of ferrihydrite on the leachability of the coprecipitated secondary metal ions Cr(III) concentrations were followed over a pH range of 7 to 11 [3]. The finding of this study was that for all Cr(III) systems examined, with the exception of that aged at pH 11, leachability was only slightly altered on ageing [3]. During the study of antimony(V) adsorption onto hematite, Ambe (1987) observed desorption of antimony(V) from α-Fe$_2$O$_3$ surfaces at pH 4 to 10 was negligibly slow [113]. Wilkin and McNeil (2003) studied the reversibility of metal adsorption (Cu, Cd, Ni, Zn, Hg, Al, Mn and metalloid As) onto zero-valent iron, noting that changes in respect to pH and redox conditions could impact on long-term performance of substrate treatment systems by changing geochemical conditions [105]. In their reversibility study over 450 hours of reaction, they adjusted the pH from the final alkaline values attained during batch runs to pH <2 and also applied reoxidation with air for 24 hours. For the acid extraction test they found metals were released once solution pH decreased below 4; however, complete metal recovery was not obtained even at pH 2. During aeration the formation of iron oxyhydroxide was evident, but detectable levels of dissolved metals were not observed in solution [105].

Understanding the desorption or dissolution of trace elements from the product of the treatment process in the environment in which it will be stored is crucial to ensuring no or negligible release of the adsorbed trace elements back into receiving waters occurs. Consequently, the leachability of trace elements from materials formed through the process of adsorption and/or coprecipitation also needs to be analysed in a conjoint study for the full process to be illuminated.
2.7 REFERENCES


[99] Yongtian He; (2003) *Chromate Reduction and Immobilisation under High pH and High Ionic Strength Conditions*. Ph.D., Ohio State University, USA.


CHAPTER THREE
VALES POINT POWER STATION: SELENIUM AND TRACE METAL REDUCTION PILOT PLANT TRIALS

3.1 INTRODUCTION

Vales Point Power Station is located on the southern shores of Lake Macquarie in New South Wales (NSW). The power station built in the 1970s comprises two 660 MW units and is owned and operated by Delta Electricity. The power station utilises black coal sourced from coal mines located in NSW.

Ash generated through the combustion of black coal is stored in a nearby ash dam. The means of transport of the ash to the dam is through a lean-phase process comprising nominally 70% estuarine water and 30% ash. The mixture is pumped from the station’s ash handling plant through ash pipes to the ash dam. The lean-phase ash mixture is pumped to the highest point of the ash dam which is at the north-eastern section as shown in Image 3.1 below. The ash is terraced to allow the ash transport water to flow down to the lowest point of the dam. From this point the ash-depleted water is pumped back to the power station by two ash pumps at a rate of about 550 litres per second to a storage tank. Ash water from this tank is utilised as required by the power station for the ash plant for further transport of ash to the dam, so that the system is continually recirculating.

Image 3.1 Vales Point Power Station and the ash dam ash water circulating system.
During the earlier years of the power station’s operation, surplus ash water from the ash dam was discharged into Mannering Bay via Wyee Creek. In 1995, a pumping station was constructed at the ash dam discharge point to return ash water to Vales Point Power Station for reuse in ash transport. Now the process utilised is a recirculating system, with the main source of additional makeup being from rainfall runoff into the dam. As depicted in Image 3.1, the catchment of the ash dam is large, covering an area of about 4.1 km², but this is reduced to about 1.3 km² with stormwater diversion channels that have been established to redirect rainfall runoff to Wyee Creek and thus minimise the amount of water entering the ash dam catchment. The ash water itself is saline in nature, with a pH of between 7.5 - 8.5 and conductivity of about 40 mS/cm. The operation of the ash water system has been established for maximum recirculation, so as to minimise release through a licensed discharge point.

The bottom ash generated through the combustion process is captured and taken off site for reuse. The ash stored at the ash dam is the remaining fly ash, with a composition consisting of the major elements silicon, aluminium, iron and calcium. Minor and trace elements present include arsenic, boron, barium, beryllium, copper, selenium, chromium, manganese, molybdenum, lead, antimony, vanadium, zinc and strontium.

The release of trace elements from ash into the transporting water is dependent on a number of factors, including the chemical characteristics of the element present in the ash, chemical reactions occurring within the confines of the ash dam and external factors such as rainfall into the catchment, seasonal variations in temperature and amount of makeup water introduced into the system and amount released. A certain fraction of the trace elements are in fact sorbed onto the fly ash, inhibiting their release into the transporting water.

To control the water height in the ash dam, additional ash water generated by rainfall into the catchment is released via the power station’s environment protection licenced discharge points into the cooling water outfall canal which discharges into Wyee Bay. The amount of ash water released from the licenced discharge points into the cooling water outfall canal ranged from 9 ML/day up to 63 ML/day between 1997 and 2009.

Image 3.2 displays the main ash return water pipeline for the power station. The pipeline tapping off to the right is one of the main licenced ash water discharge
lines entering the cooling water outfall canal to the south of the power station. The small sample line tapping off the main ash return water line at the bottom of the image is the ash water source for the selenium and trace element removal pilot plant located at Vales Point Power Station.

Image 3.2  Vales Point Power Station ash return water pipeline.

The interaction or effect of major and minor trace elements on receiving waters and ecosystems is dependent upon several factors. These include the relative concentrations present in the ash being transported to the ash dam, the sorption of trace elements by ash deposited in the dam, the amount that can be released and subsequent chemical reactions and transformations which take place once the ash water is mixed with the receiving water and lake sediments, along with the toxicity of the element released.

As covered in Chapter 1 Introduction, the environmental impact of discharging ash water into Wyee Bay has already been addressed. This chapter focuses on the pilot plant trials undertaken at Vales Point Power Station utilising a range of iron products for the generation of iron oxides and oxyhydroxides for the removal of trace elements, in particular selenium from ash water.
3.2 VALES POINT POWER STATION ASH WATER TREATMENT: 2002 PILOT PLANT TRIAL

The first pilot plant constructed at Vales Point Power Station in 2002 was initially designed utilising a single concrete trough with dimensions of 370 mm depth by 1,000 mm width and 10,000 mm (or 10 metres) in length. Waste fabric filter hanger bars were installed to provide approximately 91 m² of iron initially, it was later increased to 140 m². The first pilot plant trial only focused on the removal of selenium from ash water and did not consider other trace elements at that time.

The most dominant selenium complex present in the Vales Point ash water is selenite (SeO$_3^{2-}$), representing of the order of 95% of the total selenium, with the remainder being selenate (SeO$_4^{2-}$). At the time of testing in 2002, the selenite concentration was of the order of 18 µg/L, with total selenium being 22.2 µg/L.

The following sections outline the pilot plant trial objectives, design and materials used, operating conditions during the trial period of six months, and the outcome of analytical tests and pilot plant measurements recorded in 2002.

3.2.1 Study Objectives

For this preliminary pilot plant trial, the objectives were not just to ascertain the amount of selenite removed from the process but also to learn more about the operating parameters, and to observe during the six month period what physical transformations occur with the reacting material. Further, it was intended to determine the optimum operating conditions. The following objectives were considered in the 2002 pilot plant trials:

1. To determine the amount of selenite removed per metre square of iron oxide material at a constant flow rate of ash water.
2. To determine the optimum flow rate for the removal of selenite for the fabric filter iron bar system.
3. To ascertain if increasing the capacity of iron increases the removal of selenite.
4. To observe the flow path through the fabric filter hangers and contact time.
5. To observe the chemical properties of the ash water being treated by the process.
6. To observe the physical transformation of the fabric filter bars over the six month trial period.
3.2.2 Pilot Plant Design and Materials

3.2.2.1 Design

The concrete trough utilised in the trial as depicted below in Image 3.3 was fitted initially with rows of approximately 5,000 fabric filter hanger bars, suspended inside the trough by cross bars, with a surface area of approximately 91 m². Later, this was increased to 7,000 bars to increase the capacity to approximately 140 m² of iron. The flow rate was measured with a Signet flow monitor with a range of 1 to 5 litres per second. No flow regulator was installed on the pilot plant and as a result the flow was difficult to regulate, as the flow through the ash return line was regulated by the amount of ash water captured in the main ash water storage tank which is elevated above the line entering the power station site. As mentioned earlier, the concrete trough had a length of 10 metres, width of 1 metre and depth of 0.4 metre.

Ash water enters at the western end of the concrete trough through a PVC pipeline 120 mm in diameter at the top of the trough, flowing through the hangers in an easterly direction and exiting the trough (foreground of Image 3.3) through two PVC pipes 120 mm in diameter located at the bottom of the trough. Treated ash water is then discharged into the cooling water canal just north of the licence discharge point for ash water.

The first pilot plant was constructed during November and December 2001, with the first testing of ash water commencing on the 11th January 2002.

Image 3.3 Vales Point Power Station 2002 selenium removal pilot plant.
Figure 3.1 provides a schematic of the pilot plant trough and the likely direction of ash water flow past the fabric filter hanger bars [2]. A likely scenario for the flow of ash water would be one of turbulence, since, as the ash water passes around the bars, laminar flow is disrupted by the obstruction of the bars. Fluorescein was utilised to observe the flow of ash water and it was noted that, where larger gaps were present, the ash water flow was observed to be faster and more turbulent. If the bars do not connect with the bottom of the concrete trough or along a side then the ash water will preferentially flow along that path.

Figure 3.1  Top down schematic of pilot plant fabric filter hanger bars and ash water flow [2].

Image 3.4 provides a side view of the inlet to the concrete trough and fabric filter bars. As can be seen in this image, the bars are tightly packed in ranks side by side and the discolouration of the concrete along with evidence of oxide formation on the bars provides the height of ash water passing through the trough. Note the yellow ochre colour of the treated ash water, which is clear evidence of iron oxide or oxyhydroxide formation. The colours, when compared to colour plates of known species (Chapter 2), indicates the presence of either lepidocrocite or goethite.

Image 3.4  Inlet to the pilot plant with fabric filter hanger bars also displayed.
3.2.2.2 Materials

The fabric filter hanger bars were made from mild steel manufactured with an iron content of approximately 95%, with the remainder being approximately 3.5% manganese. The dimensions of the bars were 25 mm width by 6 mm thick and had a length of 400 mm. Prior to commencement of filling the trough with ash water, the fabric filter hanger bars were soaked initially with dilute hydrochloric acid to remove scale and promote the production of iron oxide. These bars were suspended on steel rods across the width of the concrete trough. The rods suspending the bars filled the middle section of the trough with the inlet and outlet sides free of bars so as not to obstruct the inlet pipe and to allow room for the corrosion products and suspended matter to accumulate at the end of the trough.

The mass of each bar was in the order of 400 to 450 grams and over the pilot plant trial period it was expected that the weight of each bar would increase due to the formation of the oxide coating. Image 3.5 provides a view looking down into the trough across the tops of the bars suspended from iron rods.

Image 3.5 Top view of the pilot plant fabric filter bars suspended from iron rods.

3.2.3 Pilot Plant Operating Conditions

The pilot plant was commissioned on the 11th January 2002, with testing concluding on the 8th May 2002. The initial flow rate of ash water was set at 2.5 litres per second. The pilot plant was operated continuously 24 hours per day, with the measured pH varying between 7.5 and 8.6. Total selenium in the inlet ash water ranged from 18.0 µg/L to 19.0 µg/L. The temperature of the ash water during the
period of operation ranged from 27 °C in the summer period down to 21 °C in May 2002. The flow rate and contact time were the only parameters controlled in the process. All other conditions were pre-defined by the quality of the incoming ash water, which could change due to external conditions such as the type of coal utilised by the power station, the chemical characteristic of the ash being produced or stored in the ash dam, rainfall infiltration causing dilution, and temperature effects due to weather conditions over the trial period.

### 3.2.4 Trial Process Observations

During the summer period, algal blooms were observed to be growing in the inlet side of the trough and accumulating over the surface of the fabric filter hanger bars. This unanticipated biological reaction posed a threat to the chemical process efficiency. Subsequently, the bars were removed and cleaned, with algal blooms also removed from other areas of the trough. Black plastic was placed over the top of the trough to prevent ultraviolet light from entering, thereby inhibiting further growth of algae.

On removal of the bars for cleaning, the formation of different iron oxides and oxyhydroxides was evident. At the surface, the colour of the oxide was brown with the centre being orange to ochre in colour and the ends being black. These colours are consistent with the reported colours of iron oxides or oxyhydroxides hematite, goethite, lepidocrocite and magnetite respectively. Image 3.6 depicts both the bars and colour changes arising from oxidation, along with algal growth to the inlet of the pilot plant. The plastic covering introduced provided a satisfactory control to algal problems, without limiting required air entry.

Image 3.6 Inlet to the pilot plant depicting formation of oxides and algal growth.
3.2.5 Experimental Results

3.2.5.1 Selenium Removal Trial Results

The first selenium removal trial was conducted over the period of 11th January 2002 to 25th January 2002, with the pH varying only slightly, from 8.37 to 8.59, while the average temperature was 25.7 °C. The surface area of iron totalled 90.8 m² and the flow rate was ramped up from 0.5 L/sec to 5.1 L/sec over the 14 day period. The total selenium concentration in the inlet ash water during this period ranged from 20.7 µg/L to 22.6 µg/L. It is evident from Figure 3.2 below that the lower was the flow rate, the greater was the amount of selenium that could be removed. The data refer to the first hanger bar trial and the upper range removed was approximately 1.0 µg/L, which is equivalent to a 4.5% reduction.

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

Figure 3.3 reports both inlet and outlet total selenium test results, and further illustrates how, over the trial period, the amount of total selenium removed from the system was dependent on the flow rate. The higher the flow the less selenium was adsorbed or coprecipitated on the iron oxide/oxyhydroxide surface. In this trial, the optimum flow rate was 0.5 L/sec, maximising the period for selenium to be in contact with the oxide surface. The amount removed was not high, and indicated that a surface area of 98 m² was not enough to obtain a high efficiency of removal. At this flow rate, the amount of ash water being treated per day was low at only 1800 kL.
The second trial was undertaken from 22\textsuperscript{nd} April 2002 to 8\textsuperscript{th} May 2002, with the surface area of the iron increased to \(\sim 140\) m\(^2\). The pH during this period ranged from 7.5 up to 8.3, with the temperature ranging from 23 \(\degree\)C in April down to 21 \(\degree\)C in May. The total selenium in the inlet ash water during this period ranged from 13.4 \(\mu\)g/L to 15.7 \(\mu\)g/L. The flow rate of the ash water was again ramped up over the trial period from 0.5 L/sec to 5.6 L/sec. Once again, as illustrated in Figure 3.4 below, the higher the flow rate the less contact time the ash water had with the oxides that have formed on the bars, and consequently the lower the reduction in total selenium. The optimum flow rate for this trial was 0.5 L/sec. Selenium reduction was clearly higher in this trial, at around 20%.

Figure 3.3 Trial 1 selenium inlet and outlet concentration trends; 98 m\(^2\) iron surface.

![Trial 1 Selenium Removed (\(\mu\)g/L) for Surface area of 98 Square Metres](image1)

Figure 3.4 Trial 2 selenium removed (\(\mu\)g/L) versus flow rate (L/sec); 140 m\(^2\) iron surface was employed.

![Trial 2 Selenium Reduction (\(\mu\)g/L) Versus Flow Rate (L/s)](image2)
The inlet and outlet total selenium test results for the second trial (Figure 3.5) also followed the same trend as the first trial in that the higher the flow the less selenium was removed from the system, confirming that process efficiency is reliant on having high contact time with the oxide surface.

![Trial 2 Selenium Removed (µg/L) for Surface area of 140 Square Metres](image)

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

The amount of selenium removed from the ash water, as shown above, ranged from 0.3 µg/L at high flow rates to 2.7 µg/L at the lowest flow rate of 0.5 L/sec, which is equivalent in the latter case to a reduction of 20.2%. The higher efficiency of selenium removal shown for this trial demonstrates that the addition of extra iron bars and a subsequently higher surface area of iron oxides/oxyhydroxides leads to more selenium being adsorbed or coprecipitated.

### 3.2.6 Discussion

The optimum flow determined for the trials with fabric filter hanger bars was 0.5 L/sec or lower. Whilst the plot of flow rate versus selenium removed was not perfectly linear, the coefficient of the plot $R^2$ equalled 0.8573, displaying some correlation. The preferred flow rate of 0.5 L/sec is low, allowing only 1800 kL per day to be treated by this system. However, increasing the surface area of iron improved the efficiency of selenium removal. For the highest reduction, the amount of selenite removed per m² of iron oxide or oxyhydroxide was approximately 0.02 µg/L Se per m². The pH remained reasonably stable throughout the trials, but the temperature did drop from about 25 °C in summer to 21 °C in winter, which may have a very small effect on the efficiency of removal. The concentration of inlet selenium
also dropped from 22.4 µg/L to 13.4 µg/L across the trials. The hanger bars used formed a range of iron oxides, as evident from the visual inspection and types of coloured oxides and oxyhydroxides formed. The flow of ash water was distributed reasonably past all the iron bars, as evident from visual inspection aided by dyes added to the flowing water.

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

The first pilot plant constructed at Vales Point Power Station was modified in 2003 with the addition of two concrete troughs placed in series with the first pilot plant trough, which employed fabric filter hanger bars with a surface area of 140 m². The two additional troughs were constructed on the southern side of the first trough, and were filled with sheets of iron which had been cut to fit the shape of the troughs with a gap on one side to allow ash water to flow around them. The modified pilot plant had a combined iron surface area of 250 m².

The main objective of this pilot plant trial was to determine more accurately the relationship between selenium removal to surface area of iron at the optimum flow rate. The trials also considered, for the first time, the removal of other trace elements present in the ash water.

During this trial period of February 2004 to April 2005, the total selenium concentration being measured at the inlet of the pilot plant ranged from 3.2 to 21.7 µg/L. This is a much wider concentration spread than that observed in the first trial period. However, the test period for the first trial was between January to May 2002, which is a much shorter timeframe than that of the second pilot plant trial of 14 months. Evidently, and depending on a number of factors, the concentration of selenium and perhaps other trace elements is variable. This could be due to the quantity of trace elements in the coal, chemical interactions after combustion and in the ash slurry, and external factors such as dilution through rainfall into the dam catchment.

A testing regime was established with a program for each trial period along with other tests to learn more about the process and the materials being utilised. All analysis undertaken for the first and second trials were performed by either the CSIRO or ALS Laboratory Services. Initial “round robin” samples were dispatched
to both facilities to check the quality and reproducibility of analyses before sampling and testing commenced.

The following sections outline the pilot plant trial objectives, design and materials used, operating conditions during the trial period, and the outcome of analytical tests and pilot plant measurements recorded from February 2004 to January 2005.

### 3.3.1 Study Objectives

The objectives for the second pilot plant trial were essentially to establish more accurately the relationship between the flow rate (contact time), surface area of iron and the level of selenium and trace element reduction that could be achieved from the process, whilst observing changes to pilot plant materials and ash water properties. The detailed objectives for the 2004/05 pilot plant trials included the following:

1. To confirm the optimum flow rate for the removal of selenium.
2. To determine the concentration in µg/L of total selenium removed by the 250 m² iron oxide material at a constant flow rate of ash water.
3. To ascertain what trace elements are coprecipitated or adsorbed onto the iron oxides and oxyhydroxides formed by the process.
4. To determine the concentration in µg/L of trace elements removed by the process.
5. To determine the composition of metals present in the iron bars and sheets.
6. To identify the types of iron oxides formed on the surface of the plates.
7. To observe the chemical properties of the ash water being treated by the process.
8. To observe the physical transformation of fabric filter bars and steel plates over the trial period.

### 3.3.2 Pilot Plant Design and Materials

#### 3.3.2.1 Design

The original pilot plant trough containing the 7,000 fabric filter hanger bars with an approximate surface area of 140 m² of iron was not altered during the second trial. Two additional concrete troughs were installed, as depicted in Image 3.7, on the southern side of the first trough with equal dimensions of 10 metres by 0.6 metres wide and a depth of 0.6 metres. The additional troughs were elevated above the first
trough by different amounts to ensure the ash water flowed sequentially through the first, second and third troughs, eventually discharging from the end of the final trough. The new concrete trough at the highest elevation was now the inlet to the plant and the ash water inlet was redirected to flow into the top of the first trough through a PVC pipeline 120 mm in diameter. To regulate the flow of ash water at a constant controlled rate, a GEMU control valve and regulator was installed to replace the Signet flow monitor used in the first trial. The range of the flow rate provided by the GEMU control valve was between 0.4 to 2.5 L/s, with an accuracy of ± 1%. The maximum flow rate that was achievable without overflowing the troughs was established to be 2.0 L/s. The additional troughs constructed in 2003 were fitted with steel plates with dimensions of 0.5 metres wide by 0.6 metre height, and a thickness of 0.01 metre or 10 millimetres.

Image 3.7 Modified Vales Point Power Station 2003 selenium and trace metal removal pilot plant.

Figure 3.6 provides a schematic of the additional pilot plant troughs and the direction of ash water flow past the steel plates. The plates were installed into the two troughs and were consecutively butted against the wall of the trough on opposite sides and sealed to the side walls and at the bottom to ensure the ash water flowed past all of the plates in the direction as depicted in Figure 3.6.
For the new troughs, steel plate was employed. Pieces of steel plate 10 cm by 10 cm were cut and provided to CSIRO for analysis by Inductively Coupled Atomic Emission Spectroscopy. The test results confirmed the steel plates were made from mild steel, manufactured with an iron content of approximately 97% with the remainder being 3.3% manganese. The steel was purchased in large sheets and then cut in the workshop into sheets with dimensions of 0.6 metres by 0.5 metres. When fitted in place, this allowed a gap of about 10 cm from the wall of the concrete trough for the ash water to flow through. The thickness of each plate was nominally 10 mm. Prior to commissioning the pilot plant, the plant was filled with ash water for a month to promote the production of the iron oxides or oxyhydroxides from the salt content in the water.

The weight of each steel plate was between 16 and 18 kilograms, and over the pilot plant trial period it was expected that the weight of each steel plate would increase due to the formation of the oxide coating. Image 3.8 displays a number of steel plates with iron oxide coating and also the timber support beam screwed into the top of the plate which was used to suspend the plate in the concrete trough.

The original trough, incorporated into the new pilot plant, employed fabric filter hanger bars as described earlier in Section 3.3.2.1. No change to the materials or their assembly was made.
3.3.3 Pilot Plant Operating Conditions

The modified pilot plant was commissioned in February 2004 and continued to operate for a period of 14 months, with all testing being completed by the end of April 2005. During February to April 2004 the flow rate was modified with the GEMU controller to confirm the optimum flow rate to be set for the remainder of the pilot plant operations. Table 3.1 provides the test results for total selenium measured in µg/L at the inlet and outlet of the pilot plant at varying flow rates, along with the percentage of selenium removed by the process.

Table 3.1 Total selenium test results in µg/L at the inlet and outlet of the pilot plant [1].

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Date Sampled</th>
<th>Flow rate L/sec</th>
<th>Total Selenium µg/L</th>
<th>Total Selenium Removed µg/L</th>
<th>% Selenium Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Inlet 1</td>
<td>Inlet 2</td>
<td>Inlet Average</td>
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</tr>
<tr>
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<td>12.2</td>
<td>-</td>
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<tr>
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<td>9.7</td>
</tr>
<tr>
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<td>18/3/04</td>
<td>1.5</td>
<td>8.9</td>
<td>-</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>24/3/04</td>
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<td>9.1</td>
<td>9.5</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Figure 3.7 confirms the optimum flow rate determined by the first pilot plant trial to be less than or equal to 0.4 L/sec or 24 L/min. This flow rate (0.4 L/sec) was programmed into the control valve as the set point for the remainder of the trial.
period; lower flow rates were considered inappropriate, as they would produce insufficient throughput.

![% Selenium Removed versus Flowrate L/sec](image)

**Figure 3.7** Percentage of total selenium removed versus flow rate [1].

The pilot plant was operated continuously 24 hours per day. Parameters were measured on a weekly basis, and included temperature in °C, pH, flow rate in L/min and conductivity in mS/cm. Table 3.2 provides the measured parameters, along with the date they were determined.

The flow during the trial period remained constant, with only slight deviations with the exception of the readings on the 1st and 8th February 2005, where the flow dropped to 10 L/min. The low flow rate was due to a blockage of marine growth which caused the control valve to fail. A strainer was installed to inhibit any further material from accumulating at the control valve. The pH remained reasonably constant, with only slight fluctuations throughout the 2004 to 2005 trial period. The temperature of the inlet ash water ranged from 12 °C during the winter period up to 27 °C in the summer.
Table 3.2 Pilot Plant 2004/05 measured operating parameters.

<table>
<thead>
<tr>
<th>Date</th>
<th>pH Inlet</th>
<th>Temperature °C Inlet</th>
<th>Conductivity (mS/cm)</th>
<th>Flow rate (L/min)</th>
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</tbody>
</table>

A step change is evident from the trends of operating parameters provided in Figure 3.8 for both temperature and conductivity. The change in conductivity could be due to a number of factors, including rain water infiltration and amount of salt water make up to the ash transport system.

Figure 3.8 Variation in the Pilot Plant 2004/05 measured operating conditions [1].
3.3.4 Trial Process Observations

During the 14 month trial period no algal blooms were observed growing in the troughs containing steel plates. This was likely due to the solid plates being installed with a partition gap of only ~10 cm, which significantly restricted light penetrating the ash water moving through the troughs and thus inhibited growth. The black plastic cover for the third trough containing the hanger bars remained in place after the first trial and continued to block ultraviolet light and prevent algal growth.

A number of plates were weighed before the commencement of the trial and during the trial period. The plates were weighed after 3 months of plant operation. The mass of the plates increased due to the formation of the iron oxide and oxyhydroxide layers forming on the surface of the plates, which was expected. However, over time during the trials, the mass of the plates was observed to reduce due to the oxide coating becoming separated from the parent metal surface and depositing on the bottom of the concrete troughs. Table 3.3 provides the initial mass of a number of steel plates located along the two concrete troughs along with the weights of the same plates approximately three months after commissioning of the pilot plant trial. Increases in weight of up to ~5% occurred in this period.

Table 3.3  Masses of pilot plant steel plates at commencement and during trials.

<table>
<thead>
<tr>
<th>Steel Plate Identification</th>
<th>Weight Plate (g) 14/1/04</th>
<th>Weight Plate (g) 2/4/04</th>
<th>Difference Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 – Plate 2</td>
<td>16599</td>
<td>17482</td>
<td>+883</td>
</tr>
<tr>
<td>T1 – Plate 29</td>
<td>16566</td>
<td>17051</td>
<td>+485</td>
</tr>
<tr>
<td>T1 – Plate 37</td>
<td>16731</td>
<td>17177</td>
<td>+446</td>
</tr>
<tr>
<td>T1 – Plate 45</td>
<td>16617</td>
<td>17064</td>
<td>+447</td>
</tr>
<tr>
<td>T1 – Plate 60</td>
<td>16453</td>
<td>16907</td>
<td>+454</td>
</tr>
<tr>
<td>T1 – Plate 66</td>
<td>16622</td>
<td>17074</td>
<td>+452</td>
</tr>
<tr>
<td>T1 – Plate 80</td>
<td>16661</td>
<td>16977</td>
<td>+361</td>
</tr>
<tr>
<td>T1 – Plate 92</td>
<td>16760</td>
<td>17230</td>
<td>+470</td>
</tr>
<tr>
<td>T1 – Plate102</td>
<td>16555</td>
<td>16955</td>
<td>+400</td>
</tr>
<tr>
<td>T2 – Plate 1</td>
<td>16554</td>
<td>17225</td>
<td>+671</td>
</tr>
</tbody>
</table>
On removal of the steel plates for weighing, the formation of different types of iron oxides and oxyhydroxides was evident. At the surface, the colour of the oxides varied; the colours observed included brown, black, reds and different shades of orange to ochre colours. The surface colours were more predominantly the brown, red and orange to ochre colours which are consistent with the colours of hematite, goethite and lepidocrocite. When flakes of the oxide had fallen off the plate, the colour of the oxide was black, which is indicative of magnetite. The pattern of formation could be a result of the amount of dissolved oxygen contacting the surface of the oxide and steel plate. Image 3.9 depicts the colours and the surface of the oxide coating. Note the formation of bubbles and sheets of oxides at the surface.

Image 3.9 Steel plate with varying iron oxide formation evident.

3.3.5 Experimental Results

The first trial undertaken with the modified pilot plant was to determine which trace elements were removed through adsorption or coprecipitation. On the 26th February 2004, samples were collected from the inlet and outlet of the pilot plant to analyse at the μg/L or ppb level for trace elements likely to be present in the Vales Point Power Station ash water. The flow rate was maintained at 0.4 L/sec for one week prior to sampling. The inlet temperature on the day of sampling was 20 °C and the pH 8.3. The conductivity measured at the inlet was 29.7 mS/cm at 23 °C.
Samples were collected by CSIRO and were filtered at the time of sampling with 0.45 μm Millipore filter paper and collected in 100 mL polyethylene sample bottles each containing 3 drops of concentrated nitric acid. Table 3.4 provides the test results for a range of trace elements from duplicate samples obtained from the inlet and outlet of the pilot plant troughs which had been analysed by Inductively Coupled Mass Spectroscopy, and for total selenium by atomic fluorescence spectrometry or CSIRO Analytical Method CAAC/AFSO2.

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>
<thead>
<tr>
<th>Element</th>
<th>Acid Blank (a) µg/L</th>
<th>Acid Blank (b) µg/L</th>
<th>Inlet (a) µg/L</th>
<th>Inlet (b) µg/L</th>
<th>Outlet (a) µg/L</th>
<th>Outlet (b) µg/L</th>
<th>Inlet/Outlet Difference µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (Al)</td>
<td>7</td>
<td>&lt;4</td>
<td>40</td>
<td>41</td>
<td>20</td>
<td>20</td>
<td>-20 ± 6</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>3.3</td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
<td>0</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>9</td>
<td>11</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>20</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>16</td>
<td>15</td>
<td>58</td>
<td>58</td>
<td>42 ± 2</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>130</td>
<td>130</td>
<td>120</td>
<td>120</td>
<td>-10 ± 0.3</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>0</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>11</td>
<td>2</td>
<td>1</td>
<td>&lt;0.5</td>
<td>0.5</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>12</td>
<td>11</td>
<td>9.4</td>
<td>9.8</td>
<td>-2 ± 0.3</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>10</td>
<td>10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>0</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>4</td>
<td>7</td>
<td>&lt;2</td>
<td>2</td>
<td>-3 ± 2</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>-</td>
<td>-</td>
<td>3.6</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Fluoride (F)</td>
<td>-</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
<td>1.23</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Total Selenium (Se)</td>
<td>&lt;0.1</td>
<td>-</td>
<td>9.8</td>
<td>9.7</td>
<td>7.9</td>
<td>7.8</td>
<td>-2 ± 0.1</td>
</tr>
<tr>
<td>Total Arsenic (As)</td>
<td>&lt;0.1</td>
<td>-</td>
<td>10.5</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>-7 ± 0.1</td>
</tr>
</tbody>
</table>

From the set of trace elements analysed by CSIRO, the elements which were significantly reduced in concentration from the inlet to outlet included aluminium, molybdenum, arsenic, antimony and selenium. Zinc also appeared to be slightly reduced in concentration; however, the levels of zinc being measured were close to the concentration in the acid blank.

From the analysis of these trace elements the only element detected that had increased in concentration by the process was manganese (Mn). This trace element increased from 16 µg/L to 58 µg/L, and this reflects the presence of significant amounts of manganese in the steel, some evidently being released into solution during
surface corrosion. All other trace elements analysed, apart from the above, had neither been reduced nor increased by the process. Following the above test results of the removal of trace elements, further tests were conducted only on those elements that have been significantly reduced by the process.

Arsenic and selenium were also tested on the 26th February 2004, but with samples obtained at several locations along the three troughs in addition to inlets and outlets. The data appears in Table 3.5. The selenium concentration falls in a reasonably continuous manner, but variability in concentrations for arsenic at initial sites is observed, although later positions display consistent fall-off in levels. The source of this initial variability for As data is unclear.

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>
<thead>
<tr>
<th>Sample Identification</th>
<th>Se µg/L (ppb)</th>
<th>% Selenium Removed in Process</th>
<th>As µg/L (ppb)</th>
<th>% Arsenic Removed in Process</th>
<th>Approximate Surface Area Mild Steel (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>&lt;0.1</td>
<td>-</td>
<td>&lt;0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inlet</td>
<td>9.8</td>
<td>0</td>
<td>10.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Middle Trough 1</td>
<td>9.0</td>
<td>8</td>
<td>29.2</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>Outlet Trough 1</td>
<td>8.8</td>
<td>10</td>
<td>10.8</td>
<td>0</td>
<td>54</td>
</tr>
<tr>
<td>Middle Trough 2</td>
<td>8.3</td>
<td>15</td>
<td>14.2</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>Outlet Trough 2</td>
<td>8.4</td>
<td>14</td>
<td>7.5</td>
<td>29</td>
<td>108</td>
</tr>
<tr>
<td>1/3 Trough 3</td>
<td>8.4</td>
<td>14</td>
<td>5.7</td>
<td>46</td>
<td>156</td>
</tr>
<tr>
<td>2/3 Trough 3</td>
<td>8.2</td>
<td>16</td>
<td>4.8</td>
<td>54</td>
<td>203</td>
</tr>
<tr>
<td>Outlet Trough 3</td>
<td>7.9</td>
<td>19</td>
<td>3.0</td>
<td>71</td>
<td>250</td>
</tr>
</tbody>
</table>

The test results demonstrate that removal is dependent on the surface area of the iron oxide or oxyhydroxides contacted. The results also show arsenic is more readily adsorbed or coprecipitated than selenium under the experimental conditions, with overall ~70% removal for As, compared with ~20% removal for Se. The variation with surface area of steel passed at stages throughout the process is shown in Figure 3.9. Since there is no evidence of a decay in efficiency across the plant, this suggests that a longer passage past the same iron material or else an iron material of greater surface area per occupied plant volume would enhance removal further.
3.3.5.1 Selenium

The selenium trial undertaken over the 14 month period from February 2004 to April 2005 utilising steel plates and hangers with a total surface area of 250 m² has demonstrated, with the exception of samples taken in February and March 2005, the pilot plant continuously performs in removing selenium. This was measured as total selenium, which contains mainly selenite and a small amount of selenate under the operating conditions.

Figure 3.10 provides an overview of the analytical test results for total inorganic selenium from the inlet (blue line) of trough 1 and the outlet (red line) of trough 3 for the period from February 2004 to April 2005. The blue line trends represent the concentration of total inorganic selenium for duplicate samples from the inlet to the pilot plant and the red line trends for duplicate samples from the discharge. The Practical Quantitation Limit (PQL) for the analysis of total inorganic selenium by CSIRO’s Lucas Heights laboratory is 0.025 µg/L, which is about one percent of the average concentration of selenium removed. Hence there is confidence in the analysis of total selenium and the trends presented.
Figure 3.10  Pilot plant total selenium inlet and outlet analysis (µg/L).

The overall performance of the pilot plant with iron oxides and oxyhydroxides forming on the surface of the steel plates and hangers is not high, and the percentage removal throughout the 14-month trial period was not constant, as seen by the trend lines, which do not have the same slopes. Apart from the major impediment of insufficient surface area of reacting iron oxide or oxyhydroxide material, other factors which could have an influence on process performance include pH, temperature, rate of formation of iron oxides and oxyhydroxides, the matrix of the ash water being treated, and even the initial concentration of selenium in the ash water.

The range of total inorganic selenium test results from the pilot plant was 3.2 to 21.7 µg/L for inlet samples and 3.7 to 17.5 µg/L for outlet samples. The concentration of total selenium removed from the process ranged from near zero up to 6.2 µg/L, or up to 46% selenium removed. The average percentage of selenium removed from the process stream was about 23%.

Figure 3.11 plots the percentage of selenium removed as well as pH. It does not display a strong correlation between the amount of selenium removed and the pH of the ash water. However, experiments undertaken by Baldwin in 1983 using metallic iron powder found the best reduction occurred in the pH range from 3.0 to 5.5 [3]. The pH of the pilot plant inlet ash water ranged from 6.7 to 9.8, which may be a factor in the efficiency of selenium removed apart from the surface area of iron oxide available for absorption or coprecipitation. The types of iron oxides and
oxyhydroxides formed under such conditions of basic pH could also be a contributing factor.

![Figure 3.11 Percentage of selenium removed and variation in pH in the pilot plant plotted versus sampling date.](image)

The pilot plant test results confirm selenium can be effectively removed by contact with surface oxidised iron on a continuous basis without chemical alteration of the process, apart from the control of flow. The amount of selenium removed on average in this trial was 3.1 µg/L (ppb) or 23%, which represents a removal capacity per square metre of original available surface of 0.0124 µg/L. At this capacity of selenium removal, a surface area in the order of 1,000 m² would be required to remove up to 100% selenium from approximately 35,000 litres of ash discharge water per day. Of course, this area calculation represents the initial surface, and does not reflect likely increase in the active surface area as a result of oxidation and porous oxide crust formation; the latter cannot be effectively determined.

### 3.3.5.2 Arsenic

The analytical results for arsenic samples taken during the same period as the selenium samples from February 2004 to April 2005 under identical pilot plant conditions display different inlet and outlet trends. Figure 3.12 provides the average test results and percentage reduction of arsenic from the inlet of trough 1 and the outlet of trough 3 for the period from February 2004 to April 2005. The blue line represents the concentration of arsenic for the average duplicate samples from the
inlet to the pilot plant and the red line for the average duplicate samples from the discharge.

![Graph showing arsenic analysis](image)

**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.

The test results indicate a reasonable correlation between the duplicate samples for both the inlet and outlet. It is evident from these trends that the pilot plant not only consistently performs in removing arsenic but also does so with high efficiency, averaging around 70%. The process is also continuous and does not appear to be affected by temperature, conductivity, pH or the initial concentration of arsenic in the ash water. The Practical Quantitation Limit (PQL) for the analysis of arsenic by CSIRO’s Lucas Heights laboratory is 0.025 µg/L, which is less than one percent of the average concentration of arsenic removed. Hence there is confidence in the analysis of arsenic and the trends presented.

The range of arsenic test results from the inlet and outlet of the pilot plant was in the order of 6 to 32 µg/L for the inlet samples and 1 to 22 µg/L for the outlet samples. The percentage of arsenic removed from the process ranged from 31 to 91%. The average percentage of arsenic removed from the process is 62%. The outlet trend line also follows the same pattern as the inlet trend line.

The removal of arsenic utilising surface oxidised iron yielded the highest efficiency of all the trace elements trialled in this investigation. This efficiency is most likely due to the slightly basic pH condition which would favour arsenic adsorption or coprecipitation as anionic oxides onto the iron oxides and oxyhydroxides. As discussed in Chapter 2 Background, Kanel et al. [4] found the
greatest extent of arsenic(III) adsorption occurred in the broad pH range of from 4 to 10 [4]. In the present study, the percentage of As removal was as high as 91%, and typically around 70%. The process of removal was continuous throughout the trial period of 14 months, with no evidence of saturation effects towards the end of the extensive test period.

Figure 3.13 displays the average percentage of arsenic removed from the process over the 14 month trial period as well as pH levels measured in the ash water inlet. There is some indication of a slight correlation, which presumably relates to minor variations in the concentrations of protonated/deprotonated oxyanions including species formed by aerial oxidation with pH and their differing adsorption capacities.

![Figure 3.13](image)

**Figure 3.13** The average percentage reduction in arsenic (green) and variation in ash water pH (orange) throughout the pilot plant trial.

The amount of arsenic removed on average was approximately 7.9 µg/L with the maximum amount removed being 13.9 µg/L. At the average amount of arsenic removal of 70%, the surface area of oxidised iron required to remove 100% arsenic would be in the order of 360 m² (initially) for 35,000 litres of ash discharge water per day.

### 3.3.5.3 Antimony

The inlet and outlet trends for antimony samples taken during the same period as the selenium samples from February 2004 to April 2005 under identical pilot plant conditions displays a different trend pattern to those of selenium and arsenic. The
average percentage of antimony adsorbed or coprecipitated fluctuates, but overall the trends indicate that the process is continuously removing antimony.

Figure 3.14 provides average test results and percentage reduction of antimony from the inlet of trough 1 and the outlet of trough 3 from the period of February 2004 to April 2005. The dark blue line represents the concentration of antimony for the average duplicate samples from the inlet to the pilot plant and the light blue line the average duplicate samples from the discharge outlet of trough 3. The test results indicate a reasonable correlation between the duplicate samples for both the inlet and outlet, with reduction being reasonably consistent over time, as displayed by the red line in the figure.

There is a very modest similarity between the antimony trends and the selenium trends across the study. This could be due to a common role of pH of the ash water influencing concentrations of various protonated/deprotonated species of the oxyanions present, which are the form in which both elements occur.

The highest percentage of antimony removal was 61%. The Practical Quantitation Limit (PQL) for the analysis of antimony by CSIRO’s Lucas Heights laboratory is 0.05 µg/L, which is less than two percent of the average concentration of antimony removed. The range of antimony test results from the pilot plant was in the order of 7 to 22 µg/L for inlet samples and 6 to 18 µg/L for outlet samples. The percentage of antimony removed from the process ranged from 0 to 61%.
### 3.3.5.4 Aluminium

The analytical results for aluminium display no correlation with the trends of the other trace elements sampled. Samples were taken during the same period as the other trace elements samples, under identical pilot plant conditions. Like antimony, the average percentage of aluminium adsorbed or coprecipitated fluctuates, but overall the trends show that the process is continuously removing aluminium, at times with high efficiencies. Figure 3.15 provides average test results and percentage reduction of aluminium from the inlet of trough 1 and the outlet of trough 3 from the period of February 2004 to April 2005. The test results indicate a reasonable correlation between the duplicate samples for both the inlet and outlet.

![Average Aluminium versus % Average Reduction Aluminium](image)

Figure 3.15 Analysis results for 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 percent reduction (in red) and the trend line (in black) are also shown.

There appears to be no correlation between the pH of the ash water and the amount of aluminium removed through adsorption or coprecipitation. However, as indicated in Chapter 2 Background, the reduction of aluminium is more favourable at lower pH levels, although reduction of up to 70% is achieved here at near-neutral pH. The Practical Quantitation Limit (PQL) for the analysis of aluminium by CSIRO’s Lucas Heights laboratory is 5 µg/L, which is less than ten percent of the average concentration of aluminium removed. Aluminium removed from the process was significant, with an average removal of 58%, corresponding to ~25 µg/L removed.
3.3.5.5 Molybdenum

The analytical results for molybdenum samples taken during the same period as the other trace elements samples under identical pilot plant conditions displays no correlation with any of the other trace element trends. Further, the efficiency or removal is low, somewhat like selenium. The removal trend fluctuates significantly, with at times apparently no molybdenum being adsorbed or coprecipitated. Figure 3.16 provides average test results and percentage reduction of molybdenum from the inlet of trough 1 and the outlet of trough 3 from the period of February 2004 to April 2005.

The low efficiency of molybdenum adsorption or coprecipitation is no doubt due to the pH of the ash water. In Chapter 2, it was noted that, in the study of Kim and Zeitlin (1969), the optimum pH to remove molybdenum from sea water with iron(III) hydroxide was 4, and removal decreased significantly with increasing pH to a minimum at pH 8.5 [5]. The pH of the Vales Point ash water during this trial period was is in the range of about 6.7 to 8.5, this is not conducive to Mo removal.

The Practical Quantitation Limit (PQL) for the analysis of molybdenum by CSIRO’s Lucas Heights laboratory is 2.5 µg/L, which is 20% of the average concentration of molybdenum removed. The range of molybdenum test results from the inlet and outlet of the pilot plant is 107 to 224 µg/L for inlet samples and 92 to 205 µg/L for outlet samples. The percentage of molybdenum removed from the process ranged from 0 to 29%, with on average only ~10% removed.
3.3.6 Discussion

The optimum flow for the trial steel sheets and fabric filter hanger bars was established to be no more than 0.4 L/sec or 24 L/min. This is very low, only allowing 1440 kL per day to be treated by this system; it indicates that an alternative capture medium or configuration should be sought to allow greater throughput.

Apart from selenium, other trace elements examined in this study that adsorbed or coprecipitated onto the iron oxides or oxyhydroxides were arsenic, antimony, aluminium and molybdenum. The order of efficiency of removal is As>Al>Sb>Se>Mo. The concentration of these trace elements removed by the pilot plant with solid steel is provided in Table 3.6 below.

Table 3.6 Trace element removal levels with solid steel in the pilot plant.

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Concentration of Trace Element Removed by the Process (µg/L)</th>
<th>Percentage Removal by the Process (%)</th>
<th>Average Percentage of Trace Element Removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>0 - 6.2</td>
<td>0 - 46</td>
<td>23</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1 - 22</td>
<td>31 - 91</td>
<td>62</td>
</tr>
<tr>
<td>Antimony</td>
<td>3 - 9</td>
<td>0 - 61</td>
<td>30</td>
</tr>
<tr>
<td>Aluminium</td>
<td>25 - 50</td>
<td>45 - 70</td>
<td>58</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>11 - 14</td>
<td>0 - 29</td>
<td>14</td>
</tr>
</tbody>
</table>

The continuous corrosion of the steel throughout the trial period leads to variability in amount, surface area and type of oxide/oxyhydroxide species present. This variability is no doubt reflected in the results obtained for trace element removal. The type and abundances of the different iron oxides and oxyhydroxides are likely to have a particular influence, since adsorption efficiency for ions depends on the surface character. Another likely contributing factor, apart from the key factor of the surface available, would be the pH of the ash water. The pH fluctuated during the 14 month trial period between 6.7 and 8.5. This could influence the concentrations of various protonated/deprotonated species present, and as each form has a different adsorption profile, variation in overall adsorption is then expected. Other uncontrolled parameters such as temperature and the matrix of the ash water could also be minor contributing factors to explain the variance in efficiencies of removal.
The temperature ranged from 12 to 27 °C over the 14 months of sampling and the concentrations for all elements varied over this period as well.

The presence of various iron oxides and oxyhydroxides is apparent from simply a visual inspection. From observation of the colours of oxides formed on the iron bars and steel plates, the iron oxides and oxyhydroxides appear to include goethite, lepidocrocite, hematite and magnetite. Testing of samples by XRD would confirm the presence of these and other iron oxides.

From the earlier trial in February 2004 and throughout the 14 month trial period, the average amount of total selenium removed by the 250 m² solid iron coated by oxides is 23% (or 3.1 µg/L). This equates to ~0.012 µg/L Se per square metre, which is similar to the ~0.02 µg/L Se per square metre determined in the first trial. With the volume of ash water to be treated in the order of megalitres, this process would require a large surface area of solid iron (around 500,000 m²) which is not practical using the type of material trialled. A higher efficiency may be achieved with a much higher surface area of iron per unit mass, and hence an equivalent surface formation of iron oxides during treatment. This can be achieved with a material such as steel wool. The only advantage of the use of solid iron would be the longevity of the process in not having to replenish the material as often, but the area required to establish such a plant would be substantive, expensive and not practical. Nevertheless, what this trial has established is that a number of trace elements are capable of being absorbed or coprecipitated onto the iron oxides and oxyhydroxides formed through the corrosion of the parent iron. The high salt content and hence high conductivity of the ash water is conducive to the formation of corrosion products, enabling the process.

What was observed during the 14 month trial period was the formation of a number of iron oxides and oxyhydroxides on the surface of the iron. The oxides that formed were either displaced from the surface as fine particles, settling at the bottom of the concrete troughs, or peeled off in large flakes and sheets. Despite such losses, the sample steel sheets and bars taken from the pilot plant troughs all gained weight after being in contact with the Vales Point ash water for four months, supporting the observation of the formation of varying iron oxides and oxyhydroxides.

Even though the efficiency of removal of the elements selenium, antimony and molybdenum was not high in the process tested, the amounts that were removed by this process would still contribute to lowering levels towards the Australian and
New Zealand Guidelines for Fresh and Marine Water Quality 2000 guideline levels for receiving estuarine waters.

Ultimately any process adopted at Vales Point Power Station for the treatment of ash water has to consider the large volume of ash water to be treated. Factors to consider include what type of process is to be implemented and is a purpose-built plant required or can the ash dam itself be used as the reaction vessel. The mass and cost of iron material required to treat megalitres of ash water must be considered along with the required efficiency of removal. Nominally, any process should achieve at least 80% removal of targeted trace elements, in this case selenium, before it can be considered a viable option. As the next step towards a more viable process, the use of steel wool as the process material had to be considered.

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

On completion of trials with steel hanger bars and plates in 2005, the Vales Point Power Station pilot plant was modified in 2007 to allow for trials using steel wool. The first and second troughs had their steel plates removed to allow for the insertion of wire baskets containing steel wool. The sheets of iron were again positioned in the first two troughs to force the ash water to flow through the steel wool and around each plate.

The steel fabric filter hanger bars in the third trough were removed and three sheets of stainless steel with dimensions of 1 m by 40 cm and 5 mm thick were installed. The three plates had 30 mm diameter holes cut out over the entire surface to direct the flow of ash water through the third trough. The sheets were installed about 3 m apart to allow large wire baskets to be installed between the plates. All three wire baskets were filled with loose steel wool.

The main objective of this pilot plant trial was to determine if increasing the surface area of iron and operating the plant at the optimum flow rate would result in high efficiency of removal of selenium and other trace elements. The trial also was to ascertain if the rate of removal was constant and to examine the longevity of the process by probing when efficiency declines.

The trial period using steel wool as the medium for production of iron oxides and oxyhydroxides was between July 2008 and December 2008. The total selenium
concentration measured at the inlet of the pilot plant ranged from 23 to 37 µg/L, which was higher than levels experienced in earlier trials.

The steel wool was obtained from a manufacturer of steel wool located in northern Sydney. This steel wool was in fact a waste by-product which was stored as bales with dimensions of approximately 0.5 m by 0.5 m and 1 m in length. Before being installed in the pilot plant, the steel wool was unravelled so it could be loosely packed in the wire baskets.

A program of testing for this trial period was again established. All analyses for the third trials were carried out by either the CSIRO or ALS Laboratory Services. A range of analyses were undertaken once again to determine which trace elements were removed by this process. The following sections outline the pilot plant trial objectives, design and materials used, operating conditions during the trial period and the outcome of analytical tests and pilot plant measurements recorded from July 2008 to December 2008.

3.4.1 Study Objectives

The core objective for the third pilot plant trial were to determine more accurately the highest efficiency of selenium and other trace elements that could be adsorbed or coprecipitated by iron oxides and oxyhydroxides produced through the corrosion of high surface area steel wool. Additionally, the trials were to observe what transformations of the steel wool occurred during the trial period along with the quality of ash water being treated. The objectives for the 2008 pilot plant trials include the following:

1. To determine what trace elements are coprecipitated or adsorbed onto the iron oxides and oxyhydroxides formed by the process.
2. To determine the discharge concentration in µg/L of selenium and trace elements removed by the steel wool corrosion products.
3. To determine the efficiency of selenium and other trace metals removal by the process.
4. To determine the composition of metals present in the steel wool.
5. To ascertain whether the process efficiency of removal fluctuates or is constant.
6. To ascertain if the process consistently removes selenium and other trace elements over the duration of the trial period of six months.
7. To observe the chemical properties of the ash water being treated by the process.
8. To observe the physical transformation of the steel wool over the trial period.
3.4.2 Pilot Plant Design and Materials

3.4.2.1 Design

As stated earlier, the three original pilot plant troughs containing fabric filter hanger bars and steel plates were modified so that baskets of loosely packed steel wool could be installed in each concrete trough. Only the internal components of the troughs were modified. All the plumbing into and out of the pilot plant remained the same, including the 120 mm diameter PVC pipeline and the two PVC exiting pipes of 100 mm diameter. The flow was regulated at an optimum flow rate of about 0.5 L/s. The maximum flow rate that was achievable without overflowing the troughs was still 2.0 L/s.

Figure 3.17 provides a schematic of the pilot plant troughs containing both steel wool and steel plates to control the direction of ash water flow. Once again, the plates were installed into the two troughs to be consecutively butted against the wall of the trough on opposite sides and sealed on the sides and at the bottom to ensure the ash water flow was in the direction as depicted in the image below [2]. Image 3.10 shows the wire baskets utilised to hold the steel wool.

![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 [2].](image)

![Image 3.10 Pilot plant trough 1 with steel basket containing steel wool in the base.](image)
Figure 3.18 provides a schematic of the differently configured third pilot plant trough. This contained the stainless steel plates with fabricated holes drilled over the full surface to control the direction of ash water flow in a laminar fashion, along with the steel wool packed between the stainless steel plates. The different trough configuration was deliberately chosen so as to allow testing of different flow control mechanisms while employing a common material for adsorption throughout.

![Figure 3.18  Top-down schematic of the third pilot plant trough containing ‘porous’ stainless steel plates and steel wool.](image)

### 3.4.2.2 Materials

The waste steel wool provided by SIFA Pty Ltd Manufacturers used in the final pilot plant trials contained the following constituents:

- Iron – 98.665%
- Carbon – 0.07%
- Silica – 0.09%
- Manganese – 0.92%
- Phosphate – 0.077%
- Sulfur – 0.17%
- Nitrogen – 0.008%

From the above list, the steel wool is predominantly iron with trace amounts of other elements which are typical for this type of material. The bales of steel wool supplied are compact, and before being placed into the concrete troughs were unravelled like sheets. On the outside of the bales the steel wool has a brown oxide coating, but when unravelled the steel wool on the inside has the appearance of grey metal consistent with minimal surface oxidation. Ten bales of steel wool were used for the
six month trial. The two views in Image 3.11 are of a bale similar to ones used in the trial and the pilot plant third trough modified with insertion of the steel wool.

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).

3.4.3 Pilot Plant Operating Conditions

The third pilot plant trial commenced on the 24th July 2008, with the plant in operation for a six month period. The flow rate of ash water was set at 0.4 L/s. The pilot plant was operated continuously 24 hours per day. The pH measured during the trial period ranged between 8.2 to 8.7. Total selenium in the inlet ash water ranged from 23 µg/L to 37 µg/L. The temperature of the ash water during the period of operation ranged from 13 °C in the winter period up to 29 °C in December 2008.

Like the conditions of the first two trials, the mass of steel wool used and flow rate were the only parameters controlled in the process. Even the dissolved oxygen fluctuated slightly during the testing period, ranging from 3 to 6 mg/L. The use of uncontrolled conditions is consistent with a desire to develop and test a low-cost element capture process.
3.4.4 Trial Process Observations

The third pilot plant six month trial and testing commenced on the 24\textsuperscript{th} July 2008. The ash water in the first two troughs was observed to be flowing through the steel wool and not just around the edges of the troughs. The third trough containing the stainless steel plates with 30 mm holes not only forced the ash water to flow through the steel wool but also produced eddy currents, allowing the water to mix well with the iron oxides and oxyhydroxides formed.

The steel wool changed from the grey colour of the parent metal to a red to brown colour within weeks of being installed into the troughs. Some orange flecks were observed forming in and around the darker oxide coating. The colour of the pilot plant treated water was observed to have the same orange colour as in the first two trials.

The ash water at the commencement of the trial contained 9,240 mg/L of chloride and 5,770 mg/L of sodium; sulfate as SO\textsubscript{4}\textsuperscript{2-} was 1,360 mg/L. Suspended solids during the first sampling did increase from the inlet to other areas of the troughs tested, with results ranging from 2 to 18 mg/L. The suspended solid concentration from the pilot plant discharge was 10 mg/L.

The steel wool almost completely transformed into iron oxides or oxyhydroxides during the pilot plant trial after the six month period, with corrosion products settling at the bottom of the three troughs. At no time during the trial was more steel wool added to the troughs, with only the original material employed throughout the trial.

3.4.5 Experimental Results

A number of trace element samples were obtained by ALS Laboratory Services along sections of the pilot plant troughs and analysed by ORC-ICPMS. Table 3.7 provides the analyses of these elements (in µg/L or parts per billion).
### Table 3.7  Trace metal analysis of samples taken at points throughout the pilot plant.

<table>
<thead>
<tr>
<th>Element</th>
<th>Point 1 Inlet µg/L</th>
<th>Trough 1 µg/L</th>
<th>Trough 1 Outlet µg/L</th>
<th>Point 3 Inlet µg/L</th>
<th>Trough 2 µg/L</th>
<th>Trough 2 Outlet µg/L</th>
<th>Point 5 Inlet µg/L</th>
<th>Trough 3 µg/L</th>
<th>Trough 3 Outlet µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>10</td>
<td>&lt;10</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>9.0</td>
<td>1.2</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Iron</td>
<td>10</td>
<td>9</td>
<td>&lt;5</td>
<td>6</td>
<td>9</td>
<td>14</td>
<td>6</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Manganese</td>
<td>10.2</td>
<td>89.7</td>
<td>119</td>
<td>160</td>
<td>205</td>
<td>234</td>
<td>261</td>
<td>301</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>78.3</td>
<td>76.4</td>
<td>77.7</td>
<td>77.1</td>
<td>78.2</td>
<td>78.4</td>
<td>71.5</td>
<td>71.1</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Antimony</td>
<td>23.9</td>
<td>18.9</td>
<td>17.9</td>
<td>15.9</td>
<td>13.2</td>
<td>11.2</td>
<td>10.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Vanadium</td>
<td>28.6</td>
<td>8.4</td>
<td>3.9</td>
<td>1.7</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>21</td>
<td>6</td>
<td>&lt;5</td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>2800</td>
<td>2600</td>
<td>2700</td>
<td>2600</td>
<td>2500</td>
<td>2500</td>
<td>2400</td>
<td>2400</td>
<td></td>
</tr>
<tr>
<td>Total Selenium</td>
<td>37</td>
<td>28</td>
<td>24</td>
<td>19</td>
<td>12</td>
<td>10</td>
<td>10</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>5.2</td>
<td>1.7</td>
<td>1.1</td>
<td>1.0</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

From the above table of trace metal analyses of the ash water processed by the pilot plant at Vales Point Power Station and sampled on the 24th July 2008, the elements clearly removed by the iron oxides and oxyhydroxides formed by the steel wool include the following:

- Selenium
- Arsenic
- Antimony
- Vanadium
- Chromium(III)

Surprisingly, the trace element which did not appear to be removed by the steel wool corrosion product that had been observed to be partially removed (~ 60%) during the solid steel trials was aluminium. Molybdenum concentrations near the outlet to the final trough are also only slightly lower than at the inlet, indicative of limited capture. However, diminution by only 14% was observed in earlier trials, and the drop of almost 10% observed here is not dissimilar. Whilst these elements do not appear to be removed by the process, they are still incorporated into the analysis program along with the above significantly captured trace elements.
3.4.5.1 Selenium

The selenium trial undertaken over the 6 month period from July 2008 to December 2008 utilising steel wool has demonstrated the pilot plant continuously performs in removing selenium, measured as total selenium but containing predominantly selenite and a small amount of selenate. Figure 3.19 provides analytical test results for total inorganic selenium from the inlet of trough 1 and the outlet of trough 3 during the six month trial period.

![Selenium Pilot Plant Inlet and Outlet Test Results (Steel Wool)](image)

Figure 3.19  Selenium inlet and outlet analyses (µg/L) over time for the pilot plant containing oxidised steel wool.

The total selenium inlet analysis ranged from 23 to 37 µg/L and the pilot plant outlet ranged from 2 to 9 µg/L. The pilot plant inlet and outlet test results follow the same trend, demonstrating that the process removes selenium (predominantly SeO\(_3^{2-}\)) from the Vales Point ash water to a significantly lower level.

The efficiency of selenium removal by the iron oxides and oxyhydroxides formed is high, and of the order of 85%. The process of removal over the six month period was demonstrated to operate continuously, with no sign over the trial period of tapering off or decreasing in efficiency of removal. The increase in efficiency in Trial 3 to 85% is a large increase when compared to the 5% and 23% removal experienced by the pilot plant Trials 1 and 2. The high surface area of the steel wool has significantly increased the amount and surface area of iron oxides and
oxyhydroxides available for adsorption and coprecipitation, which suggests that capture in the first two trials was limited mainly by the limited surface area.

### 3.4.5.2 Arsenic

The arsenic results utilising steel wool has demonstrated the pilot plant also continuously performs in removing arsenic. Figure 3.20 reports analytical results for arsenic from the inlet of trough 1 and outlet of trough 3 during the six month trial.

![Arsenic Pilot Plant Inlet and Outlet Test Results (Steel Wool)](image)

Figure 3.20 Arsenic inlet and outlet analyses (µg/L) over time for the pilot plant containing oxidised steel wool.

The total arsenic inlet analysis ranged from 6 to 10 µg/L and the pilot plant outlet ranged from 0.6 to 1.6 µg/L. The pilot plant inlet and outlet test results follow the same trend, demonstrating the process removes arsenic from the Vales Point ash water at a constant level. The efficiency of arsenic removal by the iron oxides and oxyhydroxides formed, at 87%, is slightly higher than that of selenium. This is to be expected, as the removal of arsenic by solid steel was also higher. Like the selenium trend, the process of arsenic removal over the six month pilot plant trial period is continuous, with no sign of tapering off or decreasing in efficiency of removal. Indeed, it should be noted that whilst the arsenic concentration of the inlet ash water increased during the trial, the concentration of arsenic at the outlet decreased.
### 3.4.5.3 Antimony, Vanadium and Chromium

The trends for vanadium and antimony shown in Figure 3.21 are not dissimilar to the selenium trends. The vanadium inlet analysis ranged from 17 to 29 µg/L and the pilot plant outlet ranged from 0.5 to 1.7 µg/L, whereas the antimony inlet analysis ranged from 24 to 30 µg/L and the outlet ranged from 1.2 to 9.8 µg/L.

The efficiency of vanadium removal is the highest of all the trace elements removed by the system at 97%. In the case of antimony, removal is slightly higher than that achieved for selenium at 87%. Like the selenium and arsenic trends, the process of vanadium and antimony removal over the six month period is indicative of continuous activity without diminution over time.

The chromium(III) inlet concentration is different to that of vanadium and antimony, being clearly lower and ranging from 1 to 9 µg/L. However, regardless of the inlet concentration, the outlet of the pilot plant was consistently around 0.5 µg/L, indicative of efficient capture. The efficiency of removal of chromium(III) by the iron oxides and oxyhydroxides formed is also high, at 80%. The inlet and outlet trends do not follow patterns similar to most other trace elements, with the outlet trend appearing essentially as a flat line due to removal of the initially low levels to a limiting value. Like the other trace element trends, the process of chromium(III) removal over the six month pilot plant trial period operates as a continuous process without any drop off in capacity observed.

![Vanadium, Antimony and Chromium(III) Pilot Plant Inlet and Outlet Test Results (Steel Wool)](image-url)

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.
3.4.5.4 Molybdenum and Aluminium

The behaviour of molybdenum and aluminium, Figure 3.22, is somewhat different to that of selenium, arsenic, vanadium, antimony and chromium; removal efficiency is not as high, with the average efficiency of removal of molybdenum during the trial being 48% and that for aluminium being 21%.

The total molybdenum inlet analysis ranged from 93 to 126 µg/L and the pilot plant outlet ranged from 9 to 78 µg/L. The pilot plant inlet and outlet test results follow the same trend pattern, with the exception of one analysis. Moreover, the trends do demonstrate that the process removed molybdenum from Vales Point ash water at a reasonable constant level throughout the trial.

The aluminium inlet analysis ranged from 10 to 60 µg/L and the pilot plant outlet of 10 µg/L. The pilot plant inlet and outlet test results for aluminium do not follow the same trend patterns and do not give confidence that aluminium is being consistently successfully removed through adsorption or coprecipitation onto the iron oxides and oxyhydroxides formed on the surface of the steel wool. Although there is an overall small drop in aluminium levels, the variability throughout is highest amongst all elements examined. The presence even in filtered samples sent for analysis of ultra-fine clay particulates or colloids, rich in aluminium, may contribute to the behaviour observed.

![Molybdenum & Aluminium Pilot Plant Inlet and Outlet Test Results](image)

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.
3.4.6 Discussion

With the flow rate of 0.4 L/sec employed, the levels of trace elements removed through absorption or coprecipitation onto the iron oxides or oxyhydroxides formed by the corroding steel wool were mostly high, and typically above 80%. The order of efficiency of removal observed was V>As>Sb>Se>Cr>Mo>Al. A summary of the control of these trace elements by the pilot plant with steel wool is reported in Table 3.8.

Other elements examined were either present at too low a level for any changes to be detected (Cd, Co, Hg, Ni and Pb), or did not change appreciably during passage through the plant (Zn, B and Fe). Although one would expect adsorption of ions of the first set to occur from their usual behaviour with iron oxide surfaces, there is simply insufficient present to probe this further. The only element to show an increase in concentration during passage through the plant was manganese, and this arises as a result of corrosion releasing some oxidised manganese (which is present to ~1% in the steel wool) into solution.

Table 3.8  Trace element depletion in the pilot plant containing steel wool.

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Pilot Plant Inlet Concentration of Trace Element (µg/L)</th>
<th>Pilot Plant Outlet Concentration of Trace Element (µg/L)</th>
<th>Average Percentage of Trace Element Removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>23 – 37</td>
<td>2 – 9</td>
<td>85</td>
</tr>
<tr>
<td>Arsenic</td>
<td>6 – 10</td>
<td>0.6 – 1.6</td>
<td>87</td>
</tr>
<tr>
<td>Antimony</td>
<td>24 – 30</td>
<td>1.2 – 9.8</td>
<td>87</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>1 – 9</td>
<td>0.5</td>
<td>80</td>
</tr>
<tr>
<td>Vanadium</td>
<td>17 – 29</td>
<td>0.5 – 1.7</td>
<td>97</td>
</tr>
<tr>
<td>Aluminium</td>
<td>10 – 60</td>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>93 – 126</td>
<td>9 – 78</td>
<td>48</td>
</tr>
</tbody>
</table>

With the high surface area of the steel wool and corrosion products readily forming on the surface, the efficiencies obtained remained high throughout. This inexpensive material is no doubt the most suitable for the process, as it removed above 80% of selenium and similar amounts of most of the other targeted trace elements. As demonstrated by all the trends, with the exception of aluminium, the
level of removal remained essentially constant throughout the six month trial period. The trends for the inlet analyses were similar to the outlet test results for nearly all trace elements. Vanadium and chromium(III) levels at the outlet were so low that they were near the level of detection, this indicates that the adsorption or coprecipitation of these elements were effectively complete. Fluctuations with pH and temperature during the six month trial period do not appear to have affected the efficiencies of removal to any marked level.

Because the system proved capable of reducing the levels of the target elements significantly even after passage through the first two troughs (see Table 3.7), it was not possible to ascertain if the design in the first two troughs or the third trough were superior. Evidently, provided water passage through the steel wool is appropriately controlled for surface contact, capture of target elements occurs readily. Examination of an array of tank configurations must await future examination prior to establishment of a working process.

The process of removal for these targeted elements has been demonstrated to occur continuously, with high efficiencies being observed even towards the end of the trial period. Over time, it would be expected that the capacity of the steel wool to removes these trace elements would diminish; however, the plant would need to be operated and be monitored continuously for at least several years to determine the longevity of the process. This was not practicable in the timeframe of this thesis. Evidently, the capacity of the system as tested is high, which indicates that this process has promise for up-scaling and subsequent application.

### 3.5 FORMATION OF IRON OXIDES AND OXIDE HYDROXIDES

 Clearly, from merely visual inspection, the oxidised iron surfaces yield an array of oxides and oxyhydroxides. Determination of species present can be achieved effectively through modern analytical methods. The following table provides a list of iron oxides and oxyhydroxides present, analysed by CSIRO in 2005 utilising XRD for the determinations. The samples were obtained by providing both sections of steel plates and hanger bars. All oxides and oxyhydroxides listed would have, through adsorption or coprecipitation, the capability to be involved in the removal of selenium and other trace elements as presented in this Chapter.
Table 3.9 Iron oxides and oxyhydroxides detected in corroded steel plate and hanger bar surfaces with XRD.

<table>
<thead>
<tr>
<th>Steel Plate</th>
<th>Steel Bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Magnetite (Fe$_3$O$_4$)</td>
<td>1. Magnetite (Fe$_3$O$_4$)</td>
</tr>
<tr>
<td>2. Goethite (α-FeOOH)</td>
<td>2. Goethite (α-FeOOH)</td>
</tr>
<tr>
<td>3. Lepidocrocite (γ-FeOOH)</td>
<td>3. Lepidocrocite (γ-FeOOH)</td>
</tr>
<tr>
<td>4. Akageneite-M (including a Cl substituted form) (β-FeOOH)</td>
<td>4. Akageneite-M (including a Cl substituted form) (β-FeOOH)</td>
</tr>
</tbody>
</table>

Samples of iron oxide were also taken from the surface of the steel plates and hanger bars in 2007, were separated in accordance with colour, and crushed in a laboratory. Image 3.12 shows the different iron oxides and oxyhydroxides found as the major species on the surface of the steel. As can be seen, the three oxides analysed at University of Newcastle in 2007 by XRD were goethite, magnetite and hematite. These oxides were anticipated, as they are common forms met in steel corrosion processes.

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).
3.6 CONCLUSIONS

The pilot plant trials utilising solid steel for the formation of iron oxides and oxyhydroxides have demonstrated that the elements selenium, arsenic, antimony, aluminium and molybdenum can be removed. However, the efficiency is not high and fluctuations between inlet and outlet test results occur, and this could be due to variations in other factors such as pH, temperature and the matrix of the ash water. This process is not practical, as the amount of solid iron necessary to treat all or even part of the Vales Point ash water is substantial, and perhaps as much as 500,000 m². The area required for such a process plant would be large and the cost high. It is evident that the low surface area per unit mass was a key factor, which was addressed in a subsequent trial.

The trials undertaken in 2008 utilising steel wool demonstrated that high efficiencies of removal can be achieved, with the process performing consistently at high efficiencies on a continual basis over six months. The steel wool trial not only removed selenium to above 85%, but also captured other elements efficiently (vanadium, antimony, arsenic, and chromium) and to a lesser extent molybdenum and aluminium. This trial confirms that low-cost waste steel wool is a viable treatment material and that the design introduced during the third pilot plant trial yields a selenium and trace element removal process that could be utilised in a larger scale plant or process to treat part or all of the Vales Point ash dam water currently being discharged into Wyee Bay.

It would appear that the iron source material contains significant quantities of Mn; this resulted in higher concentrations of Mn upon treatment than would occur from solution water treatment alone.

3.7 REFERENCES


CHAPTER FOUR
LEACHABILITY STUDIES

4.1 INTRODUCTION

The utilisation of solid iron materials (including steel wool), which subsequently undergo formation of iron oxide and oxyhydroxides, for the removal of trace elements has been demonstrated in Chapter Three. It has proven to be both a highly efficient and simple process for the removal of elements such as selenium, arsenic, antimony, chromium, vanadium, molybdenum and aluminium. Of course, efficient removal of trace elements from solution is not effective and practical if these adsorbed ions can be subsequently readily released back into the solution environment. In order for the adsorption and coprecipitation processes of trace element removal with iron oxides (such as goethite, hematite, lepidocrocite and magnetite) to be considered as an efficient and optimum treatment, the process must also demonstrate zero or minimum potential for subsequent leaching from the sludge or corrosion product produced over reasonable time periods.

The nature of the product resulting from the operating processes may be affected by a number of factors. These include ageing and external influences such as change in pH, dissolved oxygen, conductivity of the containment solution, temperature, contact with UV light, growth of organisms, and introduction of reductants such as H₂S. Changes in the adsorbing species over time that lead to structural change in the oxide may influence effective retention of adsorbed ions. Consequently, the aim of the studies reported in this chapter is an investigation into the characteristics of the corrosion products produced during the pilot plant trials over an extended period of years. A number of different experiments to ascertain the inertness of the product material, and whether trace elements eventually leach back into solution, or on a larger scale into the environment, have been conducted. The extended nature of this study is important in the context of long-term safe disposal of solids from the treatment process.
4.2 LEACHABILITY EXPERIMENTS ON STORED CORROSION PRODUCTS

As mentioned in Chapter Three, the constructed Trace Metal Reduction Pilot Plant at Vales Point Power Station for the treatment of ash water commenced operation on the 17th December 2003. The pH of the incoming ash water was 8.25 at 25 °C with the outlet pH of the pilot plant being 5.72 at 25 °C. The temperature of the incoming ash water was ~25 °C and the optimum flow for the plant was set at approximately 0.4 L/s or 25 L/hr. The three pilot plant troughs containing mild steel plates and fabric filter hangers were drained of ash water on the 11th March 2004, approximately 15 months after the plant was commissioned. Wet sludge or corrosion product was removed from each trough, and displayed a mixture of colours from orange to brown and black. The sample weights of sets of the corrosion products obtained from each pilot plant trough, measured to ±0.1 g, are provided in Table 4.1. These samples form the set employed in subsequent leachability studies.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Weight of wet sludge/ corrosion product (g)</th>
<th>Appearance of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trough 1 outlet</td>
<td>504.9</td>
<td>black and orange</td>
</tr>
<tr>
<td>Trough 1 outlet</td>
<td>300.6</td>
<td>black and orange</td>
</tr>
<tr>
<td>Trough 2 outlet</td>
<td>501.1</td>
<td>black and orange</td>
</tr>
<tr>
<td>Trough 2 outlet</td>
<td>341.5</td>
<td>black and orange</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>508.6</td>
<td>black and brown</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>316.9</td>
<td>brown and orange</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>336.8</td>
<td>brown and orange</td>
</tr>
</tbody>
</table>

Each sample was collected and placed initially in a two litre glass jar fitted with a glass stopper to seal it from the atmosphere. Subsequently, each jar of corrosion product was subject to separate long term treatment in containment with different storage solutions. The conditions employed are provided in Table 4.2 below. They represent mild conditions that may still permit leaching of adsorbed ions from the solid.
Table 4.2  Sludge or corrosion product containment conditions.

<table>
<thead>
<tr>
<th>Sample Origin Location</th>
<th>Condition of Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trough 1 Outlet</td>
<td>Ash Water</td>
</tr>
<tr>
<td>Trough 1 Outlet</td>
<td>Demineralised Water</td>
</tr>
<tr>
<td>Trough 2 Outlet</td>
<td>Ash Water</td>
</tr>
<tr>
<td>Trough 2 Outlet</td>
<td>Demineralised Water</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Ash Water</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Domestic Water</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Demineralised Water</td>
</tr>
</tbody>
</table>

The volume of storage solution added to each jar was 1.5 litres, meaning that there was a sludge:liquid ratio of between 1:3 and 1:5 applying across the sample set. Once the solution was added to each jar, the glass stoppers were placed onto the top of the jars and then each jar was further sealed by wrapping around the stopper seal with duct tape, to prevent any evaporation of the liquid. Each jar was vigorously shaken for 5 minutes and then placed inside a laboratory cupboard to be stored out of UV light for a period of 12 months. Images 4.1 – 4.4 were taken of the jars containing the sludge or corrosion product at the time of initial preparation in December 2004.

Image 4.1  Jar experiments for some samples from Troughs 1 to 3 containing ash water and demineralised water.
Image 4.2 Jar experiment (Trough 2 sample), with a close-up of the corrosion product.

Image 4.3 Further jar experiments for samples from Troughs 1 and 3 containing ash water and demineralised water.
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.

The objective of these experiments was to ascertain whether adsorbed trace elements (with the focus in this trial on selenium, arsenic, antimony, molybdenum and aluminium) are leached or released from the sludge or corrosion product under different mild solution environment conditions over an extended period of time. The aims of these experiments included the following:

1. To determine if selenium, arsenic, antimony, molybdenum and aluminium adsorbed or co-precipitated onto the iron oxyhydroxide surface will remain as a component of the insoluble iron corrosion products or will be leached, wholly or selectively, fully or partially, over time under mild storage solution conditions.
2. To determine if leaching of selenium, arsenic, antimony, molybdenum and aluminium adsorbed or co-precipitated onto the iron oxyhydroxide surface is promoted after physical agitation of each jar’s contents.
3. To ascertain the solution properties of the containment solutions at the time of sampling for testing for leached trace element levels.
On the 15th March 2005, samples of 100 mL were extracted from the solution above the sludge of each jar, which had been sealed and stored for approximately twelve months, for analysis in an air conditioned laboratory with temperature of about 23 °C. The solution in each jar was also tested for pH, conductivity and temperature at this time. After the initial samples were taken, the jars were shaken for two minutes and subsequently, following settling, further 100 mL samples were taken from each jar. Simple physical properties of each solution are provided in Table 4.3. Conductivity and temperature of the solutions were determined with a Horiba ES 14-E instrument, whereas pH analysis employed a Metrohm 744 MEP instrument; both were calibrated prior to taking measurements.

Table 4.3 The pH values and conductivities of sludge storage solutions sampled after one year of storage.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Condition of Storage</th>
<th>pH 23.9 °C</th>
<th>Conductivity (mS/cm; 23.9 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trough 1 outlet</td>
<td>Ash Water</td>
<td>7.44</td>
<td>35.6</td>
</tr>
<tr>
<td>Trough 1 outlet</td>
<td>Demineralised Water</td>
<td>7.68</td>
<td>11.2</td>
</tr>
<tr>
<td>Trough 2 outlet</td>
<td>Ash Water</td>
<td>7.28</td>
<td>33.3</td>
</tr>
<tr>
<td>Trough 2 outlet</td>
<td>Demineralised Water</td>
<td>7.85</td>
<td>9.4</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>Ash Water</td>
<td>7.49</td>
<td>32.1</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>Domestic Water</td>
<td>8.59</td>
<td>11.1</td>
</tr>
<tr>
<td>Trough 3 outlet</td>
<td>Demineralised Water</td>
<td>7.60</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The 100 mL samples were each filtered through 0.45 µm Millipore filter paper to remove any finely suspended solids, then placed in 100 mL stoppered polyethylene sample bottles and treated with 3 drops of concentrated nitric acid. The samples were refrigerated before being dispatched to the CSIRO laboratory at Lucas Heights for analytical testing by standard instrumental methods: CAAC/AES01, CAAC/MS5 and CAAC/AFS02. Sample analysis was performed within days of receipt; selected follow-up analyses indicated no changes over periods of days. The analytical test results for each jar test sample are summarised in Table 4.4 for total selenium (inorganic), arsenic, antimony, molybdenum and aluminium, with the CSIRO laboratory results provided in Attachment 1.
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 of the studies carried low levels of elements targeted, and these values are reported at the top of the table below.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Condition of Storage</th>
<th>Sample Identification</th>
<th>Se</th>
<th>As</th>
<th>Sb</th>
<th>Mo</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trough 1 Outlet</td>
<td>Ash Water</td>
<td>J1</td>
<td>0.4</td>
<td>0.75</td>
<td>&lt;0.5</td>
<td>411</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J2 (shaken)</td>
<td>0.4</td>
<td>6.73</td>
<td>2.3</td>
<td>295</td>
<td>4</td>
</tr>
<tr>
<td>Trough 1 Outlet</td>
<td>Demineralised Water</td>
<td>J3</td>
<td>1.1</td>
<td>0.31</td>
<td>&lt;0.5</td>
<td>5.2</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J4 (shaken)</td>
<td>1.3</td>
<td>10.9</td>
<td>0.7</td>
<td>6.2</td>
<td>51</td>
</tr>
<tr>
<td>Trough 2 Outlet</td>
<td>Ash Water</td>
<td>J5</td>
<td>2.1</td>
<td>0.13</td>
<td>&lt;0.5</td>
<td>576</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J6 (shaken)</td>
<td>1.8</td>
<td>0.62</td>
<td>0.9</td>
<td>603</td>
<td>&lt;4 ($\times$169)</td>
</tr>
<tr>
<td>Trough 2 Outlet</td>
<td>Demineralised Water</td>
<td>J7</td>
<td>3.1</td>
<td>1.22</td>
<td>3.3</td>
<td>657</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J8 (shaken)</td>
<td>1.2</td>
<td>4.19</td>
<td>2.7</td>
<td>230</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Ash Water</td>
<td>J9</td>
<td>0.8</td>
<td>&lt;0.05</td>
<td>&lt;0.5</td>
<td>490</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J10 (shaken)</td>
<td>0.8</td>
<td>0.79</td>
<td>0.9</td>
<td>473</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Domestic Water</td>
<td>J11</td>
<td>3.8</td>
<td>4.87</td>
<td>1.5</td>
<td>412</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J12 (shaken)</td>
<td>1.9</td>
<td>6.22</td>
<td>6.8</td>
<td>422</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Trough 3 Outlet</td>
<td>Demineralised Water</td>
<td>J13</td>
<td>0.9</td>
<td>0.84</td>
<td>&lt;0.5</td>
<td>100</td>
<td>&lt;4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J14 (shaken)</td>
<td>0.7</td>
<td>5.09</td>
<td>3.4</td>
<td>79</td>
<td>&lt;4</td>
</tr>
</tbody>
</table>

* Average levels of target elements in untreated ash water employed for tests J1, J2, J5, J6, J9 and J10; no measurable levels of the target elements were present in the distilled water used.

# A repeat analysis of trace elements for Jar test 6, at a later date.

The analytical test results provided in Table 4.4 provides evidence of no or negligible leaching of selenium, arsenic, antimony, molybdenum and aluminium from the ash water jars. In fact, levels of elements present in untreated ash water employed for half of the studies have been reduced for all but molybdenum, indicative of on-going...
adsorption during standing even of elements present at from 10 – 100 μg/L level. Some leaching of trace elements back into the demineralised and domestic water solutions has occurred, but overall the test results illustrate that at near neutral pH the leachability of each trace element back into solution is low or negligible. The sludge or corrosion product is inert under the experimental conditions with the exception of molybdenum and to a lesser extent arsenic, which were the only trace elements which produced a higher concentration than the original ash water solution concentrations. Of course, passage of ash water over the samples for 15 months provides element capture to significant levels, so even the levels reported represent very limited leaching. For example, all arsenic results were, in the case of stored ash water mixtures, lower in concentration than the concentration initially present in the added ash water solution. The tests results for added ash water actually reveal that further removal of certain trace elements continued over the sample storage period. Further examination of these results and the leaching capacities is provided in the following sections.

### 4.2.1 Samples Stored in Ash Water

#### 4.2.1.1 Results

The ash water used was very slightly basic and ranged in pH from 7.28 to 7.49. The conductivity, which ranged from 32.1 to 35.6 mS/cm, was three times higher than in the jars containing added demineralised and domestic water owing to the source being estuarine, with a high salt and trace element content. Since the ash water contained measurable levels of the elements under analysis, it was of interest to define the change in levels during storage. These changes are indicative of further adsorption/desorption processes during this time. Table 4.5 reports percentage change in trace element concentrations in the ash water itself, for experiments using ash water as the storage solution.

The percentage of selenium adsorbed or coprecipitated from the ash water by the sludge (or iron oxides and oxyhydroxides) added to the jars is high, ranging from 77 to 96%; the initial concentration in the ash water is low, at 9 μg/L. This is indicative of residual adsorption capacity in the sludge even after an extended time in the tanks. There was no evidence of selenium leaching back into solution from the solid, even when the contents of the jar were vigorously shaken. The levels of selenium present in solution are low and near to the detection limit and practical quantitation limits of the analysis of
0.005 µg/L and 0.025 µg/L respectively; this explains limited reproducibility with the repeat test for J6. Figure 4.1 provides a pictorial representation of selenium concentrations from each jar solution with and without physical disturbance. It is apparent this had negligible effect. Clearly, selenium, present as oxyanions since these represent the only stable form met in aqueous solution, is efficiently adsorbed and not subject to leaching at near-neutral pH.

Table 4.5 Percentage reduction/increase of trace elements in the added water over the storage period, for samples stored in ash water.

<table>
<thead>
<tr>
<th>Sample Location and Identification</th>
<th>Weight Wet Sludge/Corrosion Product (g)</th>
<th>Concentration and Percentage of Reduction/Increase of Trace Elements in Ash Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td></td>
<td>µg/L</td>
</tr>
<tr>
<td>Initial ash water</td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>Trough 1 Outlet J1</td>
<td>504.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Trough 1 Outlet J2 (Sample Shaken)</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Trough 2 Outlet J5</td>
<td>501.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Trough 2 Outlet J6 (Sample Shaken)</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>Trough 3 Outlet J9</td>
<td>508.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Trough 3 Outlet J10 (Sample Shaken)</td>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>

* values in red indicate increased % levels; all other values represent decreased % levels
* values in bold are repeats performed separately

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.
Arsenic levels in ash water also fell significantly (by as much as 99%), and displayed no evidence of being leached back from the solid into the container solution. Arsenic levels reduced in concentration from the initial 12.5 µg/L down to levels below 1 µg/L, with the exception of one sample which had been taken from the jar after shaking. Nevertheless, this sample was still lower than that originally in the ash water. This single outlier (see Figure 4.2) may have arisen from a trace of some very fine solid matter passing through the filter, as the levels in the solid were significantly higher than in solution as a result of continuous adsorption in the tanks prior to collection. Nevertheless, it is notable that all shaken solutions display slightly higher levels in the final solution than found in the still solution. This may indicate a general problem with ultra-fine solids passing through the filter, or else may reflect a greater tendency towards redissolution than observed with selenium. Again, like selenium, the arsenic is present as oxyanion species, which are anticipated to bind reasonably well to the oxide surface through chemisorption processes.

![Figure 4.2](#)

**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.

All analyses of antimony, with the exception of one repeat analysis, also displayed no evidence of leaching. In fact, antimony present in the added ash water was further adsorbed or coprecipitated from the sludge, which contained iron oxides and oxyhydroxides such as goethite, lepidocrocite, hematite and magnetite as determined in
Chapter Three. The highest value obtained from Jar test J2 (shaken) was 2.3 μg/L; this is close to the detection and practical quantitation limits of the analysis utilising ICP-MS in any case. The percentage of removal of antimony from the ash water solution was high, ranging from 88 to greater than 97%. Figure 4.3 provides a graphical representation of the concentrations of antimony in the ash water solution after 12 months storage. Again, shaken samples display slightly higher levels than still samples, with interpretations analogous to those given above for other elements also applicable. The slight increases found represent no substantial effect.

![Antimony Leached from Ash Water](image)

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.

Molybdenum was the only trace element in the ash water jar experiments which displayed clear evidence of leaching from the sludge back into the ash water solution. The initial concentration of molybdenum in the ash water was 153 μg/L and, as can be seen in Table 4.4 and Figure 4.4, molybdenum concentrations increased to three to four times the initial ash water molybdenum concentration.

The final molybdenum levels are, nevertheless, not significantly high, and this level of desorption is clearly manageable. It is notable that, of the elements present as oxyanions, molybdenum as molybdate alone has the capacity of forming large polyoxometalate anions. These form mostly at about pH <6 and are likely, due to their size, to adsorb less strongly than smaller oxyanions of the type formed by the other elements already discussed, which may account for the observations. The pH is also a
factor in the behaviour of MoO$_4^{2-}$ which may not adsorb strongly if protonated (pKa3.8).

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.

Aluminium displayed consistent behaviour. Unlike selenium, arsenic, antimony and molybdenum, there was no evidence of aluminium leaching from the sludge or corrosion product back into the added ash water solution. At pH 7 the main species of aluminium in solution is Al(OH)$_3$(aq). Notably, aluminium alone will be present as an aquated cation (Al$_{aq}^{3+}$, Al(OH)$_{aq}^{2+}$ or Al$_2$(OH)$_4^{4+}$), rather than as an oxyanion, which will influence adsorption behaviour. In fact, as can be seen in Table 4.4 and Figure 4.5, aluminium levels on final sampling were all very low and usually below 4 µg/L, which is close to or below the detection and practical quantitation limits of the ICP-MS analysis undertaken. From all of the jar experiments, with and without shaking, aluminium in the ash water displayed further adsorption/coprecipitation to levels either equal to or greater than 93%. The initial concentration of aluminium in the ash water solution placed in each jar was 59.5 µg/L, falling to a consistent value of <4 µg/L on final sampling. Even after 12 months of ageing, the iron oxides and oxyhydroxides retain strong adsorptive capacity for this cationic species. Actual final levels may be well below those reported, but the conditions of sampling, treatment and analysis do not permit higher accuracy, nor is it required for this relatively benign element.
4.2.1.2 Discussion

Analytical tests of trace elements selenium, arsenic, antimony and aluminium present in the ash water solution stored with trace element loaded corrosion product sludge from the Vales Point Power Station pilot plant have all been reduced significantly in concentration from the initial ash water. The corrosion product, as indicated in Chapter Three, was identified as a combination of goethite, lepidocrocite, hematite and magnetite. There was no evidence of trace elements leaching from the combination of iron oxides and oxyhydroxides stored in the jar and aged over a 12 month period. In fact, the use of ash water as the aqueous storage solution in the jars clearly showed that these four trace elements were further adsorbed or coprecipitated during the period of storage. Even with vigorous shaking of the jar contents, the concentrations generally determined amounted to reductions in element total concentrations in the ash water of at least 80%, and as high as 99%.

The stability of adsorption of selenium, in particular selenite ($\text{SeO}_3^{2-}$) which is the dominant species under the experimental conditions, and the low concentration of total selenium found in the ash water after being stored with the pilot plant corrosion product, is not surprising. Studies of adsorption of selenite on iron oxides and oxyhydroxides such as goethite, lepidocrocite and hematite have shown that the anion adsorbs over a wide range of pH levels from about 4 to 8. The pH of the ash water solution added to each jar before
storage was ~7.4. As stated in Chapter Two, Cornell and Schwertmann [1] found that selenite adsorbs strongly and specifically on goethite by a ligand exchange mechanism; that is, it is efficiently chemisorbed. Adsorption is largely irreversible [1], although it is at a maximum in the acid region and decreased to negligible values at pH 10. This trend would also be expected for the other iron oxides and oxyhydroxides lepidocrocite, hematite and magnetite, as studies of these iron oxides have found strong adsorption from acid up to pH levels of around 9; this was the case in the Duc et al. [2] study with hematite, again involving the formation of inner-sphere complexes.

Whilst final arsenic concentrations were in some cases 50% of the concentration of the ash water added to the jar with corrosion product, no analytical test results reached levels above the initial solution concentration of 12.5 µg/L, and usually were significantly below this level. There was no evidence of arsenic being leached from the loaded sludge back into solution. Studies by Manning et al. [3] on the adsorption of As(III) and As(V) with zero-valent iron surfaces found the pH range for maximum adsorption was wide, being between 4 and 10. Again, inner-sphere didendate complexes were assessed to form. The test results are consistent with that of selenium, with not only arsenic oxyanions found not to leach from the loaded iron oxide or oxyhydroxides, but also levels further reduced in the ash water solution added to the jar. Chemisorption, which involves coordinate bond formation to the oxide surface, requires substantial energy to break bonds and reverse the process, thereby allowing anion release, so leaching under moderate pH conditions is not anticipated.

Antimony also displayed the same characteristics as selenium and arsenic, in that there was no evidence of leaching from the corrosion product under mild pH conditions. Notably, the added ash water antimony concentration of 18.5 µg/L was reduced in the final solution in each jar experiment to less than 2.5 µg/L. Antimony shows a high sorption in the pH range of 3 to 7, as exemplified in the study by Leuz et al. [4] of the sorption of Sb(V) and Sb(III) onto goethite. Once again, chemisorption is favoured, and this opposes redissolution to a markedly greater extent than achieved simply by weaker, formally ion-pair interactions. Overall, behaviour of this set of elements that dominantly form simple oxyanions in solution is comparable, and fully consistent with the prior work reported on controlled surfaces or materials. The presence of a suite of oxidic materials as surfaces in the present study does not negate comparisons, as all the forms lepidocrocite, hematite,
goetite and magnetite have been demonstrated to have the capacity to act in the same manner, albeit with differing capacities and thermodynamic and kinetic properties. Molybdenum, however, displayed limited leaching from the loaded iron oxides and oxyhydroxides, with final levels after a year being two to three times that in the initial ash water. Studies of molybdenum have found adsorption on to iron oxyhydroxides like goethite are best at low pH and decrease with increasing pH above neutral. Goldberg and Foster [5] found molybdenum adsorption on goethite is dependent on particulate concentration and showed pronounced pH dependence, exhibiting a maximum at low pH and decreasing sharply with increasing pH until adsorption is virtually zero above pH 8. The pH of the ash water solution added to the jars was in the neutral to basic region of 7 to 7.5. It is evident that in the pilot plant, where the pH was lowered through the corrosion of iron to well below these levels, the adsorption of molybdenum may take place effectively. However, if the corrosion product was to be placed in an environment such as ash water with a buffering effect and neutral to basic pH range, it is likely molybdenum will experience some leaching or desorption from the loaded iron oxides or oxyhydroxides. Conversely, if the environment was acidic, such as is the case in acid sulfate environments, it would be expected molybdenum would be stable and not leach from the adsorbing material. Nevertheless, where the pH <7.5, the present study has demonstrated that molybdenum is sufficiently retained to represent no significant hazard.

It is interesting to speculate on why the oxyanion of molybdenum differs in behaviour from the oxyanions of the other elements examined. Notably, molybdenum alone can readily form polyoxometalate anions through the condensation of molybdate monomers, and this has been shown to play a role in its unwanted presence in purification of manganese ion used for making electrolytic manganese oxide [6]. If molybdate anions are slowly released from an oxide surface, they may be induced to undergo oligomerisation reactions at the surface while confined. The formed soluble polyoxometalate anion differs in size, surface charge density and thus adsorption capacity from the monomeric anion. This may lead to it being preferentially released into solution. This may be a kinetically very slow and pH-dependent process, but over a period of a year sufficient may be released to be readily detected. It suggests that storage in too basic a medium will be detrimental to retention of molybdenum, resulting in soluble oxomolybdenum(VI) species.

Aluminium concentrations in the ash water solution were very low at 4 µg/L compared to the initial concentration of 59.5 µg/L in the ash water added to the jar. The
results demonstrate high efficiency of adsorption on the corrosion product or sludge contained in the jar. Again, as has been the case with selenium, arsenic and antimony oxyanions, adsorption appears to occur in the more acidic to neutral pH range, which is consistent with conditions applying in the ash water interacting with the corrosion product containing iron oxides and oxyhydroxides. The aluminium cation is present as $[\text{Al(OH}_2\text{)}_6]^{3+}$ only at low pH, but is a small highly-charged ion that will adsorb strongly to appropriate surfaces. Replacement of a water from the coordination sphere by an oxide or hydroxide group on the solid surface leads to a chemisorbed species with a covalent Fe–O(H)–Al linkage. This leads to a very stable species that is not easily displaced. The $[\text{Al(OH}_2\text{)}_6]^{3+}$ complex does tend to undergo hydrolysis at relatively low pH, to form $[\text{Al(OH)(OH}_2\text{)}_5]^{2+}$, although this then undergoes dimerisation to form the hydroxide-bridged $[(\text{H}_2\text{O})_4\text{Al(OH)}_2\text{Al(OH}_2\text{)}_4]^{4+}$ dimer [1]. Each of these forms is capable of the same chemistry as the parent ion, leading to surface chemisorption. Release of the relatively kinetically inert and strongly bound aluminium from the oxide surface is not favoured.

4.2.2 Samples Stored in Demineralised Water

4.2.2.1 Results

The pH of the demineralised water was slightly more basic than that of ash water and ranged from 7.60 to 7.85. However, these pH levels were measured at the time of sampling and not during the initial set up of the jars with sludge and demineralised water (~pH 5). This also accounts for the reported conductivity ranging from 9.4 to 11.2 mS/cm, which is much higher than what would be expected for ultra-pure water which would normally be measured as $\mu$S/cm since the demineralised water has no detectable levels of ions present. It is evident that cations and anions, largely sodium chloride from the ash water passed over the sludge in the tanks, have been released from the sludge. These would be present as weakly adsorbed ions or arise from residual ash water entrained in the sludge. Table 4.6 reports the concentration of each trace element leached from the sludge or corrosion product in the jar experiments.

The aim of the jar experiments utilising demineralised water as the storage solution was to create a non-equilibrium environment where cations and anions may have a greater potential to leach from the sludge or corrosion product or through desorption or dissolution
from the iron oxides and oxyhydroxides. Additionally, demineralised water was chosen as it provides a starting position of no detectable ions in solution, so that leaching of trace metals of interest from the sludge or corrosion product would be better observed.

Table 4.6 Final concentrations of trace elements leached from oxide sludge into demineralised water over a 12 month period.

<table>
<thead>
<tr>
<th>Sample Location and Identification</th>
<th>Weight Wet Sludge/Corrosion Product (g)</th>
<th>Concentration of Trace Elements in Demineralised Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Se</td>
</tr>
<tr>
<td>Trough 1 Outlet J3</td>
<td>300.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Trough 1 Outlet J4 (Sample Shaken)</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Trough 2 Outlet J7</td>
<td>341.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Trough 2 Outlet J8 (Sample Shaken)</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Trough 3 Outlet J13</td>
<td>336.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Trough 3 Outlet J14 (Sample Shaken)</td>
<td></td>
<td>1.9</td>
</tr>
</tbody>
</table>

The concentration of selenium in the jar solution containing demineralised water should be less than or equal to the detection limit of the selenium analysed if no selenium has been leached from the sludge or corrosion product even with the contents of the jar being vigorously shaken. The selenium analysis for the three jar experiments displays minimal leaching of selenium, even in the experiments where the contents of the jars were vigorously shaken. Separate repeat analysis for J8 and J14 provided lower levels than the analysis of sample where the samples were taken before the jars where shaken. All test results are above the detection limit of 0.005 µg/L and practical quantitation limit of 0.025 µg/L with the lowest reading being 1.1 µg/L and the highest 3.8 µg/L. Variations may reflect minute traces of ultrafine solids passing through the sub-micron filter in some cases; at these very low levels, some variations are not unusual where ultra-clean room conditions were not available. The total selenium analysis (for combined selenite and selenate) confirms that adsorption or coprecipitation of selenium on iron oxides and oxyhydroxides is stable under the experimental conditions. Figure 4.6 illustrates the very low selenium concentrations detected. Levels observed are very similar to those obtained
in the ash water experiments. Shaking the samples may have allowed more exposure to iron oxide surfaces causing further reduction of elements such as selenium and antimony.

![Selenium Leached from Demineralised Water](image)

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.

Arsenic behaved somewhat differently to selenium in that, for all the experiments where the contents of the jars were shaken, there is evidence of some leaching from the sludge/corrosion product. Even for one jar test where the solution was taken prior to being shaken the level of arsenic was 4.87 µg/L. The lowest arsenic level analysed was 0.31 µg/L for J3, with the highest value obtained from the same jar after shaking of 10.9 µg/L. The detection limit for the arsenic analysis is 0.005 µg/L and for practical quantitation the limit is 0.025 µg/L. Whether the leaching of arsenic to a level of no more than 10.9 µg/L is considered significant depends on arsenic levels actually adsorbed or coprecipitated onto the iron oxides and oxyhydroxides that make up the sludge material. Again, the consistently higher values for shaken samples may simply reflect higher trace amounts of very fine solids passing through the filter in these cases, leading to elevated concentrations as a result of the high levels in the adsorbed solid carried through the filter.

The concentration of arsenic leached from the sludge is not uniform across the set of jar experiments as a whole. This inconsistency in the leaching of arsenic could be a result of the iron oxide or oxyhydroxide material not being uniform in type or quantity, but may point more towards particulate interference. Although the material in each jar may contain varied mixtures and quantities of goethite, hematite, lepidocrocite and magnetite, all have proven adsorption capabilities. However, the analyses of solutions from jars
before shaking were all lower in arsenic concentration than in solutions where the sludge had been disturbed by shaking. Figure 4.7 illustrates not only the variance in arsenic concentrations across jar tests, but also the pattern between samples taken before and after shaking of the contents. Overall, results are similar to those found in the ash water studies.

![Arsenic Leached from Demineralised Water](image)

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.

The antimony analytical test results were, like those of arsenic, also varied, ranging from less than the detection limit of >0.5 µg/L to 6.8 µg/L, with a similar, though less established pattern evident between samples taken before and after shaking (Figure 4.8). Again, variations in the iron oxides and oxyhydroxides present in the sludge could contribute to differences in antimony concentrations between jar experiments, as could ultra-fine particulates. Overall, the level of antimony in each analysis is not high and is close to the detection limit of 1 µg/L and practical quantitation limit of 5 µg/L for analysis. Results are comparable to those observed in ash water.

Results for molybdenum show some variations, with data from jar experiments J3 and J4 anomalous. However, the remainder of molybdenum results parallel those found in ash water and demonstrate that this trace element does undergo some leaching from the sludge or corrosion product with or without shaking, with levels as high as ~600 µg/L detected (Figure 4.9). While general variance in concentration can be assigned as discussed for other analytes, the two extremely low values are not readily explained, except it is noted that they are anomalous across the set of ash and distilled water samples.
and may represent an unintended re-adsorption during storage and transport prior to analysis.

![Antimony Leached from Demineralised Water](image1)

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.

![Molybdenum Leached from Demineralised Water](image2)

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.

The jar experiments for aluminium with demineralised water yielded results essentially the same as the experiments utilising ash water as the storage solution. The results for all experiments, with one exception, demonstrates that aluminium is not leached or released back into solution but remains chemically bound to the iron oxide or oxyhydroxide (Figure 4.10). The single analysis that determined a high aluminium concentration was a shaken sample, which suggests that some ultra-fine solids with their
high load of adsorbed aluminium may have passed through the filter. They would contribute effectively in the analytical procedure employed. This particular anomaly does suggest that limitations on filtration set by the standard 0.45 micron filters employed may play a role in these studies.

![Aluminium Leached from Demineralised Water](image)

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.

### 4.2.2.2 Discussion

The analytical test results were very similar to those performed in ash water, and similar conclusions may be drawn. The low electrolyte environment of demineralised water compared to that in ash water does not influence outcomes for any analyte significantly. Aluminium showed essentially no signs of leaching. Measured levels for total selenium, arsenic, antimony and molybdenum were above the detection limits and practical quantitation limits, illustrating for iron oxide/oxyhydroxide corrosion products stored in demineralised water a degree of leaching of these trace elements. However, the levels were not substantial for selenium, arsenic and antimony, to the point that desorption under the experimental conditions can be considered very minor. Differences in the types and abundances of the iron oxide material in the corrosion product in each jar, as well as the possibility of ultra-fine particulate passing through the filter, may account for variations in results apart from basic analytical limitations. Most concentrations were near the limits of detection. Molybdenum, as in the ash water experiments, showed the highest
capacity for desorption. Overall the stability of molybdenum at high pH levels is questionable for long term storage and re-release into the environment. However, other elements appear efficiently and essentially irreversibly bound under the conditions employed.

4.2.3 Samples Stored in Domestic Water

4.2.3.1 Results

The pH of the domestic (tap) water was more basic, at 8.59, than that of the ash water and demineralised water. The conductivity of 11.1 mS/cm is to be expected, as domestic water would contain a lower amount of cations and anions than does ash water and is similar to those measured in the final solutions for the demineralised water tests. Subsequently, the observations that the concentrations of total selenium, arsenic, antimony, molybdenum and aluminium are consistent with those found for jar experiments utilising demineralised water as the storage solution are not surprising. Table 4.7 reports the concentration of trace elements leached from the sludge/corrosion product contained in the limited jar test experiment utilising domestic (tap) water as the storage solution.

Table 4.7 Concentration of trace elements leached from the sludge/corrosion product into domestic (tap) water.

<table>
<thead>
<tr>
<th>Sample Location and Identification</th>
<th>Weight Wet Sludge/Corrosion Product (g)</th>
<th>Concentration of Trace Elements in Domestic Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Se</td>
</tr>
<tr>
<td></td>
<td></td>
<td>µg/L</td>
</tr>
<tr>
<td>Trough 1 Outlet J11</td>
<td>316.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Trough 1 Outlet J12 (Sample Shaken)</td>
<td></td>
<td>1.9</td>
</tr>
</tbody>
</table>

The concentrations of elements leached would, as for other studies, be dependent upon the types and quantities of iron oxides and oxyhydroxides present. The analytical test results of selenium, arsenic, antimony, and aluminium are illustrated in Figure 4.11.
Molybdenum was not included as the concentrations are much higher, of the order of ~400 µg/L.

![Leaching of Trace Elements into Domestic Water](image)

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

### 4.2.3.2 Discussion

Whilst the concentrations of total selenium, arsenic, antimony and aluminium are not considered to be high compared to the original solution concentrations, it is evident from the trends provided in Figure 4.11 that some minor leaching from the corrosion product does take place. Note that the amount of corrosion product is less in this case and also in the demineralised water case than that in the jar experiments undertaken with ash water. The influence of this variation in solid:liquid ratio is not obvious; however, given the low levels of ions leached overall, this is not a surprise, as saturation effects will not operate. The same overall trends for the domestic water experimental results as for demineralised and ash water is evident. The minor variations in pH across the types of solutions have had no clear effect. While background electrolyte levels vary for the three types of leach solution, it is not simple to establish any clear effect in this aspect either. Overall, it would appear that any surface or treated water that has not been subjected to gross changes in pH or added ions to which the corrosion product is exposed, even for extended periods, will not cause significant leaching of adsorbed ions, with molybdenum alone showing an enhanced potential for desorption.
4.3 LEACHATE OF CORROSION PRODUCTS STORED IN PILOT PLANT TROUGHS

Further testing of pilot plant sludge or corrosion products was undertaken on the 15th December 2007 and 8th August 2008 by a National Association of Testing Authority accredited laboratory utilising USEPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) – pH of extracting solution (pH 2.88 or pH 4.93). The first series of leachate tests undertaken were analysed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) which only yielded test results in mg/L. The second set of analyses undertaken in August 2008 utilising TCLP was analysed by Inductively Coupled Plasma - Mass Spectrometer (ICP-MS), which yielded better levels of detection. The sludge samples obtained were from troughs 1, 2 and 3, which had corrosion product or sludge that had settled in the bottom of the troughs. This product had been subjected to ageing of several years over the operation of the pilot plants since commissioning on the 17th December 2003.

The aim of the TCLP leachate tests was to ascertain, by an independent commercial laboratory, the level of leaching of trace elements including dissolved selenium, arsenic, antimony, chromium, vanadium, aluminium and molybdenum. The following sections provide the results of the analytical test results on the leaching of these trace elements from the pilot plant corrosion product, with laboratory test reports provided in Attachment 2.

4.3.1 TCLP Leachate Analysis

4.3.1.1 Results

Samples were analysed by ICP-AES in December 2007 and by the more sensitive ICP-MS technique in August 2008. Sludge samples obtained from the Vales Point Power Station Trace Metal Reduction Pilot Plant were collected on the 15th December 2007, and were dispatched to Australian Laboratory Service, the Laboratory Group for TLCP analysis, to determine the leaching of selenium, arsenic, antimony, chromium, vanadium, aluminium and molybdenum and a number of other trace elements. Table 4.8 summarises the concentrations of each trace element from the TCLP analysis of dilute acid leachable metals by ICP-AES. Data is also provided on the test procedure parameters including initial pH, pH immediately after HCl addition, and the final pH.
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>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Reporting mg/L</th>
<th>Concentration of Leachable Metal by ICPAES in mg/L of sludge samples obtained on 15th December 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Trough 1</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

**TCLP Leach Parameters**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>7.0 6.9</td>
</tr>
<tr>
<td>After HCl pH</td>
<td>2.3 2.3</td>
</tr>
<tr>
<td>Final pH</td>
<td>5.0 6.1</td>
</tr>
</tbody>
</table>

The analytical test results obtained from the sludge samples taken on the 15th December 2007 indicate that the concentrations of selenium, arsenic, antimony, chromium, vanadium, and molybdenum in the acid leach tests are all below the limit of reporting or the detection limit of the ICP-AES analysis. The detection limits for the various elements corresponds to the following levels in µg/L: selenium, <50 µg/L; arsenic, <100 µg/L; antimony, <100 µg/L; chromium, <100 µg/L; vanadium, <100 µg/L; molybdenum, <100 µg/L. Aluminium was the only trace element detected by the TCLP leachate analysis with concentrations in Troughs 1 to 3 ranging from <100 µg/L to 300 µg/L. The results indicate, overall, that there is no detectable evidence of trace elements leaching from the sludge material, with the exception of aluminium. It is interesting to note that whilst this trend is consistent with the 2005 jar experiments it was molybdenum which showed elevated levels and not aluminium. However, this present test involves acidification prior to analysis, which was not the case in the jar experiments. This could significantly influence outcomes.

Table 4.9 reports the analytical test results for trace metals detected by the TCLP leachate analysis with ICP-MS for sludge samples obtained on the 1st August 2008. The analytical test results obtained from the sludge samples taken in August 2008 also indicate that the concentration of selenium, arsenic, antimony, chromium, vanadium,
and molybdenum are all generally below the limit of reporting or the detection limit of
the ICP-MS analysis which corresponds to the following levels: selenium, <10 µg/L;
arsonic, <5 µg/L; antimony, <10 µg/L; chromium, <10 µg/L; vanadium, <10 µg/L;
molybdenum, <10 µg/L. Once again aluminium was the only trace element detected by
the TCLP leachate analysis with concentrations in Troughs 1 to 3 ranging from 100
µg/L to 800 µg/L which is somewhat higher that leachate tests undertaken in 2007,
although the detection limit in that case was lower and consequently the values
determined likely less well defined.

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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of Reporting mg/L</th>
<th>Concentration of Leachable Metal by ICMS in mg/L of sludge samples obtained on 1st August 2008.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Trough 1</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

TCLP Leach Parameters

| Initial pH       | 6.1 | 6.2 | 6.2 |
| After HCl pH     | 1.6 | 1.6 | 1.6 |
| Final pH         | 4.7 | 5.0 | 4.9 |

The results indicate, overall, that there is no detectable evidence of trace
elements leaching from the sludge material with the exception of aluminium. The low
adjusted pH in this case could promote release of some of this cation through
protonation and cleavage of adsorbed hydroxoaluminium(III) species to form more
soluble \([\text{Al(OH}_2\text{)}_6]^{3+}\), which may account for the observation and the difference from
that in the jar experiments, where near-neutral pH solutions were employed throughout
[1].
4.3.1.2 Discussion

The TCLP leachate analytical test results for the trace elements that are the focus of this thesis investigation (including selenium, arsenic, antimony, vanadium, chromium and molybdenum) were all lower than the detection limits by both ICP-AES and the more sensitive ICP-MS analysis, with the exception of aluminium. This element was the only element leached from the sludge or corrosion product material from all three pilot plant troughs, and then only to very limited levels. Given the leachate tests were undertaken 8 months apart, the results provide reasonable evidence of the majority of elements analysed being strongly adsorbed on the iron oxide or oxyhydroxide material generated by the pilot plant through corrosion of iron. Moreover, since the analytical method involves acidification to low pH, it is apparent that acidic conditions do not promote ready rapid release of the elements present. The sole exception, aluminium, has protonation/deprotonation behaviour that could lead to formation and partial release of $[Al(OH)_2]_6^{3+}$ [1]. Nevertheless, this small, highly-charged complex cation would still show significant attraction for the surface, which accounts for the low levels of aluminium detected in solution.

4.4 CONCLUSIONS

The results of the leachate studies indicate that trace elements including selenium, arsenic, antimony, vanadium and chromium are strongly adsorbed or coprecipitated onto the iron oxides and oxyhydroxides goethite, lepidocrocite, hematite and magnetite which have been identified as the corrosion products of the Vales Point Power Station Trace Metal Reduction Pilot Plant. They exhibit negligible leaching even after long periods of exposure to aqueous solutions.

Jar experiments indicate that the trace metal molybdenum is partially leached from the pilot plant corrosion product under the neutral pH conditions applying in that case. However the TCLP analytical test results for 2007 and 2008, conducted after pH adjustment to <2, shows no leaching under these acidic conditions. Clearly, this element, which apart from a presence as simple molybdate ion has the capacity to form large polyoxomolybdates, displays complex pH-dependent behaviour. Nevertheless, the levels of leaching are not particularly high under any conditions. Aluminium was
the only other element that demonstrated some capacity for leaching, but only in strongly acidic environments, and then to a very modest extent.

The test results also demonstrate that the iron oxides and oxyhydroxides formed within each trough of the pilot plant may be reasonably uniform in type and amounts of oxidic species generated. All tests undertaken for each of three separate troughs showed no variance that could indicate a difference in the process operating in each, consistent with some overall commonality in the sludge character.

Overall, the leachate experiments confirm that the use of iron as a medium to generate iron oxides/oxyhydroxides such as goethite, lepidocrocite, hematite and magnetite for the adsorption of trace elements of environmental concern is justified and effective. Not only are all target elements efficiently removed by the process, but also they remain adsorbed or chemically bound by these iron oxides and oxyhydroxides sufficiently that they are resistant to leaching under near-neutral pH environmental conditions for very extensive periods. They even resist leaching in significantly acidic environments for at least short periods. Clearly, this process offers a cheap and effective way for control of many elements of environmental concern.

4.5 REFERENCES


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

5.1 INTRODUCTION

Earlier chapters outlined the environmental impact of Vales Point ash water on the receiving environment, focusing in particular on the release of selenium and the use of iron oxides and oxyhydroxides for the treatment of ash water. Chapter 3 demonstrated that the formation of rust on the surface of solid iron or steel wool provided an efficient process for removing a number of trace elements, including selenium. The most dominant species formed through the rusting of solid iron observed in pilot plant trials were goethite, lepidocrocite, hematite and magnetite.

To gain further knowledge of the chemical and physical properties of these iron oxides and oxyhydroxides and chemical processes involved in the treatment of ash water, this Chapter focuses on the characterisation of synthetic iron oxides and oxyhydroxides, either laboratory synthesised or commercially available. The examination of essentially pure oxide/oxyhydroxide forms is important, as it allows a level of experimental control not achievable in pilot plant studies where mixtures of these species occur. Laboratory trials performed under controlled conditions to determine the amounts of selenium, arsenic, antimony, vanadium, chromium, aluminium and molybdenum removed through adsorption/coprecipitation in various ionic matrices of defined type, and in ash water, are reported.

The kinetics of removal of these trace elements from ash water with goethite, lepidocrocite, hematite and magnetite are also explored herein. These studies allow determination of the contact time required for efficient adsorption/coprecipitation, and identification of the most effective oxide/oxyhydroxide for capture of particular target elements. Although limited in scope, these studies may also provide some mechanistic insight.
5.2 SYNTHESSES AND CHARACTERISATION STUDIES OF IRON OXIDES AND OXYHYDROXIDES

The following sections provide details of the preparation and properties of the individual oxides utilised in adsorption/coprecipitation trials and recovered from sampling of the pilot plant troughs. Further, physical characterisation through determination of surface area and porosity, X-ray diffraction (XRD) and scanning electron microscopic (SEM) imagery has been undertaken.

5.2.1 Iron Oxides and Oxyhydroxides Procured and Synthesised for Laboratory Trials

Of the four oxides defined in the following sections, not all are available from commercial suppliers. Goethite and lepidocrocite were synthesised in the laboratory, with the preparation method obtained from Schwertmann and Cornell “Iron Oxides in the Laboratory – Preparation and Characterisation”. Syntheses are outlined, along with the final yields [1]. For hematite and magnetite, the properties of these commercially available iron oxides as provided by the manufacturer are presented.

5.2.1.1 Goethite

Pure goethite was not commercially available and was synthesised in the laboratory using potassium hydroxide and iron(III) nitrate. The following method reported by Schwertmann and Cornell was used in the formation of this oxyhydroxide [1].

Method of Preparation

Solution (1) was prepared by dissolving 395.6 g of iron(III) nitrate nonahydrate (Sigma Aldrich, 98%) in one litre of high purity demineralised water to obtain a 1.0 M Fe(NO₃)₃ solution. Solution (2) was prepared by dissolving 280.6 g of AR grade potassium hydroxide in one litre of high purity demineralised water to obtain a 5.0 M KOH solution.

In a one litre polyethylene bottle, 50 mL of solution (1) was rapidly mixed with 90 mL of solution (2) and then made up to one litre with high purity demineralised water. Batches of the mixture containing the red-brown ferrihydrite precipitate were
then placed in an oven set at 70 °C and left for a period of 60 hours. After this period, samples were removed from the oven and left to cool to room temperature. Once cooled, batches of the solution were centrifuged, with several washings, then the yellow-brown precipitate was collected and left to dry in the air. The dried precipitate was then crushed by hand with a mortal and pestle to a fine powder. Each one litre solution yielded 4.5 g of goethite. Batches of 40 one litre solutions were prepared weekly until about 1.2 kg of goethite was prepared, sufficient to allow for the required number of trials with 1 and 5 g samples of this oxyhydroxide.

5.2.1.2 Lepidocrocite

Pure lepidocrocite was also not available commercially. The preparation of lepidocrocite was more complex than that of goethite, this required apparatus to which there was limited access, and as such only enough of this oxyhydroxide was prepared for the selenium trials. For the preparation of this oxyhydroxide, the assembly as illustrated in Figure 5.1 was used.

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 [1].
The following method reported by Schwertmann and Cornell was used in the formation of this oxyhydroxide [1].

Method of Preparation

The solution in a 600 mL beaker was prepared with 11.93 g of analytical grade iron(II) chloride tetrahydrate (Sigma Aldrich, 99%) diluted with 300 mL of high purity demineralised water. Whilst stirring at a constant high rate, the pH was adjusted through the slow addition of 1.0 M NaOH from a burette until the pH of the solution was stable at between 6.7–6.9. The air supply was turned on and flow rate adjusted to 100–300 mL/minute. Continuous adjustment to maintain the pH at 6.7–6.9 was performed, with the colour of the solution changing over time from dark greenish blue to grey and finally to orange. After 2 to 3 hours, the final product was collected, washed with demineralised water and centrifuged several times and the precipitate left to dry in the air at room temperature, yielding ~6 g of orange product. Given the limited access to the apparatus, only 30 batches were prepared.

5.2.1.3 Hematite

Hematite (chemical formula Fe₂O₃) is commercially available and the supplier for this iron oxide used in laboratory trials was Riedel-deHaén. The quantity of hematite (of 95% purity) supplied was 1 kg, which was a sufficient quantity in a single batch for all laboratory trials.

5.2.1.4 Magnetite

Magnetite (chemical formula Fe₃O₄) was also commercially available. It was obtained in a 5 kg glass bottle (98% purity; particle size less than 5 µm) from Sigma Aldrich.

5.2.2 Iron Oxide and Oxyhydroxide Colours

In Chapter 2, the colours of iron oxides and oxyhydroxides were briefly described, with image plates provided that had been used for initial identification of various types of oxides formed on the surface of metal plates obtained from the Vales
Point pilot plant. The following sections provide a comparison of images of laboratory synthesised and procured oxides, along with the samples obtained by the pilot plant in 2005.

### 5.2.2.1 Goethite

From the plates and images for goethite below, it is apparent that the colours presented are dependent on the size of the crystals formed. The laboratory-synthesised goethite crystals display a more yellow to dark brown colour (Image 5.1) and when compared to the colours of goethite in Plates 5.1 and 5.2 it appears the size of the crystals could be in the range of 0.1 to 0.2 \( \mu \)m. Particle sizing of the synthesised goethite confirm the size of the crystals. Positive confirmation that the synthesised oxide is in fact goethite was obtained from X-ray powder diffraction studies.

![Goethite crystals](image)

**Plate 5.1** Common colour of goethite [1]. **Image 5.1** Laboratory synthesised goethite crystals. **Plate 5.2** Colours of goethite crystals [1].

### 5.2.2.2 Lepidocrocite

The colour of the laboratory synthesised lepidocrocite formed using the Schwertmann and Cornell [1] method is the expected orange colour, and this compares well with the colour plate in Image 5.3; a size of less than 0.5 \( \mu \)m is also indicated from comparison with standard samples (Plates 5.3 and 5.4). The colour also indicates that the crystals formed are the lath-like and elongated type, confirmed with the scanning electron microscope images obtained from the synthesised lepidocrocite.
5.2.2.3 Hematite

The red colour of the procured hematite (Image 5.3) is consistent with that of the colour Plates 5.5 and 5.6 below and also with smaller crystals of 0.1 μm in plate 5.6. This is an important consideration, as the higher the surface area of this iron oxide crystal the more efficient it will be in the adsorption/coprecipitation process for removing trace elements. This form of hematite appears to be the most common iron oxide mineral and has been quoted by Cornell and Schwertmann [1] as being widespread in soils and rocks. The abundance of this mineral is relevant when considering remediation of lakes and waterways containing hematite.
5.2.2.4 Magnetite

Magnetite is black, as illustrated in Plate 5.7, and the procured magnetite used in the laboratory trials depicted in Image 5.4 below is also black. The formation of magnetite in the electricity generating industry is important for power station unit chemical control. Magnetite in almost oxygen-free water is encouraged to form on the inner surface of boiler tubes to inhibit corrosion. Conversely, for the removal of trace elements from ash water, the formation of magnetite is encouraged by the corrosion of iron.

Plate 5.7 Common colour of magnetite [1]. 

Image 5.4 Laboratory synthesised magnetite crystals.

5.2.2.5 Pilot Plant Iron Oxide Samples

Iron oxide samples taken from the surface of the Vales Point pilot plant iron bars and iron plates were mixed in colour, ranging from shades of orange to brown, red and black. The oxides were collected as thin flat sheets of various sizes and separated in accordance with their colours. Four distinct coloured oxide layers were grouped together then crushed by mortar and pestle and placed in sealed containers for testing by X-ray diffraction and scanning electron microscope imaging.

Images of the four samples along with positive identification of the constituents are presented below. As can be seen from the images, the colours of the samples are not as consistent as those of the pure synthetic iron oxides and oxyhydroxides.
The distinct black colour of Sample 1 in Image 5.5 below indicates the iron oxide is predominantly magnetite. Testing of the sample confirms this, but also showed that the sample is not pure and does contain some minor constituents; this is to be expected for a sample sourced from a pilot plant. Observation during sampling found that the black coloured oxide collected from the flat sheets occurred where the sheet of oxide contacted the inner side next to the parent metal. This is where the amount of dissolved oxygen present would be lower than on the outer side due to slow diffusion.

**Sample 1**

*Major Constituent* – Magnetite  
*Semi-dominant* – None  
*Minor* – Goethite, Aragonite, Malite, FeCl₃.H₂O

Image 5.5  Pilot plant iron oxide Sample 1.

The colour of Sample 2 (Image 5.6) is dark brown, and testing of the sample found that, although magnetite was a dominant species, this oxide sample also contained a mixture of other semi-dominant species which has had an effect on the size and shape of the crystals and the overall colour.

**Sample 2**

*Major Constituent* – Magnetite  
*Semi-dominant* – Goethite and Lepidocrocite  
*Minor* – Aragonite, Malite and Calcite

Image 5.6  Pilot plant iron oxide Sample 2.
There is not a vast difference between the colours of Samples 2 and 3, except that Sample 3 (Image 5.7) is slightly lighter in colour, but is still brown. As such, the difference in colour is due in this case to the combination of several major constituents, which do not include magnetite. When considering the formation of iron oxides on the surface, it is reasonable to assume that there will be not strict separation of species in layers, but that a mixture of species of various sizes and quantities may occur.

**Sample 3**

*Major Constituents* – Goethite, Magnetite and Lepidocrocite  
*Semi-dominant* – Aragonite and Malite  
*Minor* – Calcite

![Sample 3](image)

Image 5.7 Pilot plant iron oxide Sample 3.

The orange brown colour of Sample 4 (Image 5.8) is a clear indication of the presence of large amounts of the oxyhydroxide lepidocrocite. Again, Sample 4 is not a pure substance, but does contain some minor constituents which affect the colour.

**Sample 4**

*Major Constituent* – Lepidocrocite  
*Semi-dominant* – Goethite and Magnetite  
*Minor* – Calcite, Aragonite, Malite and Gypsum

![Sample 4](image)

Image 5.8 Pilot plant iron oxide Sample 4.
5.2.3  **Structure Identification with X-ray Diffraction and Scanning Electron Microscope Imaging**

Apart from colour as a means of characterisation, as provided in the previous section, the identification of the iron oxide species can be confirmed with powder X-ray diffraction (XRD) and scanning electron microscope (SEM) imaging. The following sections provide analytical results using XRD and SEM on iron oxide samples obtained from the Vales Point pilot plant as well as the synthetic commercial or laboratory samples.

### 5.2.3.1 Pilot Plant Oxide Sample 1

The following SEM images of Sample 1 (Image 5.9 and 5.10) display a number of different crystal forms: elongated, cross sectional, plate, circular and cubic. The size of the crystals in each image also varies, with the smaller crystal clusters being the predominant form. With so many different crystal forms present, identification of smaller crystals using SEM would require magnifications higher than 5 µm and of the order of <1 µm, which were not accessible with instrumentation available. The cubic nature of the smaller clusters in Image 5.9 indicated the presence of magnetite, with the diamond like cross most likely to be goethite.

[Image 5.9  An image of pilot plant oxide Sample 1 crystallites (major constituent magnetite) from SEM at 5 µm.]
A different view (Image 5.10) again displays a number of crystal forms, but does provide to the left an image of a large octahedron (with smaller crystals formed on the surface) which is likely to be a magnetite crystal.

Image 5.10  Another view of pilot plant oxide Sample 1 crystallites (major constituent magnetite) from SEM at 5 µm.

Visual identification where the sample contains a mixture of constituents and crystal sizes is difficult. The only means of qualitatively identifying the species present is through XRD, which identifying the main constituent of Sample 1 to be magnetite, with goethite being the minor iron oxide constituent (Figure 5.2). The intensity and sharpness of peaks is consistent with a high degree of crystallinity in the sample. Diffraction data for Sample 1 had similar peak maximum intensities at d spacings of 2.5454 (100%), 2.9871 (31%), 1.4891 (28%) and 1.6125 (23 %) to those presented in Table 2.5 of Chapter 2. Table 5.1 lists the compounds identified by XRD.

Table 5.1  XRD qualitative analysis of Sample 1.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-075-0033</td>
<td>Iron(II) diiron(III) oxide</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>01-081-0462</td>
<td>Goethite, synthetic</td>
<td>α-FeO(OH)</td>
</tr>
<tr>
<td>01-071-2396</td>
<td>Aragonite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>01-072-1668</td>
<td>Halite, synthetic</td>
<td>NaCl</td>
</tr>
<tr>
<td>00-001-0132</td>
<td>Iron Chloride Hydrate</td>
<td>FeCl₃·7H₂O</td>
</tr>
</tbody>
</table>
Figure 5.2 XRD scan for Sample 1, which contains dominantly magnetite.

5.2.3.2 Pilot Plant Oxide Sample 2

The SEM images of Sample 2 (Images 5.11 and 5.12) also display different crystal structures and clusters of varying sizes of crystals, but are different from those of Sample 1. Unlike Sample 1, the SEM image (Image 5.11) of Sample 2 below has tubular crystal structures.

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.

Once again, it is difficult from the SEM images presented to be able to make a definitive identification of the iron oxides present based on the shape of the crystallites observed at the 5 µm scale. The XRD is more informative (Figure 5.3, Table 5.2).

Figure 5.3  XRD scan for Sample 2, containing magnetite as the dominant species. In this case, semi-dominant species are apparent, compared with the result for Sample 1.
The XRD scan in Figure 5.3 provides identification of the main constituent of Sample 2 as magnetite, with semi-dominant phases of goethite and lepidocrocite.

Table 5.2 XRD qualitative analysis of Sample 2.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-081-0463</td>
<td>Goethite, synthetic</td>
<td>α-FeO(OH)</td>
</tr>
<tr>
<td>01-089-2355</td>
<td>Magnetite, synthetic</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>00-044-1415</td>
<td>Lepidocrocite, synthetic</td>
<td>γ-FeO(OH)</td>
</tr>
<tr>
<td>00-005-0628</td>
<td>Halite, synthetic</td>
<td>NaCl</td>
</tr>
<tr>
<td>01-071-3700</td>
<td>Aragonite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>01-072-1652</td>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
</tbody>
</table>

From diffraction data for Sample 2, major peaks occur at d spacings of 2.5423 (100%), 2.4636 (46%), 2.4895 (45%) and 4.2219 (39%). The maximum peak for Sample 2 is the same as for Sample 1. Other peaks do not exactly match; however, this sample does contain semi-dominant phases which may have an influence.

5.2.3.3 Pilot Plant Oxide Sample 3

The size of the crystals in Sample 3 appears to be smaller than those of samples 1 and 2. A much greater magnification would be required to clearly identify the crystal shapes in sample 3. However, the clusters of crystals are spherical in shape.

Image 5.13 Pilot plant oxide Sample 3 (major constituents goethite, magnetite and lepidocrocite) crystals from SEM at 5 μm.
Another SEM image of Sample 3 (Image 5.14), whilst again displaying crystals which are difficult to define visually, does display a mixture of crystal shapes such as elongated and circular or spherical, again in cluster formations.

Image 5.14 Pilot plant oxide Sample 3 (major constituents goethite, magnetite and lepidocrocite) crystals from SEM at 5 µm.

The XRD scan (Figure 5.4) identified the main constituents of Sample 3 to be goethite, magnetite and lepidocrocite. From diffraction data for Sample 3, major peaks are at d spacings of 2.5406 (100%), 3.3124 (53%), 4.2312 (49%) and 6.3527 (47%). With all three iron oxides and oxyhydroxides present as major components of Sample 3, the XRD scan is the superior means for positive identification. Table 5.3 provides compounds identified by XRD.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-081-0463</td>
<td>Goethite, synthetic</td>
<td>α-FeO(OH)</td>
</tr>
<tr>
<td>01-088-0866</td>
<td>iron diiron(III) oxide</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>01-074-1877</td>
<td>Lepidocrocite</td>
<td>γ-FeO(OH)</td>
</tr>
<tr>
<td>01-070-2509</td>
<td>Halite, synthetic</td>
<td>NaCl</td>
</tr>
<tr>
<td>01-072-1652</td>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>00-041-1475</td>
<td>Aragonite</td>
<td>CaCO₃</td>
</tr>
</tbody>
</table>
Figure 5.4 XRD scan for Sample 3, containing goethite, magnetite and lepidocrocite.

5.2.3.4 Pilot Plant Oxide Sample 4

The platy or elongated crystals observed in Image 5.15 of Sample 4 are consistent with the presence of lepidocrocite. The spherical and elongated shaped crystals are most likely goethite and magnetite, confirmed as present by XRD.

Image 5.15 Pilot plant oxide Sample 4 (major constituent lepidocrocite, with semi-dominant goethite and magnetite) crystals from SEM at 5 μm.
The SEM Image 5.16 at 5 µm also illustrates a mixture of crystal forms, with again cluster formations. Small platy-like crystals can also be seen in the image, but again positive confirmation is required by XRD.

Image 5.16 Pilot plant oxide Sample 4 (major constituent lepidocrocite, with semi-dominant goethite and magnetite) crystals from SEM at 5 µm.

Figure 5.5 XRD scan for Sample 4, containing lepidocrocite as the major constituent.
The XRD (Figure 5.5), identified the main constituent of Sample 4 to be lepidocrocite. The semi-dominant species are goethite and magnetite. From diffraction data for Sample 4, major peaks are at d spacings of 3.3561 (100%), 3.3216 (29%), 2.4885 (29%) and 6.3566 (26%). Some of the major peaks and intensities of Sample 4 are consistent with those provided in Table 2.5 of Chapter 2. Table 5.4 lists the compounds identified by XRD for Sample 4.

Table 5.4  XRD qualitative analysis of Sample 4.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-074-1877</td>
<td>Lepidocrocite</td>
<td>γ-FeO(OH)</td>
</tr>
<tr>
<td>01-087-0246</td>
<td>Magnetite, synthetic</td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>01-081-0464</td>
<td>Goethite, synthetic</td>
<td>α-FeO(OH)</td>
</tr>
<tr>
<td>01-070-2509</td>
<td>Halite, synthetic</td>
<td>NaCl</td>
</tr>
<tr>
<td>01-085-1108</td>
<td>Calcium Carbonate</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>00-041-1475</td>
<td>Aragonite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>00-033-0311</td>
<td>Gypsum, synthetic</td>
<td>CaSO₄·2H₂O</td>
</tr>
</tbody>
</table>

5.2.3.5  Synthetic Goethite

The uniform crystal shapes and sizes in the SEM Image 5.17 are clearly illustrative of goethite crystals. The laboratory-synthesised crystals are acicular and elongated and of mostly similar size. The crystals of Image 5.17 shown with a magnification of 10 µm, are larger in size than crystals observed in the samples from the pilot plant. This could be expected, as the crystals formed in the laboratory were made under controlled conditions such as concentrations of reagents, sequence of mixing and temperature. The pilot plant conditions varied with solution matrix, temperature, pH and flow rate. Further positive identification of the goethite crystals was performed with XRD. Table 5.5 provides the compounds identified by XRD in the goethite. While goethite is dominant, as required, trace levels of halite (sodium chloride) and the mixed oxide/hydroxide/sulphate impurity known as green rust were detected.
Table 5.5 XRD qualitative analysis of laboratory synthesised goethite.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name, synthetic</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-081-0463</td>
<td>Goethite, synthetic α-FeO(OH)</td>
<td></td>
</tr>
<tr>
<td>01-088-2300</td>
<td>Halite, synthetic NaCl</td>
<td></td>
</tr>
<tr>
<td>00-013-0090</td>
<td>Green Rust                ( \text{Fe}<em>{1.3}\text{Fe}</em>{0.9}(\text{O,OH,SO}_4)_0 )</td>
<td></td>
</tr>
</tbody>
</table>

Image 5.17 Laboratory-synthesised goethite crystals at a magnification of 10 μm.

The XRD data provide positive identification of the goethite synthesised sample, with some very minor contamination by sodium chloride and green rust observed and indicative of the sensitivity of the XRD method. Diffraction data for goethite (Attachment 3) identifies major peaks at d spacings of 4.2321 (100%), 2.4678 (70%), 2.7124 (40%) and 0.3936 (31%). The first three peaks are very close to those presented in Chapter 2, Table 2.5 for goethite. Figure 5.6 provides the scanned XRD of the goethite sample.
Figure 5.6  XRD scan for a sample of the laboratory-synthesised goethite.

5.2.3.6  Lepidocrocite

The crystals of the laboratory-synthesised lepidocrocite, like goethite, are consistent in form, but the size of the crystals are much smaller than those of goethite and they are clearly different in character or crystal form from goethite. Closer examination of the crystals in Image 5.18 identifies cluster formations and grassy or hedgehog-type formations; this is the same character as shown for a sample reported in Chapter 2, where the oxyhydroxide was formed in that case under very rapid oxidation and at low pH. However, the crystalline lepidocrocite species in Image 5.18 was prepared at near neutral pH. Another sample (Image 5.19) of lepidocrocite at 10 µm is clearly similar. The use of different conditions for synthesis does not appear to lead to major differences in crystal size and form.
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.

The XRD scan for lepidocrocite also provides positive identification of the crystals, with minor contamination from sodium chloride, as shown in Table 5.6 below.

Table 5.6  XRD qualitative analysis of laboratory-synthesised lepidocrocite.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-044-1415</td>
<td>Lepidocrocite, <em>synthetic</em></td>
<td>γ-FeO(OH)</td>
</tr>
<tr>
<td>01-075-0306</td>
<td>Halite</td>
<td>NaCl</td>
</tr>
</tbody>
</table>
Figure 5.7 XRD scan for a sample of laboratory-synthesised lepidocrocite.

Diffraction data in Figure 5.7 for lepidocrocite (Attachment 3) provides major peaks at d spacings of 6.2374 (100%), 2.4740 (82%), 3.2382 (80%), and 1.9381 (56%). The four peaks have very similar d spacings to those presented in Chapter 2, Table 2.5 for lepidocrocite, but differing intensities, possibly reflecting differences in preferred orientation of crystallites between samples.

5.2.3.7 Synthetic Hematite

The hematite sample analysed by SEM and XRD was not produced in the laboratory like goethite or lepidocrocite, but was synthesised commercially and supplied as a high purity material. Further, no impurities were found by XRD (see Figure 5.8 and Table 5.7). The crystal formations seen in SEM (Image 5.20 and Image 5.21) also appear to be of uniform size and shape. The spherical shapes observed are consistent with the morphologies of synthetic hematite crystals presented in some detail in Chapter 2.
Table 5.7 XRD qualitative analysis of commercial grade hematite.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-089-0599</td>
<td>Hematite, synthetic</td>
<td>α-Fe₂O₃</td>
</tr>
</tbody>
</table>

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.

The diffraction data from the scan shown in Figure 5.8 (Attachment 3) for hematite provides maximum intensity peaks at d spacings of 2.73544 (100%), 2.5476 (73%), 1.7082 (43%) and 1.8574 (37%). The four peaks are almost identical in d
spacings to those presented for hematite in Chapter 2 (Table 2.5), with similar intensities.

![XRD scan for a sample of commercial synthetic hematite.](image)

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

### 5.2.3.8 Magnetite

The magnetite sample analysed by SEM and XRD was also synthesised commercially, and was of high purity. The typical crystal formations for magnetite are octahedral and rhombodecahedral. The SEM (Image 5.22) at 20 µm is insufficiently resolved to discern these shapes, but the crystals are uniform in size and spherical with the overall formation of the clusters taking on the octahedral shape. The only oxide found through the analysis by XRD was magnetite (Table 5.8, Figure 5.9).

**Table 5.8** XRD qualitative analysis of commercial grade magnetite.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-088-0315</td>
<td>Magnetite, synthetic</td>
<td>Fe₃O₄</td>
</tr>
</tbody>
</table>
The diffraction data from Figure 5.9 (Attachment 3) for magnetite provides major peaks at d spacings of 2.5437 (100%), 2.9851 (30%), 1.4875 (29%) and 1.4860 (24%). The three peaks are very close in d spacings and intensities to those presented in Chapter 2 (Table 2.5) for magnetite.

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

The use of advanced techniques such as SEM and XRD is essential for the determination of the iron oxides and oxyhydroxides which form on the surface of the parent iron during pilot plant trials. With the positive identification of oxide species present, a matrix of laboratory trials could be developed to better understand the mechanisms for trace element removal from ash water and also how efficient these various iron oxides and oxyhydroxides are at removing trace elements. SEM scans and XRD analyses of samples obtained from the pilot plant confirmed that on the surface of the iron a mixture of four main oxides develops, these being the well-known species goethite, lepidocrocite, hematite and magnetite. The magnetite tends to be the dominant form near the metal surface, with lepidocrocite dominant in the outermost layer; this probably relates to the variable exposure to dissolved oxygen across the layer.

The following sections provide test results arising from further characterisation of the four iron oxides and oxyhydroxides and the results of laboratory trials for the removal of trace elements from ash water and other developed matrices.

5.2.4 Surface Area and Porosity of Iron Oxides and Oxyhydroxides

5.2.4.1 Adsorption Isotherms

The background to and methodology for adsorption studies has been covered earlier in Chapter Two. Conventional experimental approaches were adopted here. The linear adsorption isotherms determined for nitrogen gas adsorption for each iron oxide (Figure 5.10) are similar to the type II adsorption isotherm curve reported in Cornell and Schwertmann (see Chapter 2, Figure 2.19) [19]. This type of isotherm for gases has been defined by these authors as being associated with multilayer adsorption. The curves in Figure 5.10 are clearly different for each oxide species; in particular, the initial rise in adsorbed volume versus relative pressure is more marked for lepidocrocite than for goethite, magnetite and hematite. The completion of the monolayer represented by the first change in the curve occurs at a very low partial pressure ($\rho/\rho_o$)
of about 0.01. The isotherm for goethite in Figure 5.10 is almost identical to those provided in Figure 2.18 of Chapter 2.

The volumes adsorbed (cm$^3$/g) at standard temperature and pressure (Figure 5.10) reflect porosity of each oxide and vary from highest to lowest in the order lepidocrocite > goethite > hematite > magnetite. Essentially, lepidocrocite has a higher porosity or volume of pores than goethite, whereas hematite and magnetite present as being essentially non-porous due to the nature of the curves. This no doubt is due to the differences in the character of the crystals themselves and their internal pore shapes and sizes.

![Graph showing adsorption isotherms for goethite, hematite, magnetite, and lepidocrocite.](image)

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

In Figure 5.11, the logarithmic representation of the isotherms for each oxide is shown. This representation allows for clear identification of any points of inflection in the curves. Most notable is that seen for lepidocrocite at a vapour pressure ($\rho/\rho_o$) of 0.001. The curve for goethite exhibits a weak inflection around the same position, whereas hematite and magnetite are shown to be almost linear.
It is apparent from the experimental results that the various oxides have markedly different adsorption capacities. Although these results relate to gas adsorption, it is likely that these differing characteristics would apply also to adsorption of molecules and ions from solution.

### 5.2.4.2 Cumulative and Incremental Volume

Porosity was described in Chapter 2 as the volume of pores in a solid which contributes to the internal surface area that influences adsorption. Figures 5.12 and 5.13 provide the trends of cumulative and incremental volumes against pore size (in Å) for each iron oxide tested. What is evident in both figures is that lepidocrocite has a much higher volume of pores (between 100 and 1000 Å), with goethite being the next highest. These results demonstrate the difference between the crystalline forms of each oxide. However, with lepidocrocite and goethite being prepared in a laboratory whereas magnetite and hematite were manufactured commercially, complementary
conditions may not have been employed, which could have some influence on the results. The performance of the set of oxides in adsorption trials is unlikely to be compromised much by this aspect, however, since synthetic routes to all these materials are limited and results for materials prepared in different locations and or batches tend to exhibit only modest variations.

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.
5.2.4.3 Cumulative and Incremental Area

The method for determination of the surface area of each iron oxide and oxyhydroxide used in laboratory trials as described in Chapter 2 is the Brunauer-Emmett-Teller (BET) method, where nitrogen is used as the adsorbate. The surface areas measured for the laboratory-prepared goethite and lepidocrocite and procured hematite and magnetite are within the ranges provided in Table 2.3 of Chapter 2. For the present adsorption trials, Table 5.9 provides the surface areas of the oxides used and tested with Micromeritics Accelerated Surface Area Porosity 2020 instrument.

Table 5.9  Surface areas of synthetic goethite, magnetite, hematite and lepidocrocite.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>25.5</td>
</tr>
<tr>
<td>Magnetite</td>
<td>7.1</td>
</tr>
<tr>
<td>Hematite</td>
<td>10.0</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>66.5</td>
</tr>
</tbody>
</table>

As provided in Table 5.9 and illustrated in Figure 5.14 (cumulative area, m²/g) and Figure 5.15 (incremental area, m²/g), lepidocrocite has the highest surface area, followed by goethite, hematite and magnetite. The surface areas can be compared with the published data of Cornell and Schwertzman (see Table 2.3 in Chapter 2) [19]. Values determined here are within the range of areas reported previously.

The lepidocrocite (surface area 66.5 m²/g) is consistent with that defined in Chapter 2 for crystals containing highly serrated terminals. The goethite (surface area 25.5 m²/g) is consistent with the twinned goethite grown from Fe³⁺ solutions at pH 12 with surface areas <40 m²/g and with acicular samples that range from 30-90 m²/g. The hematite (surface area 10 m²/g) is of similar size to spherical hematite 12.6 m²/g (Table 2.4 of Chapter 2). These spherical particles were non-porous, which confirms the linear isotherm for hematite provided in Figure 5.10. The magnetite (surface area 7.1 m²/g) is also consistent with cubic crystals presented in Chapter 2 of 5.6–6.6 m²/g, which are also reported as non-porous.
Figure 5.14 Cumulative area (m²/g) as a function of pore size (Å) for goethite, hematite, magnetite and lepidocrocite.
The determined isotherms, volumes and surface areas of the iron oxides and oxyhydroxides used for adsorption trials for the removal of selenium and trace elements have identified lepidocrocite as having the highest volume, surface area and pore size, with goethite the second highest. The overall trend observed is fully consistent with previous studies by other researchers but at the lower scale of ranges presented in Chapter 2. Assuming that these gas adsorption studies provide some guide to solution adsorption, it would thus be expected that the adsorption of trace metals will be more efficient with lepidocrocite than goethite, hematite and magnetite.

Whilst the isotherm for lepidocrocite showed this oxyhydroxide to be porous, the isotherms of goethite, hematite and magnetite indicated that these iron oxides were of limited or even for the latter two essentially non-porous. This is also consistent with the results of researchers presented in Chapter 2. Overall, the sizes of the crystals examined are small, which is also apparent from the SEM images presented in this chapter. Thus surface areas are relatively large, but this has not impacted on the observed trends to any clear extent.

5.3 LABORATORY TRIALS OF TRACE METAL ADSORPTION AND/OR COPRECIPITATION

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

From the XRD analysis of iron oxides and oxyhydroxides formed on the surface of solid iron within the pilot plant and through surface reactions taking place with Vales Point ash water, a matrix of laboratory trials was developed in consideration of the outcomes of earlier pilot plant trials.

The following table outlines the basis of the matrix developed in 2007 and employed for laboratory tests undertaken at the University of Newcastle during 2008 and 2009. The matrix employs a known amount of oxide/oxyhydroxide, a controlled
pH, known concentrations of potential adsorbate and other added electrolytes, and a controlled mixing time.

Table 5.10  Laboratory trial matrices employed for studies of the removal of trace elements Se, As, V, Cr, Sb, Al and Mo.

<table>
<thead>
<tr>
<th>Iron Oxide or Oxyhydroxide Weight (g)</th>
<th>pH (Manually adjusted until stable)</th>
<th>Adsorbate (Trace Element) ppm (µg/L)</th>
<th>Electrolyte Composition</th>
<th>Mixing Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>4.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>4.0</td>
<td>250</td>
<td>NaCl</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>250</td>
<td>Nil</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>250</td>
<td>NaCl</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>250</td>
<td>NaCl</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>250</td>
<td>Nil</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>250</td>
<td>NaCl</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>250</td>
<td>Nil</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>250</td>
<td>NaCl</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>9.0</td>
<td>250</td>
<td>Nil</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>9.0</td>
<td>250</td>
<td>Na₂SO₄</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>4.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>7.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
<tr>
<td>5.0</td>
<td>9.0</td>
<td>Actual Concentration</td>
<td>Ash Water</td>
<td>15</td>
</tr>
</tbody>
</table>

The purpose of the trials presented in Table 5.10 was essentially to observe under various conditions the optimum efficiency of reduction of selenium (predominantly selenite), arsenic, vanadium, chromium, antimony, aluminium and molybdenum using 5 g samples of goethite, hematite and magnetite. For the selenium trials, tests were also conducted with 1 g samples of these iron oxides and oxyhydroxides but also included an additional iron oxyhydroxide, being lepidocrocite.
Testing with this latter oxyhydroxide for the other trace metals was not carried out due to the small yield (of only about 70 g) of lepidocrocite prepared in the laboratory due to synthetic limitations.

The solution conditions were varied through the use of differing matrices, including preparations of 250 μg/L standards in demineralised water, and with sodium chloride or sodium sulfate also present. The sodium chloride solution concentration of 7,000 mg/L was chosen based on the sodium concentration of ash water sampled on the 24th July 2008 of 6,770 mg/L. From the same sample, the sodium sulfate concentration of 1,300 mg/L was chosen based on the ash water sulfate concentration of 1,360 mg/L.

The sodium chloride and sodium sulfate solutions were prepared in the laboratory through dilution of analytical grade reagents in volumetric flasks of 1000 mL capacity. Ash water trace metal analysis was undertaken with samples obtained in 2008 and 2009 with the range of test results provided in Table 5.11 below. The 250 μg/L trace metal standards in 500 mL aliquots were prepared from concentrated analytical grade standards with specifications given in Table 5.11 below.

Table 5.11 Trace Metal Standard Solution Specifications and Ash Water Trace Metal Analysis

<table>
<thead>
<tr>
<th>Trace Metal</th>
<th>Chemical Formula</th>
<th>Reagent Specification (1,000 mg/L ±5)</th>
<th>Range Ash Water Trace Metal Analysis 2008-09 (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>Se</td>
<td>ARC (2% HNO₃)</td>
<td>32–37</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>ARC (2% HNO₃)</td>
<td>5–6</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>Scharlau (5M HNO₃)</td>
<td>18–28</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>Scharlau (5M HNO₃)</td>
<td>2–9</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>Scharlau (2M HCl)</td>
<td>13–36</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>Scharlau (5M HNO₃)</td>
<td>20–50</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Na₂MoO₄.2H₂O</td>
<td>Univar (99-102% powder)</td>
<td>99–102</td>
</tr>
</tbody>
</table>

Each test solution were prepared in 500 mL Nalgene High Density Polyethylene (HDPE) bottles by firstly weighing in 1.00 or 5.00 g of the iron oxide or oxyhydroxide on a 310 g electronic FX-300 top pan balance to an accuracy of ± 0.001 g. The standards prepared in 500 mL volumetric flasks with varying matrices were then added to the oxides contained in the HDPE bottles, and the screw top lids fitted. The bottles were shaken slightly and then the pH adjusted (NaOH and HNO₃) according to the
matrix provided in Table 5.10. Prior to commencement of each trial, the Eutech pH meter was calibrated with buffer solutions of pH 4, 7 and 10. During pH adjustment of the samples, the pH was periodically checked. Once the pH reading was stable at the desired pH required, the sample was placed in a Ratek R4 Mixer which holds two sample containers. After preparation of two samples, the mixer was set at the highest speed, which equated to 1 revolution per second. All samples were mixed for a period of 15 minutes.

After the 15 minute mixing time concluded, samples were placed on the laboratory bench for 5 hours to allow the suspension to settle. After this period, samples were collected in 100 mL polyethylene bottles by extraction with Terumo 10 mL syringes and filtered through 0.45 µm Millipore cartridge filters. The settling period was determined based on initial trails, during which the suspension of the oxide material was observed to take hours to settle sufficiently to allow sampling from the top of the container. The resting period also allowed time for maximum adsorption to be achieved. Each sample was preserved with 3 drops of nitric acid and immediately after sampling stored in the laboratory refrigerator. Sets of samples were then dispatched to the Australian Laboratory Services (ALS) facility in Sydney to be analysed as dissolved metals by Octopole Reaction Cell-Inductively Coupled Plasma Mass Spectrometer with the Practical Quantitation Limits (PQL) presented in Table 5.12.

Table 5.12 Trace metal limits of reporting for analysis by ALS with ORC-ICPMS.

<table>
<thead>
<tr>
<th>Trace Metal</th>
<th>Limit of Reporting (µg/L)</th>
<th>ALS Method Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.5</td>
<td>Dissolved Metals by Ultra Trace ALS Method EG094F ORC/ICPMS Octopole Reaction Cell (ALPHA 3125B)</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Antimony</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Molybdenium</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Each batch of test results was checked through analysis of general trends. Any result considered to be erroneous was retested and results compared with initial tests.
Selenium (total) was analysed separately by the CSIRO Laboratory at Lucas Heights, using Atomic Fluorescence test method CAAC/AFSO2 with a Practical Quantitation Limit of 0.1 µg/L.

5.3.1.1 Selenium Adsorption/Coprecipitation

A number of studies, as provided in Chapter 2, all demonstrate the adsorption/coprecipitation or sorption of selenite onto goethite, hematite, lepidocrocite and magnetite is at a maximum in the acid region and diminishes as the pH rises above 10. This trend was also observed throughout the present laboratory trials, with procured or laboratory synthesised iron oxides and oxyhydroxides for the removal of selenite. Another trend which is evident from previous researchers, and is confirmed during these laboratory trials, is that the more abundant or higher the surface area of the iron oxide material, the higher is the removal efficiency.

The following sections provide the analytical trends of the selenium (selenite) trials, along with the examination of the effects of differing solution matrices in comparison to the Vales Point ash water trends.

5.3.1.1.1 Selenium Removal with Goethite

The trends provided in Figures 5.16 and 5.17 on the following page for selenite adsorption/coprecipitation using both 1 and 5 g of goethite present very little difference, with reductions of greater than 245 µg/L (from an initial value of 250 µg/L) for pH levels below 6 observed for all solution matrices, including ash water. Above pH 6, the removal of selenite is quite different between the samples. However, with the higher mass of goethite, the trends from tests with 5 g of this oxyhydroxide displayed a high efficiency (greater than 245 µg/L removed). This is to be expected if pH-induced limits on available sites for adsorption are being imposed, as a greater amount of goethite provides more sites. The sample containing 1 g of goethite displays a substantial variance, in the order of 5 up to 30 µg/L, depending on the solution matrix. It should be noted, nevertheless, that selenite in ash water at pH 9 was still being removed to the order of ~245 µg/L. The selenite sample in demineralised water, however, was not as efficiently adsorbed but still was reduced by ~220 µg/L. This variation suggests that
the high ionic content of ash water has an effect on either the inner-sphere or outer-

There is also a noticeable step at pH 8 in the trends with 1 g of goethite. In
Chapter 2, the study by Rovira et al. [2] using both natural goethite and hematite to
determine the sorption of selenite and selenate also profiles a shift between pH 6 to pH
8. Their application of the triple-layer model concluded that, for natural goethite,
surface complexation of selenite was via a mixture of a monodentate inner sphere
deprotonated and surface protonated complexes. This may also explain why ash water,
with its variant ionic species and ionic strengths, has the propensity to successfully
react with surface iron hydroxyl groups forming complexes of anions present, and is
likely to also promote the formation of inner sphere complexes through local surface
charge reduction due to these bound anions.

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.
Selenium Removal with Goethite (5g) at Different pH Levels
Original Concentration 250 (µg/L) (Ash Water Concentration as Analysed)

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.

5.3.1.1.2 Selenium Removal with Hematite

The trends for removal of selenite with hematite are not that dissimilar to those with goethite. The efficiencies of the adsorption/coprecipitation for ash water with 5 g of goethite and hematite are almost identical. Once again there is a step at pH 8, with selenite prepared in demineralised water exhibiting a substantially higher step. With 1 and 5 g of hematite, only 115 µg/L and 220 µg/L of selenite (from an initial value of 250 µg/L) was adsorbed/coprecipitated respectively.

In the Rovira et al. study, sorption of selenite was found to be higher for natural hematite than goethite [2]. However, it is evident that for synthetic hematite and goethite utilised in these trials there is little difference.

One difference which is observed between the goethite and hematite trends is the trend with sodium sulfate. The hematite trial displays the lowest selenite concentration or highest adsorption between pH 5 to 8; below and above these pH levels, the adsorption/coprecipitation of selenite is less. This observation could be a result of competition by the sulfate ions, which may not just compete in the formation of outer sphere complexes but inner sphere complexes. The ability of sulfate ion to chelate may be important, which may explain why sodium chloride did not provide a similar trend, as chloride ion does not have this capability. This behaviour was observed by Duc et al. [3] in experiments on sorption of selenite on hematite with two ionic strengths of sodium nitrate; nitrate is a poorer chelate than sulfate due to its
smaller ‘bite’ angle. In their summation of the effects of sodium nitrate, Duc et al. [3] assert that weakly bound ions such as nitrate and chloride can only compete with outer sphere complexes. Cornell and Schwertmann state that “selenite, sulphate and phosphate form binuclear, bidendate surface complexes with two continuous, singly coordinated hydroxyls on goethite” [19]. They also suggest from other studies this is the case for sulfate on hematite and lepidocrocite as well. What is interesting about the sulfate trend with selenite adsorption/coprecipitation on hematite is the slight change at the lower pH values of 5 to 4. This was not observed for gothite and magnetite. Its origin is unclear.

The trial with 1 g of lepidocrocite did provide a similar trend, but at much lower concentrations of selenite remaining, in the range of 2 to 3 µg/L. With 1 g of hematite, the variance between test results was in the range of about 8 to 43 µg/L of residual selenite.

Figures 5.18 and 5.19 provide the adsorption/coprecipitation trends of selenite with 1 and 5 g of hematite.

![Selenium Removal with Hematite (1g) at Different pH Levels](image)

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.
Selenium Removal with Hematite (5g) at Different pH Levels
Original Concentration 250 (µg/L) (Ash Water Concentration as Analysed)

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.

5.3.1.1.3  Selenium Removal with Lepidocrocite

Due to the small amount of lepidocrocite synthesised in the laboratory, trials used only 1 g of this oxyhydroxide. For the ash water samples alone were tests with both 1 and 5 g of lepidocrocite conducted. Results appear in Figures 5.20 and 5.21.

Selenium Removal with Lepidocrocite (1g) at Different pH Levels
Original Concentration 250 (µg/L) (Ash Water Concentration as Analysed)

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.
lepidocrocite has revealed a slightly higher efficiency for removing selenium through the adsorption/coprecipitation process in all matrices, with the exception of one sample which was prepared in demineralised water and had a pH adjustment to 9. A high adsorption/coprecipitation capacity for selenite was also observed with the other iron oxides and oxyhydroxides. The higher absorbance of selenite on lepidocrocite compared with other species seen here was also observed by Parida et al. [11] in their experiments on the adsorption of selenite as a function of equilibrium pH [11]. The higher absorbance is also consistent with the higher surface area of lepidocrocite. Once again, the trend for percentage adsorbed tapered off to lower levels after pH 6.

During the settling period and filtering of samples, the iron oxides and oxyhydroxides prepared with demineralised water remained in suspension and did not settle to the bottom of the containers like other preparations and in particular samples for pH 9 were difficult to filter. It is likely that the behaviour is a result of the low or negligible ionic content of the samples along with the negatively charged surface due to the $\text{pH}_{\text{pzc}}$ (point of zero charge) of the iron oxides and oxyhydroxides above pH 8.

### 5.3.1.1.4 Selenium Removal with Magnetite
Magnetite was the least efficient iron oxide for adsorption/coprecipitation of selenite, but the trends as a function of pH with 5 g of the iron oxide were similar to those of the other three in that the amount of selenite removed for all matrices was high and reasonably constant until pH 6, after which it starts to slightly diminish in efficiency up until pH 8, beyond which its removal capacity rapidly decreases.

The selenite adsorption/coprecipitation trends using 1 g of magnetite resembles the sorption of selenite as a function of pH in the Martinez et al. [16] experiment; they used 0.1 g magnetite and a selenite solution concentration of $2 \times 10^{-5}$ mol dm$^{-3}$ [4]. As discussed in Chapter 2, Martinez et al. [16] had found anionic selenite best fitted the two inner sphere complexes $\langle \text{FeOHSeO}_3 \rangle^{2-}$ and $\langle \text{FeOSeO}_3 \rangle^{-}$. The Vales Point ash water with magnetite had the highest removal efficiency of all matrices studied, as was the case with the other iron oxides and oxyhydroxides. Even with only 1 g of magnetite at pH 9, the residual solution concentration of selenite was 19.3 µg/L after 5 hours of contact, down from the initial concentration of 250 µg/L. This represents a reduction in the order of 96%. Figures 5.22 and 5.23 provide the adsorption/coprecipitation trends for 1 g and 5 g of magnetite.

![Selenium Removal with Magnetite (1g) at Different pH Levels](image)

**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.
5.3.1.1.5 **Discussion**

From all selenite adsorption/coprecipitation trends presented in sections 5.3.1.1.1 to 5.3.1.1.4, the overall efficiency of removal of selenite with iron oxides and oxyhydroxides exhibits the following order: lepidocrocite > goethite > hematite > magnetite. The surface area of these oxides also follows the same order from highest to lowest. In these laboratory trials at pH 8 and above, all systems displayed the following efficiency of removal in terms of the matrix of the solution: ash water > sodium chloride solution > sodium sulfate solution > demineralised water. The higher efficiency of removal of selenite from ash water may be related to the types and abundances of cations and anions present which includes monovalent and divalent ions such as $K^+$, $Na^+$, $Cl^-$, $F^-$, $SO_4^{2-}$, $Mg^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Al^{3+}$, $B^{3+}$, and others. There may be some cooperative ion pairing effects present. This mixture of cations and anions may aid in the formation of outer sphere and inner sphere selenium complexes, perhaps through elimination of competing adsorption sites or through an alteration of the electrostatic attraction of surface hydroxyl groups. The lower initial concentration of selenium in the ash water (~10% that of the standards prepared) may also play a role. The benefit of this phenomenon is the ability of iron oxides and oxyhydroxides to adsorb/coprecipitate selenite even at relatively high pH values. With
the pH of Vales Point ash water fluctuating from pH 7.5 to 8.5, this is an important aspect, given that the efficiency of other matrices was somewhat lower beyond pH 8.

5.3.1.2 Arsenic Adsorption/Coprecipitation

Arsenic in Vales Point ash water is not as abundant as selenium, but nevertheless a reduction in this trace metal is a benefit to the receiving environments. The following sections outline the adsorption/coprecipitation laboratory trials of arsenic using 5 g of goethite, hematite and magnetite and differing matrices (though identical to those used for the selenium trials).

Studies of the arsenic species arsenate(V) and arsenite(III) which were presented in Chapter 2 with a range of iron oxides, including investigations with Nano Zero Valent Iron (NZVI), will be drawn upon in the analysis of the following adsorption/coprecipitation trends.

5.3.1.2.1 Arsenic Removal with Goethite

The adsorption/coprecipitation of arsenic with 5 g of goethite (Figure 5.24) leads to greater than 99% removal. Most of the arsenic was removed from all matrices at all pH values between 4 and 9. The only slight increase in arsenic analysed was in the solution containing sodium sulfate, where at pH 4 and 9 the test results were very slightly above 0.2 µg/L at 0.4 and 0.6 µg/L. However, this variation is in the range of the limit of reporting of 0.5 µg/L.

The observed trend is consistent with the study undertaken by Manning et al. [4] with goethite as the adsorbing medium, who found that the sorbed arsenic in the forms of As(III) and As(V) after 24 hours was in the order of 99.7%. The fact that the reaction occurred in 5 hours illustrates how efficient this oxyhydroxide acts to remove arsenic under differing solution conditions.

Whilst lepidocrocite was not examined during these arsenic adsorption/coprecipitation trials, it should be noted that Manning et al. [4] had treated As(III) and As(V) with rust containing lepidocrocite. The percentage remaining in solution, as presented in Table 2.9 in Chapter 2, was 1.95% for As(III) and 0.19% for As(V), with an overall efficiency of removal of 97.9%.
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.

**5.3.1.2.2 Arsenic Removal with Hematite**

The efficiency of arsenic removed with 5 g of hematite illustrated in Figure 5.25 is essentially identical to that achieved with goethite for all matrices in the pH range of 3 to 9. The test solutions containing sodium sulfate for pH 4 and 9 yielded a slight decrease in the amount adsorbed/coprecipitated, consistent with the goethite trend, with residual levels of 1.4 and 1.1 µg/L respectively, along with the demineralised water test result of 1.4 µg/L at pH 9. There would appear to be an effect on the efficiency of removal, but it is so low and close to the accuracy of the determination that it is not significant.

As cited in Chapter 2, the effects of anions including sulfate were examined by Sun *et al.* [6], who found that low concentrations of sulfate cause inhibition of the removal of arsenic(V), while the effect was enhanced with high concentrations of above 600 mg/L Na$_2$SO$_4$ [6]. Notably, the concentration of Na$_2$SO$_4$ in these trials is 1,360 mg/L.

What is interesting with comparison of this arsenic study using arsenic(V) as the standard solution and the study by Manning *et al.* [5] is that, whilst As(V) was not detected in solution after 24 hours, As(III) was not reduced in concentration at all. This indicates that the species present in the Vales Point ash water is As(V), as nearly all
was adsorbed/coprecipitated in all test results from pH 3 to 9. It should also be noted that the pH used in the Manning et al. [5] investigation started at 5 with no further adjustments; however, this is a pH at which As(V) is efficiently removed.

![Arsenic Removal with Hematite (5g) at Different pH Levels](image)

**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.

### 5.3.1.2.3 Arsenic Removal with Magnetite

The efficiency of arsenic removal with magnetite between pH 3 and 7 in all matrix solutions (Figure 5.26) is the same as that found with goethite and hematite. However, at pH 8 to 9 the adsorption/coprecipitation of arsenic is less, except for the ash water sample. Once again, Manning et al. [5] observed for As(V) treated with magnetite at pH 5 no detectable residual levels in solution measured after 24 hours. No As(III) was adsorbed by magnetite, which reinforces the notion of the dominant species of arsenic present in ash water being As(V) as the arsenate \(H_3AsO_4\).
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.

5.3.1.2.4 Discussion

The order of efficiency of the adsorption/coprecipitation process is not so clear-cut with the arsenic trials between pH 3 and 7 as found for selenium removal. Above pH 8, magnetite presents as being the least efficient; this is consistent with the results of the selenium trials.

It is likely the main form of arsenic in ash water is As(V). The study by Sun et al. [6] discussed in Chapter 2 found that in aerobic systems As(III) is oxidised to As(V). As such, any As(III) present in ash water would be transformed to As(V) and subsequently adsorbed onto the iron oxides and oxyhydroxides present.

5.3.1.3 Vanadium Adsorption/Coprecipitation

As also discussed in more detail in Chapter 2, vanadium is mostly likely to exist in the +5 state in oxic seawater. Given that the Vales Point ash water is saline through make up with estuarine lake waters, vanadium will be present in the +5 state.

The concentration of vanadium in Vales Point ash water sampled in 2008 to 2009 was in the same order of magnitude as selenium, and between 18 and 28 µg/L. The following adsorption/coprecipitation trials were undertaken with 5 g of goethite,
hematite and magnetite. Again matrices of sodium chloride, sodium sulfate and demineralised water as used earlier were employed.

5.3.1.3.1 **Vanadium Removal with Goethite**

The removal of vanadium is not dissimilar to that of arsenic and selenium in that it is highly efficient, with removal being of the order of greater than 99%. The test results for all trends with the exception of sodium chloride all had residuals of ~0.2 µg/L, which is below the limit of reporting of 0.5 µg/L. The sodium chloride trend alone stands out from the others, as the test results from pH 4 to 9 show a continuous increase in residual solution concentration from low pH to pH 9. This may be attributable to site competition by the chloride ion. The effect is only small, however.

![Vanadium Removal with Goethite](image)

**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.

5.3.1.3.2 **Vanadium Removal with Hematite**

Similar to the adsorption/coprecipitation of arsenic onto 5 g of hematite, vanadium for all matrices (with the exception of one test result for ash water at pH 3) all showed greater than 99% vanadium removed from solution or to levels of 0.2 µg/L, which again is below the limit of reporting of 0.5 µg/L.

Trends for vanadium adsorption on goethite in Chapter 2 display a decrease in adsorption below pH 3, but this trend was not evident in the goethite trials presented.
above. This reduction in vanadium adsorption, which is really not significant, could be due to the way vanadium, which is most likely in the form of VO$_3$(OH)$^-$, is adsorbed on hematite, or may arise from further partial protonation forming a poorly adsorbed neutral species. A repeat analysis for this test confirmed that it is not just due to analytical error.

![Vanadium Removal with Hematite](image)

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.

### 5.3.1.3.3 Vanadium Removal with Magnetite

As observed from trends with previous studies using magnetite, the reaction efficiency remains high from pH 3 to 7, then drops at pH 8 and above. What is evident from the vanadium trends here, however, is the slight increase of vanadium in the sodium chloride matrix from pH 4 to 9. This slight decrease in the removal of vanadium was also observed in the goethite trend for the sodium chloride matrix, which indicates that there might be slight competition from chloride ions in the formation of surface complexes.

The greater reduction in adsorption/coprecipitation for the sample prepared with demineralised water at pH 9 is consistent with trends for magnetite adsorption of selenium and arsenic. This again is no doubt due to the low ionic strength of the sample and the pH level being above the pH$_{pzc}$. 
Vanadium Removal with Magnetite (5g) at Different pH Levels
Original Concentration 250 (ug/L) (Ash Water Concentration as Analysed)

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.

5.3.1.3.4 Discussion

Unlike selenium and arsenic, vanadium, apart from forming complexes VO$_2$(OH)$_2^-$ and VO$_3$(OH)$_2^-$ capable of adsorption, can also form didentate corner-sharing Fe$_2$O$_2$V(OH)$_2^+$ and Fe$_2$O$_2$VO(OH)$_0^0$ surface complexes (see Chapter 2). The difference in the ability of vanadium to form both weaker adsorption bonds on the surface and strong inner-sphere Fe bonded species compared with the behaviour of other target species could explain why vanadium has the highest efficiency for adsorption/coprecipitation, not just with synthesised iron oxides but also with naturally produced iron oxides, as was evident from the pilot plant trials. The slight reduction in the adsorption of the vanadium solution in the sodium chloride matrix could be due to competition of the chloride ion for the didentate corner-sharing iron bonding sites.

5.3.1.4 Chromium Adsorption/Coprecipitation

Chromium(III) is the predominant chromium form present in Vales Point ash water and as such was chosen for the adsorption/coprecipitation trials. Like arsenic, the concentration of Cr(III) in ash water is low (of the order of 2–9 mg/L, with the limit of reporting for this element being 0.5 mg/L). The trends for Cr(III) adsorbed onto 5 g of goethite in the following section are quite different to those for hematite and magnetite.
There is a definite maximum adsorption/coprecipitation of Cr(III) occurring at pH 5 and 6 which is not observed with the other iron oxides. For the other two iron oxides, as illustrated in the following sections, the change in pH in all matrices does not have an observed influence on the amount of Cr(III) removed from solution.

5.3.1.4.1 Chromium Removal with Goethite

Cornell and Schwertmann [19] reported that chromium adsorbs as the Cr$^{3+}$ cation over the pH range 2.5–4 on both ferrihydrite and goethite. This is not the case with the present Cr(III) adsorption/coprecipitation trials, as the maximum Cr(III) adsorption for all solution matrices occurs in the pH range 5–6. At lower pH levels, as illustrated in Figure 5.30, the amount of Cr(III) removed from solution decreases sharply. Nevertheless, over 90% is removed across the pH range 3–9.

![Chromium Removal with Goethite (5g) at Different pH Levels](image)

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.

5.3.1.4.2 Chromium Removal with Hematite

The following trends for Cr(III) adsorption/coprecipitation with 5 g of hematite illustrates how under varying matrix conditions this cation can be efficiently removed from solution (~99%). The only samples which displayed a slight variation were the sodium sulfate samples at pH 3, 5 and 6, which were substantially higher in Cr(III)
concentration than other test results. Also the sodium chloride sample at pH 4 gave an anomalous result.

Cornell and Schwertmann reported that anions such as chloride adsorb specifically on iron oxides, and for anions adsorption is highest for low pH values [19]. This could explain the sodium chloride result at pH 4, in that the reduction in Cr(III) adsorption may be a result of the chloride ion competing for hydroxyl groups on hematite. The very slight decrease in Cr(III) adsorption in the three sodium sulfate samples at pH 3 to 6 could also be a result of competition limiting the number of surface hydroxyl groups available for Cr(III). At the low levels involved, however, there is little value in extended speculation; overall, removal is still exceptionally high in all cases.

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.

5.3.1.4.3 Chromium Removal with Magnetite

The Cr(III) trends with 5 g of magnetite (Figure 5.32) are almost identical to those of hematite, except magnetite is more efficient in the removal of Cr(III). This observation differs from trends observed for the previous trace elements, where magnetite produced less efficient adsorption/coprecipitation trends.
Once again, Cr(III) reacting in the sodium chloride solution at pH 4 is considerably reduced, which reinforces the prospect that competition is occurring due to the chloride ion in solution either adsorbing more specifically onto the magnetite or possibly even forming chlorochromium(III) complexes of reduced charge that have a much reduced affinity for the surface.

![Chromium Removal with Magnetite (5g) at Different pH Levels](image)

**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.

### 5.3.1.3.4 Discussion

The Cr(III) trials using hematite and magnetite illustrate that high adsorption/coprecipitation efficiencies can be achieved across a large pH range. Despite the tendency for reduced adsorption using synthetic matrices containing chloride ion, ash water samples at pH 4 where the chloride ion content is high displayed no diminution of Cr(III) removal. Perhaps the presence of numerous cations and anions in ash water inhibits chloride ion from adsorbing specifically onto the iron hydroxyl surface to a significant amount through competition.

For the goethite trials, the optimum pH for adsorption/coprecipitation of Cr(III) was in the range of 5 to 6. Beyond these pHs, the amount of Cr(III) removed from solution decreases substantially, but is still significant.
5.3.1.5 Antimony Adsorption/Coprecipitation

The antimony adsorption/coprecipitation trends with 5 g of goethite, hematite and magnetite are quite different for the ash water samples at various pH levels than with other solution matrices. Reflecting the behaviour of most other systems, the trends for antimony removed from other solution matrices are higher at lower pH levels.

During the pilot plant trials with steel wool, the efficiency of removal of antimony was the same as selenium, at 87%. The concentration of antimony in ash water samples taken during 2008 and 2009 was in the range of 13 to 36 µg/L. The following sections provide the antimony trends with different synthetic matrices other than ash water, including sodium chloride, sodium sulphate and demineralised water.

5.3.1.5.1 Antimony Removal with Goethite

Between the pH values 4 to 6, antimony displays the highest adsorption with goethite (5 g samples) and in all solution matrices trialled. At pH levels above 6 the adsorption/coprecipitation of antimony decreases (Figure 5.33). In the case of ash water the decrease is significant, given the low concentration of antimony present. This experimental observation is similar to studies outlined in Chapter 2, where, in the study by Leuz et al. (2006) high adsorption envelopes occurred for goethite in the neutral to acid region in the pH range of 3 to 7, with decreasing sorption from pH 7 to 12 [7].

The sorption studies presented in Chapter 2 for goethite shows Sb(V) forms an inner-sphere edge sharing complex. Martinez-Lladó et al. [16] proposed the following complexation equation for antimony sorption on goethite:

\[
\text{Fe(OH)}_2 + \text{Sb(OH)}_6^- = \text{FeO}_2\text{Sb(OH)}_4^- + 2\text{H}_2\text{O} \quad (1)
\]

In their sorption studies, the model was determined to be a didentate edge sharing surface complex. The role of competing ions has not been explored, however, so that in the complex ionic matrix found in ash water there could be limitations for antimony adsorption or coprecipitation, and this may explain the ash water trends with hematite and magnetite.
5.3.1.5.2 **Antimony Removal with Hematite**

The trends for antimony reacting with 5 g of hematite (Figure 5.34) show that greater than 99% efficiency was achieved in all solution matrices developed in the laboratory, as opposed to the ash water samples which were only pH adjusted. Clearly, pH 6 provides the optimum condition for antimony removal (down to a residual of 2.6 µg/L). At pH levels higher and lower than pH 6 it is likely that the reduction in the adsorption of antimony is due a combination of pH-dependent antimony speciation and to the effects of other cations and anions present in the Vales Point ash water which could interfere with antimony adsorption or coprecipitation.

The antimony inner-sphere edge or didentate edge surface sharing complexes may be more affected by competing ions than other non-specific sorption mechanisms; this may account for the observed ash water results with hematite. The trends observed for antimony adsorption with hematite demonstrate that the ash water trend does not appear to be a result of sodium, chloride or sulfate ions, as the effect of these anions and cation would have been evident from trends in synthetic matrices with these chemical constituents. Either a concerted effect of a suite of such ions is involved, or else other ions present in the ash water are responsible, through competitive binding,
for the lower efficiency of antimony removal in ash water. The presence of Sb(V) at higher pH levels forms the Sb(OH)$_6^{3-}$ species which is less likely to attach to the surface of hematite. Regardless, over 95% removal of antimony is still achieved in ash water across the pH range 3–9.

![Figure 5.34](image)

**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.

### 5.3.1.5.3 Antimony Removal with Magnetite

The maximum amount of antimony removed for ash water occurs at pH 4 to 5 (Figure 5.35). At higher pH values the removal of antimony gradually decreases. It appears for this iron oxide that the influence of the pH$_{pzc}$ leads to a narrower profile, with residual antimony rising from pH. The efficiency of antimony removal for all other matrices is high across the broader pH range of from 4 to 6, beyond which it only slightly decreases, but the changes in levels are not significant. Nevertheless, even for ash water, removal efficiency is over 90% under the worst pH conditions, and ~99% efficiency is achieved at optimum pH values.
Antimony Removal with Magnetite (5g) at Different pH Levels
Original Concentration 250 (ug/L) (Ash Water Concentration as Analysed)

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.

5.3.1.5.4 Discussion

From the antimony adsorption/coprecipitation profiles presented for synthetic goethite, hematite and magnetite from laboratory trials with ash water, it is perhaps surprising that in the pilot plant trials with steel wool antimony could still be removed at an efficiency of 87%, given the pH of the ash water resides predominantly between 7.5 and 8.5. Laboratory-controlled experiments produce only ~90% removal in this pH range, indicating that high efficiency is achieved in the pilot plant. The high surface area of the steel wool may be a contributing factor. It is comforting to find that the laboratory model and field trials yield comparable outcomes.

5.3.1.6 Aluminium Adsorption/Coprecipitation

The laboratory trials of aluminium varied for goethite, hematite and magnetite at the lower and higher pH values. At neutral pH, the amount of aluminium removed in ash water and in other solution matrices by 5 g of each iron oxide is uniformly very high. The average removal of aluminium from the pilot plant trial utilising steel wool
was not high, however, at only 21%. This result is surprising, given that the efficiency of removal during laboratory trials was very high at pH levels of 6 to 8, which is in the pH domain of Vales Point ash water.

The following sections provide the aluminium removal trends, again with different matrices other than ash water, including aqueous sodium chloride, aqueous sodium sulfate and demineralised water.

5.3.1.6.1 Aluminium Removal with Goethite

The adsorption of aluminium onto goethite was investigated by Lovgren et al., and was found to occur between pH values of 3 to 8.5 [8]. This is slightly different to what was found in this adsorption/coprecipitation trial. What was found in the present goethite laboratory trials was a slight shift in the profile, with an adsorption maximum in the pH range of 4 to 9.

Lovgren et al. [8] proposed that the adsorption onto goethite best fits two monodentate surface hydroxo complexes $\equiv$FeOAlOH$^+$ and $\equiv$FeOAl(OH)$_2$ with the former represented by the following equation [8]:

$$\equiv\text{FeOH} + \text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{Fe-O-AlOH}^+ + 2\text{H}^+ \quad (2)$$

They also suggested that the strong affinity of aluminium for the goethite surface causes an initial Al(III)-substituted goethite to form.

Figure 5.36 shows that, for ash water and solution matrices with sodium chloride present, the aluminium can be almost completely adsorbed/coprecipitated between pH 5 to 9. At pH 4 to 9, the solution containing sodium sulfate and pure demineralised water also demonstrate very high removal efficiencies. This is the same as the trends established for vanadium, although the mechanisms for adsorption are somewhat different.

At pH 4, the solution containing sodium chloride only had about 60% of the aluminium adsorbed/coprecipitated. It is likely there is competition for the aluminium complexes on the surface of goethite from chloride ions, which inhibit aluminium being sorbed. Although not observed at higher pH values in the model system, a role for chloride ion in the plant environment may play a role in driving the low removal efficiency observed in that case.
5.3.1.6.2 Aluminium Removal with Hematite

The adsorption/coprecipitation removal of aluminium with 5 g of hematite between pH 5 to 7 has essentially the same profile as that found with goethite, in that over 98% of aluminium for the laboratory-made solutions is adsorbed onto hematite. There is, however, a difference with the behaviour at pH 4, where for all matrices the amounts removed in the sodium sulfate solution and demineralised water are only about 50%, whereas no aluminium was adsorbed/coprecipitated from the sodium chloride matrix at pH 4. Presumably the formation of $\equiv$FeOAlOH$^+$ is inhibited by chloride ions competing for the positive charge, or else lower charged and poorly binding complexes form. Whereas removal of aluminium in chloride-rich ash water is greater than 95% between pH 6 to 9, again (consistent with other matrices) at lower pH levels aluminium does not appear to be adsorbed/coprecipitated well. Slow coordinated water exchange in the relatively inert Al(OH)$_2$$_6^{3+}$ ion, the species dominant at low pH, compared with water exchange in hydroxo-species present at higher pH, such as Al(OH)$_2$$_3$(OH)$^{2+}$, may contribute, since this exchange process is an essential step prior to binding to surface groups.
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.

5.3.1.6.3 Aluminium Removal with Magnetite

The removal of aluminium with 5 g of magnetite provided trends which are similar to trends reported for goethite and hematite, in that the highest adsorption/coprecipitation occurs between pH 5 to 8. The only anomaly with this iron oxide was with the solution prepared in demineralised water. At pH 8, the efficiency of aluminium removal decreases and at pH 9 only 80 µg/L is adsorbed. This occurrence is likely to be directly related to there being no other added ions in solution except for aluminium and the sodium hydroxide added to stabilise the pH at 8 and 9. Drops of nitric acid to stabilise the sample were also added to sample container but NO₃⁻ is non-complexing. Perhaps in this case the monodentate surface hydroxo complex ≡FeOAl(OH)₂ is not as abundantly formed and that formation of gel-like Al(OH)₃ is more prevalent. The latter can be so fine that it is carried through micro-filters and thus can be detected in analyses. At pH 5, the only reduction in the amount of aluminium removed from solution occurs with sodium sulfate and sodium chloride solutions. The ash water samples below pH 6 are also slightly lower in residual concentration,
behaviour which also occurred for goethite and hematite samples. Overall, efficiency of removal is very high between at least pH values of 5 to 8 (Figure 5.38).

![Aluminium Removal with Magnetite (5g) at Different pH Levels](image.png)

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.

### 5.3.1.6.4 Discussion

From all laboratory trials with goethite, hematite and magnetite the highest efficiency for aluminium adsorption/coprecipitation occurs between the pH ranges of 5 to 8, irrespective of the oxide form used. In terms of efficiency of removal at the optimum pH, hematite is very slightly better than goethite and magnetite; however, given the analytical error for the determination of aluminium in solution, there is probably no significant difference in how these iron oxides and oxyhydroxides perform.

The low efficiency of aluminium removed during the pilot plant trials is notable, and unexpected based on laboratory trials. The variation may relate to the competitive loading of surfaces in the pilot plant over extended periods of time, conditions that do not relate to limited time-controlled laboratory experiments. Inertness and hence ligand exchange reactions of aluminium(III) are high compared with a range of other metal ions, as is its tendency to undergo hydrolysis to lower-charged species; these may
contribute to reduced binding. Variation in pH in the pilot plant during the extended study may also contribute.

The formation of species such as $≡\text{FeOAlOH}^+$ and $≡\text{FeOAl(OH)}_2$ complexes at the iron oxide and oxyhydroxide surface is likely to occur between pH 5 to 9 for goethite and hematite and pH 5 to 8 for magnetite. Overall, observations imply that natural waters of near-neutral pH should be appropriate for aluminium adsorption on oxidic iron surfaces.

### 5.3.1.7 Molybdenum Adsorption/Coprecipitation

Studies of the removal of molybdenum in sea water presented in Chapter 2 defined the optimum pH as occurring at a low pH of around 4. The higher the pH of the solution, the less molybdenum is removed from the process. Thus it is not surprising that molybdenum removed by the pilot plant trials was low (only ~14%) given that the pH of ash water is in the range 7.5 to 8.5.

The laboratory trials with goethite and magnetite confirms the trends observed by Kim and Zeitlin using iron(III) hydroxide [9]. However, hematite trends with matrices containing sodium chloride and sodium sulfate, and also demineralised water, displayed slightly higher concentrations below pH 5 and above pH 8.

#### 5.3.1.7.1 Molybdenum Removal with Goethite

Goldberg and Foster [10] found the pH at which essentially no molybdenum is adsorbed onto goethite was ~8. During the present laboratory trials (Figure 5.39) the pH at which adsorption/coprecipitation starts to decrease is pH 7, with a reduction in the amount removed observed in ash water and other synthetic matrix solutions. Below pH 7, the amount removed is in the order of 99% in all matrices. Above pH 9, ash water appears to remove the least amount of molybdenum with only about 4 to 20% removed in this region.

During the molybdenum study by Goldberg and Foster [10], discussed in Chapter 2, they also found the adsorption onto goethite was not affected much by other ions in solution. Trends observed in this study indicate modest effects of other ions (Figure 5-39). For example, results in demineralised water differ little from those in
ash water, consistent with the finding of Goldberg and Foster [10] that removal of molybdenum with goethite showed little ionic strength dependence. While sodium chloride and sodium sulfate solutions displayed some differences, even at pH 9 ~90% of molybdenum was removed from solution, so the overall behaviour does not vary significantly.

![Molybdenum Removal with Goethite (5g) at Different pH Levels](image)

**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.

### 5.3.1.7.2 Molybdenum Removal with Hematite

Hematite displays the highest adsorption capacity in all matrices, including ash water, at pH 6. The trends presented for molybdenum adsorption with hematite are somewhat different to those seen for goethite in that at pH values below 6 the amounts removed for aqueous sodium chloride, aqueous sodium sulfate and demineralised water are actually reduced. The demineralised water sample at pH 4 removed only ~90% compared with essentially complete removal in ash water. Whilst less efficient, it is not a marked effect, and the difference in the amount of molybdenum removed from sodium chloride and sodium sulfate matrices compared with ash water is even less significant.
The efficiency in removal of molybdenum at pH 8 is greater overall with hematite than goethite. For example, the residual solution concentration is 37 µg/L with hematite compared with 80 µg/L for goethite. The increasing adsorption after pH 7 indicates a shift in the influence of the point of zero charge for hematite, which was also seen for goethite. Beyond the pzc, it is expected that the reduction in the amount of molybdenum removed from solution will continue to rise with increasing pH, as observed (Figure 5.40).

![Molybdenum Removal with Hematite (5g) at Different pH Levels](image)

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.

### 5.3.1.7.3 Molybdenum Removal with Magnetite

The molybdenum removal trends using magnetite are almost identical to those using goethite, with the exception that the decrease in the amount removed commences from pH 6 and not pH 7. By pH 8 there is a substantial drop in the adsorption/coprecipitation of molybdenum and at pH 9 no molybdenum is removed from solution for the sodium sulfate solution and demineralised water matrices. The amount of molybdenum removed in the sodium chloride and ash water solutions was only in the order of about 60% at pH 9, however, indicating that a matrix effect operates. However, as observed for the goethite trials, the presence of added electrolyte in
solution does not have an effect on the gross adsorption profile. Overall, the magnetite trends for molybdenum removal are fully consistent with the trends observed with goethite, and with earlier studies by Goldberg and Foster [10].

From the molybdenum trends utilising magnetite (Figure 5.41), where impairment of adsorption was shown to commence from pH 6, it is reasonable to assume that the presence of magnetite on the metal surface of pilot plant material had limited effect on the removal of this trace element from the ash water, where a pH ~8 is typical. It is likely other iron oxides and oxyhydroxides with higher pzc’s are responsible for the small removal observed during the pilot plant trials.

![Molybdenum Removal with Magnetite (5g) at Different pH Levels](image)

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.

**5.3.1.7.4 Discussion**

The high efficiency of molybdenum removal at pH levels below 6 by goethite and magnetite is consistent with earlier studies. The trends for hematite, however, were not as consistent, with a slight drop in the amount removed at lower pH values for all synthetic solution matrices; however, the Vales Point ash water was an exception, as molybdenum was removed by over 99% ± 10-20%, mirroring the behaviour for the other oxides.
Kim and Zeitlin [9], in their study with iron(III) hydroxide, noted that with increasing pH there is a decrease in positive charge density. This is also expected for goethite, hematite and magnetite. Since molybdenum occurs solely in aqueous solution as oxyanions, adsorption is clearly impaired by loss of positive surface charge. Other ionic species in solution have limited influence on the removal of molybdenum, confirming what has been observed in earlier studies and that the profile found is mostly related to pH-based effects.

Given that the pH of Vales Point ash water resides in the range 7.5 to 8.5, it is unlikely without costly pH adjustments that the amount of molybdenum removed through a plant process would rise higher than the observed 14%. Further, adjusting the pH may act to impair some other ion removal processes. Of the elements of interest, molybdenum is the sole one not targeted effectively by the process. This is largely the result of its distinctive chemistry.

### 5.3.1.8 Comparison of Vales Point Ash Water Trace Metal Removal by Iron Oxides and Oxyhydroxides

The relationship between the adsorption/coprecipitation of trace elements from the three iron oxides/oxyhydroxides goethite, hematite and magnetite with varying pH values is presented in the following sections. Further, a comparison of the trends in terms of abundances of trace elements in Vales Point ash water and overall efficiency of their removal during laboratory trials is made.

#### 5.3.1.8.1 Removal with Goethite

The pH dependence of the amount of each trace element adsorbed and/or coprecipitated from ash water upon treatment with goethite is summarised in Figure 5.42. Most elements show some variability across the pH range 3 to 9 with the exception of arsenic and vanadium, which are almost completely removed from solution at any pH between pH 3 to 9. Selenium has a similar ‘flat’ trend with only slightly less removed at any pH. For chromium, aluminium, antimony and molybdenum, the effect of pH is more evident, although all display a high efficiency of removal at pH values between 5 and 6. Only chromium and aluminium show a loss of efficiency at lower pH values. As anticipated, these gross trends were also observed for
the laboratory standard solutions in different matrices, with variable but overall modest matrix effects found. In general, efficiencies around pH 8, the natural pH of ash water, are sufficient for excellent to reasonable removal of the target elements, except for chromium and molybdenum.

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.

5.3.1.8.2 Removal with Hematite

The trace metal removal trends for hematite (Figure 5.43) are not that dissimilar to goethite, and in fact the selenium removal profile with these iron oxides appears to be identical. The drop in the efficiency in the removal of aluminium and chromium occurs around the same pH (~5) as in goethite, although in this case vanadium is also less adsorbed at lower pH values. However, the residual solution levels involved are so low that this could be a result of the measurement being close to the limit of reporting. At pH 8, molybdenum adsorption starts to decline with hematite, which is the same behaviour as seen for goethite. The pH range between 5 and 8 provides the best removal efficiency for most of the trace elements; this is a slightly wider range than that of goethite. Overall, hematite is slightly more efficient in the removal of trace elements.
than goethite, with the exception of selenium where the residual concentration profiles were similar.

Given the comparable profiles, it is highly likely that the mechanism for adsorbing and/or coprecipitating the seven target trace elements is similar for goethite and hematite. With their high efficiency for removal of targeted trace elements like selenium and arsenic at pH >7, their formation in a plant process operating around pH 8 is beneficial.

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.

5.3.1.8.3 Removal with Magnetite

The trace metal removal trends for magnetite are slightly different from those of goethite and hematite in that, at the lower pH range between 3 and 6, low residual concentrations of all trace elements are displayed (Figure 5.44). However, removal efficiencies are still very high at around 99%, making this effect a minor one. From a pH value of ~7, the residual concentration of selenium and molybdenum increase markedly compared with the behaviour shown with the other target elements. For all of the other trace elements, the residual solution concentrations remain below 2 µg/L up to
at least pH 9, showing this iron oxide to be least affected by the natural pH of ash water for most elements.

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.

5.3.1.8.4 Discussion

Although some differences are apparent for magnetite compared with goethite and hematite, the differences are not sufficient to drive a need to invoke different mechanisms for adsorption. Differences observed, rather, reflect minor variations in surface structure and pzc. All materials offer good adsorption capacity for the target ions in at least one pH region, which usually includes neutral pH.

It is evident from the pH versus residual solution concentration trends for trace element adsorption to goethite, hematite and magnetite that the amount of trace elements adsorbed/coprecipitated will be affected by the natural pH of the ash water. The adsorption/coprecipitation of arsenic, vanadium and antimony have been found to be least affected by pH or oxide used, which would explain why these trace elements provided high efficiency of removal during the pilot plant trials. From determined selenium, chromium and aluminium trends, the efficiency of removal is affected by pH levels above 7 and to a lesser amount by the oxide, which may also account for lower
reductions in the concentrations of these elements observed during pilot plant trials, where the pH is near 8.

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

As already presented in the Background in Chapter 2, there have been a number of studies of the kinetics of selenium and other trace metal sorption onto iron oxides and oxyhydroxides. All studies have demonstrated that the rate of removal is quite rapid, with maximum removal found within 30 minutes to one hour. The rate equations used by researchers for selenium, arsenic, vanadium, chromium, antimony, aluminium and molybdenum adsorption studies have assumed either a simple pseudo-first order or pseudo-second order kinetic process.

The following section provides trends from kinetic trials for each trace element examined for the ash water matrix only with goethite, hematite and magnetite. Lepidocrocite was not trialled due to insufficient amounts of this synthetically difficult oxyhydroxide. However, the kinetic behaviour of lepidocrocite would be expected to be similar to that of the others.

5.4.1.1 Selenium

The performance of the three iron oxides goethite, hematite and magnetite was examined in laboratory trials where 5 g of each iron oxide was mixed with ash water and samples were taken at time intervals of 5, 15, 30, 60, 120 and 480 minutes, under conditions similar to those of earlier studies. Each sample was filtered for analysis immediately upon collection, as required in a kinetics experiment. This process was adopted universally in the kinetic studies reported in this chapter. It provides a sufficient but not detailed view of the kinetics of the processes under examination.

The rate at which selenium in Vales Point ash water is removed is very rapid; most is removed with hematite, goethite and magnetite within 5 minutes of contact. The pH of ash water is typically about pH 8.5. Figure 5.45 illustrates the profiles; from a
concentration of 37 µg/L, within 5 minutes the concentration falls to about 11 µg/L for goethite, 7 µg/L for magnetite and 3 µg/L for hematite. The percentage of selenite adsorbed in the experiments undertaken by Parida et al. for goethite at pH 3.5 is very similar to the percentage of selenium removed in this laboratory trial [11].

![Graph](image)

Figure 5.45  Residual solution selenium concentration (µg/L) in time trials of removal with goethite, hematite and magnetite.

From Figure 5.45, it is evident that the equilibrium for selenium adsorption/coprecipitation is established more rapidly for hematite (complete within 30 minutes), but more slowly for goethite and magnetite, where maximum adsorption is achieved after 6 hours.

The unusual profile in the initial stages of reaction with goethite may reflect dissolution/readsorption processes at the surface following a rapid initial adsorption. Certainly, there is a continuing but slow adsorption process operating subsequently, from the residual/time profile. A plateau region is also noted for magnetite (clearly observable in Figure 5.46) before a slow subsequent process. This apparent two stage process is not seen for hematite, or at least the second stage is too insignificant a contributor to be defined. These results do suggest that adsorption is not
mechanistically, a simple first-order process. However, detailed mechanistic information can not be obtained from a limited study like the present one.

Figure 5.46  Percentage of selenium adsorbed onto goethite, hematite and magnetite from ash water with time.

5.4.1.2 Arsenic

The removal of arsenic from Vales Point ash water with goethite, hematite and magnetite is extremely rapid; 99% was removed and equilibrium achieved within 5 minutes of mixing. Figure 5.47 illustrates the effectiveness of all three iron oxides and oxyhydroxides in very rapidly adsorbing/coprecipitating arsenic.

An earlier study by Bang et al. [12] following the percentage of arsenate adsorbed with time described the process operating as a pseudo-first order reaction. However, the trend displayed for the present study in Figure 5.47 for arsenic removal from ash water is too rapid to permit any details of the kinetics to be probed using the technique adopted and the facilities available. This is seen simply as a very rapid reaction, with a short half-life of the order of a minute. The high efficiency of arsenic removal during the pilot plant trials is likely to be related to the rapid rate of removal observed, as this requires only a short contact time of the flowing ash water with the surface-formed iron oxides and oxyhydroxides. The fact that all three iron oxides removed arsenic at essentially the same rate also indicates that, no matter which one is
formed on the iron surface, it will contribute efficiently and rapidly to the adsorption process.

![Arsenic Time Trial with Vales Point Ash Water](image)

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

5.4.1.3  Vanadium

The trends in residual vanadium concentrations in Vales Point ash water in the presence of goethite, hematite and magnetite are identical to those found for arsenic. Most of the vanadium had been removed from solution within 5 minutes of contact (Figure 5.48).

This observation is not consistent with earlier work by Bartnegar et al. [13] using metal sludge as the adsorbent material. They observed gradual uptake over several hours, consistent with pseudo-first order kinetics. Studies on vanadium adsorption or sorption on iron oxides and oxyhydroxides are limited, and other comparable reports have not appeared. What has been demonstrated by the present study is that the process in this case is rapid for all iron oxides. The use of pure oxide materials rather than a mixed sludge of indeterminate character allows for enhanced control of the study. Obviously, vanadium uptake can be rapid; so rapid, in fact, that mechanistically useful evidence was not forthcoming.
It is not surprising, given the rapid nature of the adsorption/coprecipitation process and the fact it is not dependent on any particular iron oxide, that the removal of vanadium from pilot plant trials with steel wool was very efficient. The kinetics of the vanadium removal process may be pseudo-second order, but this is purely speculative given the data available. The short contact time needed to remove almost all vanadium at pH ~7.5 in the pilot plant illustrates how viable the use of oxidised iron is for the removal of vanadium from solution.

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

5.4.1.4 Chromium

The adsorption/coprecipitation profile of chromium(III) with time is similar to that of selenium, in that hematite is more efficient than magnetite, and goethite is the least efficient. The rates of the reactions are also similar, in that most of the chromium is removed from solution with each iron oxide/oxyhydroxide in 5 minutes and then a plateau occurs. The main difference between the behaviour of selenium and chromium is the goethite trend; with selenium, the amount removed gradually increases over time, whereas for chromium the amount initially rapidly adsorbed/coprecipitated (~40%) remains essentially constant thereafter. From this behaviour it is evident that goethite is not very efficient at removing chromium from solution, and it is clearly the other oxides which are responsible for its removal from the Vales Point ash water. From Figures 5.49 and 5.50, it is apparent that hematite and magnetite remove chromium rapidly and
to a high level; hematite is particularly effective. For all solids, equilibrium is established rapidly, in less than five minutes.

![Chromium Time Trial with Vales Point Ash Water](image)

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

The investigation by Fiore and Zanetti [14] presented in Chapter 2 utilising zero-valent iron for the removal of chromium also produced a reduction in concentration versus time trend comparable to the hematite and magnetite trends found here. This rapid reduction was also observed by Wu et al. [15], using Mn-goethite at pH 4, with removal in under an hour [15]. Both these studies were limited by the absence of collected data for short time-scales, but the overall results are consistent.

![Adsorption/Coprecipitation of Chromium on Iron Oxides and Oxyhydroxides with Time](image)

Figure 5.50 Percentage of chromium adsorbed from ash water onto goethite, hematite and magnetite with time.
From this study, it is clear that the removal of chromium from Vales Point ash water in any process developed will be predominantly by hematite and magnetite.

### 5.4.1.5 Antimony

The antimony concentrations versus time profiles are somewhat different to the others examined, with the exception of the selenium removal profiles. Clearly, hematite again provides the highest efficiency of removal, but for goethite and magnetite there is a cross-over whereby goethite over time actually improves its adsorption capacity (to about 40% of antimony) more that does magnetite.

From Figure 5.51, hematite is the oxyhydroxide most responsible for the adsorption/coprecipitation of antimony in a mixed oxide system. The reaction exhibits a rapid step (<5 minutes) by which time ~60% is removed, increasing slowly over several hours to ~80% removed. Clearly, a complex series of kinetic processes are operating. The adsorption/coprecipitation by magnetite is poor, with less than 5% removed over an 8-hour period. Goethite was marginally better, and may continue to slowly adsorb antimony beyond the 8-hour window of the experiment.

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

A study by Martinez-Lladó et al. [16] provided the sorption trend for antimony(V) removal with synthetic goethite, and determined the kinetics to be pseudo...
second order. Their trend shows a continuing reduction of antimony over a period of 20 hours, with the majority of antimony removed in under 4 hours. This is a somewhat similar result to that achieved in this trial, although here antimony is still being adsorbed/coprecipitated after 6 hours (Figure 5.52). The pH of the ash water could be a contributing factor, if the kinetics show, as expected, a pH dependence. Antimony removal with hematite is very fast and may be a pseudo-second order process; it is certainly the key material for antimony removal in plant conditions.

![Adsorption/Coprecipitation of Antimony on Iron Oxides and Oxyhydroxides with Time](image)

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

### 5.4.1.6 Aluminium

The trends for aluminium concentrations versus time for goethite, hematite and magnetite adsorption are subject to errors that lead to fluctuations in the data. The likely causes of these erroneous results could be contamination of the samples via the passage of ultra-fine Al(OH)₃ colloidal gels through the filter. The hematite data is spurious, and shows an increase over time that is clearly incorrect unless there is some unusual rapid adsorption/slow redissolution process operating. Since the overall trends with goethite and magnetite follow a course consistent with removal over time, these are taken as more indicative of the process. The only trend which could be considered of sufficient quality for examination is the removal of aluminium with magnetite, which displays a reasonably consistent reduction over time. For this system, there is a rapid
reduction in aluminium concentration in solution followed by a slower process, with most aluminium adsorbed/coprecipitated after 6 hours (Figure 5.53) (Notably, all oxides show a fast first step, at least.) This trend is not dissimilar to others discussed above, and indicates a complex multi-stage kinetic process operates. The quality of data does not warrant extensive analysis, however.

![Aluminium Time Trial with Vales Point Ash Water](image)

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.

The study by Wilkin and McNeil [17] of aluminium removal with zero-valent iron presented in Chapter 2 found the reduction was rapid and followed a pseudo-first order rate reaction. This rapid reduction in aluminium concentration is replicated in the trends found herein. Clearly, iron oxides can be successful in controlling aluminium levels, with reasonably fast kinetics operating.

### 5.4.1.7 Molybdenum

The molybdenum concentration versus time profiles (Figures 5.54 and 5.55) have some similarities to those of some other trace elements, including selenium. Processes contain rapid and following slower kinetic processes. Removal of molybdenum with goethite is more efficient than that with magnetite, though kinetics for the processes appear similar from comparison of the concentration profiles. This is different to the trends observed for selenium, chromium, aluminium and to some extent
antimony. Hematite is particularly effective for molybdenum capture, with a very rapid first stage in which most molybdenum is adsorbed, and following slower stages.

![Molybdenum Time Trial with Vales Point Ash Water](image)

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

Historical information regarding the kinetics of molybdenum removal with iron oxides is limited. One study by Diebler and Millan [18] yielded a second-order rate constant, and the rapid reduction of molybdenum during these trials for hematite appears to be similar. Figure 5.55 clearly displays the difference in the rate profiles for molybdenum removal between the three oxides and the difference in the efficiency of removal by hematite compared with goethite and magnetite.

![Adsorption/Coprecipitation of Molybdenum on Iron Oxides and Oxyhydroxides with Time](image)

Figure 5.55 Percentage of molybdenum adsorbed onto goethite, hematite and magnetite with time.
5.4.1.8 Concluding Remarks on Reaction Kinetics

The rate of removal of selenium, arsenic and antimony from solution was very rapid, and largely completed within 5 minutes of mixing for all oxides used in each trial. The percentage removal for vanadium and arsenic was greater than 99%, regardless of oxide, after 5 minutes. For selenium, the percentage removed varied, with hematite displaying the highest removal (>95%) and goethite the lowest (~70%) after 5 minutes. The rapidity of reaction does not permit useful comments on the kinetics of the process.

The profiles for chromium, antimony and molybdenum show that hematite is the most efficient iron oxide, with removal rates >80% for chromium and molybdenum and >60% for antimony when sampling after 5 minutes. The percentage of removal with goethite and magnetite were varied, but still displayed a rapid reduction within 5 minutes. Whilst the profiles for aluminium were poorly defined, a rapid initial stage was apparent.

Overall the profiles revealed that the rate of removal is very rapid; the half-life of the initial (or in some cases, sole observable) process is no more than one or two minutes. During this period, the majority of adsorption occurs. Some systems exhibited clear following steps, with further adsorption occurring. The present study uses the final concentration in solution to follow the reaction. This does not allow any kinetic step that leads to surface rearrangement or structural change without change in concentrations of adsorbed material to be defined. However, it does allow identification of further processes that alter the adsorbed amount, and several such processes were identified. Thus, the kinetics of these systems is more complicated than might be anticipated for a single species adsorbing to a single oxide type and implies that there are several processes operating that lead to adsorption. This may be a result of the presence on the surface of different classes of sites, as is evident from structural studies of pure oxide crystals. Different surface sites would likely lead to reactions at different rates. The relative amounts of surface sites would also affect the amount of ions taken up at each site. Further, oxide surfaces contain pores into which solution and or ions can penetrate, but possibly slowly. This provides another kinetic control, and slow kinetic processes observed may be due to adsorption in pores, where the tortuosity involved with entry into pores leads to kinetically slow steps that are seen as slow uptake of adsorbate over time following on from initial steps. Overall, the kinetics and
mechanisms of surface adsorption may be complex, and demand a depth and form of study neither warranted nor accessible in this study.

What is apparent, in general, is the rapidity of initial processes on oxide surfaces in ash water. These suit a flow system well, and clearly contribute to the successful capture of most target ions. Further, there are clear differences with oxide type. In general, higher percentages of removal in a short period of time occur for hematite with lower percentages for goethite and magnetite, although this is not an invariable observation. What is apparent is that the type of oxide has an impact on both adsorption kinetics and capacity, and a plant that has a range of oxides/oxyhydroxides present will have broader capacity where a range of target species are sought.

5.5 REFERENCES


CHAPTER SIX
SUMMARY AND CONCLUSIONS

Historically, the generation of electricity in Australia has occurred predominantly through steam cycle processes with the use of black and brown coal. The by-product of the combustion of coal to produce steam is ash, and the ash produced by power stations around Australia is generally stored on site. It is placed in dams, with the transport medium for ash movement in most power stations being either fresh or saline water. Measures to control levels of trace elements in ash water from Vales Point Power Station discharged to Lake Macquarie in New South Wales, Australia, lies at the heart of this thesis. With a view to providing an overview on the findings, the following sections outline the core observations and/or conclusions from each Chapter and overall discussion of the findings.

Vales Point Power Station uses black coal for the production of electricity. The fly ash generated from the combustion of black coal is mixed with estuarine water from Lake Macquarie to form a lean phase (70% water) for transport to the ash dam. Whilst the water used for transportation is recycled back to the power station, rainfall input and makeup from Lake Macquarie results in discharges to Wyee Bay via a licenced discharge point located at the cooling water outfall canal of the power station.

Fly ash is predominantly composed of Si, Al, Fe, Ca, Mg, Na and K, which account for from 90 to 99% of elemental composition. However, other trace elements exist, and for Vales Point Power Station these trace elements include significant amounts of the elements Ti, P, Ba, S, Sr and minor amounts of the elements Ag, As, B, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Ge, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Se, V, W, Zn and Zr. The concentration in ash water of each of these elements may vary over time, influencing their effect on receiving water bodies and whether they are within water quality guideline levels for that type of receiving environment.
Studies of aquatic flora and fauna in Lake Macquarie, in particular Wyee Bay, indicates that the main trace elements of concern to researchers has been particularly selenium and, to a lesser extent arsenic, and at the northern extremity of the lake cadmium, lead, zinc and copper. Selenium has been of particular concern to researchers because of its impact on aquatic ecosystems. The biomagnification or bioaccumulation and biotransference of this element in aquatic flora and fauna of areas of Lake Macquarie near heavy industries such as power stations have been the subject of studies over the past 20 years.

In response to a requirement to minimise environmental impacts to receiving waters from discharges, research has been undertaken at Vales Point Power Station that includes physical controls such as reducing discharges to water and chemical controls through the development of viable treatment options which have high efficiencies for selective element removal and are economically viable. The types of treatment options considered but found not to be viable due to low efficiency of selenium removal from ash water, high operating costs or high maintenance costs included: precipitation (coagulation/flocculation), reverse osmosis, brine concentration, ion exchange, constructed wetlands and bioreactors. The treatment option for selenium that appeared most viable was exposure to oxidised metallic iron, with high efficiency of selenium (selenite and selenate) removal found. Moreover, it required low maintenance and involved the least cost of the processes examined.

Laboratory studies undertaken by Baldwin and co-workers in 1983 found up to 99% selenium removed from samples using metallic iron powder [1]. This high efficiency of selenium removal was later confirmed through studies that used steel wool by Riley and Farrell in 2001 [2]. Their laboratory trials found that over 99% of both selenite and selenate were removed from samples. Comparative laboratory trials of Vales Point Power Station ash water treated with steel bars and steel wool found that, with the high surface area of steel wool and efficient adsorption/coprecipitation that took place with the iron oxides and oxyhydroxides that formed on the metal surface, very high efficiencies of selenium removal were achieved.

A field pilot plant was set up, and the process employed was found to not only remove selenium but also other elements including arsenic, chromium, aluminium, vanadium, antimony and molybdenum. The iron oxides and oxyhydroxides that were found to form on the surface of the metallic iron included goethite, hematite, lepidocrocite and magnetite. The removal of selenium, present as predominantly
selenite, from Vales Point Power Station’s ash water occurs through a process of adsorption and coprecipitation with surface iron oxides and oxyhydroxides.

Optimising the use of iron oxides and oxyhydroxides requires an understanding of the chemical characteristics of these compounds along with their crystalline structures and the processes involved in adsorption/coprecipitation. The following Table 6.1 summarises a number of parameters for the four iron oxide/oxyhydroxide compounds found to form on the surface of metallic iron during pilot plant trials at Vales Point Power Station.

Table 6.1 Characteristics of dominant iron oxides and oxyhydroxides formed on metallic iron in ash water.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Colour</th>
<th>Crystal Structure</th>
<th>Surface Area (m²/g)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite [1]</td>
<td>α-FeOOH</td>
<td>yellow-brown</td>
<td>acicular</td>
<td>8-200</td>
<td>4.26</td>
</tr>
<tr>
<td>Hematite [1]</td>
<td>α-Fe₂O₃</td>
<td>red</td>
<td>platy and rhombohedral</td>
<td>2-90</td>
<td>5.26</td>
</tr>
<tr>
<td>Lepidocrocite [1]</td>
<td>γ-FeOOH</td>
<td>orange</td>
<td>platy or lath-like (tabular)</td>
<td>15-260</td>
<td>4.09</td>
</tr>
<tr>
<td>Magnetite [1]</td>
<td>Fe₃O₄</td>
<td>black</td>
<td>octahedral, rhombodecahedral and twinned</td>
<td>4-100</td>
<td>5.18</td>
</tr>
</tbody>
</table>

The process for the removal of trace elements such as selenium, arsenic, chromium, antimony, vanadium, aluminium and molybdenum with iron oxides and oxyhydroxides formed on the surface of metallic iron is likely to be via a number of mechanisms, influenced by the character of the compound containing the element. Core processes are adsorption, a process whereby ions accumulate and are confined at the interface between the solid and aqueous phase, and coprecipitation, where ions are removed through the formation of complex metal precipitates on the surface. A combination of these processes may actually occur simultaneously as the iron oxides and oxyhydroxides form. Precise studies on the sorption of targeted trace elements using the iron oxides and oxyhydroxides goethite, hematite, lepidocrocite and magnetite are limited. Table 6.2 is a summary of findings from various prior studies.
Table 6.2  Summary of sorption data for Se, As, Cr, V, Sb, Al and Mo on goethite, hematite, lepidocrocite and magnetite [3-10].

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Sorption Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4 – ( \Gamma_{\text{max}} ) (mol m(^{-2}))</td>
<td>(3.3±0.1) \times 10^{-6}; inner- and outer-sphere complex behaviour.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Sorbed As(_T) (t = 24 h) [As(III)-As(V)] pH 5 99.7%</td>
</tr>
<tr>
<td>Chromium(III)</td>
<td>No data found for individual iron oxides and oxyhydroxides, except for mixed Fe(III) oxide experiments with Cr(III). pH 6 provided 100% adsorption. Inner-sphere complexes form.</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Maximum adsorption from pH 3–6. Inner-sphere surface and didendate corner-sharing surface complexes formed.</td>
</tr>
<tr>
<td>Antimony(V)</td>
<td>pH 3 – ( \Gamma_{\text{max}} ) (mol m(^{-2}))</td>
</tr>
<tr>
<td>Aluminium</td>
<td>No data found for individual iron oxides and oxyhydroxides except with zero valent iron. pH 2.3 – 3.0 provided reductions in Al(III) below detection limits. Process of removal due to adsorption and coprecipitation onto iron corrosion products.</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>80-100% removal between pH 3 to 5.</td>
</tr>
</tbody>
</table>

The information in Table 6.2 highlights how, for all trace elements regardless of the type of iron oxide or oxyhydroxide used, the optimum adsorption/coprecipitation takes place in the lower pH range (<6). The sorption isotherms can vary depending on the oxide and trace metal being adsorbed and/or coprecipitated. This is dependent on the ionic species in solution and complexes being formed, which demonstrates how the efficiency of removal of targeted trace metals will vary depending on the types and abundances of individual iron oxides and oxyhydroxides formed through the rusting of metallic iron and ageing of the coating.

Existing kinetic data on the adsorption/coprecipitation process demonstrates that the reaction for removal of selenium, arsenic, chromium, antimony, vanadium, aluminium and molybdenum with iron oxides and oxyhydroxides is generally quite
rapid. Studies on the reaction kinetics of each of the trace elements are summarised in Table 6.3 below.

Table 6.3 Reaction kinetic studies for Se, As, Cr, V, Sb, Al and Mo adsorption with goethite, hematite, lepidocrocite and magnetite [3-16].

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Selenium (selenite)</td>
<td>Equilibrium reached in 2 hours. Pseudo-second order $(0.95\pm0.003 \text{ m}^2\text{mol}^{-1}\text{h}^{-1})$.</td>
<td>Equilibrium reached in 2 hours. Pseudo-second order $(1.12\pm0.002 \text{ m}^2\text{mol}^{-1}\text{h}^{-1})$.</td>
<td>No studies found.</td>
<td>Equilibrium reached in 30 hours. Pseudo-second order.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>No kinetic data found for individual iron oxides and oxyhydroxides. Process with zero-valent iron (ZVI) examined; 100% arsenate and 60% arsenite removed within 4 hours with ZVI; pseudo-first order rate reaction.</td>
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<tr>
<td>Chromium(III)</td>
<td>Data found for Mn-substituted goethite and for ZVI only. Equilibrium reached within one hour for Mn-substituted goethite and ZVI. Pseudo-first order rate reaction.</td>
<td></td>
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</tr>
<tr>
<td>Vanadium</td>
<td>No kinetic data found for individual iron oxides and oxyhydroxides. Mixed-species metal sludge examined; pseudo-first order rate reaction with equilibrium reached in 7 hours.</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Antimony(V)</td>
<td>Data found for goethite and natural iron oxide. For goethite equilibrium reached under 50 minutes with reaction being pseudo-second order. The natural iron oxyhydroxide was slower and demonstrated a pseudo-first order rate reaction.</td>
<td></td>
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<tr>
<td>Aluminium</td>
<td>No kinetic data found for individual iron oxides and oxyhydroxides, except with mixed-species Peerless iron. Pseudo-first order rate reaction observed, with equilibrium reached in less than 25 hours.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Molybdenum</td>
<td>No kinetic data found for individual iron oxides and oxyhydroxides. A study with Fe(II) reported; pseudo-second order rate reaction.</td>
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<td></td>
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</tbody>
</table>

To be viable as a process, the removal of trace elements from ash water also requires that the adsorbed species are not re-released into the environment over time. Background studies of the leachability of trace elements were also considered, with the pH a key effect influencing dissolution. The mechanisms defined for the dissolution of iron oxides and oxyhydroxides that would allow trace element release included protonation, complexation and reduction. Compounds and ions identified as promoting dissolution include chloride ions, hydrogen sulphide, hydrogen, dissolved iron, ascorbic acid, fulvic acid, biomass and bacterial matter. The pH of the solution also plays a role in the dissolution of iron oxides and oxyhydroxides, particularly at high pH levels. It should be noted, however, that selenite does adsorb particularly strongly on goethite, a process found to be largely irreversible.

Three pilot plant trials were undertaken at Vales Point Power Station from 2002 to 2008, with increasing surface area of iron being a key difference. Assembly and/or alteration of the pilot plant for each trial was a component of the study.
The first pilot plant trialled in 2002 contained up to 7,000 steel fabric filter hanger bars with a surface area of ~140 m² in a single trough. The amount of selenium removed from the process even at the lowest flow rate was only 4.5%.

The second pilot plant trial (2004 – 2005) added two additional troughs containing steel plates to the initial trough of fabric hanger bars. This modified pilot plant, with a total surface area of ~250 m², provided a further reduction of selenium in ash water, averaging 23%. Other trace elements were also observed to be reduced in concentration, including arsenic (62% removed on average), antimony (30%), aluminium (58%) and molybdenum (14%).

The final pilot plant trial investigation (2008) involved the modification of each trough, with the removal of all fabric filter hanger bars and some steel plates to allow the insertion of baskets of loosely packed steel wool. This configuration provided a high surface area of iron and yielded the highest removal efficiencies of all the trials. The removal of trace elements observed was generally high [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%)]. Trends from monitoring inlet and outlet levels for each of these trace elements demonstrated that the process retained its efficiency over the six month trial period without requiring replacement of the steel wool, with very high efficiencies of removal including that of selenium, the element of most concern.

Leachate studies employed iron oxides and oxyhydroxides formed as corrosion products from the Vales Point Power Station pilot plant operated in 2003 – 2004. Adsorbed selenium, arsenic, antimony and aluminium levels in samples stored with ash water for extended periods exhibited very little redissolution, with some only ~1%. Molybdenum, however, did display limited leaching with final levels being two to three times that in the initial ash water, attributable to the neutral pH supporting some release of polyoxo cluster species [17]. Further testing of the pilot plant sludge or corrosion products in 2007 and 2008 by the USEPA Method 1311 leaching procedure, however, provided no detectable levels of selenium, arsenic, antimony, chromium, vanadium and molybdenum. The only element which was found at concentrations above the detection limit in samples from two pilot plant troughs was aluminium, but only to a modest extent.

Overall, the leachability studies confirm that the trace elements selenium, arsenic, antimony, vanadium and chromium are strongly adsorbed or coprecipitated.
onto the iron oxides and oxyhydroxides formed by the pilot plant process and exhibit negligible leaching even after long periods in environmental waters. Molybdenum and aluminium were the only elements to display some capacity for leaching, but in modest concentrations. The processes of adsorption/coprecipitation operating are effective in maintaining target trace elements such as selenium efficiently bound by the iron oxides and oxyhydroxides goethite, hematite, lepidocrocite and magnetite.

Pure samples of the synthetic iron oxides and oxyhydroxides goethite, hematite, lepidocrocite and magnetite were obtained by controlled laboratory synthesis or from commercially available sources. These were used in a series of controlled laboratory trials of adsorption to determine the relationship between the concentration of trace elements remaining in solution and the pH of the solution. The surface area of each oxide was also defined, as well as reaction kinetic trials to determine the speed and efficiency of the adsorption/coprecipitation processes. The characterisation of these pure oxides, along with samples formed in and collected from the Vales Point pilot plant, were also examined by their colour, with scanning electron microscopy (SEM), and X-ray powder diffraction (XRD), to permit positive identification.

The colours of the pure synthetic iron oxides and oxyhydroxides were consistent with the standard Cornell and Schwertmann colour plates [10]. However the samples obtained from the Vales Point pilot plant were not identifiable from colour alone, except for a magnetite sample which was clearly black in colour. The other samples were different shades of brown and could only be identified by SEM and XRD. The presence of magnetite, goethite and lepidocrocite in some samples and predominantly lepidocrocite with minor portions of goethite and magnetite in another, clearly identified by instrumental analysis, are consistent with the lack of colour specificity found only with pure samples. Evidently, the oxide/oxyhydroxide layers in the pilot plant are a complex mixture of all four common species, with different speciation apparent in different layers.

The surface areas measured for the synthetic/commercial samples are compared to literature values in Table 6.4 below. Apart from lepidocrocite, all other values are in the lower surface area range. Since adsorption of trace elements is positively correlated with increasing surface area, in this study lepidocrocite would likely be more efficient at removal of the target elements from solution. However,
assigning effectiveness of different species on the basis of surface area alone is not really appropriate.

Table 6.4 Surface areas of goethite, hematite, lepidocrocite and magnetite (m²/g).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Surface Area (Literature) (m²/g)</th>
<th>Surface Area (Laboratory Trials) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>(\alpha)-FeOOH</td>
<td>8-200</td>
<td>22.5</td>
</tr>
<tr>
<td>Hematite</td>
<td>(\alpha)-Fe₂O₃</td>
<td>2-90</td>
<td>7.1</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>(\gamma)-FeOOH</td>
<td>15-260</td>
<td>66.5</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>4-100</td>
<td>10.0</td>
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</table>

From laboratory trials with different solution matrices (demineralised water, sodium sulfate solution, sodium chloride solution and ash water), the overall efficiency of removal of selenite with iron oxides and oxyhydroxides exhibits the following order: lepidocrocite > goethite > hematite > magnetite which follows the pattern of surface areas provided in Table 6.4 above. 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 sulfate solution > demineralised water. This is an important aspect, given that the pH of Vales Point Power Station’s ash water fluctuates between 7.5 and 8.5.

The order of efficiency of adsorption/coprecipitation for arsenic with oxide/oxyhydroxide was not clearly delineated between pH 3 and 7, as the amount removed is invariably high, with levels of arsenic being lower than the limit of detection. Magnetite proved the least efficient in the higher pH range of 8 to 9.

For vanadium, all matrices provided the highest efficiencies of removal. This behaviour was also found in pilot plant trials with steel wool, and is presumably due to the ability of vanadium to form both weaker adsorption bonds on the surface and strong inner-sphere covalently bonded species, including didendate corner-sharing surface complexes. The trends for chromium(III) adsorption were more variable. Hematite and magnetite illustrate high adsorption/coprecipitation efficiencies across a wide pH range, whereas goethite had a high chromium(III) removal efficiency between pH 5 to 6. Antimony displays for goethite, hematite and magnetite the highest adsorption/coprecipitation efficiency of removal between pH 4 to 6, dropping off in efficiency of removal at higher pH levels.
Aluminium provided high efficiency of adsorption/coprecipitation in all matrices between pH 5 to 8, irrespective of the form of the iron oxide and oxyhydroxide. The laboratory results in this case are not consistent with pilot plant trials using steel wool, where the rate of removal of aluminium is low. This could be due to a number of factors, including the tendency for aluminium(III) to undergo hydrolysis and polymerisation to lower-charged species that may contribute to reduced binding. Molybdenum provided high efficiency of adsorption/coprecipitation at pH levels below 6 for goethite and magnetite. Hematite differed, showing a drop in the amount removed in ash water, consistent with pilot plant trials. The pH of ash water (7.5 to 8.5) may therefore control removal efficiency.

The trace element removal rate profiles determined for selenium, arsenic, chromium, vanadium, antimony, aluminium and molybdenum overall revealed that they are adsorbed very rapidly, with the observed half-life of the initial process being no more than one to two minutes. As the present study provides only final concentrations, to follow the reaction the kinetic step that leads to surface rearrangement or structural change cannot be defined. However, the present study does suggest that the kinetics of each system is more complicated than what was anticipated from studies of a single species adsorbing to a single oxide type.

What is clear from the present study is the rapid and efficient removal of trace elements present in ash water through adsorption onto the iron oxides and oxyhydroxides goethite, hematite, lepidocrocite and magnetite. This results in very high efficiencies of removal, particularly for selenium, which is the trace element of most concern.

This project addressed an environmental concern, which is the release of toxic and harmful elements into natural waters from an industrial source, namely a power station ash dam. It sought and demonstrates a cost-effective practical solution, supported by development of an understanding of the chemical processes in operation. The outcomes of the research undertaken for this thesis demonstrates that the use of iron oxides and oxyhydroxides formed through the process of oxidation of steel to treat waste water such as ash water is not only rapid and efficient but an economically viable option requiring simple design and process concepts.

The concentration versus pH profiles for adsorption of target species from various matrices using goethite, hematite, lepidocrocite and magnetite has provided more detailed knowledge of the efficiencies of targeted trace element removal.
observed during pilot plant trials. The chemistry in operation in the process has been
exposed, so that an understanding of the system is more established; this will allow
the influences of other variables that may alter the process to be more readily
elucidated.

Further refinement of the process developed would be beneficial, with the
scaling up of the pilot plant to a demonstration scale an obvious step. This would
allow further detailed information to be obtained in the field, such as the quantities of
material required at a larger scale, the longevity of the process material and quantity
of waste material formed by the process over a defined period of time. Other
parameters could then also be probed and refined including the effects of flow rates,
temperature, salinity, and dissolved oxygen on a process using steel wool as the
source of iron. Initial testing of the discharge ash water should include a wide range
of trace elements from the inlet and outlet to assist in the refinement of testing
regimes. Removal and storage of spent or loaded steel wool residual solids also needs
to be addressed, as well as prospects for recovery of concentrated trace elements from
the spent oxidic iron solids.

Overall, the development of an understanding of the chemical processes in
operation in the ash water treatment plant means that scale-up and/or extension of
studies to follow the effect of additional parameters now has a firm basis from both
practical and chemical standpoints. In fact, a Demonstration Plant designed as a
seven fold scale-up of the Vales Point Power Station Pilot Plant is nearing completion
of construction and is scheduled to be commissioned in 2012. The Demonstration
Plant located at the southwest corner of the discharge point of the Vales Point Power
Station ash dam will further add to the knowledge of the processes and suitability for
large scale treatment of ash water.

Demonstration Plant trials will be designed from the learning's the Pilot Plant
trails and laboratory research work that has been the subject of this thesis.
6.1 REFERENCES


Appendix Table of Contents
For

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

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