

# **THE JAROSITE GROUP OF COMPOUNDS – STABILITY, DECOMPOSITION AND CONVERSION**

Graham Andrew Reynolds B.Sc G Cert OH&S

Submitted for the degree of Master of Science

July 2007.

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.

.....  
Graham Andrew Reynolds.

## Acknowledgements

The author would like to acknowledge the following people:

- Jodi Reynolds for her patience and assistance in the development of this thesis.
- Greg Hancock for his direction in transferring industrial results and reports into academic styles.
- Houyuan Liu for his direction and assistance in educating the author on everything about nickel laterites.
- Brendan Logan for his assistance as technician during the batch and column leaching tests.
- Nick Ebrill for his direction in the early stages of nickel laterite stabilisation testing.
- Wolf Meihack and Gary Foulds for the opportunity to utilise BHP Billiton data for the author's personal advancement.
- Sian Miller and Eric Roche for refereeing this thesis.

# **The Jarosite Group of Compounds – Stability, Decomposition and Conversion**

## **Table of Contents**

<b>1 Introduction to This Thesis and Background Information on the Extraction of Nickel from Laterite Ores</b>	<b>1</b>
1.1 The Purpose and Layout of This Thesis	2
1.1.1 Section 1: Literature Review	3
1.1.2 Section 2: Jarosite Conversion or Stabilisation	4
1.1.3 Section 3: Measuring the Stability of Jarosite	6
1.2 Introduction to Nickel Laterite Extraction Methods	7
1.2.1 Background to the Development of the Process	9
1.2.2 Current and Future Direction of Nickel Laterite Processing	14
1.2.3 Competing Technologies	15
<b>2 Current and Relevant Jarosite Issues</b>	<b>17</b>
2.1 Physical Properties and Chemical Composition	17
2.2 The Mineralogy of Jarosites	20
2.3 Naturally Occurring Jarosite Sources	21
2.3.1 Chemical Mechanisms of Formation	21
2.3.2 Acid Sulphate Soils	22
2.4 Mining and Metallurgical Sources of Jarosite	23
2.5 Jarosite Stability – Known Chemical Data	24
2.6 Measuring the Stability of Jarosite	27

2.6.1 Energy of Formation	28
2.6.2 The TCLP Test – Benefits and Drawbacks	29
2.6.3 TCLP Results for BHP Billiton Natrojarosite	31
2.6.4 Other Methods of Solid Matter Chemical Stability Measurement Used in the World	31
2.6.5 Batch Leaching and Column Testing	37
2.7 Mining and Tailings Placement Problems	39
2.8 Jarosite Storage Methods	43
2.8.1 Landfill	43
2.8.2 Dry Storage	44
2.8.3 Subaqueous Dumping	45
2.9 Alternative Uses for Jarosite	47
2.9.1 Soil Fertilisers	48
2.9.2 Ceramic Products	50
2.10 Stabilisation of Bulk Jarosite – Landfill and Embankments	51
2.11 Conversion of Jarosite to Iron Oxides	53
2.11.1 Pyrometallurgy – Thermal Decomposition	53
2.11.2 Hydrometallurgy – Thermal Decomposition	56
2.11.3 Hydrometallurgy – Basic Decomposition	57
2.11.4 Hydrometallurgy – Acidic Dissolution	61
2.11.5 Hydrometallurgy – Chlorination	62
2.11.6 Biological consumption and Dissolution	62
<b>3 Experimental Section 1: Basic Decomposition of Natrojarosite at Atmospheric Pressure – Methods and Results</b>	<b>64</b>
3.1 Hydrated Lime and Limestone Addition Methods	65
3.1.1 Experimental Aims	66

3.1.2 Equipment and Methods	67
3.1.3 Completion of the Experiment	68
3.2 Hydrated Lime and Limestone Addition Results	69
3.2.1 Experimental Results	69
3.2.2 Data Extrapolation	70
3.2.3 Liquid Chemical Analysis Findings	71
3.2.4 X-ray Diffraction Analysis	75
 4 Experimental Section 2: Thermal Decomposition of Natrojarosite at High Pressure and Temperature in an Autoclave – Methods and Results	 76
4.1 High Pressure and Temperature (Autoclave) Methods	76
4.1.1 Experimental Aims	76
4.1.2 Equipment and Methods	78
4.1.3 Completion of the Experiment	82
4.2 High Pressure and Temperature (Autoclave) Results	84
4.2.1 Chemical Analysis of the AL7 Natrojarosite Washing Process	
Prior to Autoclave Treatment	85
4.2.2 Autoclave Decomposition Kinetics Experiment Results	86
4.2.3 X-ray Diffraction Results	91
4.2.4 Results from the Effects of AL7 Natrojarosite Washing	
Prior to Autoclave Conversion	92
4.2.5 Results for Maximising Acid Production from Jarosite	
Decomposition Using AL7 Natrojarosite Material in an Autoclave	94
4.2.6 AL7 Natrojarosite Decomposition Temperature / Time Relationship Results	 98

<b>5 Experimental Section 3: Stability Testing of Natrojarosite</b>	
<b>– Methods and Results</b>	<b>100</b>
5.1 Batch Agitation Stability Testing Methods	101
5.1.1 Experimental Aims	101
5.1.2 Equipment and Method	102
5.1.3 Completion of Experiment	103
5.2 Batch Agitation Stability Testing Results	104
5.2.1 Excess Hydrated Lime and Limestone in the Solid	104
5.2.2 Gypsum Encapsulation Theory and Liquid Chemical Analysis	109
5.2.3 Salt Water Results	113
5.2.4 Equilibrium Reactions	116
5.3 Column Testing Methods	118
5.3.1 Experimental Aims	118
5.3.2 Equipment and Methods	118
5.4 Column Testing Results	120
5.4.1 Combining Batch Agitation and Column Test Results	125
5.5 Permeability Testing Methods	126
5.6 Permeability Testing Results	128
5.7 Combined Permeability and Stability Results	128
<b>6 Discussion</b>	<b>130</b>
6.1 Conclusions Drawn from Current Literature	130
6.2 Conversion of Jarosite to Iron Oxides	131
6.2.1 Hydrated Lime and Limestone Decomposition	131
6.2.2 Autoclave Conversion	133
6.3 Measuring the Stability of Jarosite	137

<b>6.3.1</b>	<b>TCLP Test versus Batch Agitation and Column Leaching</b>	<b>137</b>
<b>6.3.2</b>	<b>The Stability of Natrojarosite</b>	<b>141</b>
<b>7</b>	<b>Further Opportunities</b>	<b>145</b>
<b>8</b>	<b>Conclusions</b>	<b>147</b>
<b>9</b>	<b>References</b>	<b>149</b>
	<b>Appendix 1 – Free Acid Titration Method</b>	<b>159</b>



## List of Figures

<b>Figure 1.</b> Steam Pressure Shown in Bar and Pounds per Square Inch on a Logarithmic Scale versus Temperature shown in degrees Celcius.	<b>6</b>
<b>Figure 2.</b> Schematic of the Atmospheric Leach Nickel Laterite Process Treating Both the Limonite and Saprolite Sections of the Nickel Laterite Ore Body, Patented by BHP Billiton	<b>13</b>
<b>Figure 3.</b> Natrojarosite Production from the BHP Billiton Atmospheric Leach Plant – Newcastle Technology Centre 2001-2.	<b>19</b>
<b>Figure 4:</b> Temperature vs pH Stability Field for Potassium Jarosite.	<b>25</b>
<b>Figure 5.</b> Differential Thermogravimetric Analysis (DTA) Data for BHP Billiton Natrojarosite Sample AL7	<b>56</b>
<b>Figure 6.</b> Result for Experiment 1. Hydrated Lime ( $\text{Ca}(\text{OH})_2$ ) Added to AL7 Natrojarosite at $90^\circ\text{C}$ to Maintaining Solution pH of 11 for 90 minutes	<b>73</b>
<b>Figure 7.</b> Result for Experiment 3. Limestone ( $\text{CaCO}_3$ ) Added to AL7 Natrojarosite at $90^\circ\text{C}$ to Maintain Maximum pH for 30 Hours.	<b>74</b>
<b>Figure 8.</b> “Parr” 2Litre Titanium Autoclave Bomb and Heating Mantle used for Experiments Described in Chapter 4	<b>79</b>
<b>Figure 9.</b> Schematic of Sampling Process for the End of Each Autoclave Experiment.	<b>84</b>
<b>Figure 10.</b> Free Acid, Dissolved Sodium and Sulphur in the Autoclave Discharge Solution for Each Experiment	<b>91</b>
<b>Figure 11.</b> Free Acidity in the Autoclave Discharge for Washed versus Unwashed AL7 Natrojarosite.	<b>93</b>
<b>Figure 12.</b> Dissolved sodium and Sulphur in Autoclave Discharge for Washed versus Unwashed AL7 Natrojarosite.	<b>94</b>
<b>Figure 13.</b> Acid Production for Samples of Natrojarosite Taken from Various Locations within the BHP Billiton AL Process (single point tests).	<b>97</b>
<b>Figure 14.</b> pH Changes in Liquid Phase Associated with AL3 and AL7 Natrojarosite	

Decomposition Using the Batch Agitation Stability Method	107
<b>Figure 15.</b> Dissolved Element Concentrations and pH from AL3 Natrojarosite	
Decomposition using the Batch Agitation Stability Method.	110
<b>Figure 16.</b> Dissolved Element Concentrations and pH from AL7 Natrojarosite	
Decomposition using the Batch Agitation Stability Method.	111
<b>Figure 17.</b> Gypsum Encapsulation Theory	112
<b>Figure 18.</b> pH Measured from AL3 and AL7 Natrojarosite Salt Water Batch Agitation	
Stability Tests	113
<b>Figure 19.</b> Dissolved Element Concentrations from AL3 Natrojarosite in Salt	
Water Batch Agitation Stability Tests.	114
<b>Figure 20.</b> Dissolved Element Concentrations from AL7 Natrojarosite in Salt	
Water Batch Agitation Stability Tests	115
<b>Figure 21.</b> Batch Agitation Stability Test Results for AL7 Natrojarosite in pH 3 Adjusted	
Water.	117
<b>Figure 22.</b> Saturated Column Test Results for AL7 Natrojarosite in Deionised Water.	121
<b>Figure 23.</b> Free Draining Column Test Result for AL7 Natrojarosite in Deionised	
Water.	122
<b>Figure 24.</b> Saturated Column Test Results for AL7 Natrojarosite in Synthetic Salt Water.	123
<b>Figure 25.</b> Free Draining Column Test Result for AL7 Natrojarosite in Synthetic Salt	
Water.	124
<b>Figure 26.</b> Standard Design of a Permeability Test Rig	127

## List of Tables

<b>Table 1.</b> Chemical Analysis of Gag Island Laterite Ores Showing the Upper (Limonite) and Lower (Saprolite) Sections.	<b>9</b>
<b>Table 2.</b> Comparison between Autoclave Leaching and Atmospheric Pressure Tank Leaching of Average Nickel Laterite Ores	<b>12</b>
<b>Table 3.</b> Chemical Analysis (using X-ray Fluorescence) of the AL Natrojarosite	<b>65</b>
<b>Table 4.</b> Qualitative XRD Analyses of AL7 Natrojarosite	<b>65</b>
<b>Table 5.</b> Atmospheric Pressure AL7 Natrojarosite Decomposition Experiment Parameters	<b>68</b>
<b>Table 6.</b> Atmospheric Pressure AL7 Natrojarosite Decomposition Test Results – Hydrated Lime/Limestone Consumption and pH Range	<b>70</b>
<b>Table 7.</b> Temperature and Time Parameters for the Reaction Kinetics Experiments to Study the Conversion of AL7 Natrojarosite to Haematite	<b>80</b>
<b>Table 8.</b> Acid Production Maximisation Experiments Using AL7 Natrojarosite Sourced from Various Locations within the BHP Billiton Atmospheric Leach Process	<b>81</b>
<b>Table 9.</b> Temperature Time Relationship Experiment Matrix.	<b>82</b>
<b>Table 10.</b> Analysis of the Three Consecutive AL7 Natrojarosite Wash Solutions Prior to Autoclave Experiments.	<b>85</b>
<b>Table 11.</b> Autoclave Decomposition Kinetics Test Results for AL7 Natrojarosite.	<b>87</b>
<b>Table 12.</b> Accountabilities for Major elements Present in the Autoclave Kinetics Experiments on AL7 Natrojarosite Material.	<b>88</b>
<b>Table 13</b> Dissolved Sulphur and the Solid Phase Molar Ratio of Calcium to Sulphur for AL7 Natrojarosite Autoclave Kinetics Experiments.	<b>89</b>
<b>Table 14</b> Identification of Mineral Species Present in the Autoclave Discharge from the AL7 Natrojarosite Decomposition Kinetics Experiments by XRD.	<b>92</b>

<b>Table 15.</b> Free Acidities, Dissolved Sodium and Dissolved Sulphur Levels in Autoclave Discharge Solutions from the Decomposition of Various Natrojarosite Samples.	<b>96</b>
<b>Table 16.</b> Free Acidity in Autoclave Discharge.	<b>98</b>
<b>Table 17.</b> Dissolved Sodium in Autoclave Discharge.	<b>98</b>
<b>Table 18.</b> Dissolved Sulphur in Autoclave Discharge.	<b>99</b>
<b>Table 19.</b> Batch Agitation Stability Test Matrix.	<b>102</b>
<b>Table 20.</b> Sulphur Balance Using Iron and Sodium Association.	<b>109</b>
<b>Table 21.</b> Comparison of Calcium and Sodium Loss Results between Column Tests and Batch Agitation Tests in Deionised Water.	<b>125</b>

## Abstract

The jarosite group of compounds are yellow/brown clay like substances, both naturally occurring and synthetically produced in metallurgical processes. Jarosites have the structure  $MFe_3(SO_4)_2(OH)_6$ , where M can be numerous elements or compounds, most often potassium or sodium. The term jarosite refers specifically to the potassium form of the compound, but is synonymous with the whole group of compounds, often leading to confusion.

In nature, jarosites can be associated with acid mine drainage and acid sulphate soils as an intermediate product of the oxidation of pyrite and other iron/sulphur bearing minerals. In industry, jarosites are used in metallurgical processes, synthetically produced to precipitate an easily filterable form of solid iron. Jarosites have properties that make them a chemically unstable solid. Upon decomposition the jarosite group of compounds will generate sulphuric acid.

A literature review found many references to jarosites, their stability, methods of conversion to iron oxides, methods to extract reusable materials and environmental concerns. Most methods of recycling were unsuccessful. Accelerated conversion of jarosites to a form of iron oxide was a successful method of mitigating the risk of future acid generation. There were numerous specific ways of completing this task.

The BHP Billiton patented nickel atmospheric leach process generates natrojarosite (sodium form of the compound) as a by-product, when extracting nickel from lateritic ores. The by-product of this process was tested for stability to understand the decomposition process.

Accelerated decomposition of natrojarosite was attempted using limestone and hydrated lime at  $90^{\circ}\text{C}$ . Limestone did not react with the natrojarosite. Hydrated lime caused extensive dissolution of sodium and sulphur from the solid. However XRD analysis still reported natrojarosite as the solid material, suggesting incomplete decomposition and the formation an amorphous form of iron oxide not detected by XRD. Further decomposition tests were completed

using elevated temperatures and pressures in an autoclave. Natrojarosite was not detectable in the solid phase after treatment at a temperature of 212°C, converting to haematite at temperature above 150°C.

The stability of natrojarosite was measured using a number of methods on two natrojarosite samples sourced from the atmospheric leach process. The methods used were batch agitation, column testing and permeability testing. The aim was to provide a holistic result for the stability of natrojarosite if stored in a waste facility. Results obtained were compared against the standard TCLP test and found to be a more accurate method for measuring the stability of natrojarosite. The tests are more time consuming than TCLP testing but showed that natrojarosite was capable of decomposing to form sulphuric acid with time. This result was not obtained from TCLP tests, which suggested the solid material was stable. It was also found that salt water stabilised natrojarosite. Decomposition occurred in 40 and 80 days respectively, for two natrojarosite samples tested in deionised water. There was no evidence of decomposition after 150 and 280 days respectively for the same two samples. The common ion theory is thought to stabilise the natrojarosite which decomposes in an equilibrium reaction. Excess ions present in solution decrease the propensity for the solid to decompose.

The two natrojarosite samples tested varied in calcium concentration. Limestone and hydrated lime were added to the natrojarosite during the nickel extraction process. Gypsum is theorised to form an impermeable layer around the natrojarosite, increasing the stability of the compound. Gypsum is sourced from the neutralisation reaction between limestone or hydrated lime and the acid generated from natrojarosite decomposition.

# **1 – Introduction to This Thesis and Background**

## **Information on the Extraction of Nickel from Laterite Ores**

The term jarosite refers to a group of yellow/brown clay-like compounds found within nature with the general molecular formula of  $MFe_3(SO_4)_2(OH)_6$ . There are numerous subspecies within the jarosite group, all with iron sulphate hydroxide within their molecule. M refers to another element or compound which identifies the specific form of jarosite. Jarosite usually refers to the potassium form of the jarosite group and can lead to confusion. Other examples of jarosite forms are listed in Chapter 2.

Jarosite exists in significant concentrations throughout the earth's crust. There exists a naturally occurring abundance as an intermediate product in the weathering of iron and sulphur bearing minerals such as pyrite. Jarosite precipitation is applied in many metallurgical processes as an easily filterable scavenger precipitate of iron and other impurities. A major concern with the formation of jarosite is the potential creation of sulphuric acid during decomposition. As a result, many processes and methods have been touted as ways to minimise the potential damage to living matter by the release of acid if decomposition occurs.

The industrial production of jarosite has significant recognised problems and thus is avoided in hydrometallurgy when possible, often for scientifically confirmed problems associated with stability, but more often due to negative

sentiments surrounding its creation, storage and disposal. The zinc industry used the precipitation of jarosite to remove a readily filterable form of iron and other impurities from the product. However, the potential for jarosite to create acid on decomposition saw most of the world's zinc producers change their processes to precipitate the iron oxide species para-goethite instead of jarosite.

## **1.1 – The Purpose and Layout of This Thesis**

This thesis consists of three sections – a literature review and two experimental sections treating a metallurgically produced natrojarosite. The first section is a review of what literature and information exists on the jarosite group of compounds. The list is extensive and includes numerous types of jarosite. Most of the literature does not deal with the synthetic creation of jarosite through metallurgical processes, but is included as relevant, as similar problems occur when comparing naturally occurring and the synthetically produced forms.

The second and third sections of this thesis are two separate but interrelated experimental sections, both using a metallurgically formed, synthetic natrojarosite. The second section outlines methods to accelerate the decomposition of natrojarosite in controlled conditions to render the resultant solid material inert. Two methods are explained here – decomposition of natrojarosite using basic substances (hydrated lime and limestone) and using a



pressurised vessel. The third section describes methods of measuring the stability of natrojarosite once formed.

The experimental parts of this thesis differ from the standard layout of a thesis for clarity. That is, sections two and three contain the full methods and results for that particular experimental section.

The three parts of the thesis will now be explained in further detail.

### **1.1.1 – Section 1: Literature Review**

Chapter 2 contains a literature review and serves as a thorough introduction to the jarosite group of compounds. A large quantity of academic papers have been published on jarosite and related issues since the 1970's. This thesis describes in detail the mechanisms by which acid generation will occur when jarosites decompose and tracks methods of jarosite stabilisation. The literature review also gauges each method for its potential to minimise the impact of acid creation. Conversion methods suggested by the literature, primarily to form a more stable and thus environmentally acceptable iron oxide, as opposed to iron sulphides, are assessed. The literature review also captures any alternative uses for jarosite and their respective merits.

### **1.1.2 – Section 2: Jarosite Conversion or Stabilisation**

Chapters 3 and 4 of this thesis deal with two methods of jarosite treatment to confirm the potential described in the literature. These are firstly the stabilisation method, whereby a base such as hydrated lime is added, as used in a number of processes suggested in the literature. The second is the complete conversion of jarosite to iron oxide at various temperatures and pressures through the use of a pressurised reaction vessel or autoclave.

In Chapter 3 the addition of hydrated lime and / or limestone to jarosite is seen as the easiest method to convert the jarosite group of compounds to a more stable iron oxide form. Hydrated lime and limestone can be expensive depending on the site for the conversion process and its proximity to a source; however, the process occurs at relatively low temperatures in a simple agitated tank. Thus capital expenditure is low but operating expenditure is subject to the cost and availability of hydrated lime and limestone. From an environmental point of view this process is less favourable than one which extracts a usable product form.

The use of hydrated lime and limestone is referred to numerous times in the literature, giving this experiment relevance to many facets of stabilisation and conversion, both in naturally occurring and synthetic jarosite applications. There is the suggested use of fly ash to form an impermeable layer of gypsum around the jarosite and deep tilling of lime and limestone slurries to the same effect (Section 2.8.1). Section 2.10 relates to the addition of cement in the Jarofix and Jarochoaux processes, as well as the quoted literature in Section 2.11.3 of this

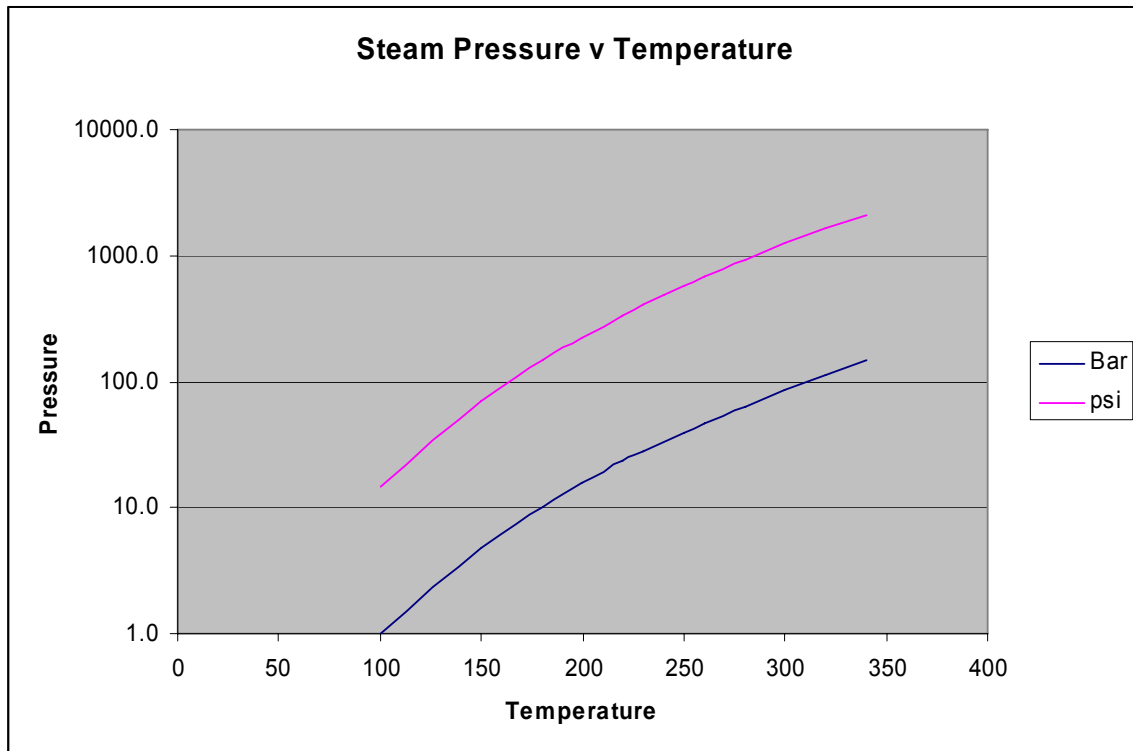
thesis referring to the basic decomposition of jarosite. However, much of the literature is contradictory, with some evidence suggesting conversion occurs, with others suggest impermeable encapsulation.

Thus the desired outcome from the first experimental section is to determine the mechanisms and the extent by which hydrated lime and limestone stabilise jarosite.

A number of researchers have used autoclaves to decompose various forms of jarosite to stable iron oxides. Autoclaves are expensive and potentially dangerous to operate, with high wear on equipment due to the contained pressures within. Operation of an autoclave is usually a batch process, adding to the complexity of a large scale operation. However, the product of conversion is haematite; a highly stable iron oxide that would require minimal management once dewatered and compacted into a tailings facility. These topics are dealt with in Chapter 4.

Lower temperature thermal conversion processes are more favoured compared to higher temperature operations, as the pressure reached inside the autoclave will be significantly lower, decreasing the risk of exposure to contained high pressure. However, decreasing the temperature is likely to increase the time taken for the reaction to reach completion. If haematite formation could occur at a lower temperature within a relatively short time period, an autoclave may be replaced by a pipe reactor. A pipe reactor is a length of pipe usually submerged in a heated medium (typically oil). Pipe reactors are much simpler and cheaper to build and operate than autoclaves. Figure 1 shows the steam pressure versus

temperature relationship. Note the logarithmic scale of the y axis. As Figure 1 shows, increases in temperature affect the pressure of operating conditions.



**Figure 1.** Steam Pressure Shown in Bar and Pounds per Square Inch on a Logarithmic Scale versus Temperature shown in degrees Celsius.

### 1.1.3 – Section 3: Measuring the Stability of Jarosite

The Toxicity Characteristic Leaching Procedure or TCLP Test is used as a standard method to determine the leachability of an element from a solid with time. As discussed in the literature review, the TCLP test only offers a snapshot of information about a particular solid product and thus may not be relevant to

risks (such as acid generation) associated with that solid over time or under varied conditions.

However, from the literature review it was noted that there is no single standard method for the determination of stability of such compounds as the jarosite group in metallurgical tailings, other than by methods that may enhance the dissolution of the mineral by processes that do not occur in nature. The findings supporting this statement are in Section 2.6. Treatment in conditions unlikely to naturally occur could thus potentially bias results from the real situation.

Chapter 5 of this thesis reports a potential method to determine the relative stability of natrojarosite residue from a metallurgical process patented by BHP Billiton. This stability measurement method was developed by Environmental Geochemistry International. Results and a critique of the method are reported in the experimental and conclusion sections.

## **1.2 – Introduction to Nickel Laterite Extraction Methods**

The world stocks of nickel ores are being gradually consumed, resulting in a need to develop methods to treat more marginal ore bodies. The preferred nickel ore is nickel sulphide, but these stocks are dwindling. Many processes for the metallurgical extraction of nickel from ore depend on the mineralogy of a specific ore body. Thus ores with characteristics that deviate from the optimal

mineralogical ore properties for particular processes are wasted, usually stockpiled and await a processing development that will unlock their value.

Approximately 70% of the remaining nickel ore stocks are of the type known as laterite ores (Dalvi *et al*, 2004). Laterite ores are divided into two sections, an upper weathered, iron rich material known as limonite and the unweathered parent rock below called saprolite. Development of laterite ore extraction processes has been determined by the marginality of the ore body. Companies must see the opportunity to make profit before they will invest capital into the development of a particular nickel laterite ore body.

Marginality is determined by a number of factors. The two main factors are the ease with which extraction occurs (this incorporates both the mining phase and the commodity extraction and purification phases) and the overall volume of the desired commodity in a body of ore of a defined size. The second factor enables an overall yield to be determined and the first factor determines a cost of production. Thus the economic value of the project can be determined, based on the current sale price for the commodity, the cost to produce it and the amount available for production.

The majority of nickel laterite ore bodies are of a low grade (<2.5%w/w nickel) but are of a size that makes mining and extraction viable. Additionally, nickel laterite deposits are often found in soft rock deposits close to the surface, thereby minimising mining costs.

### 1.2.1 – Background to the Development of the Process

In the early 1990's the then BHP Minerals research facility in Reno, USA developed a process to leach nickel and cobalt from lateritic ores, primarily aimed at the development of the Gag Island ore body in Indonesia (chemical analysis of the ore is given in Table 1). The process involved separation of the limonite from the saprolite, treating the two as separate streams. The process was novel in its approach as all other methods only extracted nickel from the limonite resource, where as this method extracted nickel from both the limonite and saprolite minerals.

**Table 1.** Chemical Analysis of Gag Island Laterite Ores Showing the Upper (Limonite) and Lower (Saprolite) Sections.

	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	S	Si	Zn
All values in %w/w of total dry solid														
Detection Limit	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.05	0.05	0.01
Gag Island Limonite	4.45	0.07	0.10	1.88	0.02	40.10	1.64	0.64	0.00	1.49	0.01	0.32	4.38	0.03
Gag Island Saprolite	1.73	0.87	0.14	1.04	0.02	13.85	14.65	0.79	0.16	1.89	0.01	0.00	17.05	0.03

In many currently used processes, the saprolite fraction is not extracted, as pressurised autoclaves are used to leach only the limonite. Limonite is high in iron and low in magnesium. Saprolite generally contains 10 to 20% magnesium which, at elevated concentrations, will severely scale an autoclave by precipitating out of solution under pressure. A nominal cut off concentration of

5% magnesium was set for autoclave feed grade. Thus, for the majority of nickel laterite ores, the deeper saprolite reserves were not and are still not planned for extractive processes.

The process employed now by BHP Billiton thus far to pilot scale (0.5t/day) involves the addition of limonite (slurried in salt water) to a three hour leach stage with concentrated sulphuric acid. Salt water is used as a number of nickel laterite ore bodies are located on small equatorial islands where fresh water availability does not allow the use of potable water in large volumes for metallurgical extraction. The high iron concentration from a primarily goethitic ore dissolves up to 95% of the original mass in approximately three hours. A reductant (e.g. sulphur dioxide gas) is used to chemically reduce the mineral asbolane, which contains most of the cobalt. Cobalt is usually present at between 0.05 and 0.1% of the limonite but markets for approximately 5 to 10 times the value of nickel and therefore is an economically viable by-product of the process.

Saprolite slurry is added to the limonite leach product. The saprolite is leached, consuming the acidity remaining in solution after the limonite leach. The acid concentration decreases and iron precipitates as natrojarosite. The iron precipitation reaction releases acid, which further leaches the saprolite, promoting reaction for approximately 11 hours.

Temperatures used in atmospheric leaching are lower than those used in autoclaves. Thus, in atmospheric leaching there is no added benefit to reaction rates from the increased pressure. For comparison, in an autoclave operation, at temperatures over 200°C iron dissolved from the limonite is precipitated during



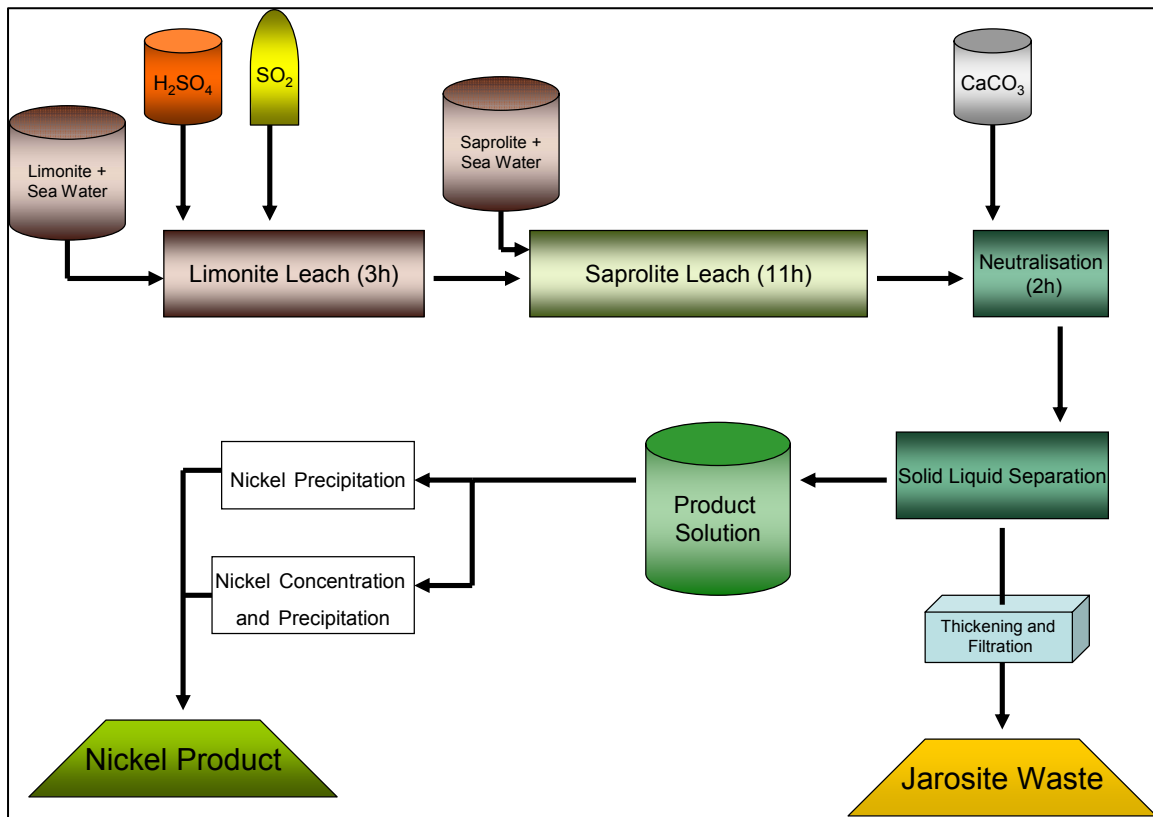
the leach as haematite; acid consumption is relatively lower as acid becomes available as iron is precipitated, leaching times are reduced by approximately a third and acid concentrations in the discharge are higher. Table 2 contains a summary of the issues in order to explain the reasons for the development of the new process.

The ability to use all of a nickel laterite ore body and not just the upper limonite layer is the major benefit of the atmospheric leach process, with simplicity of operation, minimal downtime and minimal preventative maintenance expected from a commercial scale plant. From an occupational health and safety (OH&S) point of view, the hazards associated with operating sealed units at high pressure are completely mitigated.

The disadvantages are primarily economic in operating costs, as sulphuric acid consumption is increased. Tailings management is also of concern as the stability of natrojarosite compared to haematite requires long term management.

**Table 2.** Comparison between Autoclave Leaching and Atmospheric Pressure Tank Leaching of Average Nickel Laterite Ores

<b>Parameter</b>	<b>Autoclaves</b>	<b>Atmospheric Leaching</b>
Ore Type Utilised	Limonite Only	Limonite and Saprolite
Extraction from Limonite	~100% Ni and Co	~100% Ni and Co
Extraction from Saprolite	0% Ni	60 – 80% Ni
Leach Product	Haematite - stable	Natrojarosite – relatively unstable
Leach Time	~ 1 hour (limonite)	3 hours (limonite) 11 hours (saprolite)
Acid Consumption	100 - 200kg/t ore	500 - 700kg/t ore
OH&S Considerations	Pressure (~50atm) Heat (>200°C) Acid (100g/L)	Heat (100°C) Acid (300g/L initial tank then <30g/L throughout remainder of process)
Operational Considerations	Batch process as continuous autoclaves increase wear and OH&S risks. High wear operation on equipment – high replacement and preventative maintenance costs. High cost equipment – high pressure pumps, pressure let down valves, titanium autoclave body required. Lower acid consumption costs. Higher output acid needs neutralisation – higher consumption of neutralising agents such as limestone.	Continuous process. Tank based operation. Low equipment and maintenance costs. Higher acid consumption costs. Lower acid output therefore less neutralisation agent costs.



**Figure 2.** Schematic of the Atmospheric Nickel Laterite Leach Process Treating Both the Limonite and Saprolite Sections of the Nickel Laterite Ore Body, Patented by BHP Billiton.

Figure 2 shows a schematic of the BHP Billiton patented process for atmospheric leaching of both the limonite and saprolite sections of a nickel laterite ore body. Solid liquid separation is completed using a counter current decantation process (CCD), where solids are washed and settled in a counter current direction to the product solution. The natrojarosite waste stream is neutralised with limestone and hydrated lime to a pH of 9 during the thickening

and filtration steps. After filtration, the cake moisture content is approximately 30%.

Nickel concentration and precipitation from the liquid product stream can involve a number of steps such as ion exchange, solvent extraction or preferential precipitation. The final product is usually a nickel refinery feed stock like nickel hydroxide or carbonate.

### **1.2.2 – Current and Future Direction of Nickel Laterite Processing**

Due to the perceived problems with the formation of natrojarosite, BHP Billiton Technology removed sodium from the slurry by using fresh water instead of salt water. It was found that goethite was the iron precipitant under these conditions, however some hydronium jarosite ( $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ) was also assumed to be co-precipitating, based on a sulphur balance in the solid.

The benefit of changing from a natrojarosite to goethite producing process is the formation of stable tailings that, if they were to decompose, can not form sulphuric acid. The disadvantage of changing the process is the need for fresh water as an added cost to resource, one that on a small equatorial island ore body, as a number of laterite deposits are, is not easily fulfilled.

The potential presence of hydronium jarosite in the tailings requires additional limestone to be added to the final leach neutralisation step. Conversion in basic media is covered in Chapters 2.10 and 2.11.3 and results in the formation of goethite with the release of acid. Both the conversion process and

the neutralisation of the resulting acid consume limestone, increasing operational costs for the proposed process.

Another patented adaptation of this process is a combined pressure and atmospheric leach. The limonite section of the ore body is leached in a conventional autoclave. The discharge has a relatively high acidity that requires a neutralising agent in a standard pressure leach flow sheet. However, by leaching the saprolite using the autoclave discharge there is not only a cost saving on neutralising agent, but also the major advantage of extracting further nickel from a whole of ore body process. This process is the design criteria for the Ravensthorpe laterite process in Western Australia.

### **1.2.3 – Competing Technologies**

A number of failed ventures in the late 1990's, particularly in Western Australia, saw nickel laterite ores as less favourable options for development. With this and a lack of new green field discoveries, a decrease in nickel supply caused an increase in the nickel price. The decrease in supply was coupled with large increases in demand, particularly for stainless steel by China. With advances in technology over the last ten years, more options are available to companies looking to develop nickel laterite ore bodies.

As a result, exploitation of nickel laterite deposits is again becoming popular as viable mining and processing options develop. As mentioned earlier, even though 70% of known nickel reserves are in laterite ores, they only account

for approximately 40% of world nickel production (Dalvi *et al*, 2004). Other methods of treating nickel laterites include pressure leaching, as shown in Table 2, with heap leaching now accepted as a another viable method of extraction. Methods to extract nickel through heap leaching can lead to the re-precipitation of iron in the heap. As a result, it is likely that jarosites will be present in heap leaching residues – a field of study yet to be examined in specific relation to nickel laterite heap leaching. Again, commonality between naturally occurring and synthetically precipitated jarosite and the associated problems will be relevant to heap leach residues. Heap leaching, like the atmospheric leach process, has been patented by BHP Billiton.

A number of pyrometallurgical processes exist throughout the world. Most, like Cerro Matoso in Columbia, rely on a specific ore type to be fed to the kilns for nickel extraction. This requires blending of the existing ore deposit to meet specific requirements. Suitable ores for this process will be consumed in the next twenty years. Most pyrometallurgical processes do not have flexibility to treat ores of varying grades. The capital cost of construction of a pyrometallurgical processing plant requires a large ore body of consistent grade. As previously mentioned, there have been few such findings in the last ten years.

## **2 – Current and Relevant Jarosite Issues**

The contents of Chapter 2 have been compiled from the extensive library of literature on the subject of the jarosite group of compounds. Chapter 2 acts as a background to the jarosite problem worldwide. As mentioned previously, much of the information does not directly relate to the experiments completed in this thesis. However, results obtained are applicable to the various circumstances in which jarosites are found.

### **2.1 – Physical Properties and Chemical Composition**

The term jarosite refers to a group of naturally occurring and synthetically produced minerals (Dutrizac, 1990; Al *et al*, 1994; Pelino, 1998; Hage *et al*, 1999). In nature, jarosite exists as an intermediate product of the oxidation of pyrite and thus is associated with environmental problems such as acid sulphate soils (Brown, 1971) and acid mine drainage (Long, 1992). In industry, jarosites have been extensively produced to remove dissolved iron from a product solution by precipitation (Kashkay *et al*, 1975; Dutrizac *et al*, 1983; Dutrizac *et al*, 1984). In sulphuric acid, jarosite will readily precipitate through a process of selective precipitation using pH adjustment to approximately 2. The advantage of this process is that jarosite is readily filterable, allowing for ease of solid liquid separation and is much better than iron oxides produced under similar conditions

(Loan *et al*, 2006). Specifically for the zinc industry, another advantage of this precipitation is that the formation of jarosite will also scavenge other impurities such as lead and silver from the zinc product, improving the quality of the product (see M in the formula below).

Jarosite is yellow to brown in colour, of fine clay like size, texture and appearance; with excellent water retaining properties.

Chemically, the jarosite group of compounds refers specifically to those minerals containing iron hydroxy sulphate in the formula:



where M is commonly potassium (K) or sodium (Na), or in rarer forms, ammonium (NH<sub>4</sub>), hydronium (H<sub>3</sub>O), silver (Ag), thallium (Tl), lead (Pb) or strontium (Sr) (i.e. the rarer forms often relate to metal impurities extracted from a metallurgical product solution and are not often seen occurring naturally).

The term jarosite is used for the potassium form of the compound, as this compound is the most common in nature. This can lead to confusion as the use of jarosite can refer both the group of compounds and to the potassium form. Where possible, this confusion can be avoided by naming the jarosite form. However, many authors quoted in this thesis do not specify the type and use the term jarosite in reference to the group of compounds.

It is evident that the jarosite group of compounds can form under a variety of geological conditions. The essential requirements are iron, sulphur and an



alkali earth metal in an acidic environment ( $\text{pH} < 3$ ). Once formed, however, the mineral decomposes readily upon removal from its region of stability (Figure 4). It is generally accepted that, regardless of decomposition rate, jarosite will alter to ferrihydrite (Equation 5).



**Figure 3.** Natrojarosite Production from the BHP Billiton Atmospheric Leach Plant – Newcastle Technology Centre 2001-2.

## 2.2 – The Mineralogy of Jarosites

Alunite ( $\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ ) relates to jarosite through similarities in structure and properties, with aluminium substituted for iron, and is often present associated with jarosite (Long *et al*, 1992).

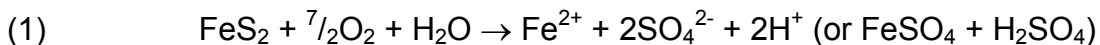
Jarosite has a well defined x-ray diffraction (XRD) pattern, which allows for clear identification by this method, even in low concentrations. However, XRD can sometimes not properly identify jarosite when it is of a very fine sized crystal or amorphous.

Jarosite species have a number of mineralogical features that correspond to associated minerals such as pyrites and limonite. Past mineralogical reports grouped jarosite and natrojarosite together as either gelbeisenerz or misy (Palache *et al*, 1951). Any crystal form is minute and indistinct, found as a crust or coating adjacent to pyrite oxidation sites. Crystals are described as pseudo-cubic or flattened with a hexagonal outline. The structure can also exist as a solid solution with alunite.

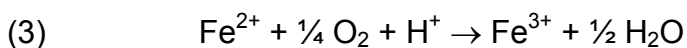
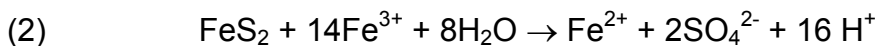
## 2.3 – Naturally Occurring Jarosite Sources

### 2.3.1 – Chemical Mechanisms of Formation

The precursors for jarosite formation are iron, sulphate and a cation source, usually an alkali earth metal (with the exception of lithium) in proximity to each other, in a temperature and pH range conducive to jarosite precipitation. These conditions occur naturally by a variety of mechanisms, most commonly from the direct oxidation of a pyritic species (Long et al, 1992; Rde *et al*, 1998) according to Equation 1:



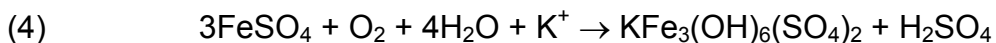
or, as occurring in acid mine drainage, a cyclic process generates Fe(III) as in Equations 2 and 3.



Sodium and potassium are readily available in some environments where the mechanisms outlined in Equations 1, 2 and 3 occur. The availability of an alkali earth metal such as sodium will ensure the formation of jarosite over an iron oxide compound like goethite for example.

### 2.3.2 – Acid Sulphate Soils

Acid sulphate soils are another source of jarosite (Brown, 1971). Acid sulphate soils were estimated worldwide to cover approximately 12.6 million hectares by Beek *et al*, 1980. Sulphide rich regions in a typical soil profile occur 0.75 to 0.85 metres below the current soil surface due to changes in the sea levels over time. At this depth, oxidation does not occur readily under natural conditions (Lin *et al*, 1998), resulting in a layer of mixed pyrite and jarosite as shown in Equations 1 and 4:



Acid sulphate soils (typically pyrite rich -  $\text{FeS}_2$ ) are an environmental problem in low-lying agricultural regions throughout the world (van Breemen, 1976). Pyrite species were deposited as coastal river plains in-filled during the last decrease in sea level. The dynamic system of conversion between pyrite, jarosite, alunite and iron oxide species is accelerated through agricultural processes such as land clearing, irrigation, drainage and harvesting. This leads in an increased acidity in the soil as described in Equations 1, 2, 4 and 5.

Acid sulphate soil management is of particular importance on the eastern coastal region of Australia (Lin *et al*, 1998) where controlled floodplains and the high intensity farming and land clearing for urban development are affecting water tables and estuarine water quality. Agricultural processes mean that soils

will be aerated and irrigated on a regular basis. This can accelerate oxidation through the inflow of dissolved oxygen, resulting in the increased formation of acid. The acid and entrained metallic ions will be mobile and thus washed from the soil through irrigation and ground water.

## **2.4 – Mining and Metallurgical Sources of Jarosite**

Sulphur bearing minerals such as pyrite are regularly associated with a wide variety of metal ore deposits around the world, examples of which are copper and nickel. Tailings from mines can produce conditions suitable for jarosite formation. By mining and processing pyrite minerals, iron sulphides are exposed to oxidative conditions. Products of the oxidation process become mobile when exposed to weathering and ground waters. Entrained metal species in the mined pyrite and the produced jarosite can be released due to the acidic conditions created. In these examples jarosite should be seen as an intermediate prior to and during the formation of acid.

The jarosite group of compounds can also be precipitated as a solid residue from a metallurgical process. For example, it can be formed during the roast-leach-electrowinning-processing of zinc sulphide ores (Kashkay *et al*, 1975; Dutrizac *et al*, 1984). The formation of a jarosite is promoted to remove dissolved iron and advantageously scavenge any contaminant metals from the solution before electrowinning occurs. This process produces as many forms of

jarosite as there are impurities in the leachate solution that will co-precipitate. However, the common types are sodium, ammonium and lead jarosite.

Jarosite continues to be regarded as a reliable and easily filtered iron precipitate, with the ability to co-precipitate other impurities from various metallurgical processes. This will continue as ore bodies become more marginal in grade and impurities increase. Examples of this include the treatment of nickel laterite ore bodies. Jarosite can be a constituent of the tailings from high-pressure acid leaching (HPAL) nickel laterite processes and the major residue from the atmospheric leaching (AL) of nickel laterite in sea water.

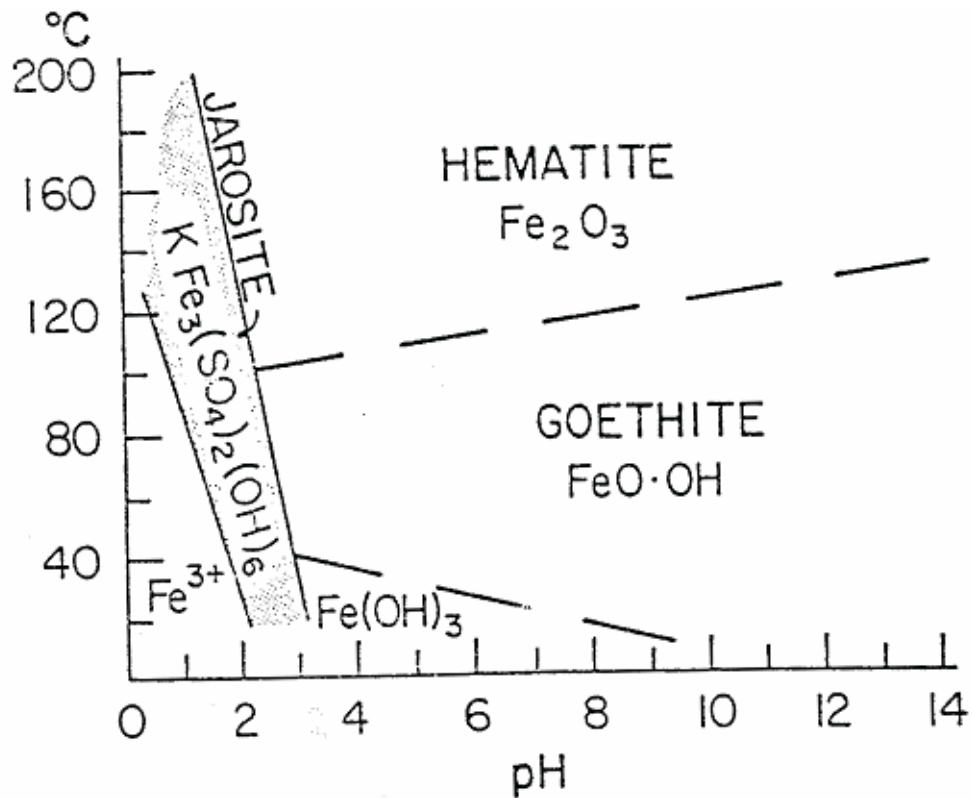
In both instances (intermediate or final product), the formation of acid during decomposition is highly likely and must be managed as a part of the metallurgical process.

## **2.5 – Jarosite Stability – Known Chemical Data**

The stability of iron oxides, hydroxides and sulphides in relation to temperature and pH is given in Figure 4. The concentration of sulphides, both in the oxidation of pyrites and in most metallurgical processes, leads to the creation of the jarosite species. Note that the stable areas defined in Figure 4 suggest what species will form if iron is precipitated under these conditions.

It should be noted that haematite, once formed, is unlikely to further decompose when exposed to conditions seen in nature, whereas all other

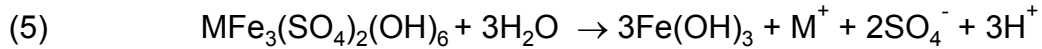
species shown in Figure 4 have the ability to decompose into other species if conditions change and the substance moves out of the defined stability region.



**Figure 4:** Temperature vs. pH Stability Field for Potassium Jarosite  
(Babcan, 1971).

As shown in Figure 4, jarosite is stable within a thin band of pH over a range of geologically significant temperatures. It is interesting to note that the formation of jarosite, as described in Equations 1, 2 and 4, releases protons, thus decreasing the pH. However, with carbonic acid buffering ( $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}$ ) it is rare for low pH levels to be maintained in nature.

It is argued that the stability of jarosite in nature is a major concern, especially for metallurgical processes that produce the substance. An example of the decomposition of jarosite in water is given in Equation 5. Basic conditions will also decompose jarosite as shown in Equation 6 (Patiño *et al*, 1994):



It can be assumed in Figure 4 that potassium can substitute with other elements to form varying types of jarosite, such as sodium (natrojarosite). To correctly define the stability of jarosite, five variables need to be considered (Brown, 1971). They are eH, pH, activity of total sulphur, activity of dissolved iron and the activity of the associated basic metal.

Results from eH variation tests have shown that iron will not precipitate from the nickel laterite leachate when iron(III) is reduced to ferrous. Thus ferric or an oxidant for iron(II) must be present before precipitation will occur.



## **2.6 – Measuring the Stability of Jarosite**

Whilst reviewing the literature related to jarosite, it was noted that no single, concise and broadly accepted method to measure the stability of the compounds was available. Chemistry based methods using empirically generated thermodynamic data such as Gibb's free energy can be useful but may be inaccurate due to impurities in or individual traits of the solid of interest, or the relevance to naturally occurring conditions in which samples will degrade over time. Such methods are described in Section 2.6.1.

Methods are used in industrial and environmental monitoring to determine the likelihood of a solid product decomposing to release constituent parts, particularly environmentally significant elements such as lead and mercury. An example of this is the toxicity characteristic leaching procedure or TCLP test (Section 2.6.2).

The TCLP Test is widely used throughout the world and is the required standard measurement of a solid waste by the Environmental Protection Agencies in all states of Australia (Australian Standard AS – 44393). It is also the standard required in the United States federal system (US EPA Proceedings, 1999). The TCLP was developed in 1984 under the Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA) (1984) and is the U.S. EPA regulatory method for classifying wastes as hazardous or non-hazardous based on toxicity (Sorini, 1996).

Many variants exist at a state level in the U.S and throughout Europe. Methods other than TCLP are explained further in Section 2.6.4.

The Australian Standard (AS – 44393) recommends the Australian requirements for sample preparation and the use of columns to test the quality of leachate produced. However, most laboratories in Australia use this only as a method for sample preparation and opt for the TCLP test as the actual stability test used.

### **2.6.1 – Energy of Formation**

Gibb's free energy could be used to compare types of jarosite to each other, as the energy of formation should be proportional to that released during decomposition. If formation is more likely for one form of jarosite over another it can be argued that decomposition is less likely under favourable conditions. There should be more of an abundance of one form of jarosite in nature if this type is more likely to precipitate and slower to decompose. Little has been completed on the thermodynamic preferences of formation and stability for jarosite species. Kashkay *et al* (1975) studied synthetic jarosite to determine Gibb's Free Energy through the stability of the molecules in equilibrium with a solution. From this work the order of stability (highest to lowest<sup>\*</sup>) was:

---

<sup>\*</sup> *Using methods other than Gibb's free energy studies hydronium jarosite is rated as least stable by Arauco and Doyle (1986), while Hage et al (2000) quotes natrojarosite as less stable than ammoniojarosite*

jarosite –  $\text{K}[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ , natrojarosite –  $\text{Na}[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ , argentojarosite –  $\text{Ag}[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ , hydronium jarosite –  $(\text{H}_3\text{O})[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ , ammoniojarosite –  $(\text{NH}_4)[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ , plumbojarosite –  $\text{Pb}\{[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2\}_2$ , strontium jarosite –  $\text{Sr}\{[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2\}_2$ .

This list conforms to the notion that stability relates to abundance. Potassium jarosite is the most abundant naturally occurring jarosite, followed by sodium jarosite (natrojarosite).

### 2.6.2 – The TCLP Test – Benefits and Drawbacks

The TCLP test is recognised by the US EPA and the various Australian environmental legislative and protection agencies as a standard for measuring the likelihood of a toxic substance being released to the environment from a solid, liquid or multiphasic material (Manahan, 1994).

For solid wastes such as jarosite, the TCLP test is initiated by determining the size distribution of particles, ensuring the material to be tested has a surface area equal to or greater than  $3.1\text{cm}^2$  or of a particle size smaller than 1mm diameter. 5g of this solid is mixed vigorously with 96.5mL of water. The pH of the resultant solution determines the extraction fluid to be used later in the test.

If the pH of the resultant solution is less than 5, the extraction fluid used is an acetic acid / sodium acetate buffer of  $\text{pH } 4.93 \pm 0.05$ . If the pH is greater than 5, 3.5mL of 1 molar hydrochloric acid is added to the solid in solution; the slurry

is stirred and then heated to 50°C for 10 minutes. After cooling the solution to room temperature the pH is again determined. If the pH is below 5 the acetic acid / sodium acetate buffer solution will be used as the extraction fluid. If above pH 5, the extraction fluid shall be a dilute acetic acid solution with a pH of  $2.88 \pm 0.05$ .

Once the extraction fluid is determined, a known dry weight of the sized solid material is added to a known volume of the chosen extraction fluid and the mixture is tipped end on end for 18 hours. The solution is then separated from any entrained solid and analysed for dissolved elements, usually by ICP-MS (inductively coupled plasma – mass spectroscopy). The results are calculated using the known mass of solid and volume of liquid to determine the total dissolved elemental mass per unit of solid (usually kilogram per tonne).

A table of accepted levels for most elements in solution has been determined by various governmental regulatory bodies around the world. The individual results from the TCLP test are compared to these tables to determine if the waste upon decomposition will produce concentrations of dissolved elements exceeding legal limits. If the answer is yes then the waste is deemed as a hazardous or toxic waste and subsequent storage and disposal requirements are set.

The TCLP test is recognised by many regulatory bodies as the standard measurement of risk for a solid material. However, such experiments tend to require a rapid analysis from a solid that may stay relatively inert for hundreds if not thousands of years. The TCLP test takes an immediate snapshot of a solid waste at any one time and does not allow for potential changes in the structure

and stability of a solid waste with time. Additionally, the process through which the extraction fluid is determined is not a realistic representation of the mechanisms that would affect a solid waste over time.

### **2.6.3 – TCLP Results for BHP Billiton Natrojarosite**

The jarosite produced from all seven operations referred to in this thesis were submitted to a NATA accredited laboratory for TCLP testing and did not return any significant amounts of dissolved metals in the leachate. Certainly no acidity in the leachate was apparent. However, as a result of higher than acceptable concentrations of nickel and manganese in the solid waste prior to TCLP testing, the waste was deemed as an industrial waste by the New South Wales EPA guidelines. These guidelines separate solid wastes into various categories based around the three increasingly dangerous headings of inert, industrial and hazardous. Thus this substance was deemed an industrial waste on chemical analysis data alone.

### **2.6.4 – Other Methods of Solid Matter Chemical Stability Measurement Used in the World**

Sorini (1996), in a paper describing the use of stability testing on coal fly ash, has completed a thorough list of method variations to the TCLP used throughout North America and Europe. Below is a summary of the findings.

#### **a) USEPA (United States Environmental Protection Agency) Methods**

- *Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA Method 1311):* The TCLP (U.S. EPA 1990c) is designed to simulate the leaching a waste will undergo if disposed in an unlined sanitary landfill. It is based on a co-disposal scenario of 95% municipal waste and 5% industrial waste.
- *Synthetic Precipitation Leaching Procedure (SPLP) (U.S. EPA Method 1312):* The SPLP (U.S. EPA 1990a). The procedure uses simulated acid rain or reagent water as the extraction fluid, depending on the constituents of interest. The extraction fluid is determined by the location in the United States where the sample of interest has come from, with the Mississippi River used as the border. To the east, an extraction pH of  $4.2 \pm 0.05$  is used. To the west, the pH is increased to  $5.0 \pm 0.05$ . When volatile organic compounds or cyanide are being evaluated, reagent water is used as the extraction fluid.
- *Multiple Extraction Procedure (MEP) (U.S. EPA Method 1320):* The MEP (U.S. EPA 1990b) simulates the leaching of a waste from repeated precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions are to reveal the highest concentration of each constituent that is likely to leach in a natural landfill (U.S. EPA 1990b). The first extraction is performed according to the Extraction Procedure (EP) Toxicity Test (U.S. EPA 1980), which was replaced by the TCLP for determining the characteristic of toxicity. Leaching involves monitoring the

pH of the waste in reagent water and using an acetic acid solution to maintain the pH of the slurry at  $5.0 \pm 0.2$ . The remaining solid is re-extracted nine times (or more) using synthetic acid rain as the leaching fluid. The synthetic acid rain leaching fluid is prepared using sulphuric and nitric acids in distilled, deionised water to give a pH of  $3.0 \pm 0.2$ . If the concentration of any constituent of concern increases from the 7th or 8th extraction to the 9th extraction, the procedure is repeated until the concentrations decrease. The method is applicable to liquid, solid and multiphasic materials.

#### **b) ASTM (American Standard Test Method) Standard Methods**

- *ASTM Method D-3987, Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM 1995a)*. This is a procedure for rapid generation of a leachate from solid waste. The final pH of the leachate is to reflect the interaction of the leaching fluid with the buffering capacity of the waste. The procedure is not intended to produce a leachate representative of leachate generated in the field and the method does not simulate site-specific leaching conditions (ASTM 1995a). The procedure involves an 18-hour contact time between a solid waste and reagent water with rotary agitation.
- *ASTM Method D-4793, Standard Test Method for Sequential Batch Extraction of Waste with Water (ASTM 1995b)*. This method is used to estimate the mobility of inorganic constituents from the waste under

specified test conditions. The final pH of the leachate is intended to reflect the interaction of the leaching fluid with the buffering capacity of the waste (ASTM 1995b). Again, this method is not intended to produce representative leachate generated in the field and it does not simulate site-specific conditions (ASTM 1995b). ASTM Method D-4793 is a serial batch test that uses reagent water as the leaching fluid. The method is applicable to inorganic constituents only and can be used to test any waste containing at least 5% solids. The leaching steps are repeated so that ten leachates are generated.

- *ASTM Method D-5284, Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid (ASTM 1995e).* A modification of ASTM Method D-4793, it uses a leaching fluid of a pH that reflects the pH of acidic precipitation in the geographic region in which the waste being tested is to be disposed (ASTM 1995e).
- *ASTM Method D-5233, Standard Test Method for Single Batch Extraction Method for Wastes (ASTM 1995d).* This is an agitated extraction test and is very similar to TCLP. The major difference between the two procedures is that ASTM Method D-5233 does not require particle size reduction. According to the method, interpretation and use of the test results are limited by the assumption of a single co-disposal scenario and by differences between the extraction fluid used in the method and the real landfill leachate (ASTM 1995d).



- *ASTM Method D-4874, Standard Test Method for Leaching Solid Waste in a Column Apparatus (ASTM 1995c)*. This column method, using reagent water in a continuous up-flow mode, is intended to provide aqueous leaching in a dynamic partitioning manner (ASTM 1995c). It is written so that many of the specific column operating conditions can be selected by the user to meet their specific objectives (ASTM 1995c). The method states that analysis of the column effluent can provide information on the leaching characteristics of the waste under the testing conditions used (ASTM 1995c). It is also stated that the method is not intended to produce results to be used as the sole basis for (1) the engineering design of a landfill disposal site or (2) classification of wastes based on leaching characteristics (ASTM 1995c).

### **c) Canadian Methods**

- *Leachute Extraction Procedure (LEP)*. The LEP (Ministry of the Environment 1985) is the regulatory leaching test used in the province of Ontario, Canada and is identical to the regulatory leaching procedure used by the Canadian provinces of British Columbia, Alberta, and Manitoba (Environment Canada 1990). The test is very similar to the EP Toxicity Test.
- *Quebec R.s.Q. (Q.R.s.Q.)*. The Q.R.s.Q. (Ministere de L'Environnement 1985) is the regulatory leaching method used in the province of Quebec,

Canada. It is very similar to the TCLP, with some procedural differences (Environment Canada 1990).

#### **d) European Methods**

- *Availability Test (NEN 7341)*. The availability test (Netherlands Normalisation Institute 1993a) is based on leaching a finely ground sample under two controlled pH conditions (pH 4 and pH 7). The purpose of the test is to indicate the quantity of an element that may be leached from a material under environmentally extreme conditions. That is, the test aims to determine elemental availability in the very long term, after disintegration of the material, when the material is fully oxidised and with complete loss of acid neutralisation capacity.
- *Column Test (NEN 7343)*. The NEN 7343 column test (Netherlands Normalisation Institute 1993b) is designed to simulate the leaching behaviour of a waste material in the short, medium and long term. This is done by relating contaminant release (mg/kg leached) to the liquid to solid ratio. The time scale relation is obtained from the height of the column and rate of infiltration. Demineralized water (pH = 4) flows upward through ground material ( $p_{95} = 4\text{mm}$ ). Seven consecutive leachate fractions are collected, corresponding to a liquid-to-solid ratio range of 0.1 to 10 L/kg. Very slow changes in mineral composition are not addressed by this test; and NEN 7343 test conditions do not correlate on a one-to-one basis with

field conditions because of several variables, such as temperature, channelling, aging and degree and length of contact.

- *French Leach Test (Agence Francaise de Normulisation 1987)*. This is the French Ministry of the Environment standard regulatory method for determining the soluble fraction of a solid waste in an aqueous solution. It requires particle size reduction and involves mechanical stirring of the sample with water in a 10:1 liquid to solid ratio for 16 hours. A second and third extraction is performed, and the cumulative extracted soluble fraction for each constituent can be determined.
- *Germun (German) Leach Test (DIN 38414 S4) (Institut fur Normung 1984)*. Generally used in Germany, the test involves table shaking of the extraction slurry for 24 hours. The liquid-to-solid ratio is 10:1. The method is applicable to solids, pastes, and sludges.
- *TVA (TVA 1988)*: This is the standard regulatory method used in Switzerland. A 100 to 200g sample is extracted using carbon dioxide-saturated water at a liquid-to-solid ratio of 10:1 for 24 hours. The continuous carbon dioxide injection is considered to represent a time-scale reduction.

#### **2.6.5 – Batch Leaching and Column Testing**

Environmental Geochemistry International (EGI) developed an experimental method (Miller, unpublished work in progress) to determine what

will happen to a solid waste when impounded in a tailings dam or a similar wet containment area common to mining and metallurgical sites throughout the world. This method uses information gathered from two different types of experiment to determine the volume of products of decomposition leaving a solid waste via dissolution. Similarities in the EGI methods can be seen throughout Section 2.6.4 of this thesis, where it is likely that favourable methods from the array of options available were taken to give a holistic approach applicable to a wide variety of samples.

The first experiment, known as batch agitation, requires a volume of the waste to be vigorously agitated in a known volume of water (or plant water<sup>†</sup>) for a set period of time and then filtered. The resultant liquid is analysed for dissolved elements to determine what, if any, of the original solid material has dissolved. The same solid is reintroduced to a known volume of water and the process repeated. The experiment is crude when referring to the conditions existing in a tailings facility, but much improved on those of the TCLP test to determine which elements, if any, are mobilised by decomposition and in what volume. The advantages are the same solid is treated over time, thus determining a rate of dissolution. Changes to stability with time can also be determined over a longer period, not relying on the “snapshot” approach offered by TCLP. Additionally, a worst case scenario can be developed by using high purity water, thereby increasing the concentration gradient for dissolution from the solid to the liquid.

---

<sup>†</sup> Some metallurgical processes will produce plant water which is recycled throughout the process and contained on site. Often this water is not potable but clean enough for the metallurgical process. Testing the stability of a solid in this water is often much more relevant than using clean water.

The second experiment uses large Buchner funnels to inundate solid samples with known volumes of water to determine if elements will dissolve under conditions more likely to be seen in tailings facilities (i.e. compacted, less permeable solids). Two tests are completed on any one sample – one free flowing and one permanently saturated. The advantages include the ability to use variation in the solutions to mimic real case conditions, as well as removing the increased surface contact likely with an agitated test such as the batch agitation or the TCLP test.

Another important parameter in devising a holistic approach to solids stability was that of the permeability. Thus experiments to determine the wet permeability were developed and tested. A multi variable stability determination included the likelihood of dissolution and then permeability of the solid for the dissolved elements to escape.

## **2.7 – Mining and Tailings Placement Problems**

The stable storage of the jarosite group of compounds is a major problem throughout the world. Menad and Björkman (1998) quote the 1998 annual production of jarosite in Europe at four hundred thousand tonnes with eight million tons already stored.

Jarosite has historically been found in proximity to pyrite and other sulphide ore mining operations (Dutrizac, 1996). It may be pyrite overburden

exposed to oxidative conditions resulting in conversion to jarosite (Herbert, May 1997; Herbert, 1997; Levy *et al*, 1997; Schuiling *et al* 1997), the result of acid mine drainage (Alpers *et al*, 1989; Taylor *et al*, 1998) or, in the case of a combined mine refinery process, tailings from the mineral recovery. Jarosite is stable in a limited range of pH values and temperature (Figure 4). Thus, outside of these conditions, the problems associated with the decomposition of jarosite will affect many abandoned mining and processing sites. The mechanics of this problem are two fold.

Firstly a mine exposes once-buried rock to oxidising conditions. Iron sulphides such as pyrite will oxidise, releasing acid and forming jarosite. This can occur on the surface or in mine shafts where surface water and air can encroach, resulting in high acid concentrations. This will cause metal species to become mobile affecting water bodies such as the water table and any river systems often required by, and found adjacent to, mining processes.

Secondly, acidic conditions while they are present will promote the stabilisation of jarosite from pyrites again (Figure 4). Once acidity decreases, either through natural carbonate buffering or mine remediation processes, the stability of the new jarosite formed will decrease, leading to further decomposition and further acid release. If this occurs near a pyrite source, the process will be replicated or, at least, jarosite stability will temporarily return, prolonging the problem. This effect can be mapped as concentric circles of the various products of oxidation around pyritic oxidation waste piles (Swayze *et al*, 2000).

Ribet *et al* (1995) claim that up to 80% of the metals associated with oxidised pyrites existing as jarosite and goethite will become available to transportation over the life of a tailings dump. This percentage would include both those metals chemically bonded to the jarosite and goethite and those adjacent existing as various oxide and hydroxide species. Zinc industry jarosites are of particular concern when considering stability as they contain chemically bonded heavy metals. These elements, such as lead and mercury, are extremely toxic and will be released by decomposition and made mobile through solution by the low pH.

The problems associated with decomposition must be considered when deciding on methods of waste disposal. If jarosite is stored in proximity to a source of drinking standard water, the potential leaching of heavy metals will be extremely detrimental to the water resource (Al *et al*, 1994; Herbert, 1997). There is some evidence that sodium sources, such as those found in brine water tables or in ocean dumping, increases the stability of jarosites, favouring these avenues of disposal (Alpers *et al*, 1992; Nolch, 1995).

In addition, tailings ponds can have inherent problems based on the geology and climate of the site. There have been numerous papers published about the management and rehabilitation of jarosite tailings dams (McGregor *et al*, 1998; Davis *et al*, 1999; Johnson *et al*, 2000). Generic management plans for tailings facilities are available (Bédard *et al*, 1998) and most point to the need for stabilised tailings prior to impoundment.

Jarosite has a reasonable settling rate but requires flocculation. Pressure filtration can reduce moisture content but in turn increases the specific resistance to filtration (SRF) (Sengupta *et al*, 1992). Generally jarosite tailings dumps require at minimum an impermeable membrane lining to stop leachate from leaving the site (Arregui *et al*, 1979).

Whilst jarosite has good settling rates, water is held within the particles either chemically bonded or as pore water (Davis *et al*, 1999). This increases the volume of the waste. Filtered jarosite from a hydrometallurgical process will commonly contain approximately 25% water. Drying of the jarosite is ineffectual for two reasons. Firstly it poses an additional cost to the process. Secondly, it makes the waste susceptible to aeolian transportation. This could increase the risks to health as inhalation of entrained metals increases exposure.

The density of jarosite is often lower than the ore being processed. This increases the volume of tailings produced when compared to the volume of ore removed. For these reasons jarosite tailings ponds are “soft”, making capping and rehabilitation a necessity but difficult to complete.



## 2.8 – Jarosite Storage Methods

Three main storage facilities are used to deal with jarosite waste.

### 2.8.1 – Landfill

Landfill is the most common way to store jarosites. Old mine workings are often filled with the waste product. The susceptibility of jarosites to acid leaching requires landfill sites to be lined, usually with either plastics or chemical barriers (Arregui *et al*, 1979). Many solutions have been attempted to alleviate the problematic nature of jarosite. Methods to increase the strength of jarosite in a dump have been attempted and are discussed later.

Ribet *et al* (1995) investigated layering a jarosite tailings dump with activated carbon, such as that found in sewage sludge and other municipal waste, to promote chemical reduction in the upper layers. This was found ineffectual as the presence of high microbial concentrations in the waste increased the rate of decomposition, especially of sulphur containing compounds. With the lack of oxygen, microbes will prefer sulphur as an electron donor (Manahan, 1994).

Another potential method for waste control is self-sealing isolation through the addition of fly ash or a similar basic waste product (Ding *et al*, 1998). The method creates pore filling within the particle resulting in a reacted layer around the outside of a body of jarosite that is impermeable to oxygen and water flow.

The theory relies on no further inclusions through the reacted layer once it is in place, although the authors do point to a self-repairing mechanism from the excess hydroxide present.

Davis *et al* (1999) quoted the use of deep tilling lime-limestone slurry into sulphide tailings exposed from an abandoned mine by flood events. A fish kill in 1989 was attributed to metal concentrations in a nearby estuarine system. Poorly revegetated areas, such as those where soil acidity affects plant growth, are especially susceptible to erosion. The slurry was added by weight depending on the depth of tailings exposed and deep ploughed. Revegetation was then promoted to minimise future erosion. The method was successful in minimising metal transport to the estuarine system. This method has reportedly proven a success for both new and old jarosite dumps.

### **2.8.2 – Dry Storage**

The costs of land storage of waste are continually under review. Consideration needs to be made of the life expectancy of the dam and the additional cost of future rehabilitation. With this in mind, Minson and Williams (1999) have surveyed the option of dry storage of tailings. Advantages listed include:

- the full return of any plant water to the processing plant system, thus decreasing water consumption,

- greater use of existing tailings storage facilities as dry tailings may be stacked higher without the risk of breakout,
- little percolation through the tailings once in place due to high densities and
- lower overall running costs over the life of the facility.

Several existing facilities are mentioned along with the reasoning behind their change to dry tailings deposition. Key reasons for dry storage are lack of space and geological risks in an area such as tectonic faults. However, dry storage is not common due to the higher initial capital costs.

### **2.8.3 – Subaqueous Dumping**

Subaqueous dumping of waste is the most controversial method of tailings disposal used. As the name implies, waste is dumped under water, be that in oceans, lakes or wells.

The practice has been in place for numerous years and many have argued for and against its use. Those in favour point to the anoxic environment the deep water provides. It is argued that this will stabilise jarosite indefinitely. 1000mm of stagnant water is enough to provide anoxic conditions (Stogran, 1997). Little has been written about the potential for future exposure to oxidative conditions. Opponents to this type of waste dumping question environmental impacts such as sea bottom ecosystem burial, an “out of sight out of mind” mentality and the chance of heavy metal accumulation throughout the food chain.

There are two methods to consider with respect to subaqueous dumping. Deep-sea tailings placement (DSTP) involves piping the tailings to accurately place them in a precise area of the ocean floor. Whilst rarely practiced, a number of companies have studied this as a viable option for waste removal. Ocean dumping is the release of waste at the surface, usually from a barge or similar vessel. The final placement of the waste is then left to the random currents of the ocean and the settling rate of the solid. The London Convention of 1975 banned ocean dumping of waste, with industrial waste added to the 1996 Protocol to the London Convention, to which Australia was a signatory.

A number of past studies related to the ocean dumping of jarosite into the Tasman Sea off Hobart in Tasmania, Australia. This process removed waste from the Pasminco EZ zinc refinery in Hobart and was undertaken from 1973 until 1997. A concession from the London Protocol until 1997 was granted to the Australian Government to dump jarosite in order to develop alternative process technologies. Four million tons of jarosite was deposited (Harris *et al*, 1999) into an area of two nautical miles radius in waters approximately 2000 metres deep on the edge of the continental shelf.

It was estimated that approximately 60% of the jarosite dissolved or remained in suspension and was transported by currents out of the dump site. 37% of the insoluble portion reached the sea floor (Mackey and Sainsbury, 1994). Harris *et al* (1999) postulated that the jarosite dumped was immediately shifted over the continental shelf into the East Tasman Saddle, an area of deeper water. Here, mixing and therefore further dilution took place with other sediments

being washed from the continental shelf. Seabed cores returning thin strips of zinc and lead concentrations higher than background levels confirmed these findings.

Potential heavy metal accumulation in fish was also studied (CSIRO, 1994). The livers and flesh of numerous species from all depths were tested and compared these results to those from fish caught off New Zealand and South Africa. Predators such as sharks and the Southern Bluefin Tuna were studied, as higher members of the food chain are most likely to show accumulation effects.

Nolch (1995) reported the findings showed no obvious signs of accumulation in any species outside of natural variability, with the exception of selenium. The CSIRO studies also mention this finding, but pointed to the fact that selenium is only available at trace levels within the jarosite dumped and therefore did not relate this finding to jarosite dumping.

## **2.9 – Alternative Uses for Jarosite**

With the jarosite group of compounds representing a problem, many studies have been completed to extract economic benefit from products associated with its production. Numerous studies have looked at jarosite as a potential fertiliser for crops due to the high sulphur and iron contents but none have shown overly promising results. There are no reported commercial practices. Some attempts have been made to convert jarosite waste into value

adding products for the building and road construction industries. However, the extent of jarosite stocks worldwide would require the generation of large volumes of these products. Such volumes would have difficulty finding a market requirement to fill.

### **2.9.1 – Soil Fertilisers**

Ryan and Stroehlein (1976) used jarosite from a copper smelter in a jarosite / sulphuric acid mixture as an iron source for crop soils. The jarosite used was sparingly soluble in water (58ppm). Jarosite by itself proved to be ineffective as an iron source since the rate of release into the soil was very low. Adding sulphuric acid to the mixture increased the iron in solution and as such, the jarosite became an effective fertiliser. The jarosite samples were treated with varying concentrations of sulphuric acid. Water was added and the sample stirred for at least one hour. A ratio of 2:1 jarosite to sulphuric acid was found to be the optimum for fertilising.

The paper quoted the use of sulphuric acid to improve iron concentrations in iron deficient soils. This practice would not be acceptable under international standards as the soils would be acidified by the addition of sulphuric acid. Also, there was no reference to other metals entrained in the jarosite such as lead or mercury, which would also become available to the plants. Few plants are resilient enough to grow in acidic soils.

Kanabo and Gilkes (1992) experimented with a number of synthetic “low contaminant” jarosites, primarily plumbojarosite and ammoniojarosite (low contaminant in this case referred to the purity of the jarosite sample produced and had no reflection on the potential for biological contamination). The material was compared with standard fertilisers in glasshouse experiments on wheat, clover and rice.

The jarosite was shown to be inadequate as a nitrogen supply for wheat and inadequate as potassium and sulphur supplying fertiliser for clover. To successfully supply enough nitrogen to the soil, the concentration of low contaminant jarosite would be greater than 150 ton per hectare. At this very high rate of fertilisation, the heavy metal concentrations taken up by plants would make them unfit for consumption, not to mention the effects on soil stability. Similarly, grazing cattle would also be affected by heavy metal concentrations. Authors Kanabo and Gilkes reported low contaminant jarosite might be useful for mine rehabilitation or forestry fertilisation but consideration of the effect on the water table was required.

Williams *et al* (2000) attempted to use jarosite as a sulphur and potassium fertiliser in a sandy, coastal plain soil, which was typically too poor for agricultural activities given the high leach rates of the soil and its inherent low organic matter. Experiments showed that the jarosite did not dissolve into the soil at a sufficient rate, nor was the equilibrium solubility of the jarosite in the soil high enough. No mention was made of heavy metal adsorption by plants. Future improvements suggested the use of smaller, more permeable particles to increase surface area,

thus increasing the area for dissolution. Another suggestion was to add elemental sulphur or similar dissolution inducing compounds.

### **2.9.2 – Ceramic Products**

Pelino (1998) completed a thorough investigation into the conversion of jarosite and granite waste into numerous ceramic and glass products. The motivation was the large quantities of the waste being expensively stored in leach-controlled facilities, as well as the estimated European Union market for ceramics and vitreous products of 15 to 20 million tons per year. The study included evaluating the properties of the various jarosite samples investigated, the recovery of heavy metals and sulphur during the glass making process and, most importantly, the quality of the glass and ceramic products produced (quality was measured through thermal conductivity, specific heat, chemical durability, abrasion resistance, hardness, impact strength and thermal expansion).

Three methods of sulphur removal and zinc recovery were employed; each evaluated against industrial zinc production costs. Two methods involving preheating and a sulphuric acid wash have proven economically viable in extracting zinc and sulphur from jarosite prior to a final melting stage. Magnetic separation was used to extract 94% of iron from the glass batch. 96.5% sulphur removal was quoted – a contaminant in glass that causes corrosion. Overall, Pelino concluded the process was a success and could be used to minimise the quantities of jarosite in land storage facilities.



Karamanov *et al* (1999) mentioned that the conversion of industrial waste to building ceramics has been applied in the former Soviet Union since it was proposed in 1959. The products have excellent properties but lack the aesthetics associated with clear or opaque ceramics.

To improve the appearance of the finished product, Karamanov *et al* suggested sinter crystallisation. This involved a two stage thermal treatment of the waste. The first crystallises the bulk of the waste. That which did not crystallise was separated and removed. The crystals, in the order of millimetres in size, were then melted and re-crystallisation commences from the surface, passing to the inside. The resulting effect matched a texture similar to marble.

Problems were, however, encountered involving the iron content of the waste. As re-crystallisation occurred, a number of iron oxide species were encountered that detracted from the appearance of the product. Results confirmed haematite on the surface and pyroxene/magnetite in the bulk. Further work was suggested to determine the effects of nitrogen cooling, removing oxygen from the crystal structure.

## **2.10 – Stabilisation of Bulk Jarosite – Landfill and Embankments**

Studies have been undertaken to stabilise jarosite in a cement type medium, creating a product that can be used for break walls, dam walls and various road bases.

Mymrim and Vaamonde (1999) combined a mixture of jarosite, dumped ferrous slag and what was termed a liquid activator in a press and allowed the resulting compacted mixture to harden under 98% humidity. Addition of 1 - 4% w/w Portland cement increased the strength considerably. Few product details were reported but it was claimed that the new material conformed to the Spanish Government heavy metals leaching standard tests.

Chen and Dutrizac (1996) also used Portland cement to increase the strength of jarosite waste. The products of this process are known as jarofix products. Jarofix products containing greater than 15% Portland cement pass all environmental criteria for waste disposal based on USEPA guidelines. The use of Portland cement allows higher stacking of jarosite waste, removing the need for large volume tailings ponds. Additionally, Jarofix product has an extremely low porosity, minimising the effects of solution through put into the future.

The Jarochaux process (Ek, 1986) involves the addition of calcium compounds such as slaked lime, quick lime and milk of lime to stabilise the waste prior to placement as landfill or embankments.

The suitability of Jarofix and Jarochaux has been indirectly examined by Levens *et al* (1996) in a report into the environmental impacts of cemented mine waste backfill. The study concluded that the addition of cement greatly decreased the exposure of sulphides to oxidising agents. This, in turn decreased the release of sulphuric acid and hence the movement of entrained heavy metals into water supplies. No mention was made of the additional costs of treatment or the future use of the land once these products were in place.

As previously mentioned, these methods rely on no further disruption of the solid once in place, to ensure no fresh surfaces of sealed jarosite are exposed.

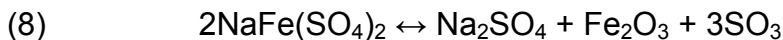
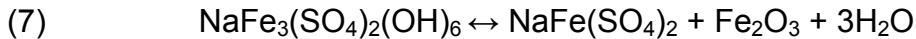
## **2.11 – Conversion of Jarosite to Iron Oxides**

Many studies into various uses of and methods to stabilise jarosite were published during the 1990's and 2000's, possibly reflecting the need for a sustainable solution to jarosite tailings disposal.

Dutrillac and Jambor (2000) have thoroughly reviewed the available literature on jarosite mineral alteration or conversion. Many aspects of their review are cited in the sections below. Most of, if not all of the techniques listed below have been studied on a bench scale only. Four main groupings can be applied to the methods attempted. They are pyrometallurgy, hydrometallurgy, biological consumption and alternative uses. Most of the work has been completed in hydrometallurgy.

### **2.11.1 – Pyrometallurgy – Thermal Decomposition**

Jarosite minerals will decompose during heating, with water being expelled close to 400°C in dynamic heating experiments (Dutrillac and Jambor, 2000). This decomposition is expressed by Equations 7 and 8:



The exact thermal decomposition reactions are somewhat debatable; however, the decomposition of natrojarosite is given in Figure 5. Kunda and Veltman (1979) quoted the formation of iron (III) sulphate (as opposed to sodium ferrosulphate as in Equation 7) and haematite between 400 and 500°C, with complete conversion to haematite above 700°C. However, pyrite, goethite and jarosite are found associated in nature. Thus, under geological conditions, there is a great deal of evidence already quoted pointing to the formation of goethite (FeOOH) rather than haematite (Fe<sub>2</sub>O<sub>3</sub>), especially in established tailings dumps.

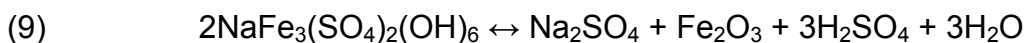
Peacey and Hancock (1996) completed a thorough review of pyrometallurgical methods for the conversion of jarosite. Again, this work primarily focussed on zinc industry jarosite and thus was interested in not only the conversion of jarosite to haematite for tailings placement, but also the potential for the recovery of impurities for later resale. As a result, extremely high temperatures (>1400°C) were required to vaporise contaminants such as zinc and lead. The chosen processes had to meet four criteria. These were:

- To produce saleable and or disposable products.
- Commercially proven process.

- No net increase to environmental emissions from the zinc industry process.
- Low capital and operating costs.

As all methods required high temperatures and large capital costs for off gas and hot stream handling, no method was deemed economically viable in the report.

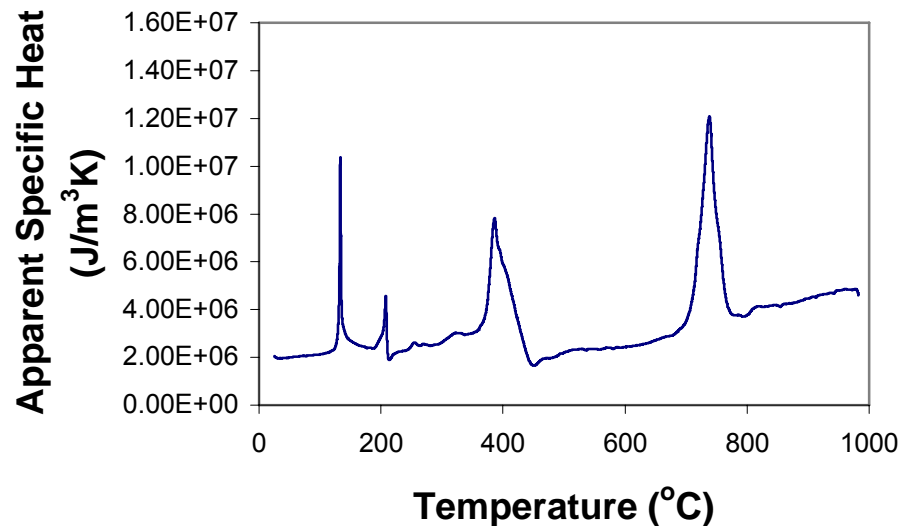
The natrojarosite to haematite hydrolysis reaction at 225°C produces sulphuric acid and sodium sulphate in addition to haematite, as expressed in Equation 9:



The goal is to convert jarosite to haematite for storage, with the advantage of potentially retrieving  $\frac{2}{3}$  of the initial acid used for a process. This method is based on hydrometallurgical processes described by Dutrizac (1990). Sulphuric acid will boil at 337°C (Aylward and Findlay, 1998), forcing Equation 9 to the right. It was proposed to attempt this conversion in a recirculating fluidised bed at 350°C whilst scrubbing the off gas to retrieve sulphuric acid. Initial testing has developed a differential thermogravimetric analysis (DTA analysis) of the natrojarosite waste. The results are shown in Figure 5.

As previously mentioned, Dutrizac found that the hydrolysis of jarosite occurs at 225°C. These results were confirmed by Das *et al* (1995) who used

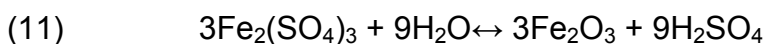
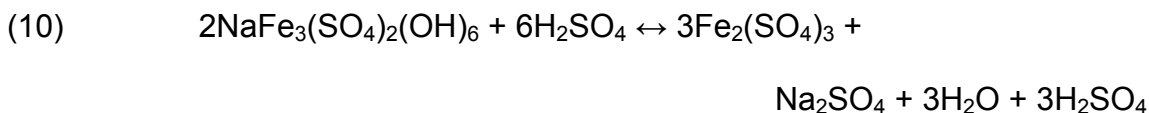
thermogravimetric analysis to map the thermal decomposition of ammoniojarosite.



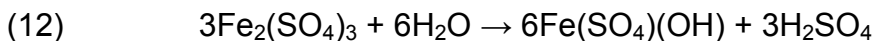
**Figure 5.** Differential Thermogravimetric Analysis (DTA) Data for BHP Billiton Natrojarosite Sample AL7 from Strezov (2001) (the major peaks in a DTA plot show at what temperature a change of phase or chemical composition occurs).

### 2.11.2 – Hydrometallurgy – Thermal Decomposition (Wet)

The reaction in Equation 9, when completed wet in an autoclave, proceeds with no initial free acid and takes two hours for almost complete conversion of the natrojarosite to haematite. Dutrizac (1990) as well as Das *et al* (1995) also found that the decomposition was promoted within an environment containing free acid and proceeded according to the following equations:



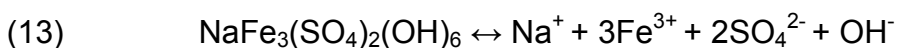
It was found that increasing the initial sulphuric acid concentration promoted the dissolution of the natrojarosite. The only problem was, however, that the higher sulphuric acid concentration reversed the iron(III) oxide precipitation reaction and tended to favour the formation of basic iron sulphate, generating considerably less acid:



The presence of haematite seeds seemed to suppress the basic iron sulphate formation and thereby allowed the haematite precipitation reaction to proceed in a more acidic media than usual.

### 2.11.3 – Hydrometallurgy – Basic Decomposition

In neutral or alkaline solutions, natrojarosite exists in equilibrium with sodium, iron(III), sulphate and hydroxyl ions as shown in Equation 13:



When the pH of the solution is increased by the addition of ammonia, lime or caustic soda, the relatively low concentration of dissolved iron is precipitated as ferrihydrite or goethite (Salinas *et al*, 2001), for example as shown in Equation 14:

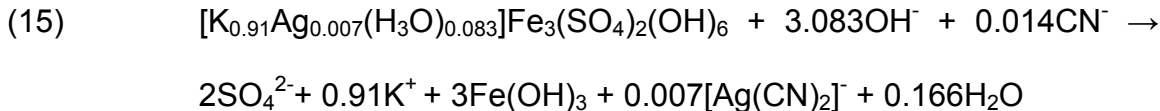


The formation of goethite causes depletion of dissolved ferric iron resulting in the formation of more goethite. The final result, as it occurs in nature over many years, is the complete transformation of natrojarosite to goethite. Synthesised acceleration of the natural process has been achieved in the laboratory by many researchers and is more in line with those findings at established tailings dumps.

Salinas *et al* (2001) and Roca *et al* (1999), using zinc industry jarosite seeded by the addition of franklinite, converted natrojarosite to goethite successfully in both hydroxide and hydroxide / cyanide media.

Cruells *et al* (2000) showed that sodium hydroxide and lime were both quite effective in decomposing a synthetic mixture containing predominantly jarosite, with some argentojarosite and hydronium jarosite. An SEM micrograph showed the formation of a decomposition shell surrounding an impermeable jarosite core. The presence of this impermeable layer confirms that also found by adding fly ash as a method to isolate jarosite. The stoichiometry of the decomposition as quoted from Cruells *et al* is given in Equation 15:





Both increased temperature of reaction and concentration of free hydroxide slowed the reaction rate. Lime had lower activation energy and less of an induction period than sodium hydroxide.

Kunda and Veltman (1979) studied the use of ammonia at various temperatures to completely transform ammoniojarosite to haematite or magnetite and water-soluble ammonium sulphate salts within 15 minutes (U.S. Patent 4,150,095 17/4/1979). An excess of ammonia was used in accordance with Equation 16:



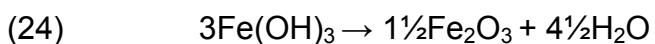
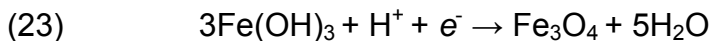
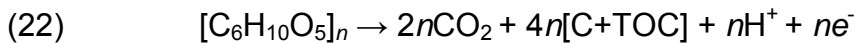
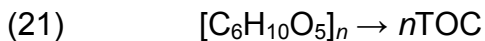
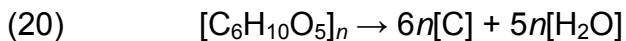
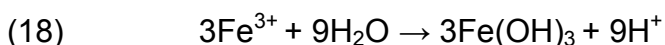
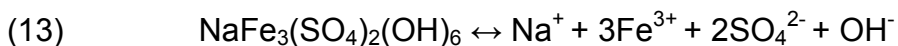
The decomposition commenced at 25°C, with 88% decomposition occurring within one hour. Filterability of the haematite produced improved with increased reaction temperatures up to 100°C, as did the percentage of decomposition up to 99%.

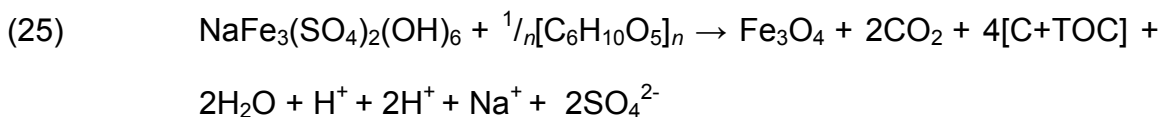
The conversion of ammoniojarosite to magnetite occurred when the reaction in Equation 16 was attempted in the presence of ferrous ions. This was achieved by adding iron(II) sulphate to the reaction solution as described in Equation 17:



These methods may show some potential for ammoniojarosite producing processes, as there is the possibility of recovering ammonium.

Hage *et al* (1999) reported successfully using magnesium oxide and cellulose at 250°C at 40 bar to convert natrojarosite to magnetite, haematite and magnesium sulphate hydroxide. Free sulphur was in the form of sulphate and readily formed solid magnesium sulphate. Iron was preferentially oxidised before reforming sulphates, with the breakdown of cellulose creating an electron source. Whilst there was no isothermal proof for the reaction mechanism, the authors suggested that the reaction followed the path as described in Equations 13 to 25 (note that Equation 13 is repeated as the initial step):





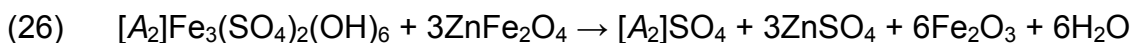
The authors concluded that the reaction depended on the availability of both a reducing agent and a neutralising agent. The products of the reaction could be controlled by the ratios of these agents, monitored by the total dissolved organic carbon (TOC). An increase in the TOC was an indicator that electrons were being released during the conversion of goethite to magnetite.

#### **2.11.4 – Hydrometallurgy – Acidic Dissolution**

Weber and Schuler (1998) suggested a multi-stage dissolution of zinc industry jarosite, with the preferential precipitation of impurities resulting in the formation of a highly pure goethite. Sulphuric acid was used to dissolve the zinc industry jarosite. The pH of the solution was “well defined and stabilised” through a series of four reaction vessels resulting in an extraction – precipitation – extraction procedure that preferentially removed heavy metal precipitates, slowly purifying the iron in solution. Sodium hydroxide was added to the final stirred reactor to adjust the pH to 4.5. This was the optimum pH for the formation of “clean goethite”, i.e. impurities were left in solution.

### 2.11.5 – Hydrometallurgy – Chlorination

Tailoka and Fray (1998) treated sodium, potassium and ammoniojarosite (species represented by *A* below) in order to recover usable metal species such as zinc and iron from the solid phase. To promote the chlorination of jarosite, a sample was pre-treated by heating to 400 - 600°C for four hours either on its own or in the presence of zinc ferrite, which reacted according to Equation 26:



The sulphate residues are separated from the iron oxide ready for chlorination with either hydrochloric acid or recycled polyvinylchloride (PVC) and recovery was achieved between 850 and 1000°C. The authors claimed up to 70% recovery of zinc, cadmium and lead from the feed with 90% removal. The iron oxide would be of an iron-making grade.

Menad and Björkman (1998) confirmed the results of Tailoka and Fray, using numerous plastics as the source for chlorine, finding the volatilisation of metal chlorides would occur between 800 and 1000°C.

### 2.11.6 – Biological Consumption and Dissolution

Biological degradation is slow and not favoured by hydrometallurgical processes producing large amounts of jarosite that need more immediate

remedies. Biogeochemical cycles that operate in oxic systems are better understood than those that operate under anoxic systems (McKee and Skei, 1999). Both oxic and anoxic conditions must be considered when looking at the problems associated with the jarosite group of compounds. It can be assumed that thermal and chemical conditions will favour a number of species over others at all stages of pyrite oxidation, jarosite formation and jarosite decomposition. It is also considered that microbial activity is often a precursor to chemical decomposition, lowering required activation energy and facilitating reactions either as a catalyst or as a consumer.

*Sulfobacillus thermosulfidooxidans* and *Sulfobacillus acidophilus* are two identified species of bacteria that grow autotrophically on reduced sulphur. Bigam, Schwertmann and Pfab (1996) reported the oxidation of ferrous ions in sulphate rich wastewaters (such as those found in acid mine drainage and sulphate soils) and this may be induced by a number of geochemical agents but generally by iron oxidising thiobacilli at pH values below 4.5.

### **3 – Experimental Section 1: Basic Decomposition of Natrojarosite at Atmospheric Pressure – Methods and Results.**

Experiments in this section of the thesis were completed on a synthetically produced natrojarosite known as AL7. The chemical analysis of AL7 is given in Table 3 (Table 3 also includes the analysis of the AL3 material used later in this thesis). The natrojarosite was produced during operations of the BHP Billiton AL pilot plant in 2001 (Figure 2). Whilst termed natrojarosite, the waste material also contained un-leached remnants of the limonite and saprolite feeds to the process. This is shown in the XRD analysis of the solid (Table 4) as the minor presence of goethite (remnant limonite) and the moderate to minor presence of quartz (remnant saprolite).

Whilst many of the experiments quoted in the literature review used low solids concentrations to enhance the extent of reaction, all experiments in this section of the thesis were completed at or near to pilot plant output concentrations (~25% solids w/w). This was to ensure that the process was viable at full scale.

**Table 3.** Chemical Analysis (Using X-ray Fluorescence) of the AL Natrojarosite

	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	S	Si	Zn
All values in %w/w of total dry solid														
<b>AL3</b>	1.12	1.91	0.00	0.99	0.01	20.54	2.19	0.03	2.29	0.16	0.00	8.17	10.08	0.00
<b>AL7</b>	1.24	5.19	0.00	0.72	0.01	19.99	1.28	0.11	2.27	0.16	0.00	10.45	6.29	0.00

**Table 4.** Qualitative XRD Analyses of AL7 Natrojarosite.

Natrojarosite	Anhydrite	Goethite	Haematite	Quartz
Major	-	Minor	-	Moderate - Minor

### 3.1 – Hydrated Lime and Limestone Addition Methods

The method used in this section was developed from the work of Cruells *et al* (2000), referenced in the first paragraphs of Chapter 2, Section 2.11.3. As mentioned, hydrated lime and limestone addition are seen as the easiest methods to treat the problem of jarosite decomposition, as this is often completed as a part of common metallurgical processes to stabilise and neutralise waste. Conversion of jarosites to an iron oxide without the use of an autoclave would be beneficial from an economic and occupational health and safety point of view.

### 3.1.1 – Experimental Aims

Experiments were carried out on the AL7 natrojarosite material at atmospheric pressure with the following parameters:

1. pH maintained at or greater than 11 using 20% w/w hydrated lime slurry.
2. Temperature of 90°C.
3. Where used, 20% w/w limestone slurry was added to the solution to adjust the pH to as high a level as possible.
4. Haematite powder added as a seed to promote the formation of haematite.

AL7 was chosen for this work as it was available in the greatest supply and was generated from an optimised experimental method and thus was seen as representative of the solid product from a larger scale project. Based on the results from Chapter 5, the AL3 natrojarosite samples should have been tested in conjunction with these experiments to see any variation. There were not enough solids generated to allow this.

Limestone was used as a neutralising agent in addition to hydrated lime, as limestone is much more readily available to industry at a much lower cost. The desired outcome from these experiments, if successful, is that a less expensive neutralising agent like limestone can be used, rather than a source of basicity such as hydroxide available from hydrated lime.



### 3.1.2 – Equipment and Methods

A glass, two-litre reaction kettle was placed within a heating mantle and heated to the desired experimental temperature (90°C). The reactor was sealed with a glass lid. Attached to the lid was a condenser, a 25mm polypropylene three-blade agitator, a glass thermometer and a sampling port sealed with a rubber cork.

250g dry weight of natrojarosite (AL7 material) was slurried with a total of 750mL of deionised water and added to the kettle (see comments regarding solids loading in Section 3.0). Any sample moisture was calculated by drying a separate sample of the solid and included in the 750mL liquid total.

Solid and liquid samples were taken every five minutes by extracting 5mL of the slurry with a syringe. The concentration results received after the experiment were converted to reflect the loss of volume from sampling in the experiment. Note that sampling of the 30 hour experiment took place at random intervals, rather than every five minutes.

Five experiments were completed to determine whether the decomposition of natrojarosite to either goethite or haematite could be achieved by adjusting the pH. The experiments are outlined in Table 5.

**Table 5.** Atmospheric Pressure AL7 Natrojarosite  
Decomposition Experiment Parameters.

Experiment Number	Dry Mass of Tailing (g)	Water Added (mL)	Temperature (°C)	pH Target	pH Adjusted With	Time (h)	Amount of Hematite Seed Added (g)
1	250	750	90	11	Lime	1.5	-
2	250	750	90	7.8	Limestone	1.5	-
3	250	750	90	7.8	Limestone	30	-
4	250	750	90	11	Lime	6	80
5	250	750	90	11	Lime	6	240

### 3.1.3 – Completion of the Experiment

The contents of the kettle were filtered hot using a Whatman 5A filter paper. The liquid was representatively sampled and analysed using ICP.

The solids were washed twice using a known volume of deionised water by repulping the filter cake and agitating. This removed as much entrained liquid phase between particles of the solid as possible to ensure the solid / liquid relationship measured was reasonably accurate. The filter cake was dried overnight in an oven at 80°C, then a representative sample taken using a sample riffle and submitted for chemical analysis by x-ray fluorescence. Wash solutions were also analysed by ICP to complete the mass balance. The solid sample was also analysed by x-ray diffraction to identify the compounds present.

## **3.2 – Hydrated Lime and Limestone Addition Results**

The bulk of these results are from experiments 1 and 3 in Table 5, i.e. hydrated lime addition over 90 minutes (1.5 hours) and limestone addition over 30 hours, both at 90°C. The other experiments conducted did not provide any results that gave further explanation than those from these two experiments.

### **3.2.1 – Experimental Results**

The starting solution pH was 7. The results from the atmospheric pressure thermal decomposition tests are summarised in Table 6. The actual pH range quoted refers to the final pH reached after hydrated lime or limestone addition, if any change occurred. In the case of the first experiment, a second number is quoted, as the pH varied during the first hour. This was not as noticeable in the later lime experiments. The two limestone experiments showed no variation in pH.

**Table 6.** Atmospheric Pressure AL7 Natrojarosite Decomposition Test Results – Hydrated Lime / Limestone Consumption and pH Range.

pH Target	pH Adjusted With	Time (h)	Amount of Hematite Seed Added (g)	Ca(OH) <sub>2</sub> /CaCO <sub>3</sub> Addition (g)	Actual pH Range
11	Hydrated Lime	1.5	-	222.7	11 – 9.8
7.8	Limestone	1.5	-	250	Remained at 5.5
7.8	Limestone	30	-	250	Remained at 5.5
11	Hydrated Lime	6	80	222	11 – 10.8
11	Hydrated Lime	6	240	222	11 – 10.8

### 3.2.2 – Data Extrapolation

The chemical reaction for the basic conversion of jarosite to an iron oxide such as goethite was shown in Sections 2.5 (Equation 6) and 2.11.3 (Equations 13 and 14). The following data extrapolation was made to ensure that excess hydrated lime was present during the reaction.

Using Equation 6 and assuming a purity of 100% and perfect stoichiometry, 250g of natrojarosite (molecular weight of 484.7) represents 0.52 moles. Five times this number of moles is required as hydroxide. Hydrated lime has the chemical formula Ca(OH)<sub>2</sub> and thus two moles of hydroxide are available in every mole of lime. Thus 2.5 moles of lime will supply 5 moles of hydroxide. 2.5 moles of lime weighs 185.3g.

Using Equations 13 and 14 and assuming a purity of 100% and perfect stoichiometry, 250g of natrojarosite (molecular weight of 484.7) would produce 86.4g of ferric ions. This is calculated from Equation 13, which tells us that 1

mole of jarosite produces 3 moles of ferric ions. 250g of jarosite represents 0.52 moles, which would produce 86.4g iron.

Referring to Equation 14, 86.4g or 1.55 moles of ferric iron would require 4.65 moles or 171.9g of lime to react to form goethite. Before considering the likely purity of the natrojarosite produced through the BHP process, the lime consumed to reach a steady pH in these experiments was 120% the stoichiometric requirement (using Equation 6) and 130% (using Equations 13 and 14). Thus hydrated lime in excess of that required to complete the reaction remained in the solid after the reaction.

This excess of hydrated lime would increase as the purity of the jarosite formed from dissolved iron during saprolite addition to the atmospheric leach process is likely to be less than 100%. Many inert minerals would be unaffected by the leaching conditions seen (100°C and mild acid concentrations of less than 30g/L sulphuric acid), thus surviving the leach process intact as a solid, passing through to the tailings and diluting the concentration of jarosite in the final solids product.

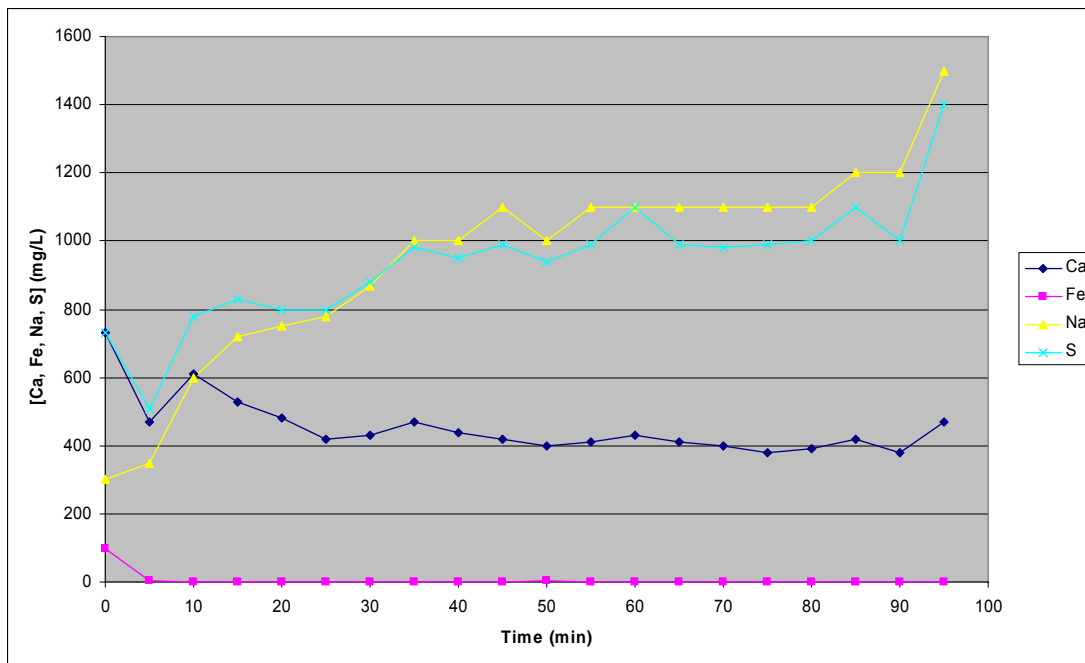
### **3.2.3 – Liquid Chemical Analysis Findings**

Liquid samples taken throughout the first lime experiment showed sodium and sulphur (sample analysis reported sulphur, however this is assumed to be sulphate) present in the liquid phase, suggesting decomposition of the natrojarosite, similar to that predicted by Equations 6 and 13. These results are

shown in Figure 6 for the lime based experiments at 90°C and Figure 7 for the limestone based experiments at 90°C. Note that the length of the experiment was much greater for limestone than lime. The limestone experiment was extended to 30 hours to see if the experiment could reach equilibrium.

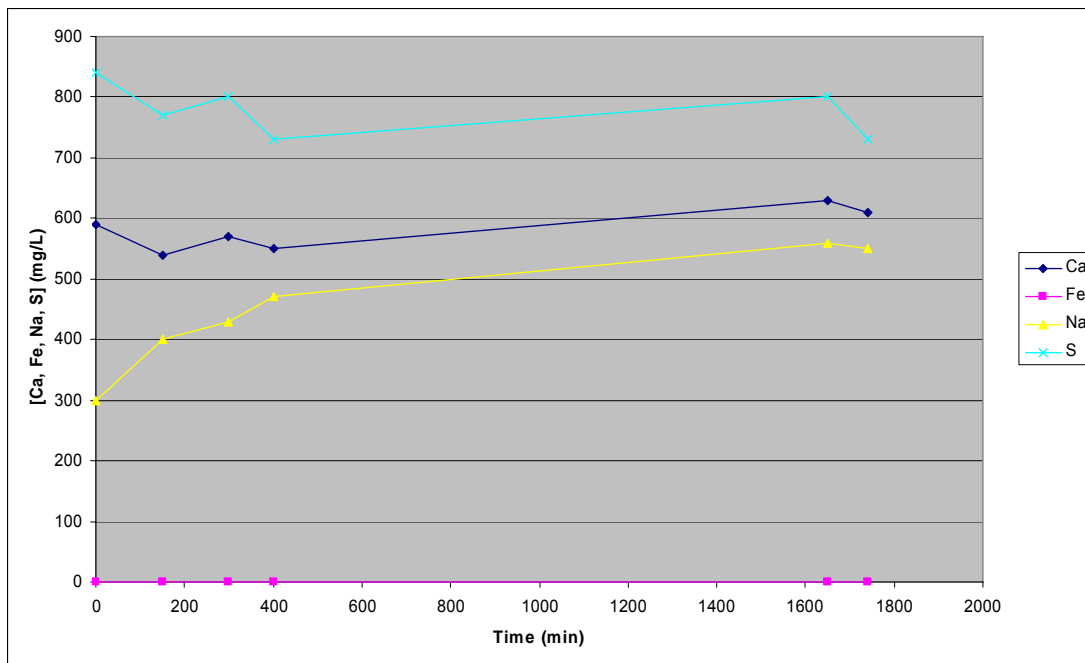
Sodium and sulphur (likely to be  $\text{SO}_4^{2-}$ ) in solution suggests the decomposition of natrojarosite to iron oxide, particularly as iron is not present in solution during the experiments (Figures 6 and 7). That is, iron remains as a solid throughout whilst sodium and sulphur as sulphate dissolve.

The energy provided by heating the natrojarosite slurry to 90°C is enough to initiate decomposition. Sodium concentrations commence at 300mg/L. Unlike the hydrated lime experiment, the sodium concentration remains relatively low throughout the limestone experiment, suggesting that hydrated lime has a much greater affect on the rate at which natrojarosite decomposes.



**Figure 6.** Results for Experiment 1. Hydrated Lime ( $\text{Ca}(\text{OH})_2$ ) Added to AL7 Natrojarosite at  $90^\circ\text{C}$  to Maintain Solution pH at 11 for 90 Minutes.

Both Figures 6 and 7 suggest that the reaction is not complete as the sodium and sulphur concentrations in solution are increasing. However, the reaction rates are extremely slow and therefore would not be viable in this industrial application.



**Figure 7.** Result for Experiment 3. Limestone ( $\text{CaCO}_3$ ) Added to AL7

Natrojarosite at  $90^\circ\text{C}$  to Maintain Maximum pH for 30 Hours.

In the hydrated lime experiment the final concentration of sodium in solution suggested that full decomposition of natrojarosite occurred. 250g dry weight of natrojarosite was used, containing 2.27% sodium (Table 3). This equates to 567 mg of sodium available to dissolve during decomposition. The final solution taken from the hydrated lime addition test had a sodium concentration of 1500mg/L. The final volume of the experiment was approximately 655mL of solution (750mL minus 19 x 5mL samples), or 982.5mg. The source of the excess sodium was the salt water medium in which the solid had been stored.

The calcium concentrations measured during the hydrated lime test were interesting. The concentration was constant throughout, showing that additions of



hydrated lime to the solution were immediately being consumed by the decomposition of natrojarosite. Gypsum, already present in the natrojarosite due to the tailings neutralisation process (Figure 2), dissolved during the heating up stage, reaching the saturation concentration of calcium (as seen in the sodium results).

#### **3.2.4 –X-ray Diffraction Analysis**

Solid samples removed during the conversion experiments underwent x-ray diffraction (XRD) analysis to determine the compounds present. Throughout the first lime addition test, jarosite was evident in the XRD analysis. In the final sample, after adding all the lime, jarosite was still observed by XRD but there was no evidence of goethite. As the solution analyses had suggested decomposition, goethite may have been present in an amorphous form and thus undetectable by XRD. The sodium analyses also suggested full decomposition. However, this was not the case with natrojarosite evident by XRD.

Analysis of the solids from the limestone addition experiments showed the existence of jarosite and limestone only. The XRD analysis was similar to that of the original samples, suggesting that no reaction had taken place.

Analysis of the solids from the later hydrated lime experiments with haematite seed addition showed natrojarosite and haematite as the major compounds present.

## **4 – Experimental Section 2: Thermal Decomposition of Natrojarosite at High Pressure and Temperature in an Autoclave – Methods and Results**

The methods used in this section of the thesis were based on the work of Dutrizac (1990). The methods described by Dutrizac were modified to answer specific questions posed by the production of jarosite in a metallurgical process and a need to understand the kinetics of the decomposition reaction, optimising the reaction to find the most economically viable conversion process. The four key questions to be answered are listed in Section 4.1.1.

Section 3.0 gives the composition of the AL7 natrojarosite material used in this section of the thesis.

### **4.1 – High Pressure and Temperature (Autoclave) Methods**

#### **4.1.1 – Experimental Aims**

There were four experimental aims to be addressed:

- i. Reaction kinetics. The changes in the chemistry and mineralogy of the solids and liquids produced were compared against the starting materials to understand the reaction kinetics. The experiments used washed natrojarosite treated at high temperature in the autoclave for two hours.

- ii. An effect of washing. A pre wash step was removed from some of the experiments to determine whether dissolution could commence prior to the two hour autoclave treatment and if this had any effect on the outcome of the experiment. A comparison of the chemistry and mineralogy of the solids and liquid produced under the same conditions was completed for the washed and unwashed starting material.
- iii. Maximising acid production. Ways of maximising the acid produced from the conversion of natrojarosite to haematite were tried in order to extract a useful chemical product from the decomposition i.e. sulphuric acid. During the BHP Billiton AL process, limestone and hydrated lime are added at various stages for metallurgical benefit. However, this is likely to have a detrimental effect on maximising acid production from the decomposition of natrojarosite as acid produced by decomposition will be immediately consumed by excess basic material. Thus samples taken from the stages prior to any limestone addition and during the limestone addition were analysed. The concentration of free acid in the product liquid was used to measure any changes occurring during the two-hour decomposition process.
- iv. Temperature versus time relationships. By varying the time at temperature for the autoclave, it was possible to measure a minimum time in which the conversion reaction could take place. This was helpful to minimise the cost of conversion created by heat input and to assess the possibility of using a pipe reactor rather than an autoclave.

#### 4.1.2 – Equipment and Methods

The autoclave used was a 2 litre titanium bodied vessel, pressured rated to 10.3MPa or 1500lb/in<sup>2</sup> (Figure 8 – the equipment shown was manufactured in the United States of America and thus safety equipment such as the burst disc rating and the pressure gauge is rated in imperial units of pounds per square inch). The head contained a bleed valve, an emergency bursting disc, a pressure gauge, a control thermocouple, a magnetic drive to allow agitation and a cooling water heat exchanger. The head was affixed to the cylinder of the bomb using two half ring locking sleeves, each containing three bolts tightened until secure using a ring spanner.

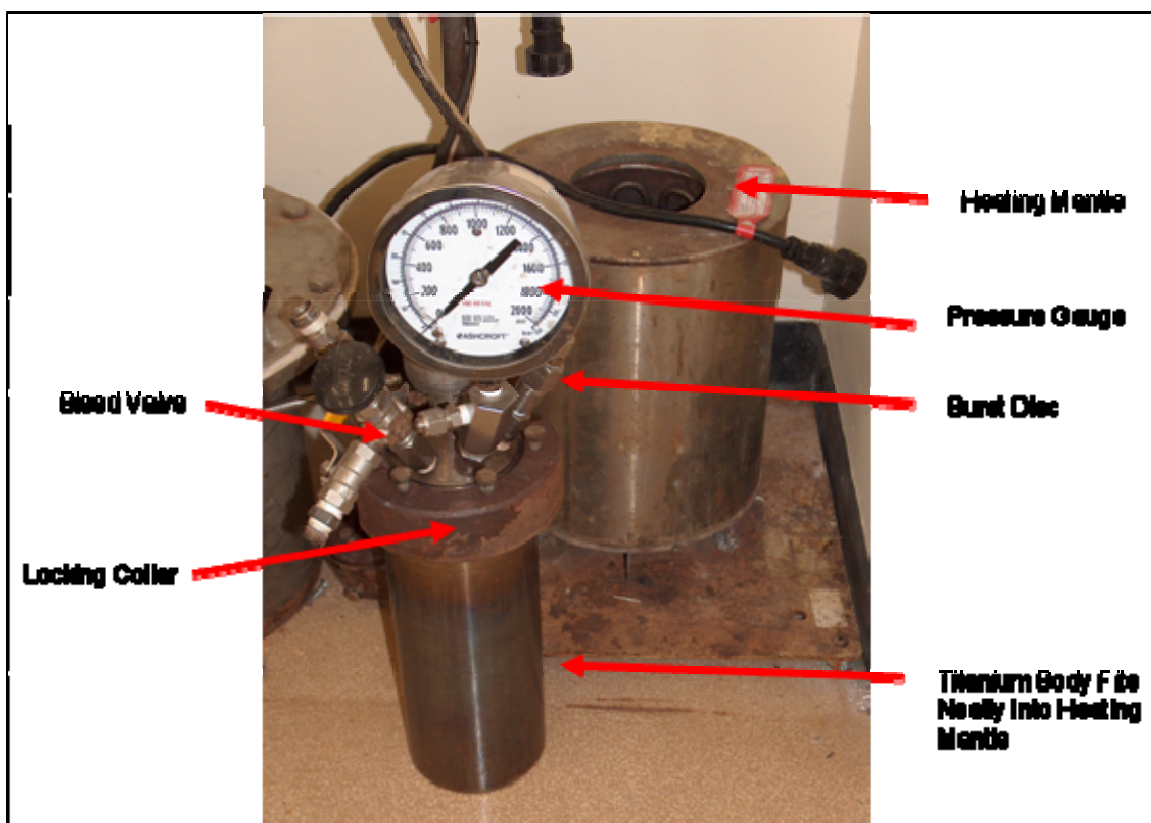
Natrojarosite of a known moisture concentration was slurried with deionised water, both by weight. The dry weight of natrojarosite was calculated allowing slurry of known solids loading (25% measured for each experiment – see solids loading comments in Chapter 3.0). The resultant slurry was mixed using a 50mm stainless steel agitator for approximately 45 minutes (or until no agglomerated particles remained in the slurry) and added to the bomb prior to sealing the lid.

The bomb was placed into the heating mantle, controlled from a Type K thermocouple measuring the solution temperature sheathed inside the bomb. The solution was stirred with a dual four-blade agitator via a magnetic coupling at 300rpm. The time taken to reach the target temperature was measured, as well as any overheating caused by the lag between the temperature controller for the

heating mantle and the solution thermocouple. The experimental time started when the target temperature was reached.

The experiments for each of the four aims mentioned above are listed below:

- i. A series of nine experiments were completed to determine at what temperature the conversion of AL7 natrojarosite to haematite took place. These are summarised in Table 7.



**Figure 8.** “Parr” 2 Litre Titanium Autoclave Bomb and Heating Mantle used for the Experiments Described in Chapter 4

**Table 7.** Temperature and Time Parameters for the  
Reaction Kinetics Experiments to Study the Conversion of AL7 Natrojarosite to  
Haematite.

Target Temperature (°C)	Time (min)
125	120
150	120
160	120
170	120
180	120
190	120
200	120
210	120
220	120

ii. A sample of AL7 natrojarosite was washed in deionised water by slurring with a known amount of deionised water for 45 minutes. The solid and liquid were separated using a Buchner funnel. The process was repeated three times. The solution was analysed using ICP to see what elements were dissolving in the presence of water with no added heat. The washed natrojarosite was used in all other experiments in the autoclave. One experiment in the autoclave was completed at 190°C using unwashed natrojarosite and the results compared to those from experimental aim i. The advantage of not washing the natrojarosite would be in time savings and capital and operational costs within a full scale operation.

iii. The third aim of the natrojarosite decomposition experiments related specifically to the BHP Billiton process and ways of optimising the flow diagram

to recycle or retrieve sulphuric acid. Three experiments (Table 8) were completed using natrojarosite from various sources within the BHP Billiton atmospheric leach process. Samples were taken from immediately before (tank number ST10) and immediately after the two hour neutralisation step (tank number ST2), after saprolite leaching (Figure 2). The theory was that maximising acid production would require the purest natrojarosite available. Certainly the natrojarosite should not include any additional lime or limestone (used within the process to promote iron precipitation), as this would potentially neutralise acid produced.

A fourth experiment was completed using a higher solids loading in the slurry, thus increasing the relative volume of jarosite present in order to determine if more solids could generate more acidity in the autoclave discharge..

**Table 8.** Acid Production Maximisation Experiments Using AL7 Natrojarosite Sourced from Various Locations within the BHP Billiton Atmospheric Leach Process.

Material Tested	Target Temperature (°C)	Time (min)
Final Tailings (Washed)	220	120
After Neutralisation (NT2)	220	120
Before Neutralisation (ST10)	220	120
Increased Solids Concentration	220	120

iv. Ten experiments were conducted to determine any temperature - time relationship in the decomposition process. An eleventh result was obtained from

the experiments from experimental aim i. The experimental points are shown as the shaded boxes in Table 9 .

**Table 9.** Temperature Time Relationship Experiment Matrix. Shaded boxes indicate test parameters completed; unshaded boxes were not completed.

	0 min*	5min	15min	120min
180°C				
200°C				
220°C				
240°C				

\* - Cooling the solution as soon as the target temperature was reached stopped the experiment. This was referred to as 0 minutes.

#### 4.1.3 – Completion of the Experiment

Cold tap water was allowed to flow through the cooling coil inside the autoclave, removing heat from the reaction slurry, with pressure within the autoclave dropping immediately. However, using this method to cool the autoclave can take up to 30 minutes due to latent heat in the walls and lid of the bomb and in the heating mantle. After the contents had cooled to below 40°C, the valve in the lid of the bomb was slowly opened to release any remaining pressure and the locking sleeves removed to separate the lid from the cylinder of the bomb. The sampling process is shown diagrammatically in Figure 9.

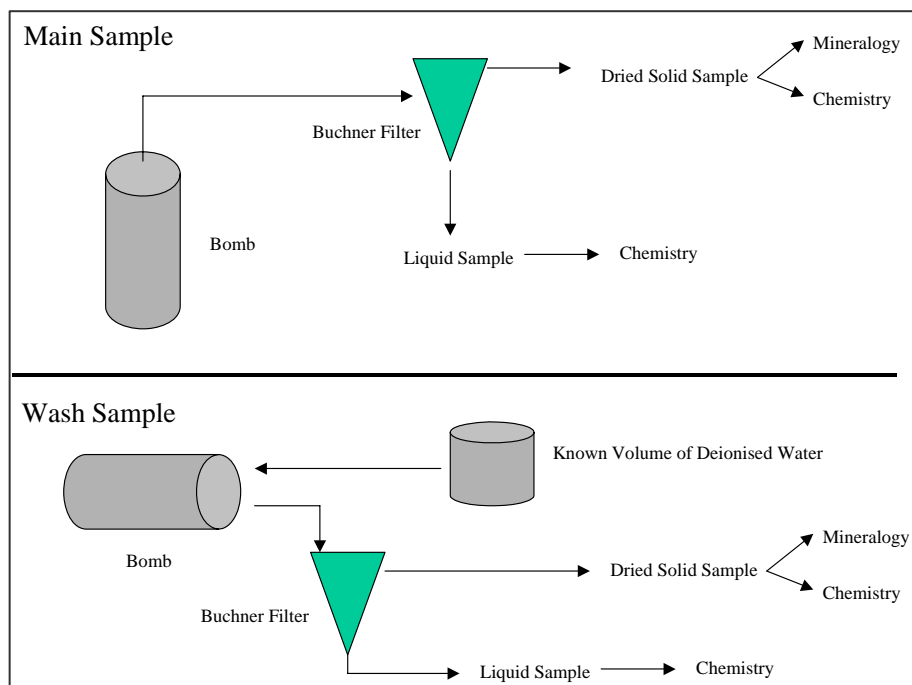


The contents of the bomb were filtered using Whatman 5A filter paper in a Büchner funnel and the filtrate solution volume measured using a measuring cylinder. Residues from both the lid (including the impellers and cooling coil) and the walls of the bomb cylinder were washed into a container using a known volume of deionised water. This was kept separate from the main solution to allow for an accurate mass balance.

The solid sample was washed twice using deionised water to remove any entrained acid. The filtered solid was added to a beaker, broken up and repulped prior to re-filtering. The volume of the wash solution was measured and a sample submitted for chemical analysis.

The initial filtrate was mixed and sampled. The free acidity of the solution was determined by titrating 1mL of solution (in a matrix of potassium oxalate solution; Appendix 1, Free Acid Titration Method) with 1N sodium hydroxide, with the remaining portion undergoing elemental analysis by ICP. The liquid from the lid, the bomb and the second solids washing was also analysed to complete the mass balance.

The solid sample was dried at 80°C overnight, weighed and a representative portion submitted for analysis by acid digestion and ICP. A second representative sample was submitted for characterisation by x-ray diffraction and scanning electron microscopy. A dried solid sample of untreated natrojarosite was submitted for both chemical analysis and mineralogical characterisation to allow for comparison.



**Figure 9.** Schematic of the Sampling Process for the  
End of Each Autoclave Experiment.

## 4.2 – High Pressure and Temperature (Autoclave) Results

The autoclave temperature control was poor during these experiments. This was caused by a delay between the temperature controlling software, the thermocouple housed in the autoclave head and the time it took the heating mantle to react. Latent heat remained in the autoclave body, the elements and the insulation after the temperature controller had deactivated. The result was a sine curve heating profile, where the temperature was exceeded then underachieved over the time of the experiment. To show this effect, temperature

is reported throughout Section 4.2 as a range, rather than the specific targeted temperatures shown in Section 4.1.

#### 4.2.1 – Chemical Analysis of the AL7 Natrojarosite Wash Process Prior to Autoclave Treatment

The AL7 natrojarosite samples used in the autoclave experiments were washed in deionised water three times to remove any entrained liquid phase material (such as sodium from the salt water media). The chemical analyses of the wash solutions are given in Table 10. Each solution was extracted from the slurry by filtration after a one-hour agitation period.

Sodium, sulphur and magnesium dissolved in decreasing amounts over the three washes, suggesting that these elements were entrained, while calcium increased during the washing process, suggesting dissolution from the solid.

**Table 10.** Analyses of the Three Consecutive AL7 Natrojarosite Wash Solutions Prior to the Autoclave Experiments.

Element	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	S	Si	Zn
All results reported in mg/L														
<b>Detection Limits</b>	1	1	1	1	1	1	1	1	1	1	1	1	1	1
<b>Wash 1</b>	0	480	0	0	1	0	1100	1.2	810	0	0	1900	28	0
<b>Wash 2</b>	0	510	0	0	0	0	490	0	380	0	0	1200	28	0
<b>Wash 3</b>	0	530	0	0	0	0	240	0	190	1.3	0	850	28	0

#### **4.2.2 – Autoclave Decomposition Kinetics Experiment Results**

The results from the nine experiments completed for experimental aim i are summarised in Tables 11, 12 and 13. Table 11 reports the percent solids of the slurries at the start of the experiments and the specific gravity of the slurries prior to the experiment.

The elemental accountability was calculated as the output from the experiment divided by the input from the experiment for all elements of interest. The percentage weight of the solid (natrojarosite input) is converted to a total weight in grams by multiplying by the dry weight of natrojarosite. The same calculation is used on the solid residue, with the grams of element reporting to the solid added to the grams of element found in the liquid phase after the reaction.

Overall, the desired outcome is 100% recovery of elements after the reaction. A 5% variation (results of 95 to 105) during the experiment is considered acceptable, as errors will occur when comparing solid and liquid chemical analysis. Using XRF for solids analysis and ICP-MS for liquid analysis will inherit error, particularly at or near detection limits. Additional errors may be caused by small sample losses during cleaning and filtering and through the accuracy of weight measurements.

**Table 11.** Autoclave Decomposition Kinetics Test Results for AL7 Natrojarosite.

Reaction Parameters		Before Reaction		After Reaction				
Temperature Range (°C)	Time (min)	% solids	Liquid SG	Final Solution Free Acidity (g/L)	Fe Accountability	Fe in Solid (% wt)	Na Accountability	Na in Solid (%wt)
108 - 129	120	21.46	1.17	0.0	102	101.65	103	91.21
147 - 163	120	22.58	1.17	2.9	97	97.32	102	78.35
160 - 170	120	21.69	1.16	7.6	100	99.25	104	68.53
170 - 178	120	22.01	1.17	7.3	98	98.01	101	66.31
180 - 189	120	21.86	N/A	7.8	101	100.20	102	56.93
190 - 204	120	21.84	1.17	17.7	102	101.30	107	45.06
204 - 212	120	21.69	1.17	23.5	120	118.05	105	29.81
208 - 221	120	21.80	1.17	24.0	99	98.05	102	23.71
217 - 231	120	21.91	1.16	24.0	96	94.76	100	20.22

Iron remained in the solid phase with 100% (+/- 5% error) of the initial iron remaining in the solid phase iron at the end of the experiment. Sodium dissolved from the solid phase to form aqueous sodium sulphate. However, 20% of the original sodium remained in the solid phase in the 217 - 231°C test, where XRD results showed no natrojarosite present (Table 12). The solids were thoroughly washed after the experiment to remove any entrained liquid. Thus it is difficult to explain the existence of the remaining solid phase sodium, other than to suggest the formation of another solid sodium species.

Most of the accountabilities for those elements present in measurable quantities were acceptable. The accountabilities are given in Table 12 and results confirm the validity of the experiments. The method to develop a mass balance is given in Section 4.2.2.

The conclusions reached are therefore based on mathematically acceptable evidence.

**Table 12.** Accountabilities for Major Elements Present in the Autoclave Kinetics Experiments on AL7 Natrojarosite.

Temp. Range (°C)	Al (%)	Ca (%)	Cr (%)	Fe (%)	Mg (%)	Mn (%)	Na (%)	Ni (%)	S (%)	Si (%)
108 - 129	107	101	111	102	111	103	103	102	104	108
147 - 163	93	89	89	97	81	88	102	97	96	90
160 - 170	99	98	96	100	102	95	104	98	98	97
170 - 178	94	92	88	98	89	109	101	102	99	93
180 - 189	100	97	97	101	100	91	102	125	100	101
190 - 204	90	87	83	102	78	93	107	101	97	88
204 - 212	113	117	106	120	99	99	105	91	104	106
208 - 221	96	96	90	99	91	105	102	92	97	93
217 - 231	90	99	85	96	94	94	100	98	98	93

Table 13 shows the results for the dissolved sulphur analysed in the liquid discharge from the autoclave. All experiments lasted 120 minutes. The Table also reports the molar ratio of calcium to sulphur in the solid phase autoclave discharge.

**Table 13.** The Dissolved Sulphur and Solid Phase Molar Ratio of Calcium to Sulphur for AL7 Natrojarosite Autoclave Kinetics Experiments.

Temp. Range (°C)	Dissolved Sulphur (mg/L)	Solid Phase Calcium: Solid Phase Sulphur
108 - 129	0.76	0.80
147 - 163	15.41	0.85
160 - 170	19.73	0.92
170 - 178	23.89	0.94
180 - 189	27.95	1.03
190 - 204	37.81	1.17
204 - 212	40.65	1.33
208 - 221	51.29	1.48
217 - 231	51.67	1.51

The ore used for leaching contained a low concentration of calcium (0.87%w/w in the saprolite; Table 1). Limestone and hydrated lime were added at the end of the process to enhance the precipitation of iron as natrojarosite and to neutralise the tailings from the acid leach process. Thus all calcium in the natrojarosite as a solid prior to leaching will be present as gypsum (calcium sulphate) and un-reacted limestone and lime.

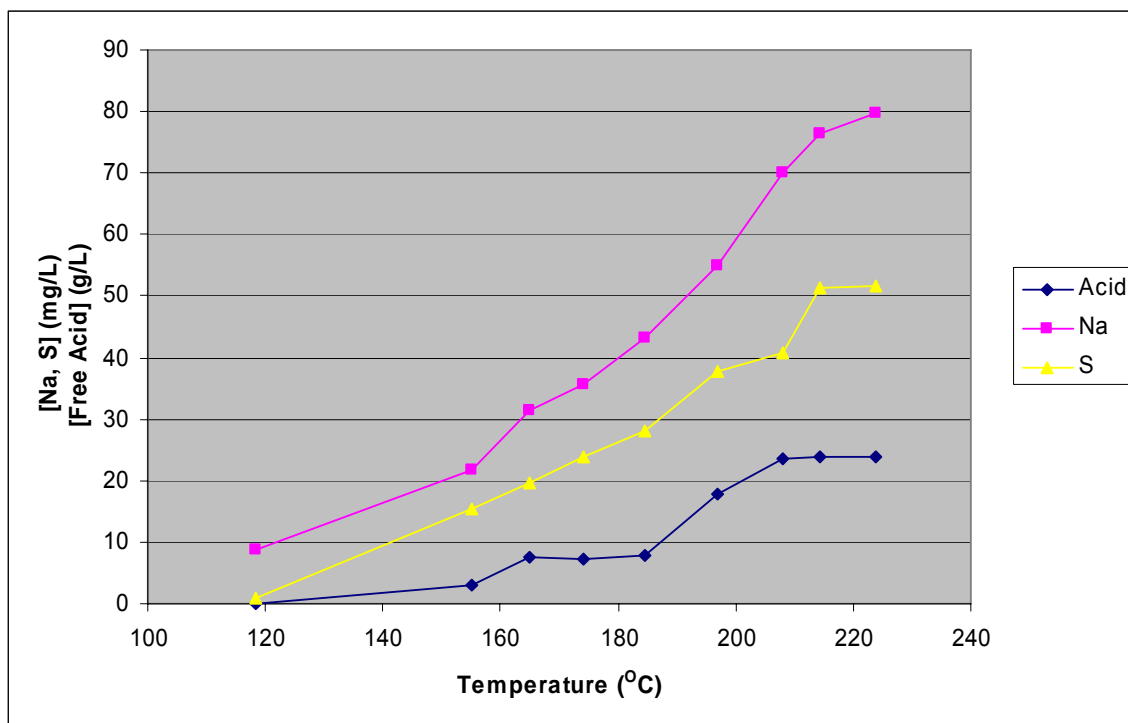
The molar balance between calcium and sulphur in the solid phase reported in Table 13 suggests that, at a temperature around 180°C, the molar ratio of calcium to sulphur was 1:1. Calcium sulphate has the same molar ratio (1:1) and thus was likely to be the only solid form of these elements present under these conditions, as acid created during the decomposition of natrojarosite would react with excess limestone and lime, forming gypsum. This suggests that

the natrojarosite decomposed at 180°C, as calcium accounted for all of the sulphur in the solid phase.

At temperatures lower than 180°C there was an excess of sulphur in the solid phase, associated with the presence of natrojarosite. At temperatures above 180°C there was less sulphur in the solid phase than was required to account for all the calcium in the solid phase, suggesting that the calcium sulphate itself may have been decomposing.

Figure 10 shows the profile of free acidity and dissolved sodium and sulphur levels for each test in the kinetics series. It should be noted that the temperatures shown refer to the mid point of the temperature range seen during the experiment, rather than the targeted temperature.





**Figure 10.** Free Acid, Dissolved Sodium and Sulphur in the Autoclave Discharge Solution for Each Experiment.

#### 4.2.3 – X-ray Diffraction Results

Table 14 gives the XRD results for the washed solid autoclave discharge. As mentioned previously, the solids were washed as thoroughly as possible to ensure that entrained liquid did not affect the solid product results.

**Table 14.** Identification of Mineral Species Present in Autoclave Discharge from the AL7 Natrojarosite Decomposition Kinetics Experiments by XRD.

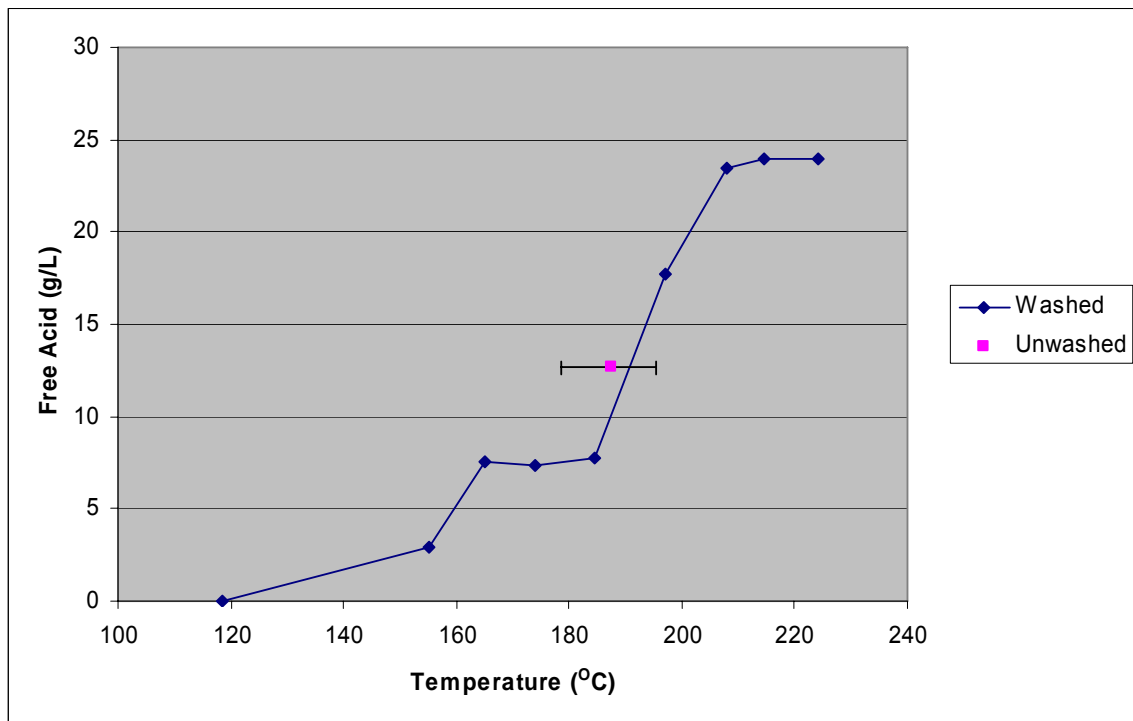
Temp. Range (°C)	Natrojarosite	Anhydrite	Goethite	Haematite	Quartz
108 - 129	Major	-	Minor	-	Moderate - Minor
147 - 163	Major	Moderate - Minor	Minor	Moderate - Minor	Moderate - Minor
160 - 170	Moderate	Major	Minor	Moderate - Minor	Minor
170 - 178	Moderate	Major	Minor	Moderate	Minor
180 - 189	Moderate	Major	Minor - trace	Moderate	Minor
190 - 204	Moderate	Major	-	Moderate	Moderate - Minor
204 - 212	-	Major	-	Moderate	Minor
208 - 221	-	Major	-	Moderate	Minor
217 - 231	-	Major	-	Moderate	Minor

Natrojarosite was not detected in the solids from the 204°C and higher temperature experiments. Haematite is present in increasing concentrations in the solids from the 147°C and higher temperature experiments. Dutrizac (1990) suggested that at 220°C natrojarosite would readily convert to haematite. These results suggest that the minimum required temperature is lower.

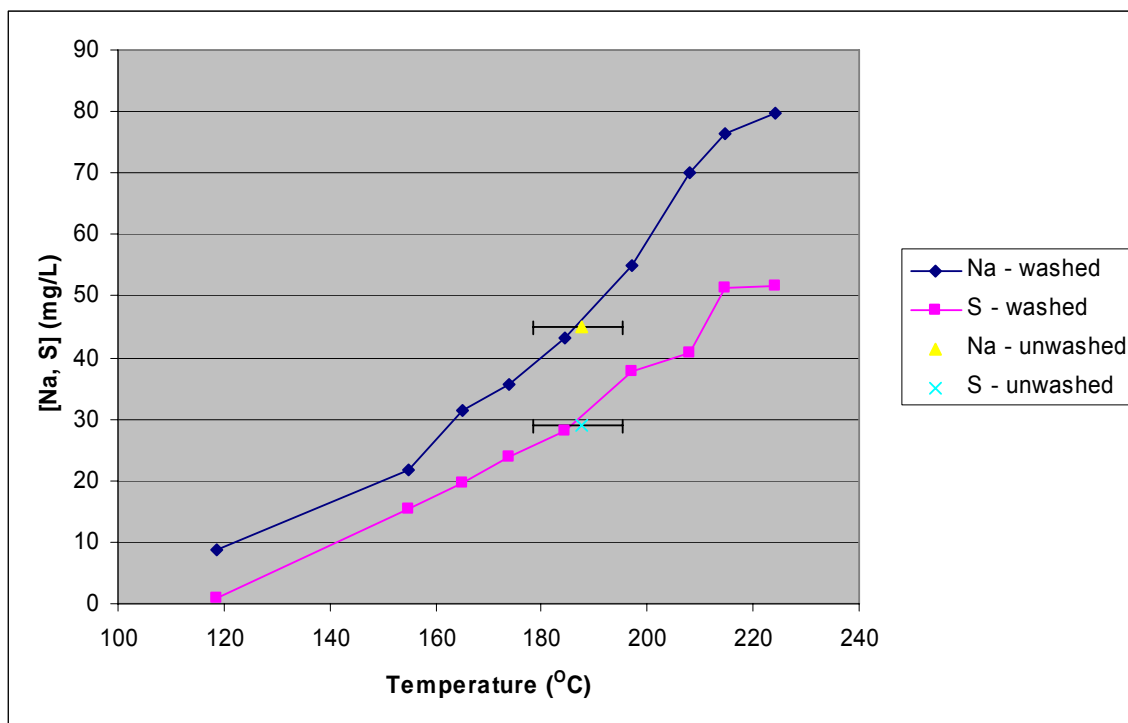
#### 4.2.4 – Results from Using Unwashed AL7 Natrojarosite Prior to Autoclave Conversion

An unwashed AL7 natrojarosite sample was tested at one temperature to determine if the unwashed natrojarosite sample would behave differently to the washed natrojarosite. The selected temperature was 190°C. However, the same issues with poor temperature control already mentioned arose and the

temperatures in Figures 11 and 12 have error bars representing the variation in temperature during the two hour experiment. The results for washed natrojarosite are taken from Figure 10.



**Figure 11.** Free Acidity in the Autoclave Discharge for Washed versus Unwashed AL7 Natrojarosite.



**Figure 12.** Dissolved Sodium and Sulphur in Autoclave Discharge for Washed versus Unwashed AL7 Natrojarosite.

The results obtained for the washing stage suggested that there is no difference between the results using washed or unwashed material. This would be a potential saving in a plant scale operation, as there would be no need for a preliminary wash prior to conversion.

#### **4.2.5 – Maximising Acid Production from Jarosite Decomposition Using AL7 Natrojarosite in an Autoclave**

Converting jarosite to haematite is advantageous, not only because it forms a stable waste material for disposal, but also because there is the

opportunity to extract a reusable material from the conversion process. The cost of acid is the greatest operating expense in the AL process and thus recycling of acid from natrojarosite decomposition could potentially save money.

As described in Section 4.1.1 – iii, samples were taken from various stages within the BHP Billiton atmospheric leach process. The intention was to find a balance between the acid generated from natrojarosite decomposition and the buffering capacity of limestone added to enhance the precipitation of iron during the process.

One sample was taken from the final tank of the saprolite leach (ST10) and so contained dissolved iron and no added limestone. Another sample came from the second of two tanks (NT2) where the initial two hour limestone neutralisation occurred. Limestone was added to a pH of 2 to complete iron precipitation prior to solids / liquid separation.

The results obtained from the autoclave experiments completed over two hours are given in Table 15, with Figure 13 showing the results compared to those in Figure 11. Two samples were tested and compared to the final product. The mean temperature over the two hour period is reported.

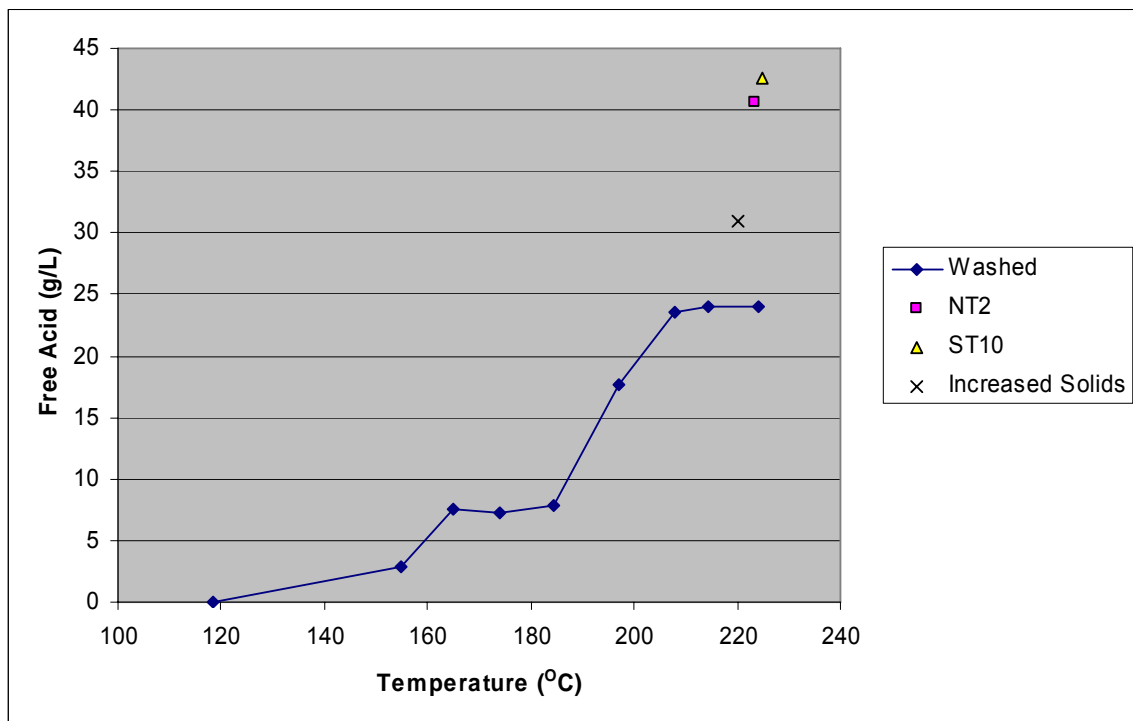
**Table 15.** Free Acidities, Dissolved Sodium and Dissolved Sulphur Levels in Autoclave Discharge Solutions from the Decomposition of Various Natrojarosite Samples.

<b>Material Tested</b>	<b>Temperature (°C)</b>	<b>Free Acidity (g/L)</b>	<b>Dissolved Sodium (% of initial solid)</b>	<b>Dissolved Sulphur (% of initial solids)</b>
Final Tailings (Washed)	217 - 231	24.0	79.8	51.7
After Neutralisation (NT2)	216 - 231	40.6	79.5	69.0
Before Neutralisation (ST10)	220 - 229	42.6	77.0	79.8

Table 15 shows that acidity in the autoclave discharge increased between the final tailings of the AL process and the natrojarosite neutralised to pH 2 (NT2). This suggests that there was an excess of limestone and hydrated lime present that neutralised the acid as it formed during the decomposition reaction. The increase in acid production measured when the samples taken from ST10 and NT2 decomposed was minimal. The extent of natrojarosite precipitation was comparable between the two samples and limestone added at NT2 was consumed completely to precipitate iron i.e. there was minimal un-reacted limestone present. In all, the acid produced by the decomposition of the AL natrojarosite is not of a high enough concentration to be of commercial value.

A fourth experiment was conducted to determine whether increasing the solids loading of the slurry would maximise acid production (Figure 13). These results are compared in Figure 13 to those for washed natrojarosite from Figure 10.

The maximum solids loading achievable whilst still having flowing slurry was an increase in solids from 250g/L to 416g/L. This should have resulted in increased acid production from 24.0g/L to 38.7g/L. However, the result was actually 30.9 g/L, suggesting that increasing the solids loading may also increase the buffering capacity of excess limestone and hydrated lime present in the solids. Mass transfer issues may also have arisen with the increased solids loading and the capacity of the high solids concentration to accommodate acid in solution.



**Figure 13.** Acid Production for Samples of Natrojarosite Taken from Various Locations within the BHP Billiton AL Process (single point tests).

#### 4.2.6 – AL7 Natrojarosite Decomposition Temperature / Time Relationship

##### Results

The results for the various time and temperature combinations tested are given in Tables 16, 17 and 18. Free acidity, dissolved sodium and dissolved sulphur levels (as percentages of their respective totals in the initial solid) in the autoclave discharge were used as indicators of decomposition.

**Table 16.** Free Acidity in Autoclave Discharge.

	0 min*	5min	15min	120min
180°C				7.3
200°C		9.8	12.3	17.7
220°C	11.3	16.7	17.6	24.0
240°C <sup>#</sup>	16.7		23.5	24.0

**Table 17.** Dissolved Sodium in Autoclave Discharge.

	0 min*	5min	15min	120min
180°C				43.1
200°C		35.9	54.5	54.9
220°C	51.2	61.7	72.7	76.3
240°C	72.6		80.6	79.9



**Table 18.** Dissolved Sulphur in Autoclave Discharge.

	0 min*	5min	15min	120min
180°C				27.9
200°C		21.2	29.5	37.8
220°C	33.6	40.2	47.5	51.3
240°C	49.0		52.0	51.7

NOTES for TABLES 16, 17 and 18:

\*0 minutes – heating element set to full power with the sample quenched as soon as the temperature was reached.

# 240°C – actually 231°C due to poor temperature control.

The relationship from the temperature versus time experiments showed that, based on acid production, maximum decomposition was achieved at 220°C after 120 minutes. That is, 24.0g/L free acid was produced as the highest concentration of free acid. However, the dissolution of sodium and sulphur suggested that maximum decomposition occurred after 15 minutes at 240°C (80.6% dissolved sodium and 52.0% dissolved sulphur). The result for sodium dissolution agreed with the result seen in Table 11, where 20% of the initial mass of sodium remained in the solid phase after the reaction.

## **5 – Experimental Section 3: Stability Testing of Natrojarosite – Methods and Results**

Issues with the TCLP test as a method of measuring the stability of an inherently unstable compound were raised in Chapter 2. Various alternatives were noted, including the holistic approach developed by Environmental Geochemistry International (eGi). The methods used in the batch leaching and column testing sections of this chapter were developed from the methods described by eGi. Permeability testing was added to understand the relevance of the results obtained from the stability tests. The methods for permeability testing come from Lambe and Whitman (1979).

In all these experiments the natrojarosite was tested wet and never dried, other than for chemical analysis. When dry weights are mentioned it is an estimation of the true weight of solid material used in the experiment, based on the drying of another sample of the natrojarosite tested. Dried natrojarosite is likely to react to stability testing differently to wet natrojarosite, as the chemical composition will change if allowed to dry in direct sunlight or in an oven above 80°C, with the loss of waters of hydration.

## **5.1 – Batch Agitation Stability Testing Methods**

### **5.1.1 – Experimental Aims**

The aim of the batch agitation tests is to create an unrealistic environment in which solids may dissolve. Agitation was used to maximise the surface to liquid contact. Deionised water was used to maximise concentration gradients between the solids and the surrounding solution, thereby maximising both the dissolution gradient and the chance of detecting the products of dissolution.

Sea salt solution was made by adding 27g/L dried sea salt to water. This solution was used to determine the effects of excess alkali metal (sodium) in the solution surrounding a decomposing jarosite species and to determine if brine media (as seen in some underground water supplies and in deep sea tailings placement) would have any effect on the stability of the residue.

Table 19 shows the experiments completed on AL3 and AL7 natrojarosite residues from the BHP Billiton atmospheric leach process (Table 3 contains their chemical analyses). The number in the matrix indicates the number of tests at those parameters completed.

**Table 19.** Batch Agitation Stability Test Matrix.

Test solution Residue	Deionised water	27g/L sea salt	pH 3 water
AL3	3	1	0
AL7	2	1	1

### 5.1.2 – Equipment and Method

Tests were conducted in 2L polypropylene containers. A three bladed, 25mm polypropylene agitator was placed in a multi test chuck, similar to those used in flocculation testing. These chucks allow up to six tests at once, all at the same revolutions per minute.

The sample of natrojarosite to be used in the batch agitation test was dried to determine the initial moisture. From this, a wet mass was added to the test bottle to provide the equivalent of 250g dry sample. 1000mL of the test solution, either deionised water or synthetic sea water was added to the container.

Agitation was maintained for sixteen hours, after which the agitators were stopped and removed. Lids were placed on the containers and the solutions allowed to settle for 24 hours. The supernatant above the solid was decanted and any entrained solids filtered and returned to the experiment container. The volume of liquid was recorded to calculate the total mass of dissolved elements.

The pH of the liquid sample were measured using a hand held pH probe, with a sub sample was submitted for chemical analysis (various methods subject to the element of interest including ICP and AAS).

Another volume of test solution equal to the volume removed was added to the batch agitation test container and the process repeated.

### **5.1.3 – Completion of the Experiment**

The process of sixteen hour agitation, settling and decantation was repeated until the pH of the decanted solution dropped below 3. This pH was nominally chosen to indicative of when acid production resulting from natrojarosite decomposition was significant.

Once pH change occurred, the solid and liquid components were separated by filtration. The final liquid volume was measured and a sample submitted for chemical analysis. The solid sample was dried at 80°C, weighed and a representative sample submitted for acid digestion and chemical analysis. A second solid sample was sent for mineralogical characterisation.

## **5.2 – Batch Agitation Stability Testing Results**

Dissolution of the solid occurred in all experiments, with a similar rate and order of dissolution. In decreasing order of concentration: calcium, sodium (where salt water was used as it was not possible to detect sodium dissolving from the natrojarosite), silica and magnesium all dissolved from the solid residue.

After 48 days (48 cycles of agitation, settling and decantation) in deionised water, sample AL3 decreased in pH to below 3. Sample AL7 did not show this trend. The decrease in pH was accompanied by a dissolution of elements into the liquid phase.

### **5.2.1 – Excess Hydrated Lime and Limestone in the Solid**

A comparison of the initial natrojarosite chemical assays was completed to determine the difference between the AL3 and AL7 samples (Table 3). One obvious difference was the calcium concentration. Calcium is present due to hydrated lime or limestone added to the tailings during the neutralisation process, i.e. as un-reacted hydrated lime or limestone in excess of that required to neutralise the tailings, and as gypsum, the product of the neutralisation of acid.

It is thought that AL3 may not have received as much limestone and hydrated lime during neutralisation, possibly due to pilot plant operations error caused by tube blockages. Log books from the pilot plant operation were inconclusive in this regard.

A theory developed to associate calcium concentration in the natrojarosite and the release of acid during decomposition was that, as natrojarosite decomposed and acid was produced, excess limestone or hydrated lime neutralised the acid production, thus masking the drop in pH associated with decomposition. Once excess limestone or hydrated lime present in the tailings was consumed, the effects of decomposition (i.e. pH decreases as acidity increases) became apparent. Acidity appears in solution as a drop in pH, with associated elements such as sodium and sulphur present in the liquid phase in increasing concentrations.

Other elements present but not chemically bonded to natrojarosite in the atmospheric leach tailings sample will also dissolve as acidity increases (see Table 3 for other elements present in the tailings). These elements will be associated with leach residues and precipitates formed.

All samples under investigation were continually undergoing decomposition, buffered in solution by the presence of excess limestone or hydrated lime, suggested by the dissolution of calcium and sodium in all samples within the first weeks of testing. Acid created by decomposition was neutralised in situ by the excess limestone and hydrated lime, forming gypsum.

All salts of calcium have a low solubility – for gypsum, which is relatively high compared to other calcium salts, it is 0.21g/100mL (Aylward and Findlay, 1998). Gypsum can form a semi impermeable layer, sealing the natrojarosite from further decomposition. This theory correlates to those in the literature

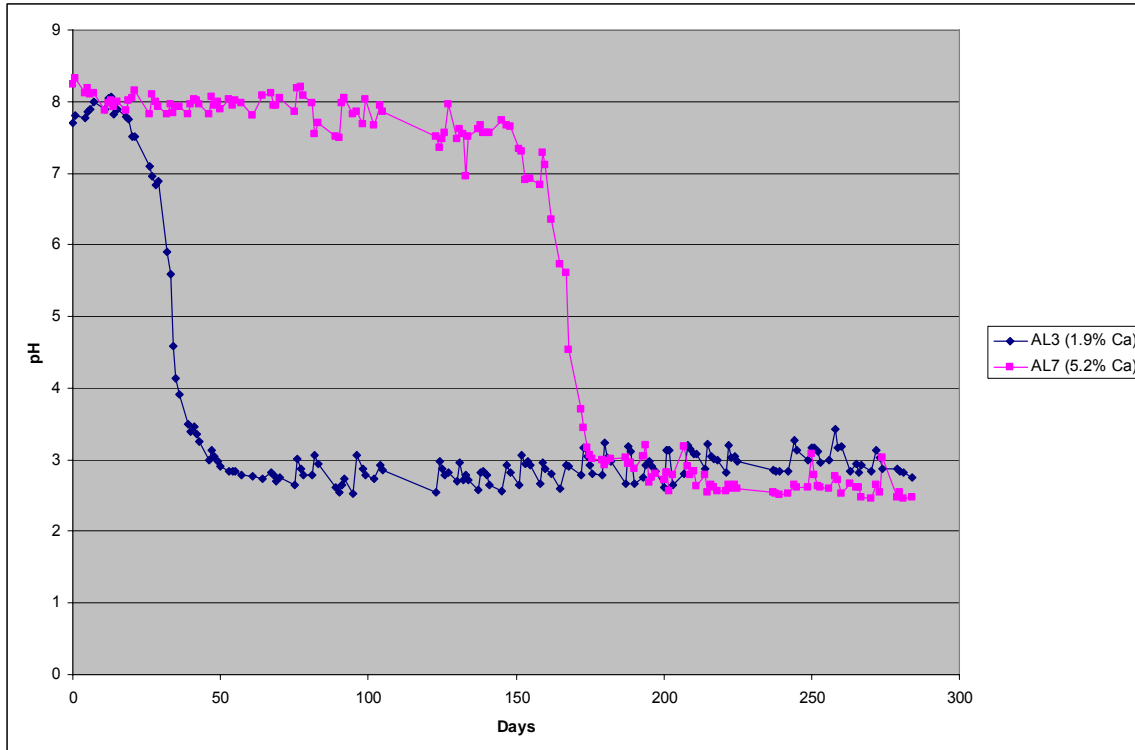
mentioned in Chapter 2, where limestone and lime were added to stabilise jarosite and in the Jarofix and Jarochoaux processes.

An estimate was made of the decomposition time for the AL7 natrojarosite. This was done by multiplying the number of days for AL3 natrojarosite to decompose by the ratio of calcium in AL3 and AL7, shown in Equation 27. A linear reaction rate was assumed. However this may not have been the case as increases in the thickness of the gypsum layer may slow the reaction.

$$\begin{aligned}
 (27) \quad \text{Days to Decompose (AL7)} &= \text{Days to Decompose (AL3)} \times \frac{[\text{Ca}] (\text{AL7})}{[\text{Ca}] (\text{AL3})} \\
 &= 48 \text{ days} \times \frac{5.19}{1.91}
 \end{aligned}$$

Equation 27 suggests that the AL7 natrojarosite should have decomposed after 130 days. However, as Figure 14 shows, this was not the case.





**Figure 14.** pH Changes in the Liquid Phase Associated with AL3 and AL7 Natrojarosite Decomposition Using the Batch Agitation Stability Method.

AL7 material decomposed after 180 days, 50 days beyond the estimation based on calcium concentrations in the solids. As mentioned previously, the assumption of linearity may have caused the result to be incorrect. Another cause of the error may have been the assumption that the calcium present in the solid phase was un-reacted limestone or hydrated lime, without accounting for precipitated gypsum.

A sulphur balance was used to account for the gypsum. By calculating the sulphur associated with iron as jarosite the assumption can be made that remaining sulphur in the solid phase is associated with gypsum. A back calculation can then be made to calculate excess calcium and associate this with

un-reacted limestone and hydrated lime. The calculations used are shown in Equations 28 and 29 with the results in Table 20.

$$(28) \quad S_{(Total)} - \frac{Na_{(natrojarosite)}}{S_{(natrojarosite)}} \times Na_{(Total)}$$

$$(29) \quad S_{(Total)} - \frac{Fe_{(natrojarosite)}}{S_{(natrojarosite)}} \times Fe_{(Total)}$$

The ratios of sodium to sulphur and iron to sulphur in natrojarosite were needed to calculate the percentage of sulphur in natrojarosite. Both sodium (Equation 28) and iron (Equation 29) are used, as the sulphur balance method can only be an approximation. Using iron alone is flawed as iron may coexist in the solid waste as iron oxides. Using sodium alone is also flawed as there is likely to be excess sodium from the salt water. The sulphur associated with the sea water matrix was negligible, as the solution was synthetic in origin. The sulphur not tied up in natrojarosite was calculated by subtracting from the sulphur in the solid analysis (Table 3).

Calcium present as gypsum was calculated by multiplying the results of Equations 28 and 29 by the ratio of calcium to sulphur in gypsum (40.08 / 32.06 or 1.25). This gave a percentage of calcium reporting as gypsum which, when subtracted from the total calcium in Table 3, gave excess calcium, which can be assumed to be excess limestone or lime.

**Table 20.** Sulphur Balance Using Iron and Sodium Association.

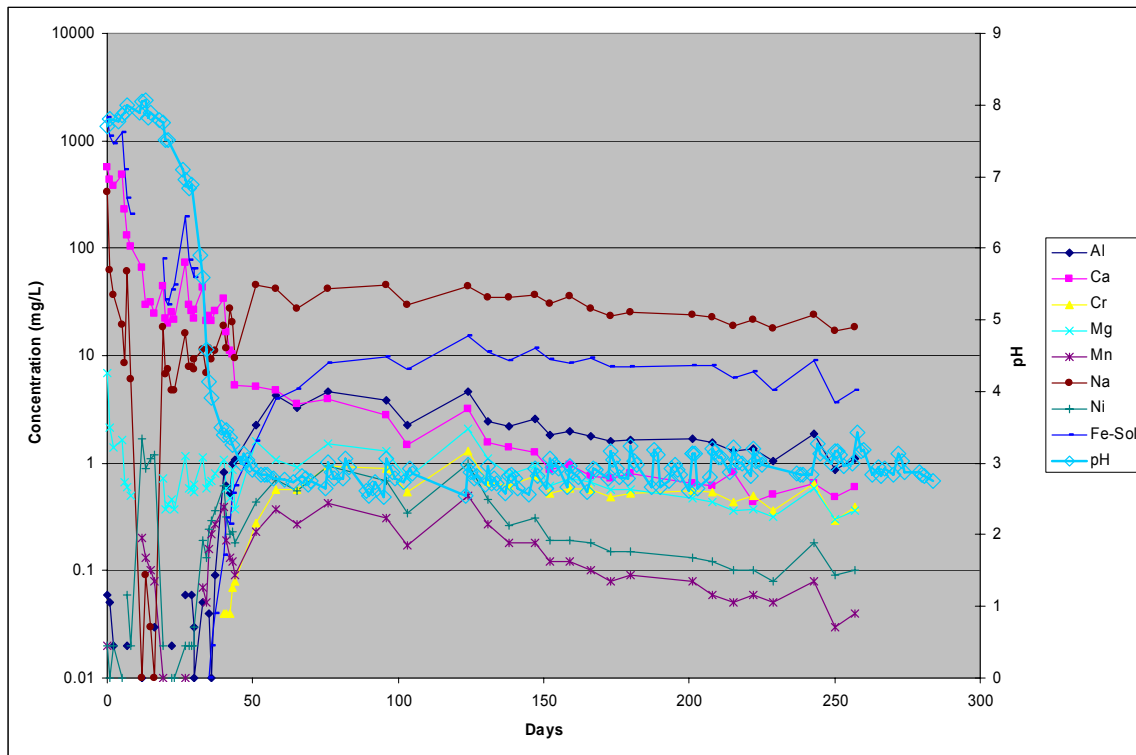
<b>AL3</b>	<b>Iron Method</b>	<b>Sodium Method</b>
% S Associated in Jarosite	7.86	6.39
Excess % S in Solid	0.31	1.78
Resulting % Ca Associated as Gypsum	0.39	2.23
% Calcium as Limestone or Lime	1.52	-0.32
<b>AL7</b>		
% S Associated in Jarosite	7.65	6.33
Excess % S in Solid	2.80	4.12
Resulting % Ca Associated as Gypsum	3.50	5.15
% Calcium as Limestone or Lime	1.69	0.04

For both AL3 and AL7, the iron method suggested a greater excess of calcium than that calculated by the sodium method. This may be inaccurate due to the presence of iron oxide in the leach residues. Overall the result suggests the presence of a small amount of un-reacted hydrated lime and limestone. Most, if not all, of the calcium is present as gypsum.

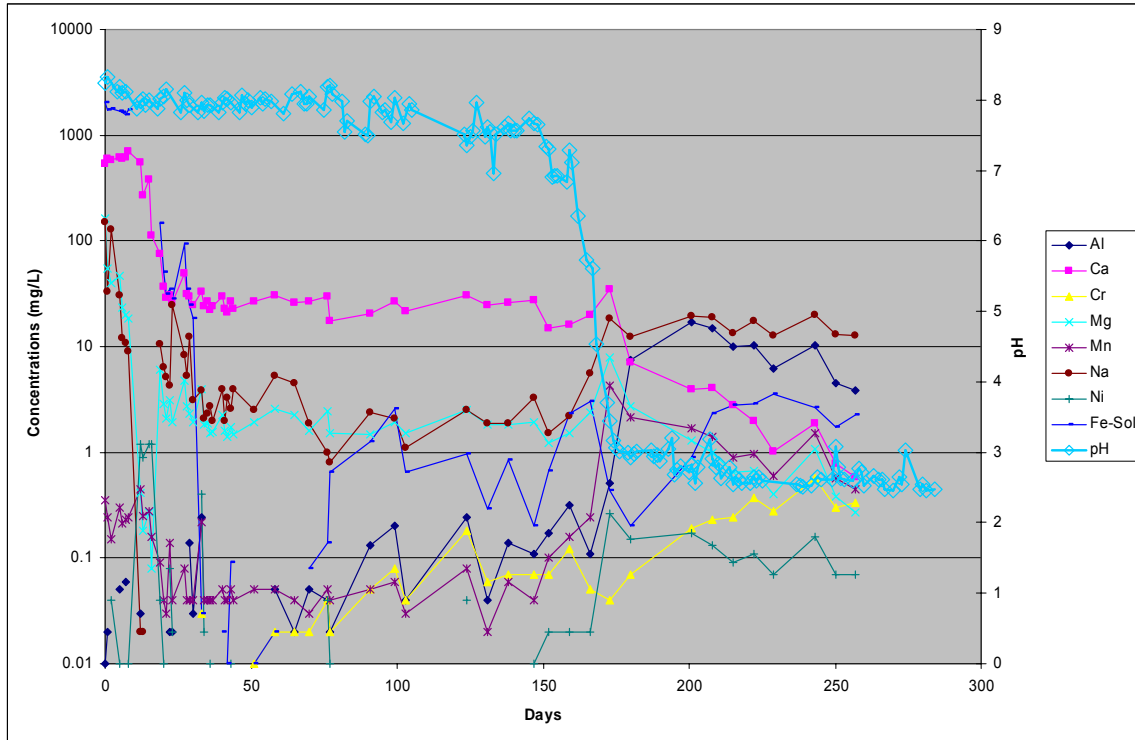
### **5.2.2 – Gypsum Encapsulation Theory and Liquid Chemical Analysis**

The ability of the higher calcium containing solid to buffer decomposition was seen in the liquid analysis samples. Figures 15 and 16 show the dissolution of elements into the liquid phase as decomposition occurred. Note the logarithmic scale for the elemental concentrations. Occasional points and incomplete plots were due to certain elements reporting below detectable limits. The acidity generated by decomposition will dissolve other elements from the AL

tailings not chemically bonded to the natrojarosite. It can be seen that calcium passing into solution decreased with time, whilst sodium remained relatively constant throughout.



**Figure 15.** Dissolved Element Concentrations and pH from AL3 Natrojarosite Decomposition Using the Batch Agitation Stability Method.



**Figure 16.** Dissolved Element Concentrations and pH from AL7 Natrojarosite Decomposition Using the Batch Agitation Stability Method.

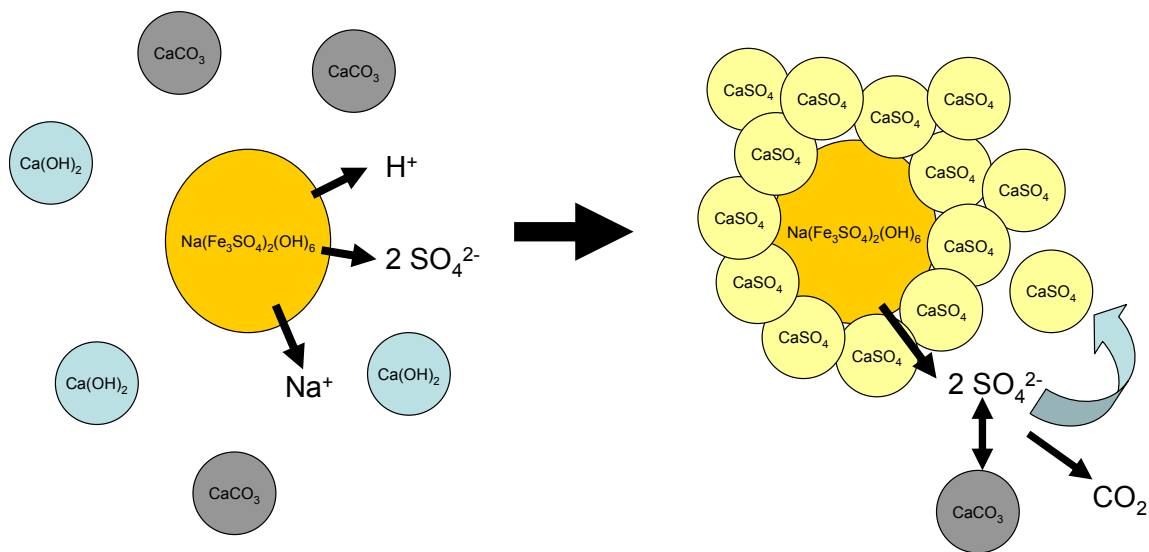
Figure 17 shows the gypsum encapsulation theory. The more natrojarosite decomposes the greater the thickness of gypsum coating the surface. There is assumed to be a very small concentration of free limestone or hydrated lime present in the solid material (based on the results from Section 5.2.1) and thus the reaction shown in Figure 17 must represent the solids stabilisation within tailings neutralisation in the BHP Billiton AL process.

As natrojarosite decomposed, the sodium, sulphate and hydrogen ions passed into the liquid phase. Iron converted to an oxide (not shown) and remained as a solid, although again, there was no evidence of iron oxide present in the solid when analysed by XRD. This may have been due to the iron being

amorphous (not defined crystal structure) and thus was not detectable by x-ray diffraction.

The results of Ryan and Stroehlein (1976) suggested that jarosite was a poor iron source as a plant fertiliser, which supports the poor availability of iron in seen here in the liquid phase. Figures 15 and 16 show iron present in the liquid phase, but only when the acidity drops below 3. Thus, if the acid remains in proximity to the decomposition reaction, iron may dissolve as a sulphate.

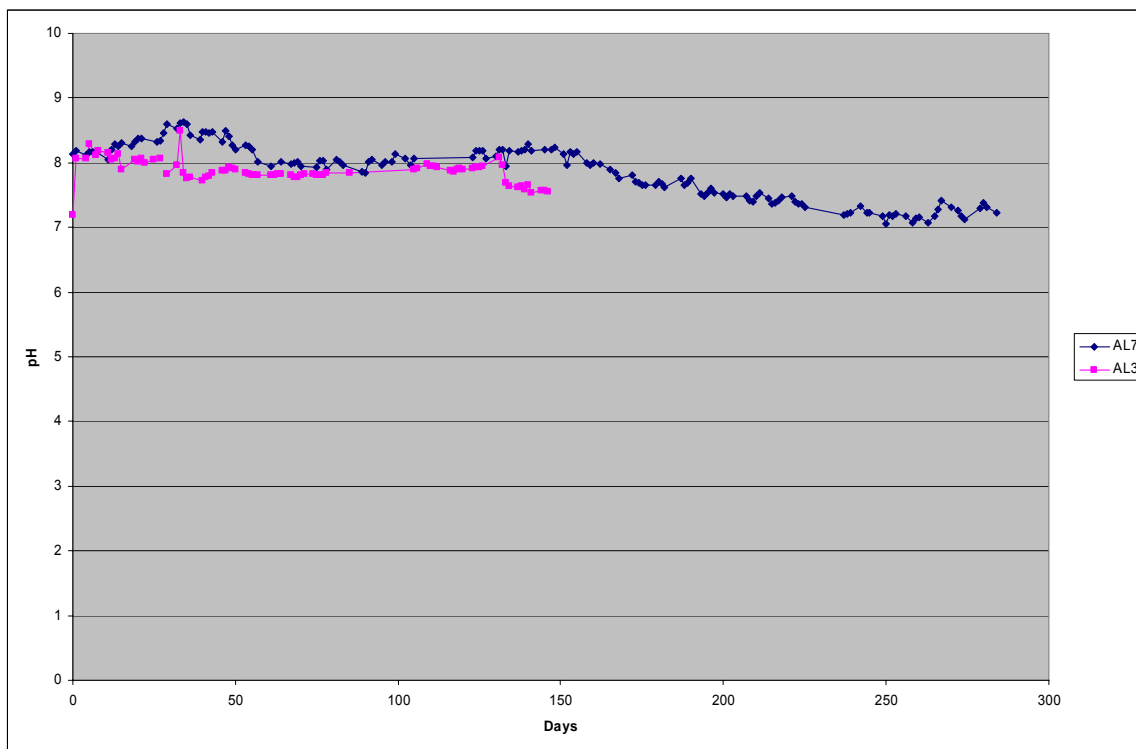
The sulphate ion combines with either limestone or hydrated lime forming gypsum immediately at the point where the dissolution occurred. This increases the width of the gypsum coating. Similarly, liquid does not readily contact the surface of the natrojarosite, further inhibiting dissolution.



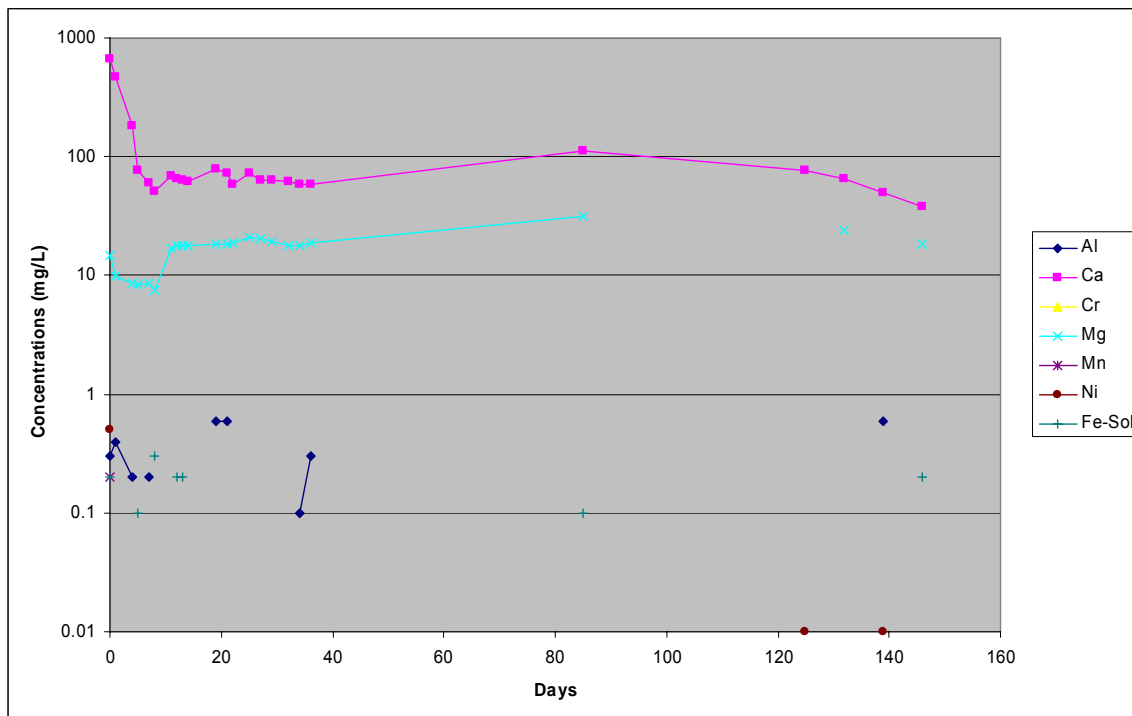
**Figure 17.** Gypsum Encapsulation Theory.

### 5.2.3 – Salt Water Results

Interesting results were obtained from the batch agitation tests using salt water as the test solution. Figures 18, 19 and 20 show the pH measurements for the AL3 and AL7 materials, as well as the liquid chemical analysis diagrams. These three figures are dramatically different compared to the results shown in Figures 14, 15 and 16.

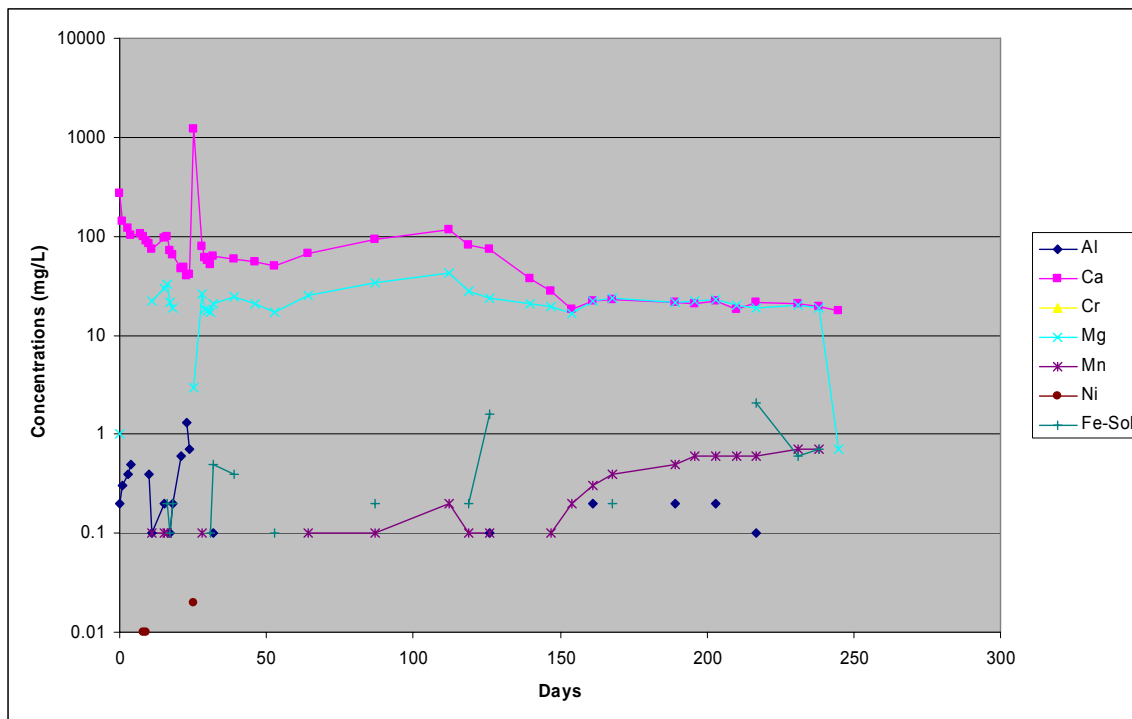


**Figure 18.** pH Measured from AL3 and AL7 Natrojarosite Salt Water Batch Agitation Stability Tests.



**Figure 19.** Dissolved Element Concentrations from AL3 Natrojarosite in Salt Water Batch Agitation Stability Tests.





**Figure 20.** Dissolved Element Concentrations from AL7 Natrojarosite in Salt Water Batch Agitation Stability Tests.

It was found that there was no significant formation of solution acidity and no significant dissolution of elements during the salt water batch agitation tests. The same natrojarosite was used in both the salt water and deionised water tests. These results show that the decomposition seen in deionised water is non-existent when using salt water. This result agrees with empirical data from the field-based findings of Alpers *et al* (1992) and Nolch (1995), who found that jarosites were stabilised when in the presence of a saline media. Further to this, these results provide an experimental explanation for the findings by the CSIRO (1994), where there was no accumulation of heavy metals in higher order species of fish stocks off the Hobart coast post jarosite dumping at sea by

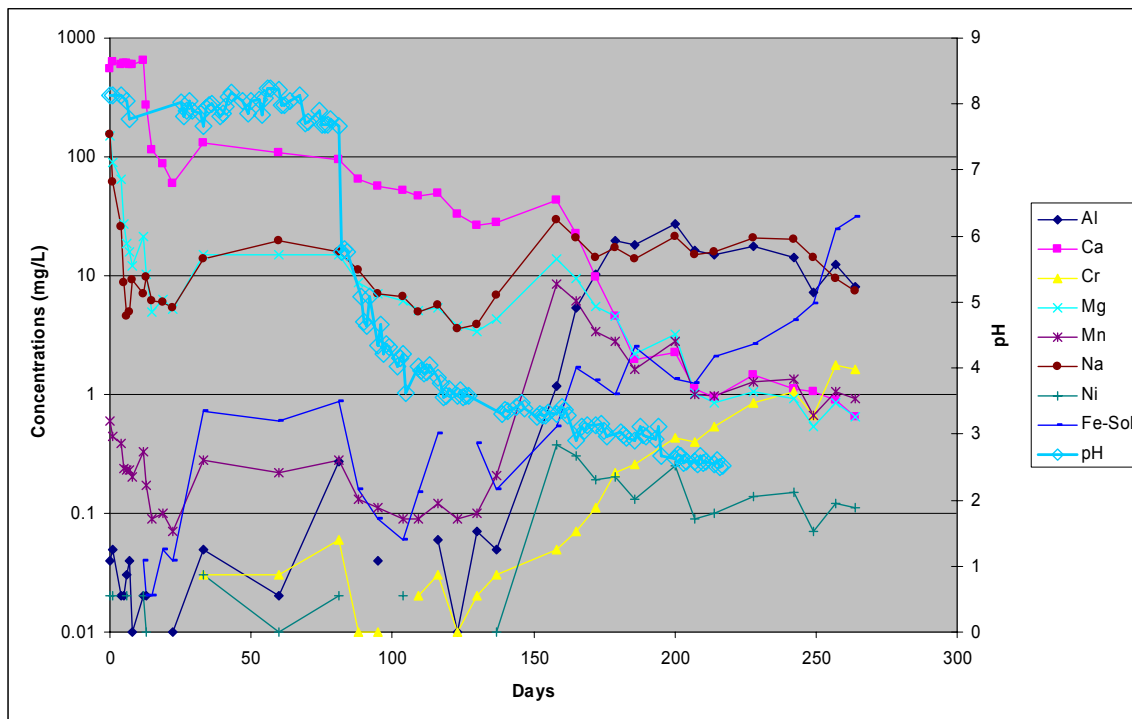
Zinofex, Hobart. The result also refutes part of the theory of Wilson (from Mackey and Sainsbury 1994), who suggested that 60% of ocean dumped jarosite either dissolved or remained suspended. Suspension is a possibility but dissolution is very unlikely.

#### **5.2.4 – Equilibrium Reactions**

The salt water results suggested the mechanism of natrojarosite decomposition. If an excess of sodium in solution inhibits the decomposition of natrojarosite, the actual decomposition mechanism itself is likely to be an equilibrium reaction, as suggested in Equation 9 and discussed in Section 2.9.3.

The presence of excess sodium is enough to stop decomposition from occurring. Sodium is one product of decomposition, along with iron, sulphate and protons. Iron remains in the solid phase during decomposition and thus would be ineffectual as a retardant in solution.

To test the equilibrium theory, an excess of acid was tested by using water adjusted to pH 3 with sulphuric acid as the test solution. The acid in solution was buffered by the natrojarosite for 80 days or cycles. Figure 21 shows the concentrations of the various elements in solution over time and the pH over time for the AL7 sample.



**Figure 21.** Batch Agitation Stability Test Results for AL7 Natrojarosite in pH 3 Adjusted Water.

Solution concentrations from about 150 days onwards in the pH 3 media are comparable to those seen after decomposition commenced in deionised water, i.e. after about 180 days in Figure 16. Free acid in the test media expends the buffering capacity of the gypsum present in the solid, decreasing the time to decomposition from 180 to 150 days.

The evidence from these experiments suggests that sodium dissolution is the trigger for natrojarosite decomposition and this decomposition can be slowed or stopped by the use of sodium rich solutions as the storage media and this would include the use of under sea or saline lake storage. However, this does not justify the use of ocean dumping. There is as yet no definitive study on the

detrimental effects of ocean floor sedimentation on localised and larger ecosystems.

## **5.3 – Column Testing Methods**

### **5.3.1 – Experimental Aims**

Column testing provides conditions more like those seen in the placement and storage of natrojarosite in a large dam or settling pond. This testing was done by packing a large sample (larger than that used in the batch agitation test) of natrojarosite into a column or fixed bed and allowing solution to percolate through the sample under gravity. The results were then compared to the batch agitation tests to determine differences in the dissolution rates caused by water percolation compared to an agitated slurry.

### **5.3.2 – Equipment and Method**

3kg dry weight of AL7 natrojarosite was moistened into a paste and spread over the surface of the filter cloth to an even depth in a large (400mm diameter) Buchner funnel. The depth of the 3kg sample in the funnel was approximately 100mm. Vigorous compaction, as well as any trapped air pockets were avoided where possible. Two separate experiments were completed for

each test condition and sampled as described in Chapter 2 of this thesis. The test conditions are described below.

Test solutions were used to determine if the matrix surrounding the natrojarosite could affect the results gained from the column tests. Two test solutions were used - deionised water and synthetic seawater (27g/L sea salt in water).

Two types of column test were used:

#### **a. Free Draining Tests**

The free draining column tests involved adding a set amount of test solution to the surface of the natrojarosite. The volume of solution added was subject to the permeability of the sample but was generally 1L of test solution per week. The percolation flow was collected out of the base of the Buchner funnel and tested for pH and eH using hand held probes. A representative sample of the solution was taken for chemical analysis to determine what elements, if any, had dissolved.

#### **b. Saturation Tests**

The saturation tests involved fitting a tap on the drain of the Buchner funnel to restrict the amount of flow leaving the natrojarosite bed. By doing this, the natrojarosite remained saturated at all times. Enough test solution was added when required to maintain a head of water above the bed. The volume of water

collected was measured, then tested for pH and eH using hand held probes, as well as a representative sample taken for chemical analysis. These tests usually required 1L of test solution every two weeks.

## **5.4 – Column Testing Results**

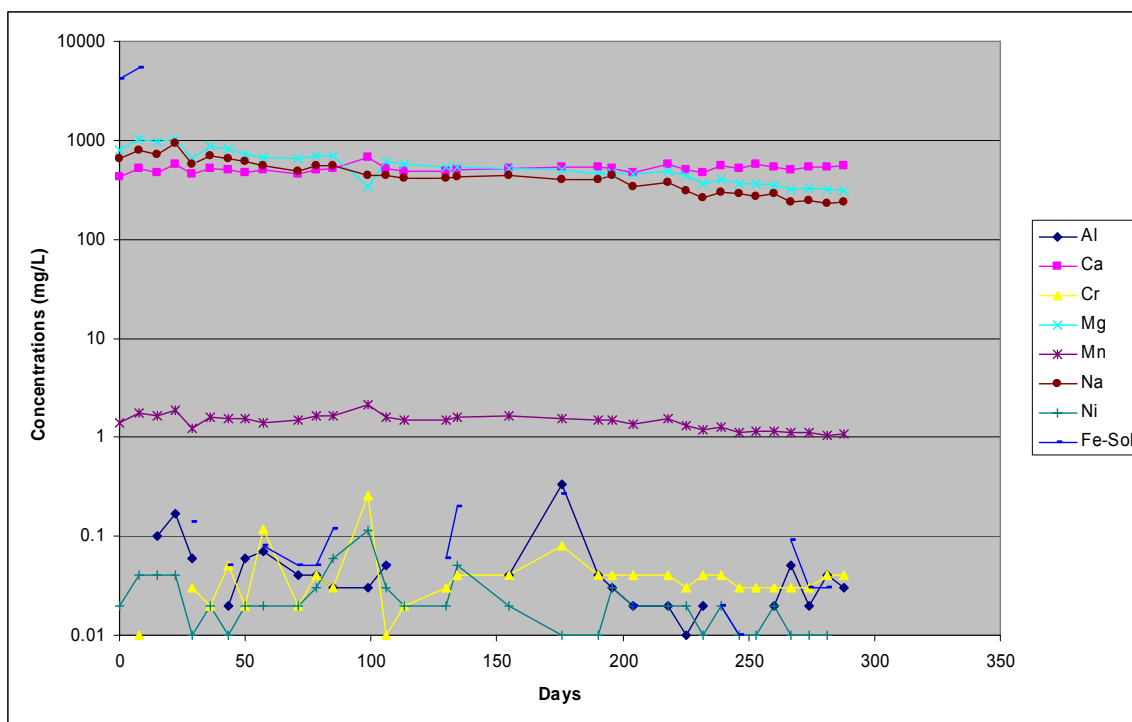
No changes to the pH or eH of the percolation solution during the column tests were seen. The pH remained at 5.8 and the eH was 550mV (v Ag/AgCl probe). Two reasons for this were:

1. The added buffering capacity of the increased mass of natrojarosite – 3kg as opposed to 250g in the batch agitation tests.
2. Solution flow under gravity as opposed to vigorous agitation, decreasing the solid to liquid contact.

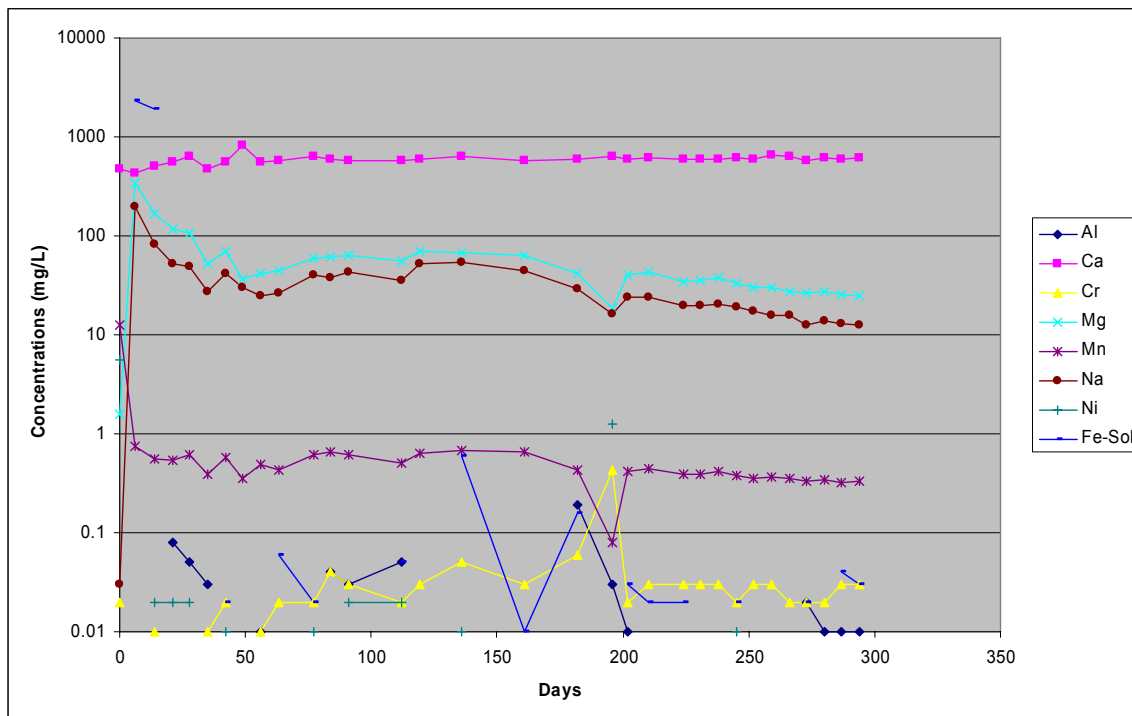
The difference between batch agitation and column testing was that the system was no longer closed. That is, solution did not remain in complete contact with the solid for the 18 hour mixing time seen in batch agitation testing, but rather stayed in contact for as long as it took to seep through the bed of solid. Thus, the results from the column testing are less conclusive as stand alone tests. The results must be viewed in conjunction with the information provided by batch agitation testing.

The results obtained for the AL7 natrojarosite, in free draining and saturated columns and in deionised and salt water are summarised in Figures 22

to 25. Occasional points and incomplete plots were due to certain elements reporting below detectable limits.

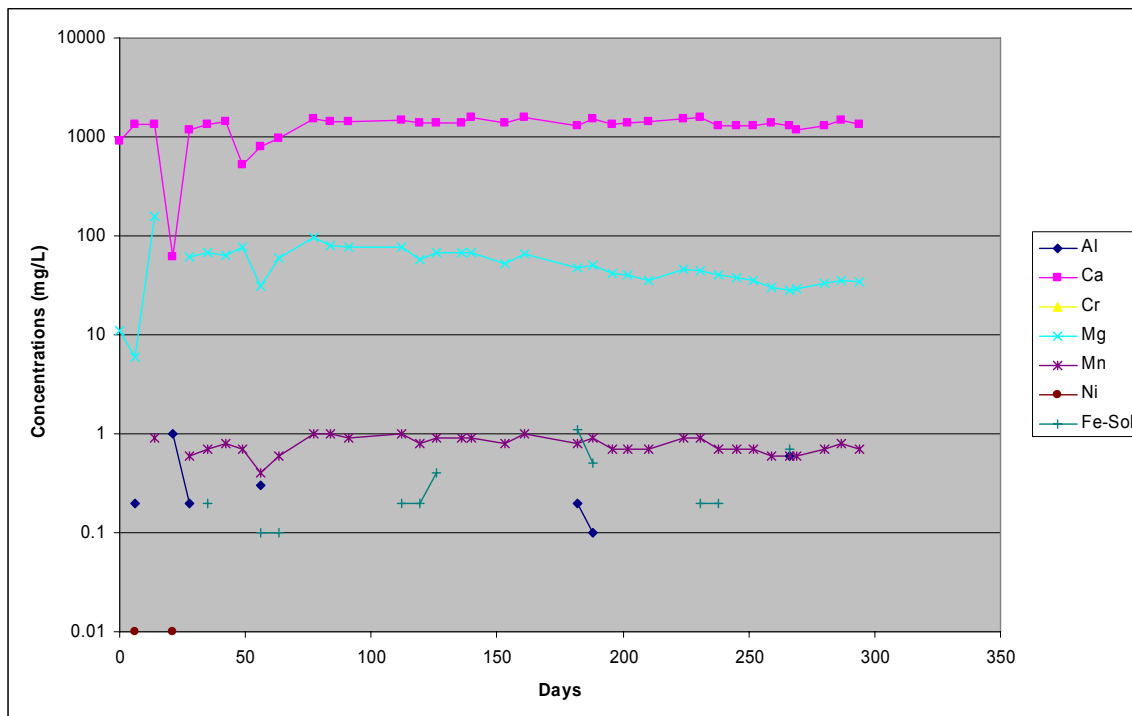


**Figure 22.** Saturated Column Test Results for AL7 Natrojarosite  
in Deionised Water.

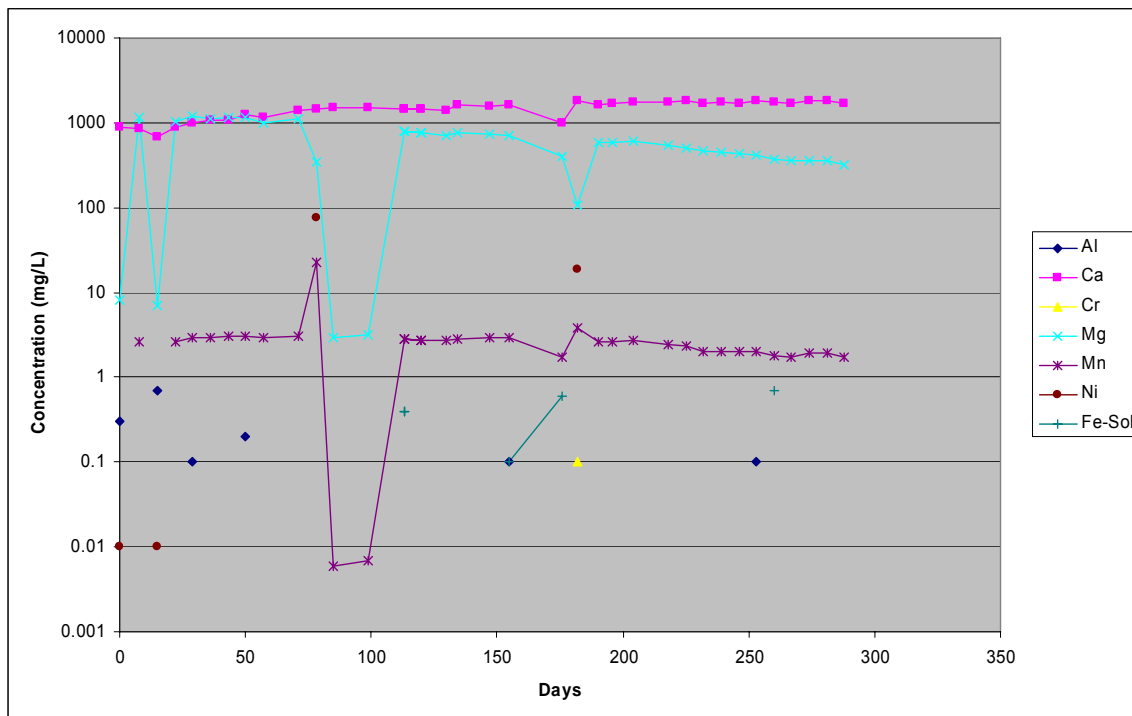


**Figure 23.** Free Draining Column Test Result for AL7 Natrojarosite in Deionised Water





**Figure 24.** Saturated Column Test Results for AL7 Natrojarosite  
in Synthetic Salt Water.



**Figure 25.** Free Draining Column Test Result for AL7 Natrojarosite in Synthetic Salt Water.

Comparisons between Figure 22 and 24 or 23 and 25 show a decrease in the dissolution of elements when using salt water as the test solution. Additionally, comparison between Figures 22 to 25 and the batch agitation test results in Figures 15 and 16 show the amount of dissolution occurring during the column tests is much less than that seen in batch agitation testing.

The results shown in the column tests using deionised water match those found in the very early stages of the batch agitation tests. Calcium, sodium and magnesium all appear in the analysis in high concentrations when compared to all other elements tested. Magnesium dissolves from the solid at a greater rate in the saturated column tests than in the free draining column tests, suggesting that

longer contact time is required between the solid and liquid phases for magnesium to dissolve.

#### 5.4.1 – Combining Batch Agitation and Column Test Results

The dissolution rates of calcium and sodium from the deionised water column tests were combined with the results obtained from the batch agitation tests. The total calcium and sodium released from the columns was divided by 12 (3000g of natrojarosite in the column tests divided by 250g in the batch agitation tests). The results are given in Table 21. Note that the values quoted for the batch agitation test are after 180 days, when the pH of solution dropped below 3.

**Table 21.** Comparison of Calcium and Sodium Loss Results between Column Tests and Batch Agitation Tests in Deionised Water.

	Days	Total Calcium Loss (mg)	Total Sodium Loss (mg)
<b>Batch Agitation Test</b>	180	6563	554
<b>Free Draining Test</b>	294	1574	92
<b>Saturated Test</b>	288	1418	1216

The results for calcium loss from the column tests were comparative to the first two days of batch agitation testing for both the free draining and saturated tests.

Much more sodium was leached from the saturated column than from the free draining column. The sodium loss from the free draining column tests

compared to the sodium loss calculated in less than one day of batch agitation tests. However, in the saturated column test, sodium dissolution was more than twice that of the batch agitation test at the time where decomposition had occurred.

One possible cause was that decomposition of natrojarosite is occurring in the saturated column, but was masked by gypsum buffering.

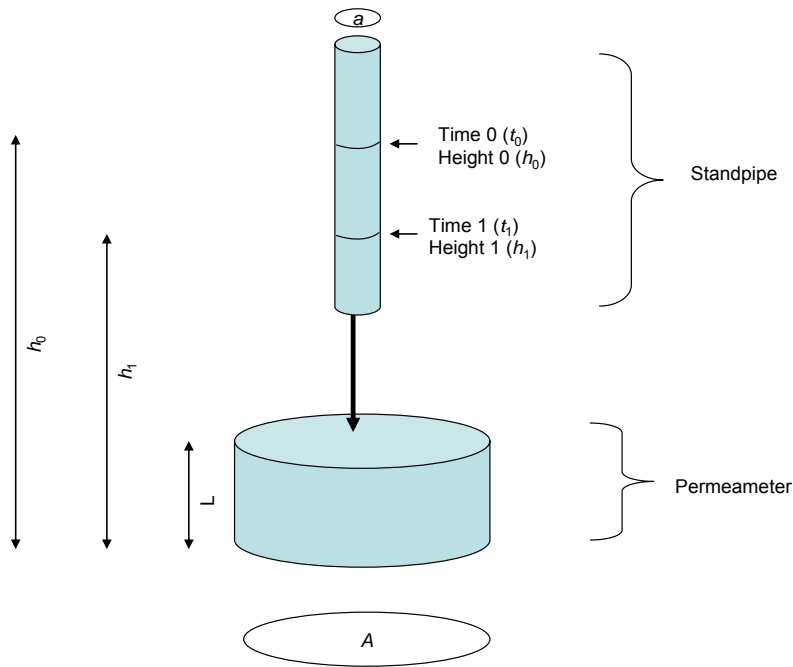
X-ray diffraction analysis of the saturated samples would have been unlikely to help confirm this conclusion, as in 3kg of jarosite there is 4.7% sodium or 142g. Just 1.2g total was dissolved. XRD was not completed on these samples.

## **5.5 – Permeability Testing Methods**

The permeability of a certain mineral or compound measures the likelihood of water egression through the tailings facility. The data from permeability testing can be combined with that obtained from both the column testing and the batch testing to determine whether a particular compound has the potential to decompose with time. For example, jarosite decomposition is an expected result when stored under oxidising conditions; however, decomposition may not occur if there is no movement of water through the bed due to poor permeability.

Permeability was tested using the falling head method taken from Lambe and Whitman (1979). A known volume of natrojarosite was contained in a sealed

cylinder with an entry and exit port. The entry port was connected to a head of water in a standpipe and the exit allowed to drain freely. The design of the test rig (taken from Lambe and Whitman, 1979) is shown in Figure 26.



**Figure 26.** Standard Design of a Permeability Test Rig

The permeability of the bed was determined using Darcy's Law, referring to Figure 26 for the parameter used:

$$(30) \text{ Permeability} = \frac{2.303 \times a \times L}{A \times (t_1 - t_0)} \times \log_{10} \frac{h_0}{h_1}$$

This result was obtained using a permeameter bed, 400mm in diameter, 200mm tall. The head was 75mm in diameter, with a starting height of 1500mm.

A relatively large bed diameter was used to minimise wall effects in the permeameter.

## 5.6 – Permeability Testing Results

The permeability of the AL7 natrojarosite was calculated to be  $5.58 \times 10^{-6} \text{ cm/s}$ .

## 5.7 – Combined Permeability and Stability Results

Using a worst case scenario, based on the percentage of sodium loss from the batch agitation test when decomposition occurred, a calculation of the time a  $1 \text{ m}^3$  sample of natrojarosite would take to decompose was performed. To estimate the decomposition time, the following equation was used:

$$(31) \quad \text{Time} = \frac{\text{Volume of Solids} \times \text{SG} \times \% \text{ Moisture} \times \% \text{ Sodium} \times \% \text{ Loss to Decompose} \times 10^3}{\text{Average Sodium Released to Solution} \times \text{Permeability} \times \text{Area of Test}}$$

The result obtained for the AL7 natrojarosite at 25% moisture content was:

$$\text{Time} = \frac{1 \times 2.6 \times 75\% \text{ Solids} \times 2.27 \times 9.8 \times 10^3}{0.012 \text{ g/L} \times 5.58 \times 10^{-6} \times 1}$$

$$\text{Time} = 6.39 \times 10^{12} \text{ years}$$

This result was based on the average sodium dissolution rate (9.8%) seen in the AL7 batch agitation tests. This does take the buffering result seen in the saturation column test into account and would increase dramatically if the results obtained from the free draining tests were used.

These results are indicative of a long term stability of natrojarosite in a correctly managed tailings facility. However, the ability to decompose is not mitigated by storage under these conditions, merely delayed for a long period of time. Long term management of a tailings facility means long term expenditure.

## **6 – Discussion**

The jarosite group of compounds are problematic, as seen in both the literature review and from the results obtained in this thesis. Particularly of concern are those results showing the compound's ability to generate acid upon decomposition. As a result, the production and storage of jarosites in metallurgical applications will continue to require management long after the resource is expended. Many processes continue to move away from jarosite production for this very reason. However, as ore types become more and more marginal and new methods are developed to extract numerous commonly used elements, jarosite will continue to be examined as a method for controlling and removing iron as an impurity from aqueous media, whether intentionally or by accident.

### **6.1 – Conclusions Drawn from Current Literature**

The findings from the literature show that there has been a large body of work completed in order to find alternative uses for the jarosite group of compounds, understand the mechanisms of decomposition and stabilise existing jarosite placements, all with varying levels of success. Current suggestions for alternative uses are neither beneficial nor economical and thus stabilisation or conversion surpass recycling as preferred options for jarosite treatment. The use



of the jarosite group of compounds as a fertiliser can be ruled out due to the acidity and addition of impurities associated with the solid product to the soil. Certainly for jarosites generated through the zinc refining industry, metals such as lead, silver and mercury associated with the jarosite are of environmental significance. Such metals, if released during decomposition, are toxic in low concentrations and will be mobile in solution.

The manufacture of building materials, including ceramics, using jarosite was not without success. The concern with this option is finding a market for the products. Unless a market is available, the cost of converting these products to saleable commodities such as glass, ceramics and building products would not be refunded to the producer. In this case, conversion to iron oxide would be the preferred treatment as the cost to convert to a building product would probably equal the costs of using an autoclave to convert the jarosite to iron oxide.

## **6.2 – Conversion of Jarosite to Iron Oxides**

### **6.2.1 – Hydrated Lime and Limestone Decomposition**

The results obtained in this study suggest that the lab scale processes attempted in some papers may work for a pure, synthetically produced jarosite, but would fail on an industrially produced natrojarosite produced in the atmospheric leach process.

At lower temperatures, the addition of lime resulted in no change to the presence of natrojarosite when examined by x-ray diffraction, suggesting conversion had not taken place. Examination of the contents of the resulting solutions, however, saw concentrations of sodium and sulphur present in the liquid phase. The concentrations observed in the liquid chemical analysis were suggestive of a near complete dissolution of the natrojarosite.

This process of stabilisation (or decomposition), used in such variations as the Jarofix and Jarochaux processes, stabilises jarosite, most likely through the formation of an impermeable layer of calcium sulphate. The gypsum formation results from the reaction between the acid formed from jarosite decomposition and a neutralising agent in limestone or hydrated lime. The stability of the gypsum encapsulation layer should be questioned, as future disturbance could expose the surface of the jarosite to further reaction, defeating the purpose of the stabilisation process. Future disturbances are minimised through the use of cement, but this in turn creates a large volume of concrete that needs to be used in an economically and environmentally acceptable way. Sustainability of such a process must also be of consideration.

The use of limestone in stabilising the jarosite group of compounds needs to be questioned. The results obtained in this thesis showed that limestone can only be used to stabilise natrojarosite when pH is low. Under these conditions natrojarosite is likely to be either decomposing or newly formed. The use of limestone will precipitate gypsum from the free acid present, causing natrojarosite to precipitate from dissolved iron. This is the likely stabilisation

mechanism suggested during the batch agitation chapter. Once formed, however, natrojarosite will not be further decomposed or stabilised by the addition of limestone.

The literature review indicated that natrojarosite was second in stability to potassium jarosite. It could be proposed that natrojarosite does not possess the high instability required to decompose in the presence of limestone. The higher basicity of hydrated lime was required to destabilise the natrojarosite and cause conversion to iron oxide.

### **6.2.2 – Autoclave Conversion**

Higher temperature and pressure resulted in natrojarosite conversion. The conclusion drawn was that natrojarosite required time and a temperature of 212°C to complete the conversion.

These results found a lower temperature than that recommended in the work of Dutrizac (1990), who quoted 225°C as the minimum temperature required to produce haematite from an iron sulphate solution. The use of a solid iron sulphate in jarosite lowers the temperature at which this reaction starts to approximately 150°C. However, full conversion still requires the higher temperature.

The work of Hage *et al* (1999) quoted in the literature review used carbon and temperature to convert jarosite to magnetite and haematite. The temperature used by Hage was 250°C, at 40 bar pressure. Using the work of Dutrizac in

conjunction with the work completed in this thesis, a carbon source is not required, as jarosite will autonomously convert under these conditions.

The autoclave discharge from the natrojarosite conversion experiments did not produce an acidic solution that contained a high enough concentration of acid to be immediately useful. For example, the atmospheric leach process upon which this thesis was based used 98% sulphuric acid to leach limonite. To achieve this concentration of acid, the natrojarosite conversion process would need to be accompanied by an acid plant concentrator, adding to the capital and operating costs.

If the natrojarosite conversion process was accompanied by a process that required a lower acid concentration, such as heap leaching or pickling, then the conversion process may be viable. However, the cost of purchasing new, low concentration acid is much cheaper than the operating costs of an autoclave or pipe reactor. Therefore the economic viability for a jarosite conversion process would come from the creation of a stable waste stream (iron oxide) that did not require long term management. Additional cost will be generated from the need to neutralise the waste stream prior to disposal if there is no use for the low concentration acid associated with the conversion process. As many commodity producers around the world have realised, advantage is gained from not producing jarosite in the first place.

Another problem with the conversion process when applied specifically to the zinc industry is the re-dissolution of scavenged impurity metals, removed in conjunction with iron, by jarosite precipitation during product solution purification.

Examples include silver ( $\text{Ag}[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2$ ) and lead ( $\text{Pb}\{[\text{Fe}(\text{OH})_2]_3[\text{SO}_4]_2\}_2$ ) which, when jarosite is converted to an iron oxide, dissolves into the liquid phase. It may be possible to control this accelerated decomposition, but it must be considered when assessing the viability of the conversion process. That is, there will be a waste stream containing environmentally sensitive elements such as silver and lead in solution that will need to be controlled and disposed of correctly.

A further conclusion from the natrojarosite conversion work is that the conversion process on an industrial waste is incomplete. Approximately 20% of the available sodium remained in the solid phase, suggesting either the time required for full conversion exceeded that used in these experiments, or the sodium remains in some solid form other than as natrojarosite. Similarly, the acid produced could not be maximised by increasing the solids loading or by improving the purity of the solids, suggesting that other compounds present in the solid either inhibit acid production or neutralise or buffer the product.

This may be caused by the presence of calcium. However the results indicate that it does not exist in the solid as calcium sulphate (gypsum) as the correct ratio is not found. If the temperature and pressure in the autoclave promote the desulphurisation of the gypsum, the calcium oxide formed may be able to neutralise the acid produced from natrojarosite decomposition. This reaction cannot be prevented, as the temperature at which the calcium oxide is formed is also required for natrojarosite decomposition.

The natrojarosite sample tested from the stage prior to limestone neutralisation in the atmospheric leach process (ST10) suggested that, whilst the acid production level was the highest achieved, it was still not stoichiometric to indicate full decomposition of natrojarosite, meaning compounds other than gypsum also affect this result.

Overall, the ability to convert the jarosite group of compounds either to an iron oxide or to usable or saleable products in a relatively inexpensive manner is unlikely using current methods. The advantages of producing a stable iron solid can only be derived from the decreased need to monitor a tailings facility storing goethite or haematite. This saving, however, is sizeable, as jarosites need management when being stored. This includes, but is not limited to, geomembrane isolation and water catchment management, with these risk mitigating practices expected to be a long term concern. Whether or not this saving is enough to make the conversion process economically viable is subject to the costs of constructing and operating an autoclave under the conditions at which jarosite formation occurs.

It is timely to mention that the atmospheric leach process was developed in order to eliminate the use of autoclaves, which are currently used to leach limonite and transitional material (a transition zone between the limonite and saprolite ore usually exists at varying depths and of varying thicknesses) up to a magnesium concentration of approximately 5%. If the formation of natrojarosite requires the use of an autoclave to convert to iron oxide, the advantage of removing autoclaves from the extraction process is lost. However, there may be

some ore bodies that justify this approach. A final stage jarosite conversion process may be economically viable if the ore contains a high proportion of magnesium.

The washing of the natrojarosite prior to autoclave conversion did not positively affect the temperature at which conversion occurred, or the amount of acidity produced in the autoclave discharge solution. However, the results from the chemical analyses of the liquids matched the results obtained from the column and batch agitation tests. Calcium was removed by washing the natrojarosite at a constant rate, with sodium, sulphur and magnesium levels decreasing with each subsequent wash. If plotted, these results would mimic those seen in the deionised water batch agitation tests and the free draining column tests.

## **6.3 – Measuring the Stability of Jarosite**

### **6.3.1 – Toxicity Characteristic Leaching Process Test versus Batch Agitation and Column Leaching**

The toxicity characteristic leaching process (TCLP) test is used extensively throughout the world. It gives results that are extremely useful for characterising many solid materials. Its strength is in its ability to test a wide variety of solids, basing the leach process on the natural pH of a liquid contacted

by the solid. It is relatively quick but this speed in obtaining a result is also its weakness. By taking a quick snapshot of the stability of a solid such as the jarosite group of compounds, the result may not be a true indication of stability with time.

The weakness of using the TCLP method alone was highlighted through the study of AL3 and AL7 natrojarosites. The TCLP test uses the pH of a solution contacted with the solid to determine the chemistry of the final leaching media. If the TCLP test was carried out on freshly produced natrojarosite, the initial solution test using water contacted with the solid would produce a solution of pH greater than pH 5. That would trigger the use of 1M hydrochloric acid solution as the second extraction solution.

Batch agitation testing in pH 3 buffered solution showed that AL7 natrojarosite has buffering capacity that neutralised the low concentration acidity for approximately 80 days. The hydrochloric acid used as the second extraction solution would be buffered, resulting in a solution pH greater than 5. This would trigger the final leach solution to be a dilute acetic acid solution of pH 2.88. Again, natrojarosite can last for 80 days at this pH only leaching calcium, sodium and magnesium. This is the result as reported in Section 2.6.3, where none of the natrojarosite produced from the seven atmospheric leach experiments reported any significant findings from the TCLP tests.

This should be compared to the concentrations of dissolved metals when AL3 natrojarosite decomposition commenced (Figure15). The leachability result from TCLP testing of an aged natrojarosite would be very different. If the TCLP



test was the sole method of determining the stability of the solid material, the age of the sample would affect how the solid was disposed of. Additionally, decomposition with time would not necessarily be expected from the solid unless prior knowledge of the jarosite group of compounds was available.

Thus, the age of the sample would have a major impact on the results from the TCLP test. The results from a freshly produced sample of jarosite may suggest the waste is safe to dispose of by standard practices such as landfill. The results from an aged sample of jarosite would recommend the product is not fit for storage, let alone disposal. Associated metals would affect this result as well. A “pure” natrojarosite would lose acid and sodium. A zinc industry jarosite would lose environmentally significant elements such as lead.

Combining the data from a vigorous stability test such as the batch agitation tests, the column leaching tests and the permeability measurements provides an overall picture of the stability of the product. The results take much longer to generate than TCLP testing, as some batch and column testing could take over a year to complete. However, decisions made on a tailings facility that has a long life expectancy should be based on the potential risks associated with the solid and the likely exposure to those risks, not on experimental methods based on expediency. As seen in these results, the AL3 natrojarosite was more unstable than the AL7 natrojarosite. This difference was only made apparent using the batch agitation method, as no difference was seen in TCLP testing. What effect would this result have had on the management of an actual tailings

placement facility, particularly when taking into consideration the permeability of the natrojarosite?

Using test methods that relate to specific metallurgical and environmental processes generates a better understanding of the likely risks associated with a waste such as natrojarosite. An example was the use of salt water media to see if decomposition would occur. Whilst the under sea storage of industrial wastes has environmental impacts far beyond the risk of acid production through decomposition, an interesting result from the batch agitation test was that the risks were mitigated by this storage method – a result that would not have been generated through use of the TCLP test.

Overall, when comparing the TCLP test to batch agitation and column leaching tests, use of the latter will give a holistic result on the stability of the solid waste. If the waste is to be stored in a tailings facility, time to generate results must not be an issue, as time needed in the management of an unstable waste stream will far outweigh the time taken to fully characterise the waste. The TCLP test is an excellent measurement of stability for many solids generated both in the industrial and domestic environments. However, its usefulness will be limited by intermediate solids such as the jarosite group of compounds that degrade in stability with time.

### 6.3.2 – The Stability of Natrojarosite

The mechanism by which natrojarosite decomposes is via the dissolution of sodium from the solid into the liquid phase. The permeability of natrojarosite will allow percolation to occur, albeit slowly. The decomposition of natrojarosite will release protons to the liquid phase causing a decrease in solution pH. This is accelerated where there are lower calcium concentrations in the solid, likely to be associated with a buffering or inhibiting capacity provided by gypsum. As acid generation increases, more elements in proximity to or directly contained within the natrojarosite are dissolved into solution.

It is important to understand the relationship between gypsum and natrojarosite, particularly when designing process flow charts, in order to stabilise and potentially convert the natrojarosite to iron oxide through the addition of lime at elevated temperatures. Such a step is not uncommon in the treatment of tailings produced from an acidic leach process and thus should not impose added cost to a process.

The decomposition of natrojarosite was impeded by excess sodium in solution. This result provides laboratory based empirical data to support the findings of Alpers *et al* (1992) and Nolch (1995) who found that the jarosite group of compounds were stabilised when stored in saline medium such as a hyper saline lake. These results also support other findings from numerous studies into the effects of the ocean dumping of jarosite off Hobart, Australia, throughout the 1980's. These findings were mentioned in Chapter 5.

Relating the findings of the above studies to those in this thesis expands the results obtained to more than just natrojarosite. Natrojarosite was stabilised by the presence of sodium in solution. Jarosites in the work of Alpers *et al* (1992), the CSIRO (1994) and Nolch (1995) were those from the group of compounds associated with the zinc industry. As sodium is not the metal associated with the iron sulphide hydroxide compound in many zinc industry jarosites, sodium's presence in solution should not slow an equilibrium dissociation reaction. Le Châtelier's Principle or the common ion theory can explain this result. Le Châtelier's Principle states that if a system at equilibrium is disturbed by a change in temperature, pressure or the concentration of one of the components, the system will shift in equilibrium position so as to counteract the effect of the disturbance (Brown and LeMay 1991).

The presence of sulphate salts in sea water may also inhibit decomposition of the sulphate compound in jarosites. Le Châtelier's Principle suggests that the potential for further ion dissolution from a solid into a high ionic liquid concentration is decreased. Further work with other solutions and compounds such as potassium jarosite would be interesting to see if a potassium rich liquid medium inhibits decomposition.

Another finding from the column testing of AL7 natrojarosite was the increased dissolution of sodium when the tailings remained saturated. Similar total volumes of water passed through both columns but when there was a drying and subsequent wetting phase, the total dissolved sodium decreased dramatically. This may be due to the fine, clay like structure of the natrojarosite

and its ability to hold pore water. If the water was absorbed into the natrojarosite during inundation, then dried out, any dissolved sodium would remain with the natrojarosite. A volume of water equal to that of the holding capacity would be required to rewet the solid before any significant volume of sodium could be washed out. Thus decomposition should be delayed. Again, this result has implications for how a storage facility should be managed to minimise the risk of jarosite decomposition.

By taking information from the batch agitation, column and permeability tests, a list of best storage practices can be generated. The batch agitation tests showed that decreased calcium concentrations in the natrojarosite resulted in faster decomposition. How this relates to stability can be seen in the hydrated lime and limestone decomposition experiments, where the concentration of sodium in solution suggested near to complete dissolution of natrojarosite. However, XRD suggested natrojarosite was still present in the solid.

The use of sodium in the solution media inhibited decomposition. If possible, saturation in a saline solution may increase long term storage capabilities. This suggestion, when engineering such a facility, may make this option economically unviable.

The column tests showed that a drying phase rather than storage saturated in water also decreased the total amount of sodium dissolving. This result corroborates the batch agitation test results where sodium in solution inhibits decomposition. It is likely, if it could be successfully designed and constructed, that a bulk natrojarosite storage facility saturated in salt water would

find equilibrium between the solid and liquid phases and would thus inhibit further decomposition. In this case, egress of solution could not be allowed.

When these results are combined with a relatively low permeability of  $5.58 \times 10^{-6} \text{ cm/s}$ , successful storage of the jarosite group of compounds seems to be a viable option. However, again, the long term need for successful management, in conjunction with historic problems associated with jarosites have led to many producers moving away from production of the compound.

The storage of the jarosite group of compounds must be managed to limit the ingress of water into the facility. Saline solutions should not affect the stability of natrojarosite, however, the fine particle size of natrojarosite may become entrained and thus cause other problems associated with transportation. Certainly jarosite facilities should not be allowed to leach into fresh water supplies, the results of which witnessed in the fish kill described by Davis *et al* (1999).

Whilst commenting on storage options, dry storage of jarosite was proposed in the literature review as a viable option. The cost of a drying facility associated with an area that could store dried solid (without allowing aeolian transportation) would need to be compared to the cost of an autoclave facility. In particular, dried jarosite still contains sulphur, allowing potential acid generation some time in the future. However, the output of haematite from an autoclave would be free of acid generating compounds, needing less strict storage. The cost of driving water from a wet jarosite would be comparable to the cost of operating an autoclave.

## 7 – Further Opportunities

Potential further experimental work is suggested from both the literature and from the experimental work completed in this thesis. This work should be completed on laboratory, pilot and full scale operations. Laboratory based work should be completed to understand if:

- Salt water will stabilise other forms of jarosite other than natrojarosite. This will confirm the relationship between the result for natrojarosite and the findings from the work of Alpers *et al* (1992), Nolch (1995) and the CSIRO (1994).
- Further to this, work should be completed using the batch agitation stability method to rank various jarosite types for stability over time.
- The kinetics of decomposition in an autoclave should be completed on other forms of jarosite to see any variation from the natrojarosite results obtained.
- The eventual location and form of toxins such as mercury and lead from zinc industry jarosites is of particular interest in determining the viability of using autoclaves to treat existing dumps. If the toxins are in the liquid form, there will be serious repercussions for the treatment of autoclave discharge from this process to contain and stabilise the toxin. If present in the solids, the stability of the compound must be understood to ensure greater stability than that of the jarosite group of compounds, otherwise the process is pointless.

From a larger scale metallurgical perspective, there are opportunities to employ results from this thesis into process flow sheets. The primary learning from this thesis is that the neutralisation of tailings by adding limestone and lime to a target pH should not be seen as a simplistic process. An optimal method of neutralisation should be determined and employed to maximise the stability of natrojarosite. Further to this:

- Consideration should be made of the temperature at which the process occurs, the method of agitation, the neutralising agents used and the target pH.
- The use of salt water to stabilise natrojarosite should be considered if a viable engineering method can be developed. This should not include the reintroduction of ocean dumping as this has other detrimental effects not discussed in this thesis. However, areas where water table salination has already occurred may be suitable jarosite storage areas. The addition of salt to the solid may promote stability; however, keeping the salt in proximity to the jarosite with time may prove difficult.

Alternative uses should continue to be explored, particularly with a view to extracting useful commodities from the waste. Any recycling of acid would benefit a project by saving costs of consumables.

Finally, there is limited knowledge associated with naturally occurring jarosites. It would be beneficial to see what results from this thesis (and from the extensive literature on industrial jarosite) might be applied to the treatment of jarosites associated with acid mine drainage and acid sulphate soils.



## 8 – Conclusions

The jarosite group of compounds have numerous problems associated with their decomposition. Production in industry is in decline, although still favoured as an easily filterable removal process for iron from a liquid product. A large volume of jarosites exists world wide, most in controlled and monitored waste dumps, with a small proportion in older mine and processing sites. Numerous methods to decompose, stabilise and recycle the compounds have been suggested with varying levels of success. Most methods of recycling and stabilisation are short term solutions. The complete conversion to an iron oxide is the only permanent solution.

Measurement of the stability of natrojarosite is difficult and subject to the age and storage environment of the solid. The batch agitation stability test method is suitable to testing solids with inherent variation in stability with time. TCLP testing of a solid like natrojarosite will not give a true indication of its stability. The drawback of the batch agitation method is the additional time required to fully assess the stability of the solid.

During batch agitation testing it was found that natrojarosite can be stabilised by contacting the solid through storage in synthetic salt water. The concentration of salt only needs to be that of ocean water (approximately 27g/L). This had been recognised in the literature by way of anecdotal evidence. These results provide laboratory based data, specifically relating to natrojarosite, to confirm field findings from the broader jarosite group of compounds.

Natrojarosite ranked second behind potassium jarosite in stability. This may have caused the suggested conversion method using limestone to fail with natrojarosite produced from the atmospheric leach process, as the stability of the compound was enough to inhibit the reaction.

The likely mechanism by which limestone and hydrated lime stabilises natrojarosite involves the formation of a layer of gypsum around the particles. Acid production through decomposition of natrojarosite was increased where samples had been dosed with less limestone and hydrated lime. Thus, the addition of neutralising chemicals, both for metallurgical purposes and for final tailings stabilisation, is fundamental to the eventual stability of the final product. Changes to the methods of limestone and hydrated lime addition should be thoroughly tested to ensure optimisation of the process.

## 9 – References

Al T.A., Blowes D.W., Jambor J.L., Scott J.D.; "The geochemistry of mine-waste pore water affected by the combined disposal of natro-jarosite and base metal sulfide tailings at Kidd Creek, Timmins, Ontario", *Canadian Geotechnical Journal*. 31(4) pp 502-512, 1994 Aug.

Alpers C.N., Nordstrom D.K., Ball J.W.; "Solubility of jarosite solid solutions precipitated from acid mine waters, Iron Mountain, California, USA", *Sciences Geologiques (Bulletin)*, in *Thermodynamique des processus naturels; Contributions au premier symposium international*, B.Fritz editor, v.42, no.4, pp 281-298, 1989.

Alpers C.N., Rye R.O., Nordstrom D.N., White L.D. King B.S.; "Chemical, crystallographic and stable isotopic properties of alunite and jarosite from acid-hypersaline Australian lakes". *Chemical Geology*, (96) pp 203-226, 1992.

Arauco, H., and Doyle, F.M., "Hydrolysis and Precipitation of Iron during Pressure Leaching of Zinc Sulphide Materials", *Hydrometallurgical Reactor Design and Kinetics*, Eds. R.G. Bautista, R.J. Wesely, G.W. Warren, TMS, 187-207, 1986.

Arregui, V., Gordon, A.R., and Steintveit, G., "The Jarosite Process, Past, Present and Future", *Lead- Zinc Tin '80*, Eds. J.M. Cigan, T.S. Mackey, and T.J. O'Keefe, TMS of AIME, 97-123, 1979.

Aylward G., Findlay T.; *SI Chemical Data*, 4<sup>th</sup> Edn, Jacaranda Wiley Ltd, 1998.

Babcan J.; "Synthesis of Jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ", *Geol. Zb.*, 22(2), pp 299-304, 1971.

Bédard C., Duval J., Ferguson K., Gardiner E., Gladwin D., Jansons K., Lang D., Lewis B., Maltby J., Matthews J., McCann M., Mchaina D., Poirier P., Puro M., Schwenger R., Siwik R., Vezina S., Welch D., West S.; *A Guide to the Management of Tailings Facilities*, The Mining Association of Canada. 1998.

Beek, K.J., W.A. Blokhuis, P.M. Driessen, N. van Breemen, R. Brinkman and L.J. Pons. Problem soils: their reclamation and management. In: *Land Reclamation and Water Management: Developments, Problems, and Challenges*. ILRI Publication 27, Wageningen, pp. 43-72, 1980.

Bigham J.M., Schwertmann U., Pfab G.; "Influence of pH on Mineral Speciation in a Bioreactor Simulating Acid Mine Drainage" *Applied Geochemistry*, (11) pp 845-849, 1996.

Bridge T.A.M., Johnson D.B.; "Reduction of soluble iron and reductive dissolution of ferric iron-containing minerals by moderately thermophilic iron-oxidizing bacteria", *Applied & Environmental Microbiology*. 64(6) pp 2181-2186, 1998.

Brown, J.B., "Jarosite-Goethite Stabilities at 25\_C, 1 atm.", *Mineral Deposita (Berl.)*, 6, 245-252, 1971.

Brown T.L., LeMay jr H.E; "Chemistry – The Central Science". Prentice-Hall International. 1991.

Chen T.T., Dutrizac J.E.; "Mineralogical Study of Jarofix Products for the Stabilization of Zinc Industry Jarosite Residues", *Proceedings from the 2<sup>nd</sup> International Symposium on Extraction and Processing for the Treatment and Minimisation of Waste*, The Minerals, Metals and Materials Society, 1996.

Cruells M., Roca A., Patiño F., Salinas E., and Rivera I.; "Cyanidation kinetics of argentian jarosite in alkaline media", *Hydrometallurgy*, (55) pp 153-163, 2000.

CSIRO Research Team – Brief from a Public Meeting 20/12/1994.

Dalvi A.D., Bacon W.G., Osborne R.C.; "The Past and the Future of Nickel Laterites", PDAC 2004 International Convention, Trade Show and Investors Exchange. 2004.

Das G.K., Anard S., Acharya S., Das R.P.; "Preparation and Decomposition of Ammonojarosite at Elevated Temperatures in  $\text{H}_2\text{O}-(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4$  Media", *Hydrometallurgy*, (38) pp 263-276, 1995.

Davis A., Eary L.E., Helgen S.; "Assessing the efficacy of lime amendment to geochemically stabilize mine tailings", *Environmental Science & Technology*. 33(15) pp 2626-2632, 1999.

Ding M., Geusebroek M., Vandersloot H.A.; "Interface precipitation affects the resistance to transport in layered jarosite fly ash", *Journal of Geochemical Exploration*. 62(1-3) pp 319-323, 1998 Jun.

Dutrizac J.E., Dinardo O.; "The Co-precipitation of Copper and Zinc with Lead Jarosite", *Hydrometallurgy*, (11) pp 61-78, 1983.

Dutrizac J.E., Chen T.T.; "Mineralogical study of the Jarosite Phase Formed During the Autoclave Leaching of Zinc Concentrate", *Canadian Metallurgical Quarterly*, Vol 23, No 2, pp 147-157, 1984.

Dutrizac J.E.; "Converting jarosite residues into compact hematite products" (Research Summary), *J.O.M.* pp.36-39, June 1990.

Dutrizac J.E.; "The Effect of Seeding on the Rate of Precipitation of Ammonium Jarosite and Sodium Jarosite", *Hydrometallurgy*, (42) pp 293-312, 1996.

Dutrizac J.E., Jambor J.L.; "Jarosites and their Application in Hydrometallurgy", *Iron and Aluminium Hydroxysulfate Minerals*, Reviews in Mineralogy and Geochemistry, Volume 40. pp 405-451, Mineralogical Society of America, Geochemical Society. 2000.

Ek C.; "Jarosite treatment and disposal by the 'Jarochaux' process", *Iron Control in Hydrometallurgy*, Toronto, Canada, pp 719-729, 1986.

Hage J.L.T., Schuiling R.D., Vriend S.P.; "Production of magnetite from sodium jarosite under reducing hydrothermal conditions. The reduction of Fe(III) to Fe(II) with cellulose", *Canadian Metallurgical Quarterly*. 38(4) pp 267-276, 1999 Oct.

Hage J.L.T., Schuiling R.D.; "Comparative column elution of jarosite waste and its autoclaved product – Evidence for the immobilization of deleterious elements in jarosite", *Minerals Engineering*. 13(3) pp 287-296, 2000 Mar.

Harris P.T., O'Brien P.E., Quilty P., McMinn A., Holdway D., Exon N.F., Hill P.J., Wilson C.W.; "Sedimentation and continental slope processes in the vicinity of an ocean waste-disposal site, southeastern Tasmania", *Australian Journal of Earth Sciences*. 46(4) pp 577-591, 1999.

Herbert R.B. (1); "Partitioning of heavy metals in podsol soils contaminated by mine drainage waters, Dalarna, Sweden", *Water, Air, & Soil Pollution*. 96(1-4) pp 39-59, 1997 May.

Herbert R.B. (2); "Properties of goethite and jarosite precipitated from acidic groundwater, Dalarna, Sweden", *Clays and clay minerals*, 45 (2), pp.261-273, 1997.

Johnson R.H., Blowes D.W., Robertson W.D., Jambor J.L.; "The hydrogeochemistry of the Nickel Rim mine tailings impoundment, Sudbury, Ontario", *Journal of Contaminant Hydrology*. 41(1-2) pp 49-80, 2000 Jan 31.

Kanabo I.A.K., Gilkes R.J.; "Low-contaminant jarosite waste as a fertilizer amendment", *Journal of Environmental Quality*, 29 pp 679-684, 1992.

Karamanov A., Taglieri G., Pelino M.; "Iron-rich sintered class-ceramics from industrial wastes", *Journal of the American Ceramic Society*. 82(11) pp 3012-3016, 1999 Nov.

Kashkay C.M., Borovskaaya Y.B. and Babazade M.A.; "Determination of  $\Delta G_{298}$  of synthetic jarosite and its sulfate analogues", *Geochemistry International* 12, pp 115-121. 1975.

Kunda W., Veltman H.; "Decomposition of Jarosite", *Metallurgical Transactions*, (10B) pp 439-446, 1979.

Lambe and Whitman: "Soil Mechanics – SI Edition", John Wiley and Sons, 1979.

Levens R.L., Marcy A.D., Boldt, C.M.K.; "Environmental impacts of cemented mine waste backfill", *Report to Investigations 9599*, United States Department of the Interior/United States Bureau of Mines, 1996.

Levy D.B., Custis K.H., Casey W.H., Rock P.A.; "A comparison of metal attenuation in mine residue and overburden material from an abandoned copper mine", *Applied Geochemistry*. 12(2) pp 203-211, 1997 Mar.

Lin C., Melville M.D., Islam M.M., Wilson B.P., Yang X., van Oploo P.; "Chemical controls on acid discharges from acid sulfate soils under sugarcane cropping in an eastern Australian estuarine floodplain", *Environmental Pollution*. 103(2-3) pp 269-276, 1998.

Loan M., Newman O.M.G., Cooper R.M.G., Farrow J.B., Parkinson G.M.; "Defining the Paragoethite Process for Iron Removal in Zinc Hydrometallurgy". *Hydrometallurgy* 81, pp 104 – 129, 2006.

Long D.T., Fegan N.E., McKee J.D., Lyons W.B., Hines M.E., Macumber P.G.; "Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: Lake Tyrell, Victoria, Australia", *Chemical Geology*. (96) pp183-202, 1992.

Mackey D.J., Sainsbury K.J.; *Research on Jarosite Dumping at Sea*. CSIRO. 1994.

Manahan S; "Environmental Chemistry", 6<sup>th</sup> Edition, Lewis Publishers – CRC Press, 1994.



McGregor R.G., Blowes D.W., Jambor J.L., Robertson W.D.; "The solid phase controls on the mobility of heavy metals at the copper cliff tailings area, Sudbury, Ontario, Canada", *Journal of Contaminant Hydrology*. 33(3-4) pp 247-271, 1998 Oct.

McKee B., Skei J.; "Framvaren Fjord as a Natural Laboratory for Examining Biogeochemical Processes in Anoxic Environments", *Marine Chemistry*, 67 pp 147-148, 1999.

Menad N., Björkman B.; "Polyvinyl chloride used as a chlorinating and a reducing agent", *Resources Conservation & Recycling*. 24(3-4), pp 257-274, 1998 Dec.

Miller, S – Environmental Geochemistry International (Sydney, Australia). Internal method of analysis – unpublished.

Minson D.N., Williams C.E., "Filtering Systems for Dry Tailings Deposition", *MetSoc Solid/Liquid Separation, 29<sup>th</sup> Annual Hydrometallurgical Meeting*. pp 205-219. 1999.

Mymrin V., Vaamonde A.V.; "New construction materials from Spanish jarosite processing wastes", *Minerals Engineering*. 12(11) pp 1399-1402, 1999 Nov.

Nolch G.; "Jarosite dumping not harming the marine environment", *Search*. 26(1) pp 9, 1995 Jan-Feb.

Palache C., Berman H., Frondel C.; "The System of Mineralogy", Vol 2, Wiley and Sons, pp 555-565, 1951.

Patiño F., Viñals J., Roca A., Nuñez C.; "Alkaline Decomposition – Cyanidation Kinetics of Argentinian Plumbojarosite", *Hydrometallurgy*, (34), pp 279-291, 1994.

Peacey J.G., Hancock P.J.; "Review of Pyrometallurgical Processes for Treating Iron Residues from Electrolytic Zinc Plants", *Iron Control and Disposal – Second International Symposium on Iron Control in Hydrometallurgy*, Ottawa, Canada, pp 17 – 35, 1996.

Pelino M.; *Interceram*, 47(1), pp22-26, 1998.

Ribet I., Ptacek C.J., Blowes D.W., Jambor, J.L.; "The potential for metal release by reductive dissolution of weathered mine tailings", *J.Contam.Hydrol.* Vol.17 (3), pp 239-273, 1995.

Roca A., Viñals J., Arranz M., Calero J.; "Characterisation and alkaline decomposition/cyanidation of beudantite-jarosite materials from Rio Tinto gossan ores", *Can. Metall. Q.*, 38(2) pp 93-103, 1999.

Rüde T.R., Vogelsang A., Petri E. and Wohnlich S. "Pyrite Oxidation and Water Quality in a Former Open Pit Lignite Mine". 1998.

[www.hydrogeologie.uni-muenchen.de/publications/1998/PyriteIAH.html](http://www.hydrogeologie.uni-muenchen.de/publications/1998/PyriteIAH.html)

Ryan J., Stroehlein J.L.; "Copper Industrial Byproducts for Improving Iron Deficient Calcareous Soils", *Agronomy Journal*, 68 pp 79-82, 1976.

Salinas E., Roca A., Cruells M., Patiño F., Córdoba D.A.; "Characterization and Alkaline Decomposition-Cyanidation Kinetics of Industrial Ammonium Jarositer in NaOH Media", *Hydrometallurgy*, (60) pp 237-246, 2001.

Schuling R.D., Vangaans P.F.M.; "The waste sulfuric acid lake of the TiO<sub>2</sub> plant at Armyansk, Crimea, Ukraine. 1. Self sealing as an environmental protection", *Applied Geochemistry*. 12(2) pp 181-186, 1997 Mar.

Sengupta D.K., Hamza H.A.; "Dewatering Behaviour of Jarosite Sludge from the Zinc Industry", *Proceedings of the International Symposium on Waste Processing and Recycling in Mining and Metallurgical Industries*, pp 331-342. Aug 23-27, Edmonton, Alberta. 1992.

Sorini S: "Leaching tests: commonly used methods, examples of applications to coal combustion by-products, and needs for the next generation", *Coal Combustion By-Products Associated with Coal Mining, Transcript from the Office of Surface Mining, Mid-Continent Region USA*, October 29-32, 1996.

Strezov V.; Internal BHP Billiton Newcastle Technology Centre Report. 2001.

Stogran S.W., Elliot L.C.M., Liu L.; "Subaqueous Deposition of Acid Generating Tailings into an Acidic Environment: Pilot Column Test Results", *Proceedings to the Fourth International Conference on Acid Rock Drainage*, Vancouver 31/5-6/6 1997.

Swayze G.A., Smith K.S., Clark R.N., Sutley S.J., Pearson R.M., Vance J.S., Hageman P.L., Briggs P.H., Meier A.L., Singleton M.J., Roth S.; "Using imaging spectroscopy to map acidic mine waste", *Environmental Science & Technology*. 34(1) pp 47-54, 2000 Jan 1.

Tailoka F., Fray D.J.; "Recovery of zinc from jarosite residues by chlorination with both chlorine and scrap polyvinyl chloride", *Transactions of the Institution of Mining &*

*Metallurgy Section C-Mineral Processing & Extractive Metallurgy*. 107 pp C60-C64, 1998  
May.

Taylor R.M., Robbins R.G.; "Treatment of Berkeley Pitlake Water using the Green Precipitate Process", *Proceedings from the 1998 Conference on Hazardous Waste Research*.

Proceedings from the US EPA Leaching Meeting. July 1999.

van Breemen N.; "Genesis and Solution Chemistry of Acid Sulphate Soils in Thailand", *Pudoc*, Centre for Agricultural Publishing and Documentation, Wageningen, 1976.

Weber T., Schuller D.; An Alternative to the Deposition of Industrial Residues: The Possibility of Working up of Jarosite, *Environmental. Technology Letters*, 9, pp 163-170, 1988.

Williams S.N., Gilkes R.J., Bernard N.G.; "Waste jarosite and alunite will be ineffective sulfur and potassium fertilisers", *Australian Journal of Soil Research*. 38(2) pp 493-500, 2000.

## **Appendix 1.**

### **Free Acid Titration Method.**

#### **BHP Billiton Newcastle Technology Centre Standard Operating Procedure**

#### **(Hydromet – 009)**

##### **Background:**

Free acid must be determined without interference from dissolved elements, particularly iron. Oxalate in the form of potassium oxalate will complex any dissolved metals, leaving only free protons to react with sodium hydroxide, thus determining true free acid.

##### **Requirements:**

Potassium Oxalate Crystals

1M Sodium Hydroxide Solution

0.1M Sodium Hydroxide Solution

##### **Method:**

280g/L potassium oxalate (KOx) solution should be made. Use a stirring bar as the crystals will take time to dissolve. Add a small amount of sulphuric acid to adjust the final KOx solution pH to 7.5.

Add 20mL of KOx solution to a beaker, with 20mL water. Add 1mL of the solution to be tested to the beaker and stir.

Titrate using either 1M or 0.1M NaOH solution, depending on the amount of free acid present. Titrate back to the starting pH of 7.5 using a pH probe.

Using 1mL of test solution and 1M NaOH the volume of titrant should be multiplied by 49.04 to give the free acid in grams per litre. If using 0.5mL of test solution multiply by 98.08 and if using 0.1M NaOH multiply by 4.904.