

Recovering resources from abandoned metal mine waters: An assessment of the potential options at passive treatment systems



Matthew Thomas Bailey

Thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

July 2016



School of
**Civil Engineering
& Geosciences**

Abstract

Remediation of metal-rich discharges from abandoned mines entails capture of metals within a treatment system and, typically, disposal of the waste. A preferable option would be to recover the metals for reuse. For many long-abandoned mines metal loads are often relatively small, albeit they often cause significant environmental pollution. Low-cost passive treatment systems, in which metals are retained in some form of treatment substrate, such as compost, are often preferred. This thesis investigates the amenability of such treatment systems to resource recovery. Two down-flow compost bioreactors, treating zinc-rich discharges, were the focus of the research: a pilot-scale unit at Nenthead, and a full-scale system at Force Crag, both in Cumbria, England. Laboratory investigations of the Nenthead substrate identified 7,900mg/kg zinc in the upper horizons of the substrate, and 2,400mg/kg in the lower horizons, after two years of operation. Acid leaching tests effectively de-contaminated the substrate with respect to zinc and cadmium. Complete recovery of zinc was observed after ≤ 30 hours across a range of acid leach tests, although 23-37 days were required before equivalent recovery was achieved by biological leaching. The Force Crag system removed $>95\%$ zinc over the first year of operation and, removal rates suggest that after 10 years of operation $>20,000\text{mg/kg}$ zinc will have accumulated in the substrate. Substrate de-contamination could offer substantial life-cycle cost savings at passive treatment sites, especially by limiting volumes of material for disposal to landfill. Furthermore, recovery of metals has important implications for resource sustainability and circular economics. Other resource recovery options may exist at abandoned mine sites. At Force Crag 1.6kW of kinetic energy exists in flowing mine water, in addition to thermal energy which could be recovered for space heating applications. Recovering this energy would convert this site into a net-generator of power. Because of their often remote locations, renewable energy may be of particular value to off-grid facilities at some mine sites.

Acknowledgements

Firstly, I must thank my first supervisor Dr Adam Jarvis for his generous support and patience during my time at Newcastle. Thanks are also extended to my secondary supervisors, all of whom have provided valuable assistance: Prof. Paul Younger, Dr Simon Reed, Dr Ian Watson and especially Dr Catherine Gandy. This PhD was partially funded by The Coal Authority, and I am indebted to the efforts of Tracey Davis, without which I would not have had the fortune of indulging in this research degree. My appreciation also extends to friends and colleagues at The Coal Authority for their assistance when faced with continued requests for information.

Over the last three years, I have spent many enjoyable hours both in the beautiful Lake District and in the immaculate laboratories of the Devonshire Building with Jane Davis and Patrick Orme. Their help and shared experience was invaluable to successful completion of this research. Additional assistance has been provided by other staff across the School of Civil Engineering and Geosciences, in particular Dr Angie Sherry for her help with the microbes. Thanks are also extended to Leon Kirk of Acumen Waste Ltd. and Hein Schade of Helix Projects Ltd. who provided insider knowledge of the waste and minerals industry. The information they provided was crucial in forming some of the economical calculations presented in this thesis.

Behind the scenes, my wonderful wife Claire has been a continued source of reassurance, inspiration, and above all, a fantastic companion. Thanks also for proof reading my Thesis, along with my old man. Dad, one day I'll know where to put those punctuation marks!

Foreword

In the intervening period following first submission of this thesis for examination, the United Kingdom (UK) held a landmark referendum on membership of the European Union (EU). The result, ‘Brexit’, was a shock to many and bitter blow to UK science, in which the EU heavily invests. Furthermore, in the context of this thesis, the environmental agenda in Great Britain relies upon EU directives – specifically clean-up of pollution from abandoned metal mines (Water Framework Directive) and managing wastes (Waste Framework Directive). The EU is also promoting the Circular Economy, with the central aim of closing the loop on product life-cycles through greater re-cycling and re-use.

Immediately following the Brexit result, a new UK Prime Minister was appointed (Theresa May – Conservative Party) and with this a substantial shake up of the Cabinet occurred, including the abolition of the Department of Energy and Climate Change. This Department had been central to supporting the clean-up of pollution from abandoned mines through its funding of The Coal Authority and, had supported the development of de-centralised renewable energy.

As a consequence of these factors, there is now a great deal of uncertainty surrounding the UK Governments environmental commitments. Nevertheless, protecting water resources, managing wastes effectively and recovering materials and energy are important factors in a sustainable economy, and will no doubt be high priorities for progressive governments throughout the world. In these respects, Brexit has little implication on the fundamental principles of the research presented in this thesis.

Contents

Abstract	I
Acknowledgements	III
Foreword	V
Contents	VII
List of Figures	XIII
List of Tables	XVII
Chapter 1. Introduction	1
1.1 Background and scope	1
1.2 Aims and objectives	2
1.3 UK legislation driving mine water remediation	3
1.4 Mine water pollution	4
1.5 Study site – Nenthead	6
1.5.1 Pilot treatment system	6
1.6 Study site – Force Crag	8
1.6.1 Mine water discharges	8
1.6.2 Force Crag mine water treatment system installation	10
1.6.3 Vertical flow ponds	10
1.6.4 Wetland	11
1.6.5 Resource recovery potential	12
1.7 Thesis structure	13
Chapter 2. Assessment of the resource potential of metal mine waters	15
2.1 Introduction and chapter contents	15
2.2 Realising the resource potential from mine abandonment	16
2.2.1 Mine water characteristics which might offer recoverable resources	16
2.3 Potential energy of mine waters	18
2.3.1 Mine water discharge flows	19
2.4 Micro-hydropower for potential energy recovery	21
2.4.1 Hydroelectricity generation	21
2.4.2 Types of turbine	22
2.4.3 Applications of hydropower systems in mine water environments	23

2.5	Thermal capacity of mine waters	23
2.5.1	Metal mine water temperatures	24
2.6	Exploitation of mine waters for heating and cooling	28
2.6.1	Principles of pumping heat	28
2.6.2	Coefficient of performance	29
2.6.3	Mechanics of a Rankine cycle heat pump	30
2.6.4	Applications of heat pumps in mine water environments	31
2.7	The metal content of metal mine waters in England and Wales	32
2.8	Mine water treatment systems	34
2.8.1	Treatment of ferruginous mine drainage	35
2.8.2	Ferruginous drainage treatment waste	36
2.8.3	Treatment of metalliferous mine drainage	37
2.8.4	Active treatment	37
2.8.5	Passive treatment systems	39
2.8.6	Summary of treatment technology and potential for metal recovery	43
2.9	Passive treatment system lifetime	45
2.9.1	Database of known systems tackling zinc	46
2.9.2	Limits on system lifetime and estimates from the literature	46
2.10	Possibilities for extending passive treatment system life-times	49
2.10.1	Increasing labile carbon	49
2.10.2	Selective harvesting and replenishment of substrates	50
2.10.3	Overcoming reduction in porosity and permeability	50
2.11	Management of spent passive treatment system wastes	51
2.11.1	Landfill disposal	51
2.11.2	Micro-fertiliser applications	51
2.11.3	Recovery of metals from passive treatment wastes	52
2.11.4	Characterisation of mine water treatment wastes	53
2.12	Methods for metal recovery from passive treatment substrates	54
2.12.1	Physical separation	54
2.12.2	Pyrometallurgy	56
2.12.3	Hydrometallurgy and soil washing	57
2.12.4	Biohydrometallurgy	59
2.13	Removal of metals from pregnant leach solutions	62
2.13.1	Direct precipitation methods	62
2.13.2	Solvent extraction	63

2.13.3	Electrowinning	63
2.14	Active treatment and combined treatment and recovery systems.....	64
2.15	Passive treatment vs. active and combined treatment recovery systems	65
2.16	Conclusion to Chapter 2.....	66
2.16.1	Energy	66
2.16.2	Mine water treatment and potential for metal recovery	67
2.16.3	Resource recovery impacts on life-cycle costs	68
2.16.4	Gaps in literature	69
Chapter 3.	Methods.....	71
3.1	Introduction and chapter contents.....	71
3.2	Nenthead pilot treatment system decommissioning	71
3.2.1	Substrate sample collection.....	71
3.2.2	Sample preparation	72
3.3	Laboratory investigations – Nenthead substrate characterisation	73
3.3.1	Investigating metal content in relation to particle size	73
3.3.2	Investigating metal content in different locations.....	76
3.3.3	Sequential extraction procedure	76
3.3.4	Analysis of sequential extraction solutions.....	79
3.4	Laboratory investigations – Nenthead chemical leaching tests	80
3.4.1	Leach test procedure	81
3.4.2	Leach test variables.....	82
3.4.3	Acid concentration.....	82
3.4.4	Pulp density.....	83
3.4.5	Metal recovery from pregnant leach solutions	84
3.4.6	Aqua regia digests.....	85
3.4.7	Metals analysis of leach and digest solutions.....	86
3.4.8	Leach solution filtrate analysis for sulphate	87
3.5	Laboratory investigations – Nenthead bioleaching tests	88
3.5.1	Leach solution and inoculum	89
3.5.2	Bioleach test procedure.....	89
3.5.3	Bioleach test variables	91
3.5.4	Chemical analysis of bioleach solutions.....	92
3.5.5	Microbial analysis.....	93
3.6	Field based investigations – Force Crag.....	94
3.6.1	Water sampling and field analysis	94

3.6.2	Flow measurements	96
3.6.3	Analysis of water samples	97

Chapter 4. Results and Discussion – Nenthead Substrate Characterisation and Metal Recovery99

4.1	Introduction and chapter contents	99
4.2	Characterisation of treatment system substrates.....	100
4.2.1	Particle size characterisation.....	100
4.2.2	Sequential extraction procedure.....	101
4.2.3	Zinc data for sieved samples	102
4.2.4	Metal distribution in samples from different locations	105
4.2.5	Partitioning of metals	117
4.2.6	Sequential extraction reproducibility.....	119
4.3	Metal recovery from treatment system substrates: Chemical leaching.....	121
4.3.1	Leaching with variable acid concentrations	121
4.3.2	Leaching with variable pulp densities	125
4.3.3	Leach test reproducibility and controls.....	130
4.3.4	Metal removal from substrate	131
4.3.5	Separation of solids from pregnant leach solutions.....	132
4.3.6	Metal content of leach solution residues.....	137
4.4	Metal recovery from treatment system substrates: Bioleaching.....	142
4.4.1	Key variables during bioleaching	143
4.4.2	Metal recoveries during bioleaching.....	147
4.4.3	Reproducibility of bioleaching experiments.....	148
4.5	Conclusions.....	151
4.5.1	Summary of investigations	151
4.5.2	Substrate characterisation	151
4.5.3	Acid leaching tests and metal recovery.....	153
4.5.4	Bioleaching tests.....	154

Chapter 5. Force Crag: Resource Recovery to Offset the Cost of Mine Water Treatment.....157

5.1	Introduction and chapter contents	157
5.2	Treatment system performance.....	158
5.2.1	Metal removal over monitoring period.....	159
5.2.2	Zinc.....	160
5.2.3	Alkali and alkaline earth metals and secondary contamination	164

5.2.4	pH, conductivity, sulphate and alkalinity	164
5.2.5	Electroneutrality	168
5.3	Life-cycle costs of mine water treatment	169
5.4	Force Crag substrate lifetime	173
5.4.1	Forecasting VFP substrate lifetime	173
5.4.2	Possibilities for extending substrate lifetime.....	174
5.5	Substrate re-use and metal recovery.....	175
5.5.1	Metal content of used substrates.....	175
5.5.2	Alternative uses for used substrates	177
5.5.3	Metal recovery potential	179
5.5.4	Waste reduction potential	181
5.5.5	Cost of metal recovery	182
5.6	Renewable energy	184
5.6.1	Small scale hydropower	184
5.6.2	Mine water heat recovery	188
5.6.3	Energy recovery to offset operational costs.....	190
5.7	Financial assessment of active vs. passive treatment	191
5.7.1	Hypothetical active mine water treatment system design.....	192
5.7.2	Comparison of active vs. passive life-cycle costs.....	192
5.7.3	Composition of wastes.....	194
5.8	Conclusions	195
5.8.1	Treatment system performance and metal accumulation	195
5.8.2	Life cycle cost estimates.....	196
5.8.3	Resource recovery to offset operational costs	196
5.8.4	Life-cycle cost scenarios.....	198
Chapter 6. Conclusions and Recommendations		199
6.1	Chapter contents and overview.....	199
6.2	Addressing thesis aims and objectives	199
6.2.1	Objective 1. Review the resource potential of metal mine waters nationally and identify ways in which resources can be recovered	199
6.2.2	Objective 2. Characterise distribution of metals within passive metal mine water treatment system substrates.....	201
6.2.3	Objective 3. Assess the options for metal recovery from passive treatment system substrates and undertake lab-scale proof-of-principle metal recovery tests	202

6.2.4	Objective 4. Monitor the performance of a passive treatment system to gain an understanding of rates of metal accumulation and thereby forecast future metal concentrations in the substrate	204
6.2.5	Objective 5. Estimate life-cycle costs associated with an operational metal mine water treatment system and determine how resource recovery from the mine water might offer a mechanism of offsetting these costs.....	205
6.3	Research contribution	207
6.4	Study limitations.....	208
6.5	Recommendations.....	209
6.6	Final remarks	209
References	211
Publications Arising from Research	247
Appendices	249

List of Figures

Figure 1.1 Ferruginous discharge at Handbank Colliery, Yorkshire, UK (left); and a metalliferous mine discharge with low iron concentrations, Nentsberry Hags Pb-Zn Mine, Cumbria, UK (right) (photographs courtesy of The Coal Authority).....	5
Figure 1.2 Rampgill Horse Level mine water discharge, Nenthead (Digimap 2014)	6
Figure 1.3 Nenthead compost-based pilot treatment system, note inlet pipes to right (photograph taken during spring 2012)	7
Figure 1.4 Force Crag Mine location (Digimap 2014)	9
Figure 1.5 Schematic drawing of Force Crag VFP configuration	11
Figure 1.6 Force Crag mine water treatment system in plan, gravity main flows shown in purple (modified from Atkins, 2014a)	12
Figure 2.1 Spot readings of metal mine water discharge flows across England and Wales (unpublished Environment Agency data, 2015).....	19
Figure 2.2 Location of metal mine discharges in England and Wales discussed in review.....	20
Figure 2.3 Suitability of hydropower turbines for a range of heads and flows, after Paish (2002)	22
Figure 2.4 Pelton turbine (left) and crossflow turbine (right) after Paish (2002).....	23
Figure 2.5 Woodend Low Level discharge, Threlkeld Mine, emanating from the foot of Blencathra Mountain in the English Lake District National Park.....	26
Figure 2.6 Threlkeld Mine Woodend Low Level discharge water temperatures, January 2012 – July 2014 (unpublished Environment Agency data, 2015).....	27
Figure 2.7 Barney Craig Mine water temperatures, November 2013 – February 2015 (unpublished Environment Agency data, 2015).....	27
Figure 2.8 Pumped mine water temperature in the Cleveland Orefield, June 2013 – February 2014 (unpublished Coal Authority data, 2014)	27
Figure 2.9 Ground sourced heat pump schematic (Banks and Robins, 2002)	30
Figure 2.10 Installation of a 'blade' type heat exchanger at Caphouse coal mine water treatment system, Yorkshire, UK (photograph courtesy of Prof. Paul Younger). Note black lines which circulate glycol heat carrier to and from a heat pump.	32
Figure 2.11 Saltburn passive treatment system tackling ferruginous mine water from ironstone workings (photograph courtesy of The Coal Authority).....	36
Figure 2.12 Soil types associated with zinc deficiency, shaded brown (Alloway, 2008)	52

Figure 3.1 Sample plan of Nenthead pilot treatment tank (diagram courtesy of P. H. A. Orme, Newcastle University)	72
Figure 3.2 Spex™ liquid nitrogen pulveriser, inset showing pulverised substrate sample	75
Figure 3.3 Flow chart showing sample C4B preparation using wet and dry sieving techniques	75
Figure 3.4 Leach test experimental configuration.....	82
Figure 3.5 Hydroxide solubility of Mn(II), Zn, Cd, Cu, Pb, Ni, Fe(III) as a function of pH, redrawn after Cortina et al. (2003).....	85
Figure 3.6 Stained cells in the Threlkeld Mine drainage under 100x magnification with oil immersion	93
Figure 3.7 Photograph of Force Crag mine water treatment system VFPs (note that at the time of the photograph, a fluorescein tracer test was being conducted on the right hand VFP)	96
Figure 4.1 Zinc content of wet and dry sieved substrate	102
Figure 4.2 Comparison of zinc partitioning according to particle size (as % of total determined by Tessier extraction), showing data for wet and dry sieved substrate samples .	104
Figure 4.3 Copper partitioning in different sample locations	107
Figure 4.4 Lead partitioning in different sample locations.....	108
Figure 4.5 Zinc partitioning in different sample locations.....	109
Figure 4.6 Zinc partitioning in upper 0 – 23cm compost layer: pie charts positioned approximately at sample locations.....	110
Figure 4.7 Zinc partitioning in lower 23 - 46cm compost layer: pie charts positioned approximately at sample locations.....	110
Figure 4.8 Zinc distribution for blank compost sample.....	111
Figure 4.9 Cadmium partitioning in different sample locations.....	113
Figure 4.10 Nickel partitioning in different sample locations	114
Figure 4.11 Iron partitioning in different sample locations.....	115
Figure 4.12 Manganese partitioning in different sample locations	116
Figure 4.13 Metal partitioning using aggregated data, ordered in terms of sulphide solubility products for metal sulphides.	117

Figure 4.14 Zinc concentrations in triplicate samples of two unsieved replicates as determined by Tessier extraction (additional 5mL H ₂ O ₂ added to triplicates 2(iii) and 3(iii) in step 4).....	119
Figure 4.15 Metal extraction efficiencies during leach-test where acid concentration was varied, compared to metals extracted by aqua regia digest (mean values of duplicates)	123
Figure 4.16 Metal extraction efficiencies across a range of solid: liquid ratios compared to metals extracted by aqua regia digest (mean values of duplicates)	127
Figure 4.17 Dosing of pregnant leach solutions with sodium hydroxide (left – at time of dosing; right – one day after dosing)	133
Figure 4.18 Filtration residue (left) and after drying and grinding (right)	137
Figure 4.19 Metal mass in leach solution residues compared to metal mass in the unleached substrate.....	139
Figure 4.20 Plots showing sulphate, pH and temperature over time, and pH vs. sulphate during bioleaching experiments	144
Figure 4.21 Metal recovery efficiencies and pH during bioleaching experiments	148
Figure 4.22 Zinc recovery from bioleaching tests showing replicates	149
Figure 5.1 Zinc removal at Force Crag. Final effluent is a combined flow of VFPs 1 and 2 after having passed through a small aerobic wetland (note log scale)	161
Figure 5.2 Alkalinity, pH, conductivity and sulphate at the Force Crag treatment system. Final effluent is a combined flow of VFPs 1 and 2 after having passed through a small aerobic wetland.....	165
Figure 5.3 Force Crag treatment system cost in relation to monetised benefits (financial data used to produce conceptual model was supplied by The Coal Authority, see text for further explanation).....	172
Figure 5.4 Zinc accumulated in treatment system substrates from cases in the literature, and projected for Force Crag. Force Crag substrate zinc content as mg/kg dry weight (substrate density 0.32). Nenthead and Standard Mine sites shown in red.....	176
Figure 5.5 Elevation of Level 1 discharge compared to mine water distribution chamber and treatment system, note location of former mine office building near the distribution chamber at base of Grisedale Pike	186
Figure 5.6 Level 1 flow rates at Force Crag Mine measured from April 2014 to March 2015, inclusive	187
Figure 5.7 Force Crag Level 1 and Coledale Beck temperatures April 2014 - March 2015.....	188

Figure 5.8 Whole life costs for different treatment scenarios, assuming passive treatment substrate life of 10 years (left) and 5 years (right). Note capital build costs only include system design and construction for comparison purposes. 194

Figure 5.9 Left - predicted composition of active treatment sludge (Schade, 2015). Right - metal concentrate recovered from acid leaching of the Nenthead passive system substrate with 0.1M H₂SO₄ and 1.875% pulp density..... 195

List of Tables

Table 1.1 Force Crag Mine discharge water flow data from various sources.....	9
Table 2.1 Features of mine water discharges which may have resources associated with them	17
Table 2.2 Flow and head data for flows at abandoned mine sites, taken from Roberts (2011)	20
Table 2.3 Gravity discharge temperature and flow data for free draining metal mines in England and Wales	25
Table 2.4 Heat pump performance (COP) data (Heat Pump Test Centre WPZ Switzerland, 2012)	30
Table 2.5 High ranking polluting metal mines in England and Wales, ordered by zinc load (unpublished Environment Agency data, (2015) after Mayes et al. (2013); Jarvis et al. (2010a)).....	33
Table 2.6 Summary of combined metal fluxes in England and Wales from abandoned metal mines, and indicative market value of some metals.....	34
Table 2.7 Solubility products of metal sulphides (from Hedin et al., 1994)	42
Table 2.8 Performance for a range of experimental metal mine water treatment systems tackling zinc	44
Table 2.9 A range of techniques used by the contaminated land industry for soil washing adapted from CL:AIRE (2007)	56
Table 2.10 Metal removal efficiencies from contaminated soils by soil washing.	58
Table 2.11 Top 10 mine water discharges in England and Wales ranked by zinc loading, compared to zinc load treated at an active sulphate reducing bioreactor at a site in the USA (BioteQ, no date; unpublished data courtesy of the Environment Agency, 2015);	65
Table 2.12 Energy resources associated with mine waters at sites in England and Wales identified from review of the literature and unpublished data	67
Table 2.13 Metals in metal mine waters cumulatively discharged throughout England and Wales (unpublished Environment Agency data, 2015)	67
Table 3.1 Sequential extraction procedure, after Tessier et al. (1979)	78
Table 3.2 ICP-OES calibration standards for Tessier Extraction	80
Table 3.3 ICP-OES calibration standards for acid leach tests.....	87
Table 3.4 Variables for bioleaching experiments.....	92

Table 3.5 Force Crag field samples and measurements	95
Table 3.6 Analytical parameters adopted for Force Crag water sampling analysis	97
Table 3.7 ICP-OES calibration standards for Force Crag mine water metals analysis	98
Table 4.1 Masses of compost following sieving of quarters 1 and 4 of sample C4B (quarters 2 and 3 were not sieved)	101
Table 4.2 Rampgill Horse Level water quality, after Jarvis et al. (2014); Gandy and Jarvis (2012)	106
Table 4.3 Metal content of mine water treatment substrate used for variable acid concentration tests	122
Table 4.4 Metal content of mine water treatment substrate used for variable pulp density acid leaching tests and biological leaching tests	126
Table 4.5 Zinc and cadmium recovery efficiencies for acid leaching after 100 hours	129
Table 4.6 Average metal content of (1) contaminated Nenthead substrate, (2) substrate after leaching with 0.1M acid and (3) blank substrate which was used in the mine water treatment system, as determined by aqua regia digests	131
Table 4.7 Final pH of leach solutions from variable pulp density leach test, prior to filtration	132
Table 4.8 Metal content and pH of pregnant leach solutions after 5 day leach test	133
Table 4.9 Metal content and pH of leach solution after dosing with NaOH and filtration	134
Table 4.10 Major species in leach solution after dosing with NaOH and filtration.....	135
Table 4.11 Metal mass of residues obtained from leach solutions, determined as product of residue mass and total metals by aqua regia	138
Table 4.12 Residue and substrate masses, and mass and efficiency of zinc recovered.....	141
Table 4.13 Chemical analyses of the Threlkeld Mine discharge used for bioleaching tests	143
Table 4.14 Sulphate and pH measurements upon completion of bioleaching experiments, showing replicates	146
Table 5.1 VFP treatment performance showing mean values for April 2013 - March 2014, inclusive.....	159
Table 5.2 Comparative mean zinc removal rates and efficiencies from a range of bioreactor systems harnessing bacterial sulphate reduction.....	162
Table 5.3 Construction costs for Force Crag mine water treatment system (courtesy of The Coal Authority)	169

Table 5.4 Operational costs (forecast) for the Force Crag mine water treatment system (courtesy of The Coal Authority)	171
Table 5.5 Comparison of pre- and post-leach substrate from the Nenthead pilot system with SGVs (Cd, Ni) or GAC (Zn, Pb, Cu) for human health exposure and PAS 100 threshold (see text for further details).....	178
Table 5.6 Metal recovery potential at Force Crag based upon current performance, showing metal accumulation rates and metal recovery potential, using Nenthead substrate leach efficiencies	180
Table 5.7 Value of metals potentially recoverable from Force Crag based upon first year of operation	181
Table 5.8 Costs of substrate decontamination	183
Table 5.9 Factors affecting small hydropower installation in watercourses and mine discharges	185
Table 5.10 Construction and operational costs of active and passive treatment and passive treatment with substrate washing for the Force Crag site	193
Table 6.1 Summary of costs associated with mine water treatment scenarios at Force Crag Mine: active, passive, and passive with substrate decontamination.....	207

Chapter 1. Introduction

1.1 Background and scope

In England and Wales, drainage from abandoned mines represents the single greatest source of metal pollution affecting the water environment. A greater quantity of lead, and similar quantities of cadmium and zinc are discharged from metal mines compared to the total of all other permitted discharges (Mayes et al., 2010).

Unfortunately, the owners of abandoned metal mines are often untraceable given the elapsed time since abandonment, and the burden for clean-up consequently falls on the state. In Great Britain, The Coal Authority has been dealing with pollution from abandoned coal mines for more than twenty years, and in the last five years has been tasked with delivering a programme of remediation at the most polluting metal mine sites in England (The Coal Authority, 2015a; The Coal Authority, 2015c). This entails both strict budgetary challenges and complex stakeholder management issues in often highly sensitive and remote settings, such as national parks and areas of outstanding natural beauty (e.g. Harris et al., 2014). As a result of these factors, passive treatment systems are typically preferred, which can act to enhance, rather than harm the landscape and environment (Parker, 2003). Unlike conventional active treatment systems, passive systems do not require a supply of chemicals or power, rather harnessing natural processes for treatment (PIRAMID Consortium, 2003; Hedin et al., 1994a). Despite representing a relatively low-cost option, there remains an increasing desire to identify areas where passive treatment system life cycle costs may be reduced or offset. For example, these systems often produce voluminous metalliferous wastes, which require periodic and wholesale disposal at a significant cost. In fact, disposal of passive treatment wastes has been identified as one of the most substantial life cycle costs associated with systems tackling metal mine drainage, particularly since these materials can constitute hazardous wastes (Atkins, 2014b; Gusek et al., 2006).

This thesis explores ways in which the cost of passive mine water treatment might be reduced or offset, by extending system life-times and recovering resources.

In order to achieve this, data have been collected by field and laboratory investigations at two pioneering passive treatment systems in England. In particular, this research focused upon the amenability of passive treatment system wastes to resource recovery. Findings are discussed in the context of reduced life-cycle cost scenarios, considering both recovery of resources from system wastes and also the potential for renewable energy generation. This research may not only have important commercial implications for system operators and funding bodies, but also upon wider environmental issues of responsible resource management and low-carbon economics.

This introductory chapter firstly presents the thesis aims and objectives and then discusses the legislation and issues associated with mine water pollution. Distinction is made between iron rich and more metalliferous waters which entail different strategies for remediation. Subsequently, study sites at Nenthead and Force Crag are introduced, and the thesis structure is outlined.

1.2 Aims and objectives

The overarching aim of this thesis is to examine the potential for recovering resources from metal mine waters in order to minimise the full life-cycle costs of passive treatment systems. The objectives of this thesis are to:

1. Review the resource potential of metal mine waters nationally and identify ways in which resources can be recovered.
2. Characterise the distribution of metals within passive metal mine water treatment system substrates.
3. Assess the options for metal recovery from passive treatment system substrates and undertake lab-scale proof-of-principle metal recovery tests.
4. Monitor the performance of a passive treatment system to gain an understanding of the rates of metal accumulation and thereby forecast future metal concentrations in the substrate.
5. Estimate life-cycle costs associated with an operational metal mine water treatment system and determine how resource recovery from the mine water might offer a mechanism for offsetting these costs.

1.3 UK legislation driving mine water remediation

Metal mining in Great Britain was once a vast industry with a peak in mining output occurring in the mid to late 19th Century (Hudson-Edwards et al., 2008). Slightly later, coal mining peaked, with 250 million tonnes extracted in 1910, before widespread closure of entire coalfields in the late 20th Century following nationalisation (Parker, 2003). This nationalisation, however, did not apply to non-coal mines such as those which extracted base metals (Johnston et al., 2008). Upon re-privatisation of the industry in 1994, The Coal Authority was formed, which is now statutorily responsible for coal reserves in Great Britain along with many tens of thousands of coal mines which were abandoned before the Coal Industry Act (1994). Upon formation, The Coal Authority was specifically tasked with managing mine water emissions, as set out by Lord Strathclyde, and, as such, it has developed a successful programme of remediation (Parker, 2003). This is of particular importance since no responsibility exists for polluting water discharging from mines abandoned before Lord Strathclyde's assurances on the 1994 Bill: Section 89.3 of the Water Resources Act 1991 as originally enacted, stated that 'A person is not guilty of the offence of causing or knowingly permitting the pollution of controlled waters if he is merely permitting a discharge from an abandoned mine'. This loophole applied to both coal and metal mines until 31 December 1999 (McGuinness, 1999); although, by this time, a programme of remediation had been addressing pollution from abandoned coal mines for more than fifteen years.

Mayes et al. (2009a) identified 464 'waterbody'¹ river catchments throughout England and Wales which are either known to be, or thought to be, impacted by non-coal (largely base metal) mine water discharges, out of a total of 7,815² waterbodies. Yet, until recently, there has been no statutory organisation provided with a remit to deal with the legacy of abandoned non-coal mines. Over recent years, however, and principally driven by introduction of the EU Water Framework Directive (2000/60/EC), political pressure for The Coal Authority to deal with pollution from non-coal mine waters has heightened.

¹ Waterbodies are defined management units (typically river catchments) under the EU Water Framework Directive (EEC, 2000)

² Changes in the River Basin Plans boundaries mean that there are less waterbodies at the time of writing (*pers comm.* Dr A. P. Jarvis, Reader in Environmental Engineering, Newcastle University 2015)

The Energy Bill received Royal Assent on the 18 October 2011, extending The Coal Authority's remit to work associated with non-coal mines (Energy Act, 2011) and, subsequently, government funding was granted to deliver a programme of remediation in England. Since initiation of this programme, feasibility studies have been conducted and two treatment systems installed at abandoned metal mine sites (The Coal Authority, 2015b). Concurrently, research efforts have increased in order to tackle the many technical issues associated with this ground breaking programme (The Coal Authority, 2015b). Specifically, in the case of this thesis, investigations into resource recovery to reduce or offset system life-cycle costs have been conducted.

1.4 Mine water pollution

Mine waters range widely in quality depending upon the strata through which they pass (Banks et al., 1997). Often, iron minerals exposed within the mine workings can lead to generation of waters characterised by elevated iron concentrations, which may also be known as ferruginous mine waters (Banks et al., 1997). These are typical of both discharges from coal mines, and some metal mines (Parker, 2003; Younger, 2002). This thesis makes the distinction between waters which are dominated by high iron loadings (ferruginous), and metalliferous waters which suffer elevated concentrations of other metals such as zinc and cadmium. Ferruginous waters are typical of coal mine waters in Britain (although not exclusively) and waters where iron is not the dominant pollutant are characteristic of many metal mines; specifically in Britain, these metal mine sites pose particular problems due to zinc, amongst other metal loads (Mayes et al., 2013; Johnston et al., 2008; Younger, 2000). Figure 1.1 illustrates a ferruginous mine water discharge from an abandoned coal mine, and a non-ferruginous discharge from a metal mine with elevated zinc concentrations (for information on discharges see: Jarvis, 2006; Nuttall and Younger, 1999).



Figure 1.1 Ferruginous discharge at Handbank Colliery, Yorkshire, UK (left); and a metalliferous mine discharge with low iron concentrations, Nentsberry Hags Pb-Zn Mine, Cumbria, UK (right) (photographs courtesy of The Coal Authority).

This distinction has important implications for treatment process and waste generation, which are discussed in Chapter 2. In particular, aerobic passive treatment processes which have been widely established for the treatment of net alkaline coal mine waters, both in Britain and overseas, would not be effective at treating metalliferous mine waters (Jarvis et al., 2012b). The reason for this is that iron removal is normally achieved by hydroxide precipitation, forming an iron hydroxide solid which settles from solution to form hydrous ferric oxide or ‘ochre’ sludge (Younger et al., 2002). Metals such as zinc have much higher hydroxide solubilities than iron and, therefore, are not removed easily under these conditions (Jarvis et al., 2012b). As a consequence, alternative passive treatment approaches are required, such as removal of metals as sulphides within organic matrices; yet these approaches are likely to generate more complex wastes requiring costly disposal (Gray et al., 2012).

This thesis investigates the characteristics of wastes generated by passive metal mine water treatment systems, and their amenability to metal recovery, using data collected from two candidate sites: the Nenthead pilot scale system and the Force Crag full-scale system. Wider resource recovery options are also considered, in conjunction with system life-time optimisation, as a means of reducing or offsetting long-term treatment costs.

1.5 Study site – Nenthead

Drainage from abandoned metal mines severely impacts the water quality of the upland River Nent in Cumbria, which is ranked 3rd in the Northumbria region for its severity of mining related pollution (Mayes et al., 2012). One significant discharge arises from the Rampgill Horse Level located at Nenthead (Figure 1.2), which drains the Rampgill Mine Complex and Smallcleugh Mine (Gandy and Jarvis, 2012; Nuttall and Younger, 1999). The Rampgill discharge has characteristically low iron concentrations, is net-alkaline and circum-neutral in pH, yet contains elevated concentrations of zinc (typically between 2 – 2.5mg/L) (Gandy and Jarvis, 2012; Nuttall and Younger, 2000; Nuttall and Younger, 1999). This pollution is typical of other metal mine-impacted catchments of the area, known as the North Pennine Orefield, which was mined intensively for lead and zinc until the early 20th century (Jarvis et al., 2014; Gozzard et al., 2011).

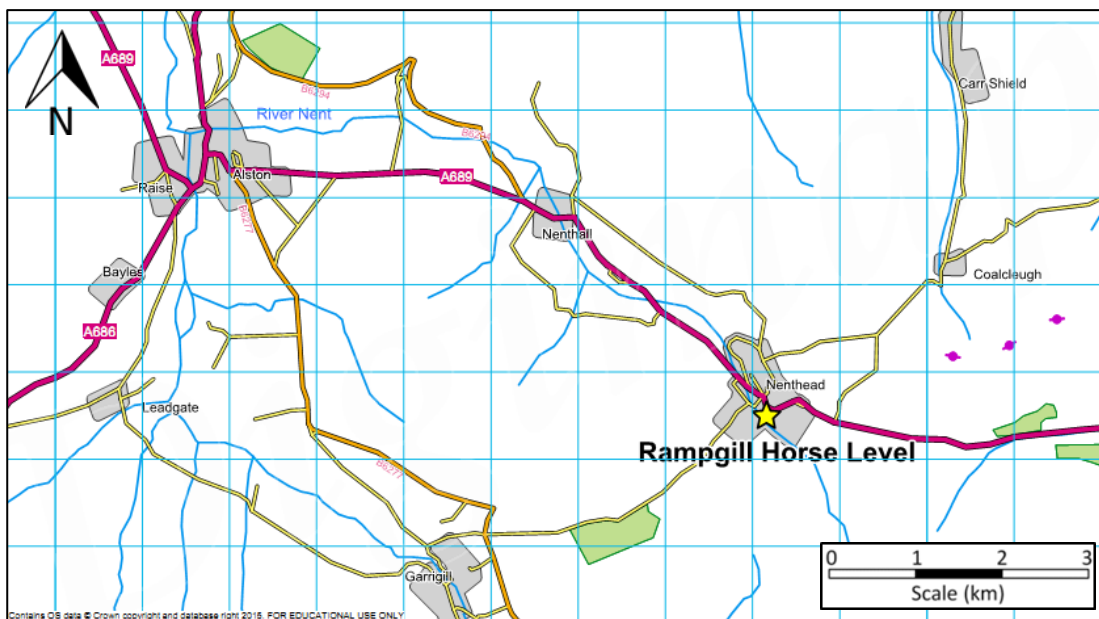


Figure 1.2 Rampgill Horse Level mine water discharge, Nenthead (Digimap 2014)

1.5.1 Pilot treatment system

Between 2010 and 2012, a pilot scale system treating a small flow of the Rampgill mine water was operated at Nenthead by Newcastle University (Jarvis et al., 2014). Funding for the treatment system was provided by the Department for Food and Rural Affairs (Defra) (Jarvis et al., 2014). Figure 1.3 shows the pilot treatment system in operation.

The treatment system comprised a tank 2.5m x 1.5m x 1.0m (height) configured so that mine water passed vertically down through a substrate of mixed PAS100 municipal waste compost (45% v/v); wood chips (45% v/v) and digested sewage sludge (10%) (Jarvis et al., 2014). PAS100 certified municipal waste compost conforms to a range of stringent parameters, including source control and limits on metal content (BSI, 2011). Below the substrate, a layer of limestone gravel facilitated under draining (Jarvis et al., 2014). 1.1L/minute of mine water was fed into the top of the treatment system using a Watson Marlow peristaltic pump to achieve a residence time of approximately 19 hours (Jarvis et al., 2014). The compost substrate was completely submerged in water, with the water level controlled by the invert height of the raised outlet pipe (Jarvis et al., 2014; Gandy and Jarvis, 2012). This pilot system was designed to operate anaerobically, harnessing microbial sulphate reduction in order to remove metals as their sulphides (Gandy and Jarvis, 2012).



Figure 1.3 Nenthead compost-based pilot treatment system, note inlet pipes to right (photograph taken during spring 2012)

Decommissioning of the pilot treatment system at Nenthead took place in August 2012, and a large number of substrate samples were taken and stored at Newcastle University. Data collection from the Nenthead site is limited to laboratory investigations on these

substrate samples, encompassing geochemical characterisation and metal recovery tests. These investigations are presented in Chapters 3 and 4.

1.6 Study site – Force Crag

Installation and commissioning of a full-scale passive metal mine water treatment system at Force Crag Mine coincided with this PhD research, a coincidence which allowed detailed study of a system of this type during its first year of operation. In particular, it was possible to review the resource recovery possibilities at this remote site by collection of field data. Accordingly, a more in-depth description of the site is provided, compared to Nenthead.

Located in an upland area at the head of the Coledale Valley near Braithwaite in Cumbria, the Force Crag Mine is one of a number of metal mines within the English Lake District National Park (Figure 1.4 shows the site location). Operating intermittently for c.150 years, the mine was finally abandoned in 1991 following collapse of the Level 0 mine entrance. The principal ore mined at Force Crag was baryte (BaSO_4), but sphalerite (ZnS) and galena (PbS) were also abundant and were commercially exploited (Dumpleton et al., 1996).

1.6.1 Mine water discharges

In addition to catalysing its closure in 1991, collapse of Level 0 (one of eight levels accessing the mine and draining water) also altered the hydraulic regime of the mine (Dumpleton et al., 1996). A driving hydraulic head is believed to exist behind the blockage in Level 0, with the main drainage for the mine exiting from Level 1 which is located higher in the valley (Dumpleton et al., 1996). Very small flows discharge from Level 0 as shown in Table 1.1, although the metal load is of little consequence (Jarvis et al., 2012a). Flows from Level 1, however, represented a substantial source of pollution to the Coledale Beck and downstream waterbodies prior to installation of a treatment system (Jarvis et al., 2012a). The Newlands Beck, to which the Coledale Beck drains, and River Derwent both failed Environmental Quality Standards (EQS) for zinc and cadmium under the Water Framework Directive as a result of pollution from Force Crag Mine; although an additional pollutant load from the Threlkeld Mine (also known as Gate Gill, located some 14km WNW of Force Crag) is known to contribute to the pollution of Bassenthwaite Lake and the River Derwent (The Coal Authority, 2014).

Chapter 1. Introduction

Bassenthwaite Lake has received recent attention due to rediscovery of the rare vendace fish in 2014 which were believed to have been extinct from the area due, in part, to pollution (Winfield, 2014; Winfield et al., 2013).

Table 1.1 Force Crag Mine discharge water flow data from various sources

Discharge	Flow data source/ date collected	Flow range during dry conditions (L/s)	Flow range during wet conditions (L/s)	Storm event flows (L/s)
Level 0	BGS, 1996 (Dumpleton et al., 1996)	4		
	Entec, 2006 – 2010 (Pomfret et al., 2009)	0.5 – 2	3 - 9	>15
	Newcastle University 2012 (Jarvis et al., 2012a)	1.2 – 3.9 (across a range of flow conditions)		
Level 1	BGS, 1996 (Dumpleton et al., 1996)	6		
	Entec, 2006 – 2010 (Pomfret et al., 2009)	7 – 11	15 - 30	>50
	Newcastle University 2012 (Jarvis et al., 2012a)	8.5	19.0	

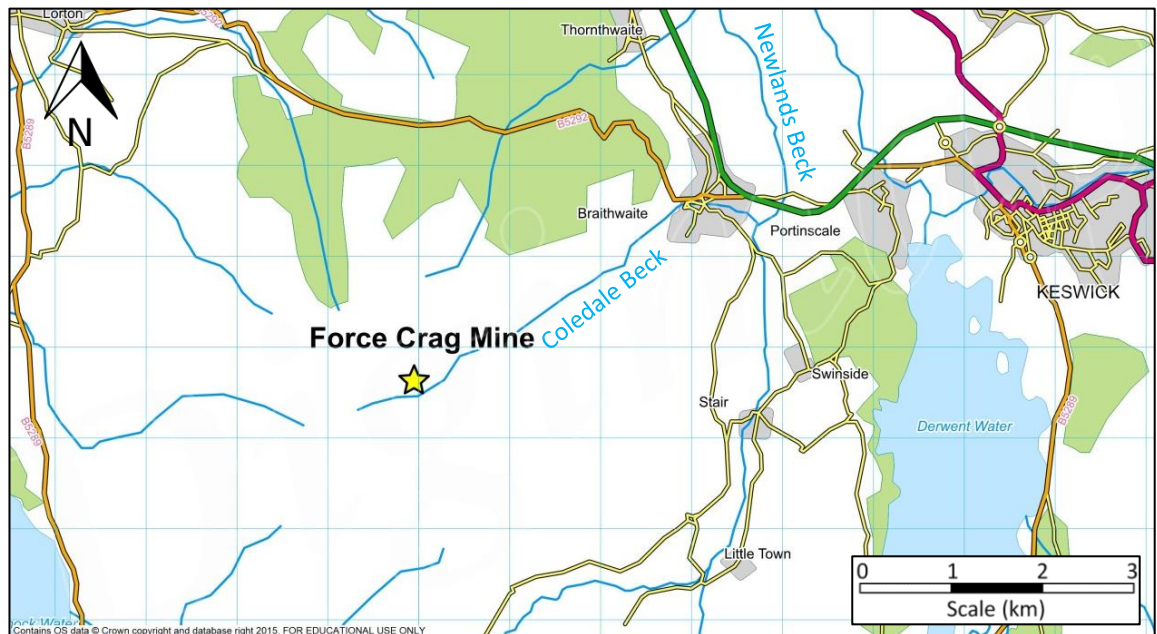


Figure 1.4 Force Crag Mine location (Digimap 2014)

1.6.2 Force Crag mine water treatment system installation

Installation of a large pilot scale treatment system based around a pair of Vertical Flow Ponds (VFPs) was completed in March 2014. A total flow of 6L/s from Level 1 is directed into the treatment system, with any excess discharging untreated to the Coledale Beck via an engineered overflow. No treatment is provided for water emanating from Level 0.

Force Crag mine water treatment scheme was a collaborative project involving The Coal Authority, Environment Agency, National Trust (which owns the mine) and Newcastle University, with Defra funding (Harris et al., 2014). System design was led by Dr Adam Jarvis (Principal Investigator at Newcastle University) with engineering provided by Atkins Ltd. and construction undertaken by J N Bentley Ltd. (Moorhouse et al., 2015). The Coal Authority was responsible for managing the design and build of the system, and is responsible for its ongoing operation (Moorhouse et al., 2015).

1.6.3 Vertical flow ponds

The main treatment units consist of a pair of earthworks-formed VFPs. These contain a 500mm layer of compost comprising 10% digested sewage sludge, 45% wood chips and 45% municipal waste compost (PAS100 specification) (Jarvis et al., 2014). This is underlain by a 200mm coarse limestone gravel drainage layer and a network of perforated drainage pipes. Mine water flows into the VFPs, before passing vertically through the compost substrate and collecting in the basal pipe network, where it leaves the treatment system as shown in Figure 1.5. In each VFP, there are four isolated drainage pipe networks, each draining one quartile of the treatment system (Atkins, 2014a). This is in part to test for, and guard against, the formation of preferential flow paths through the substrate (*pers comm.* Dr A. P. Jarvis, Newcastle University, 2014). VFP effluents pass through a swan-neck arrangement, the key objective of which is to control the water level within the VFPs: the water level is maintained at 350mm above the substrate to ensure the system operates anaerobically (Jarvis et al., 2015). This design, similarly to Nenthead, promotes bacterial sulphate reduction (BSR) for removal of dissolved metals and sulphate as insoluble metal sulphides (Jarvis et al., 2015; Jarvis et al., 2014).

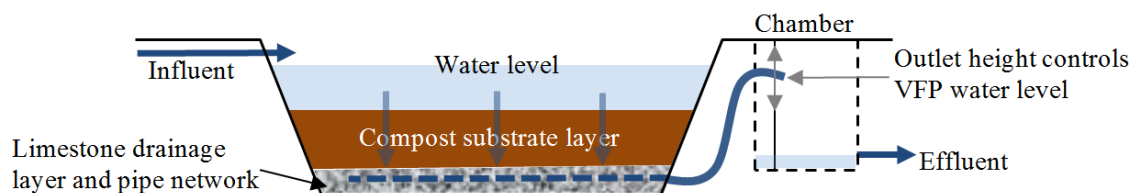


Figure 1.5 Schematic drawing of Force Crag VFP configuration

System size was designed to achieve a residence time of 19 hours, based upon scaling of empirical data from the Nenthead pilot system (Jarvis et al., 2014) to the 6L/s flow rate. On the basis of the designed residence time and flow rate, the system has a total substrate volume of 840m³ (Jarvis et al., 2014). Flow is carefully controlled via an arrangement of penstocks and gate valves to ensure each VFP receives a constant flow of 3 L/s (Jarvis et al., 2014).

1.6.4 Wetland

The VFP effluent water passes through an aerobic wetland before final discharge to the Coledale Beck (Jarvis et al., 2014). The aerobic wetland consists of an unlined shallow earthworks lagoon, planted with indigenous soft rush (*Juncus effusus*) to facilitate oxygenation and removal of suspended particles (Moorhouse et al., 2015).

Additionally, it has been suggested that wetlands act to remove residual metals within effluents by direct uptake into plants, and formation of plaque deposits around roots and rhizomes (Batty, 2003). However, given the small size of the wetland (Atkins, 2014a), it is likely that this effect will be minimal. The layout of the treatment system is shown in Figure 1.6 after Atkins (2014a).

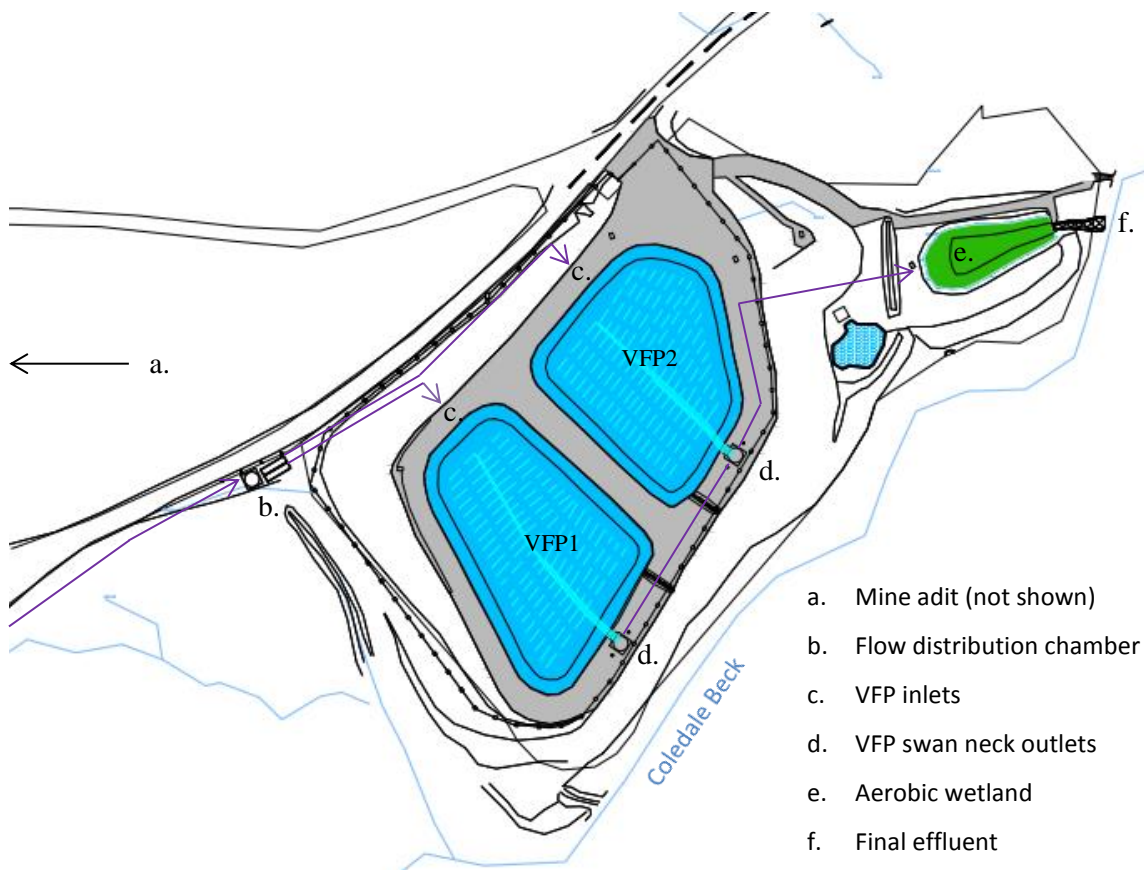


Figure 1.6 Force Crag mine water treatment system in plan, gravity main flows shown in purple (modified from Atkins, 2014a)

1.6.5 Resource recovery potential

The Force Crag treatment system case study provided a unique opportunity for this research to study, in real time, metal accumulation rates at a passive metal mine water treatment system, given that at the time of writing it was the only system of its kind in the UK. It is passive in the truest sense: water is diverted from the mine and through the treatment system by gravity, and metal removal is achieved by passive processes within vertical flow ponds and a wetland (Jarvis et al., 2015). Minimal operational intervention should be required to keep the system operational, given its passive nature; however, there will become a time at which the substrate of the vertical flow ponds will require replacing (Gray et al., 2012; Gusek and Clarke-Whistler, 2005). Analysis of a substrate taken from the Nenthead pilot system (on which the full-scale Force Crag system was based) identified that the material constituted hazardous waste due to zinc content, which would entail very high disposal costs (Atkins, 2014b). Yet, it has been suggested that the metals which accumulate in these systems may represent a resource (Gusek et al., 2006; Gusek and Clarke-Whistler, 2005). This raises the possibility that recovery of metals from passive compost-based treatment substrates could be used to

offset life-cycle costs. Additionally, other resources may exist in mine waters that may be amenable to recovery, either to be used beneficially at site or to generate revenue. These scenarios are explored in Chapter 5, supported by data obtained by experimentation with the Nenthead substrate, in addition to measurements at Force Crag and data sourced from the literature.

1.7 Thesis structure

In accordance with the first objective, Chapter 2 discusses metal mine water treatment processes, and provides a broad inventory of the resource potential associated with mine waters in Great Britain, based upon published and grey literature. It considers methods of recovering resources, in particular those relating to passive metal mine water treatment systems which is a key focus of this work.

Experimental methods to investigate the resource potential at the two case study sites, Nenthead and Force Crag, are presented in Chapter 3.

Chapter 4 documents the main phase of experimental work, which comprises a detailed geochemical analysis of mine water treatment substrates from the Nenthead pilot treatment system. Metal recovery from these wastes is trialled, using inorganic acid leaching and biological leaching.

Treatment system performance and potential for resource recovery at Force Crag is evaluated in Chapter 5. Metal accumulation rates are calculated, based upon data collected in the field, compared to other examples in the literature. Life-cycle cost scenarios are presented, with and without resource recovery. This is then compared directly to the estimated life-cycle costs of active treatment.

Chapter 6 concludes the thesis, summarising its main findings, positioning them in the current knowledge landscape and stating this thesis' claims to an original contribution. Recommendations for further research are also provided.

Chapter 2. Assessment of the resource potential of metal mine waters

2.1 Introduction and chapter contents

The resource potential of abandoned metal mine waters forms the key focus of this chapter, considering data from both the published literature and grey literature available to the author. By understanding the potential for, and viability of, resource recovery, strategies may be developed to exploit this as a means of offsetting the life-cycle costs of mine water treatment systems. On the other hand, extending treatment system life-time may provide a mechanism to reduce these costs. Both of these strategies are reviewed and discussed in this chapter in order to address the first objective of this thesis:

- Review the resource potential of metal mine waters nationally and identify ways in which resources can be recovered (Objective 1, Chapter 1).

Firstly, energy resources are outlined with a focus on potential and thermal energies of mine waters and a selection of data are presented that detail power that may be recoverable. Metal mine waters are identified to contain significant quantities of valuable metals, yet disposal of metal laden wastes from passive treatment systems represents a substantial cost. This review, therefore, explores ways in which metals might be recovered as a resource, instead of disposed of as waste. While this is an investigation into the resources associated with abandoned metal mines, reference will be made to both metal and coal mine case studies since useful information on resource recovery can be gained from both. The chapter concludes with a summary of the resource potential at abandoned metal mine sites, identifying knowledge gaps which require further investigation to facilitate its exploitation.

2.2 Realising the resource potential from mine abandonment

Mine closures are brought about for any number of reasons; however, the driver is often financial, where the economics of extracting the resource(s) becomes unprofitable (e.g. Laurence, 2006). By its very nature, the mine has completed its life as a provider of capital resource and may thus be considered exhausted, particularly once flooding and collapse of workings has occurred to render any remaining capital resources inaccessible (Younger et al., 2002). Upon abandonment, mines sites can often remain as unsightly derelict areas of land, host to numerous liabilities such as mine entries, land contamination and instability, derelict buildings and gas and water emissions (Fernández-Caliani et al., 2009; Yu et al., 2009; Holmes, 2008). From this perspective, the abandoned mine might therefore pose risks to human health and the environment (Holmes, 2008; Johnston et al., 2008).

Coal mine methane, for example, has been previously documented as an environmental and health and safety liability at coal mine sites (Jackson and Kershaw, 1996). In the years following the widespread abandonment of the coalfields of Britain, this liability has been managed through careful predictive modelling and venting. In some instances, the resource potential of coal mine methane has been realised (see: Flores, 1998). Methane is not the only hazard associated with abandoned mines that may also be viewed as a potential resource. To date, there has been little consideration of the resource potential of mine waters, yet by recovering resources, the cost of managing this liability might be offset. The following sections identify characteristics of metal mine waters which may be amenable to resource recovery.

2.2.1 Mine water characteristics which might offer recoverable resources

A mine water discharge is where water emanates, directly or indirectly, from underground mine workings, and can be at locations distant from mine sites (Watson, 2007; Younger et al., 2002; Younger, 1993). Depending upon the hydrogeology and mine workings, the water quality can vary considerably between locations, from good quality groundwater to poor quality metalliferous, saline and acidic waters (see: Banks et al., 1997). Mine water discharges were sometimes purposefully engineered during development of a mine to provide free drainage of workings. These drainage levels, sometimes known as soughs, form shallow gradient tunnels that can de-water significant proportions of orefields and are thus characteristically high in volumetric

flow rate (Younger et al., 2002). Conversely, where topography or other factors do not allow free-drainage, active pumping must be employed to keep workings dry during mine operation (Younger et al., 2002). Upon mine closure, however, mine water levels can recover and flow out in uncontrolled discharges at surface (e.g. Bailey et al., 2011; Younger, 2002). In many of these cases, mine waters are sourced from deep voids, little affected by surface temperature fluctuations, yet are warmed by geothermal heat (Banks et al., 2003). This water may represent a resource if used for the extraction of heat for space heating, for example. Table 2.1 provides a summary of some key features of mine waters and an outline of the potential resources associated with them.

Table 2.1 Features of mine water discharges which may have resources associated with them

Feature	Potential resource
Waters cascading from mine entries and within treatment system pipe ranges	Potential energy in pipe ranges may be harnessed by hydroelectric devices (McNabola et al., 2014)
Heat contained within mine waters flowing from or within mines; capacity of waters to store heat	Large volumes of water with perennially stable temperatures may be used for heating or cooling (Verhoeven et al., 2014; Banks et al., 2009; Watzlaf and Ackman, 2006; Jessop, 1995)
Mine water passing through treatment systems	Waste substrates and sludges from treatment process, particularly the metals contained within them (Gray et al., 2012; Zinck, 2005). Treated or untreated water of good quality may be suitable for potable supplies. In some cases, poorer quality waters could be used in industrial applications such as water treatment (Banks et al., 1996) and hydraulic fracturing (Macy et al., 2015).

Other resources may be recoverable from metal mine waters, for example electrochemical potential of ferric iron oxidisation (Cheng et al., 2007) or entropic potential of mixing of saline and fresh waters (Skilhagen et al., 2008; Aaberg, 2003). These are only emerging technologies, however, and will not be considered further in this thesis.

Remnant infrastructure, whilst not necessarily representing a resource itself, should be considered for its potential in facilitating the adoption of resource recovery schemes. Typically, mine sites demanded good transport and power connections to operate effectively, and often such infrastructure remains at the site (USEPA, 2011). An

example of this would be a connection to the National Grid which might be adapted to allow feed in of electricity generated by a hydroelectric turbine at a site (USEPA, 2011).

2.3 Potential energy of mine waters

Many abandoned metal mine sites are located within upland areas of Britain. For example the orefields of Llanrwst-Harlech, Mynydd Parys and Halkyn-Minera in western and northern Wales, and in England the North Pennines and Lake District, as defined by Mayes et al. (2009a). Additionally, the location of mine water discharges is often within steep-sided valleys, typically engineered in these locations during mine development in order to drain workings (Younger et al., 2002). Consequently, it is not unusual for there to be a close proximity of high energy upland watercourses to polluting mine water discharges and possible treatment sites. Potential energy from upland watercourses could be harnessed using small-scale hydroelectric systems (Gray et al., 2012). Additionally, unregulated outflows from long-abandoned mines exist, which cascade from mine entrances, or where treatment systems exist, flow down gravity pipelines (e.g. Moorhouse et al., 2015; Nuttall and Younger, 1999).

Potential energy from cascading and flowing water can be calculated using Equation 2.1 after Harvey et al. (1993):

$$(2.1) P = \rho Qgh$$

Where P = power in watts (W); ρ = density of water (1 kg/L); Q = flow in L/s; g = gravitational acceleration (9.8m/s^2) and h = hydraulic head in m.

Thus, as power is a product of flow and hydraulic head, a reasonably accurate estimation of these two variables can yield the potential energy at a given site. Few data are known to exist for hydraulic head at mine water discharges and therefore potential power generation capacity cannot be calculated even where flows are known. While this information could be approximated from map contours, significant errors would be present (Harvey et al., 1993). As a result, it would be necessary to undertake both a desk study of mine plans and a site survey in order to accurately gauge the potential energy at a mine water discharge site.

2.3.1 Mine water discharge flows

Reliable flow data for metal mine water discharges are limited, in period at least, due to the lack of legal responsibility of mine owners after mine abandonment prior to 1999 (McGuinness, 1999) and lack of government intervention before changes to legislation (Energy Act, 2011). Efforts were made by the Environment Agency and academic colleagues to collate metal mine pollutant flux data for the entirety of England and Wales, largely for the NoCAM Project (Jarvis et al., 2010b) and subsequent catchment scale investigations (Jarvis et al., 2012c). Out of 365 sites for which data are available, 126 have flow readings for mine discharges attributed to them (unpublished data courtesy of Dr H. A. B. Potter, Environment Agency, 2015). Figure 2.1 provides an illustrative overview of discharge flow rates from abandoned metal mines in England and Wales, showing that the vast number of flows are below 100L/s ($n=149/159$), with more than half of all measured flows below 10L/s ($n=84/159$). Further data collection to determine hydraulic heads would be required before the potential energy at these sites could be determined.

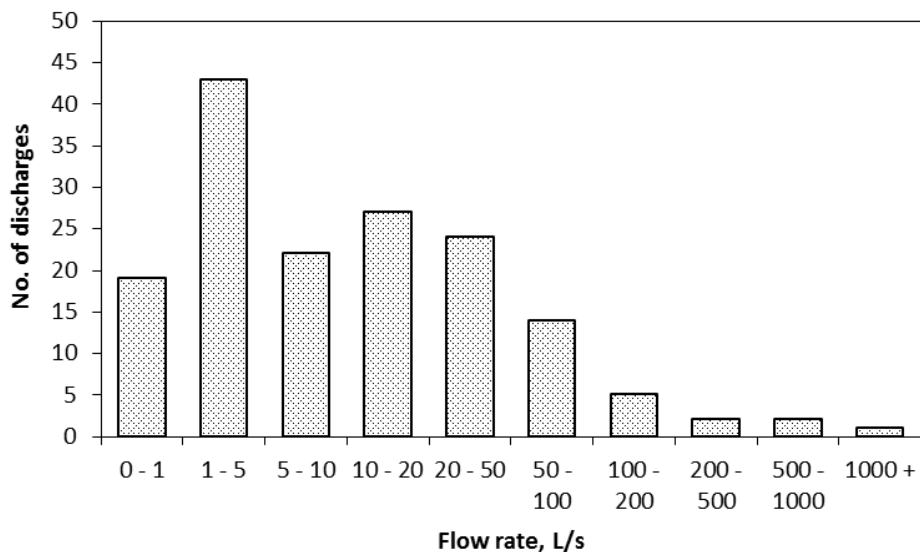


Figure 2.1 Spot readings of metal mine water discharge flows across England and Wales (unpublished Environment Agency data, 2015).

Roberts (2011) conducted a series of scoping investigations for hydroelectric potential of metal mine sites in northern England and mid Wales. A summary of the data is provided in Table 2.2, which shows that the two greatest flows (in terms of combined head and flow rate) are streams, rather than mine water discharges. Because hydraulic head was determined by Roberts (2011), it was possible to calculate the potential power (in kW) available. This shows that there is a modest amount of power which might be

Chapter 2. Assessment of the resource potential of metal mine waters

recoverable from mine water flows/streams at these abandoned metal mine sites. The individual locations of these sites, in addition to others in England and Wales discussed in this review, are displayed in Figure 2.2.

Table 2.2 Flow and head data for flows at abandoned mine sites, taken from Roberts (2011)

Site	Site type	NGR	Mean Flow (L/s)	Available head (m)	Potential Power (kW)
Pugh's Adit	Mine discharge	280100, 274400	7.41	2	0.145
Pugh's Adit	Stream	280100, 274400	31	80	24.33
Frongoch Adit	Mine discharge	271237, 274259	55	12	6.48
Cwm Rheidol Level 6	Mine discharge	273022, 278330	8.4	80	6.59
Cwm Rheidol Level 9	Mine discharge	272936, 278239	0.87	60	0.512
Force Crag Level 1	Mine discharge	319921, 521623	10.6	25	2.6
Low Force	Stream	319920, 521524	25	80	19.62

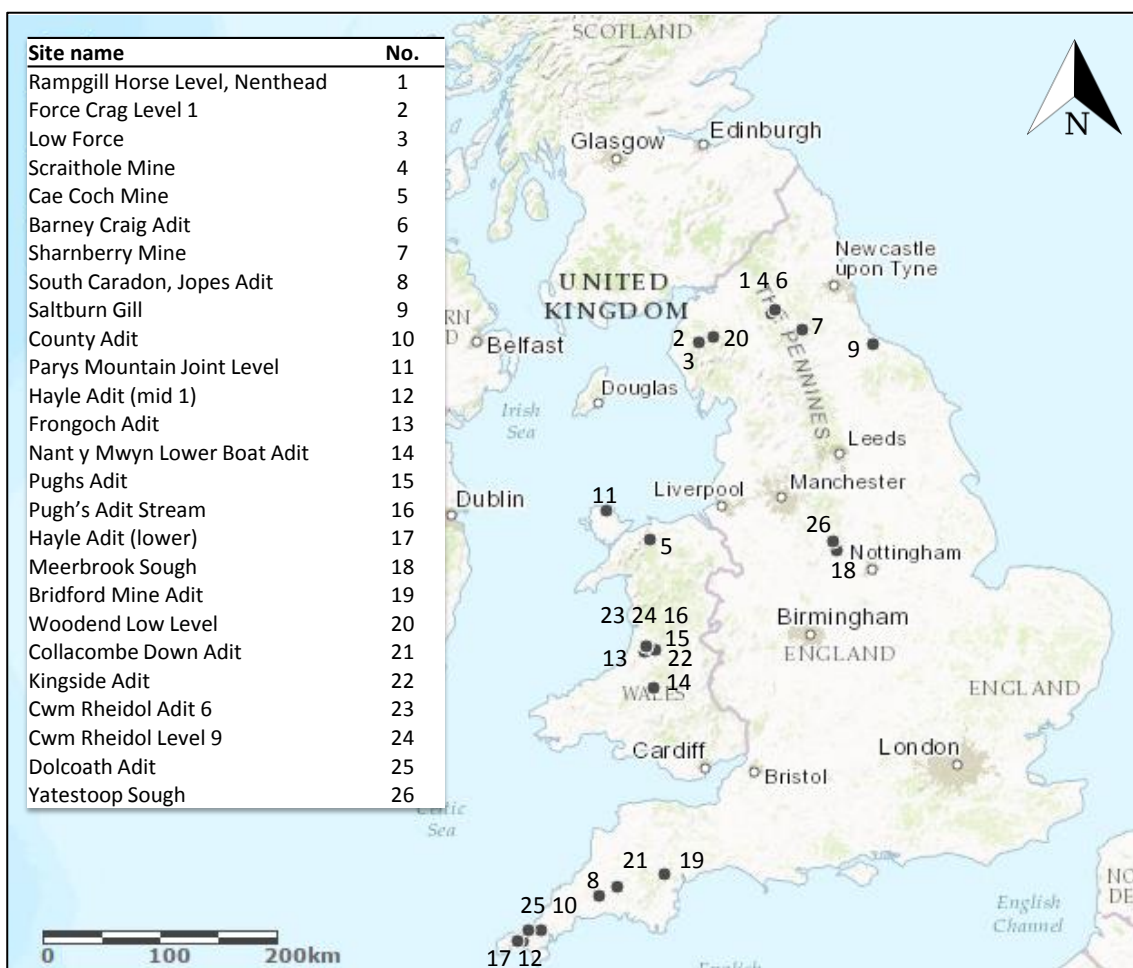


Figure 2.2 Location of metal mine discharges in England and Wales discussed in review (Digimap 2016)

2.4 Micro-hydropower for potential energy recovery

Cascading waters have the potential to yield power by Equation 2.1, which can be harnessed by hydropower systems. Often, hydropower systems are coupled to electricity generators in hydroelectric systems, but equally can be directly coupled to machinery to undertake mechanical work (Meier and Baumer, 1985). Classification of small-scale hydropower into mini-hydro, micro-hydro and pico-hydro (in descending order) depending upon power capacity is commonplace in the literature, yet there is incomplete agreement between authors on the boundaries between the classes. For example, Ashok (2007) defines micro-hydro as >100kW; whereas Harvey et al. (1993) suggests micro-hydro applies to systems between 200W and 300kW. Paish (2002), on the other hand, claims that micro-hydropower is generally accepted to range between 10kW and 500kW, with pico-scale systems defined as below 10kW; and mini-hydro from 500kW to 2MW. Small scale hydropower systems are generally installed to harness the power of rivers and streams (Gallagher et al., 2015a; Paish, 2002); and whilst there have been some investigations into potential for use in the water industry more widely (Gallagher et al., 2015b; McNabola et al., 2014), there is little evidence of consideration for use with mine waters.

2.4.1 Hydroelectricity generation

Use of hydropower systems coupled to electricity generators can provide a versatile source of power which may be either used for a process within a mine water treatment system, to supply a nearby property or to be fed into the electricity grid for revenue generation (Gray et al., 2012). Hydroelectric system efficiencies are affected by a number of factors as defined by Harvey et al. (1993), expressed by Equation 2.2.

$$(2.2) \quad e_0 = e_{(civils\ works)} \times e_{(penstock)} \times e_{(turbine)} \times e_{(generator)} \times e_{(power\ lines)}$$

e_0 is the net system efficiency, a product of the efficiencies, e , of various system components.

Determination of these factors would be required before a realistic electrical power output of a hydropower system could be determined for a given site.

2.4.2 Types of turbine

Turbines vary in design based upon the driving head and flow rate of water source and can be subdivided into two categories: impulse turbines, such as Pelton/Turgo wheels or crossflow turbines, or reaction turbines such as Francis, Propeller or Kaplan types (Harvey et al., 1993). Figure 2.3 shows how these different turbine types suit different hydraulic conditions.

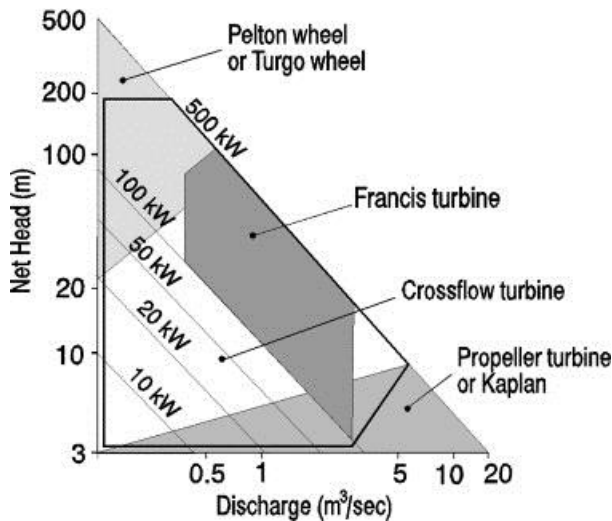


Figure 2.3 Suitability of hydropower turbines for a range of heads and flows, after Paish (2002)

Considering typical abandoned metal mine sites flows (Table 2.2) generally offer <25kW of power (or <7kW for mine water flows), yet generally with high driving heads >12m (excepting Pugh's Adit), it is anticipated that crossflow or Pelton/Turgo type wheels or crossflow turbines would be suitable. The Pelton wheel system consists of split buckets attached to a wheel which capture almost all of the energy from a high-pressure jet of water, allowing it to then spill into a discharge channel at the base, as shown in Figure 2.4 (Paish, 2002). Pelton systems operate efficiently with small heads only where power generation is fairly modest, for example <20m for 1kW capacity (Harvey et al., 1993). The Turgo turbine is similar in design, but the water jet is angled to avoid interaction with the spill water (Paish, 2002). Crossflow turbines consist of a drum runner with radially curved blades attached (Harvey et al., 1993). The water is injected in a parallel stream across the full width of the runner before falling through the drum, and providing an additional strike of the blades on its exit, as shown in Figure 2.4 after Paish (2002).

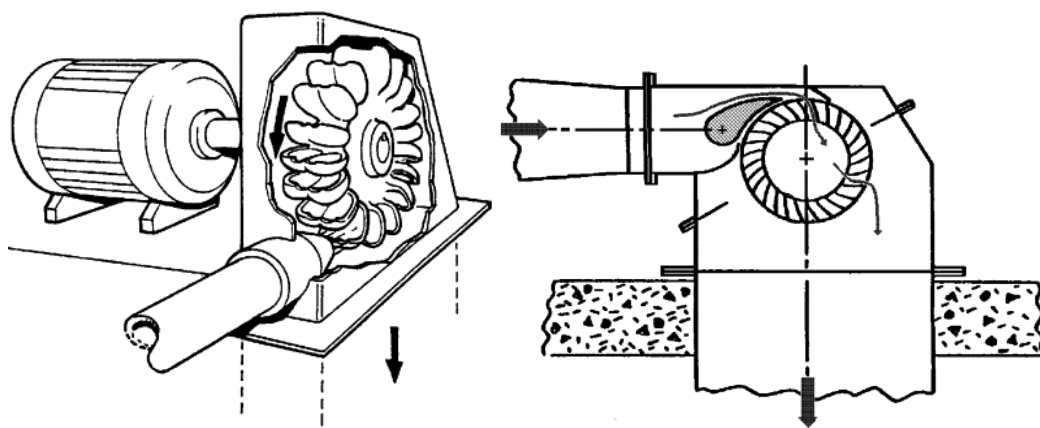


Figure 2.4 Pelton turbine (left) and crossflow turbine (right) after Paish (2002)

2.4.3 Applications of hydropower systems in mine water environments

Geochemical analysis by Rose (2015) of the Level 1 mine water at Force Crag Mine in Cumbria indicate that several minerals are oversaturated. As a consequence, there is a risk that these minerals may precipitate within a hydropower system at this site causing operational difficulties (Rose, 2015). Technical issues of corrosion of turbines have also been identified from acid mine water impacted flows (Sharma et al., 2010), and consequently further technical assessment of turbine applicability would be required at any specific site. In the favour of harnessing mine water flows, however, it appears unlikely that normal regulatory obstacles would apply (for example, see Environment Agency, 2013a), because mine waters do not have the same environmental sensitivities as rivers.

2.5 Thermal capacity of mine waters

Deep coal mine waters often have a perennially consistent temperature throughout extensive mine networks and thus can provide either a useful source or sink of heat (Preene and Younger, 2014; Banks et al., 2003). Calculations suggest that a resource of approximately 3,000MW_t exists in abandoned coal mines throughout Europe (Díez and Díaz-Aguado, 2014). It is likely that a similar situation exists at abandoned metal mine sites, albeit that in Great Britain, metal mines are generally shallower than some coal mines thereby receiving a reduced effect from deep geothermal heat (Gray et al., 2012). Mine water discharges (i.e. where water discharges by gravity) may also represent significant sources of heat and, without the need for active abstraction from workings, a heat recovery system would have improved overall efficiency.

Mine water sourced heat pumps for space heating and cooling are discussed by Banks et al. (2003) and examples of full scale systems exist at former mine sites in Scotland (Banks et al., 2009), Spain (Loredo et al., 2011), Canada (Jessop, 1995) Germany, Norway and the USA (Hall et al., 2011), and in the Netherlands (Verhoeven et al., 2014; Roijen, 2011).

Potential power from individual mine water sources can be estimated using the following simple Equation 2.3 (after: Banks et al., 2003):

$$(2.3) P = Qc\Delta T$$

Where Q = flow in litres per second; c = specific heat capacity in kJ/L/°C (assumed as 4.2); ΔT = temperature change of source in °C and P = power is in kW.

2.5.1 Metal mine water temperatures

Temperature monitoring data for metal mine water flows have been obtained for several metal mine sites from the literature and provided by the Environment Agency, as detailed in Table 2.3 and shown in Figure 2.2. Average temperatures are presented where data cover the majority of a full year or more. As can be seen, there is significant variability between sites. One possible reason for this is differences in subsurface hydrogeology which may lead to waters arising from differing depths where temperature varies due to geothermal gradients (Jessop, 1995).

Chapter 2. Assessment of the resource potential of metal mine waters

Table 2.3 Gravity discharge temperature and flow data for free draining metal mines in England and Wales

Site	NGR	Temp (°C)	Temp Range/date	Flow, (L/s)	Power (kW _t)	Source
Scraithole Mine	380300, 546900	7.3	Feb 2006 - Dec 2006	2.1	35	(Mayes et al., 2009b)
Cae Coch Mine	277523, 365326	9	May 1988 – May 1990	N.D.	-	(McGuinness and Johnson, 1993)
Parys Mountain Joint Level	243800, 389950	9		10	168	(Johnson, 2003); Environment Agency unpublished data**
Threlkeld Mine, Woodend Low Level	332514, 526142	14.28	April 2012 - April 2014	10.6	178	Environment Agency unpublished data**
Barney Craig Adit	380400, 546700	9.57	Jan 2014 - Dec 2014	18.1	304	Environment Agency unpublished data**
Sharnberry Mine	401325, 530804	7.95	Oct 2011 - Sept 2012	19.3	324	Environment Agency unpublished data**
South Caradon, Jopes Adit	226555, 069817	12.4	July 2012 - Jan 2013	N.D.	-	Environment Agency unpublished data**

*Assuming ΔT of 4°C after Banks et al. (2003) **Data courtesy of Dr H. A. B. Potter, Environment Agency 2015

The Woodend Low Level of Threlkeld Mine was visited by this Author during the winter of 2015 and field measurements taken using a calibrated Myron 6P Ultrameter. At the time of the visit, the temperature of the discharge from the mine was 13.6°C which is close to the annual average of 14.3°C, measured over two years by the Environment Agency (S.D. 0.2, $n=20$). At the time of the visit the ground had a light coating of snow and the air temperature was <5°C, yet through nitrile gloves the mine water was appreciably warm to the touch (Figure 2.5).



Figure 2.5 Woodend Low Level discharge, Threlkeld Mine, emanating from the foot of Blencathra Mountain in the English Lake District National Park

Regular temperature measurements at the Threlkeld Woodend Low Level discharge are presented in Figure 2.6. Similarly stable temperatures have been observed at other sites such as Barney Craig Mine in Northumberland (Figure 2.7), albeit temperatures are on average lower at 9.6°C (S.D. 0.2, $n=12$) (unpublished data courtesy of Dr H. A. B. Potter, Environment Agency, 2015). Pumped flows from the Cleveland Orefield (NGR 467370, 519835) are on average 16.9°C (S.D. 2.3, $n=179$), albeit with a decreasing trend in temperature from the start of pumping (Figure 2.8). Stable temperatures seen in waters from deep mines are of particular use for heat extraction during winter, as they are generally warmer than the air in the winter (Banks et al., 2003). On the other hand, it has been suggested that during summer months, the mine waters may offer a means of disposing of heat energy to keep buildings cool (Preene and Younger, 2014; Banks et al., 2003).

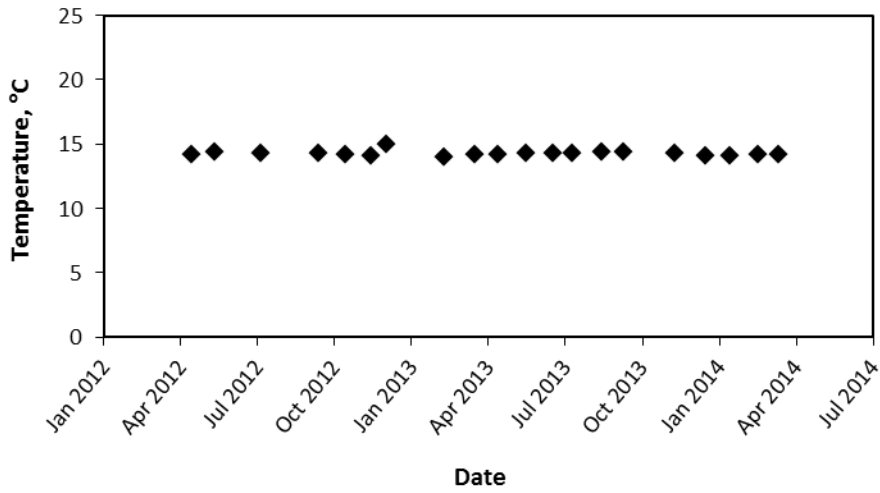


Figure 2.6 Threlkeld Mine Woodend Low Level discharge water temperatures, January 2012 – July 2014 (unpublished Environment Agency data, 2015)

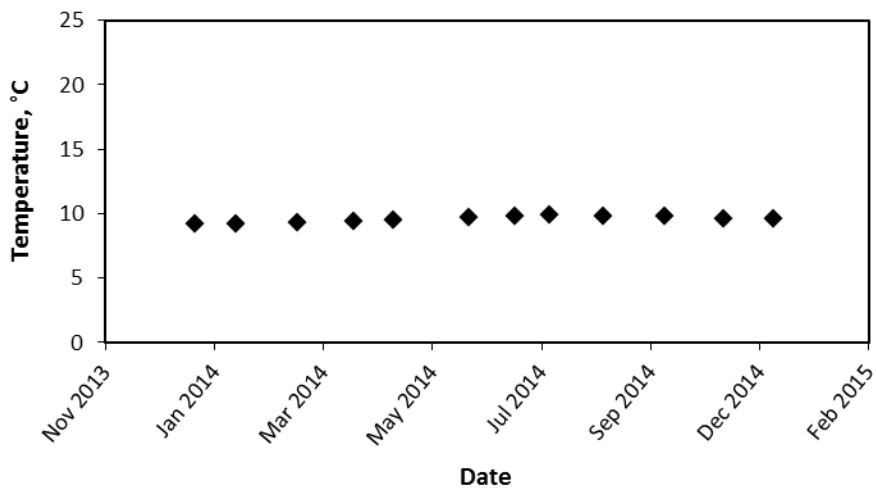


Figure 2.7 Barney Craig Mine water temperatures, November 2013 – February 2015 (unpublished Environment Agency data, 2015)

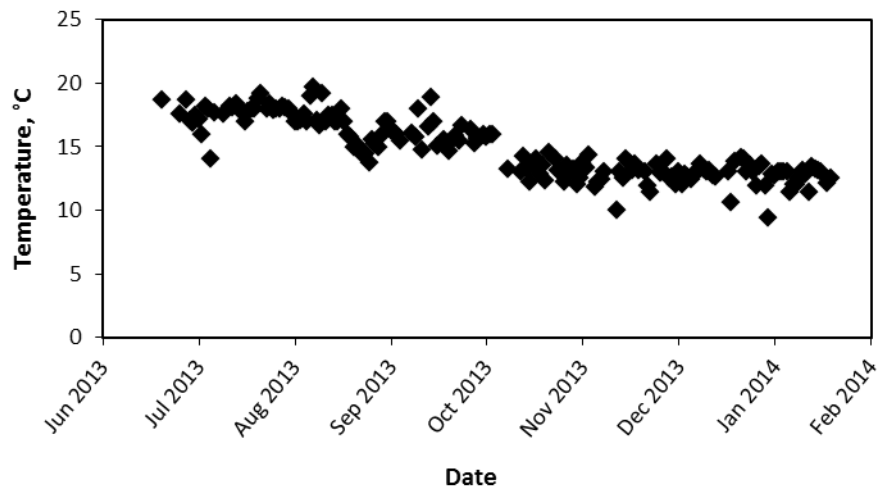


Figure 2.8 Pumped mine water temperature in the Cleveland Orefield, June 2013 – February 2014 (unpublished Coal Authority data, 2014)

2.6 Exploitation of mine waters for heating and cooling

Vast void spaces left by mining activities provide a considerable advantage for open-loop mine water sourced heating and cooling systems, for the following reasons (after: Wieber and Pohl, 2008; Banks et al., 2003; Watzlaf et al., 2002):

- Mined voids provide excellent heat exchange with surrounding bedrock.
- Significant depths can be readily accessed from mine entries.
- Substantial volumes of water are accessible and abstractions can be highly productive.
- High flow discharges often pre-exist, or mine water pumping takes place for operational or environmental reasons.

Despite these factors, there has been a certain reluctance to adopt mine water sourced heating schemes over conventional ground sourced systems, potentially attributable to high capital costs (Preene and Younger, 2014; Hall et al., 2011).

2.6.1 Principles of pumping heat

Shallow subsurface strata have the potential to store large quantities of thermal energy. Ground sourced heating and cooling is a relatively well established practice (e.g. Yang et al., 2010; Lund et al., 2004; Sanner et al., 2003) where heat energy can either be extracted or deposited within soils, rocks or groundwater; or from mine waters (Preene and Younger, 2014). While it is feasible to extract heat from these sources by circulating fluid through pipes within workings or a heat exchanger where mine water is at the surface, the relatively low temperature heat is of little use for practical applications (Banks, 2008). It is likely, therefore, that heat pumps will be required to pump heat against the thermal gradient, thus enhancing the heating or cooling available by passive methods (Banks, 2008; Banks et al., 2003).

Sadi Carnot proposed an ideal thermodynamic cycle which can create a temperature difference (between θ_1 and θ_2) by doing a given amount of work. This cycle is ideal due to its reversibility and is described by Equation 2.4: changes in entropy and losses from mechanical inefficiencies are not considered (Banks, 2008).

$$(2.4) \quad E_{max} = \frac{W}{H_{in}} = \frac{(\theta_1 - \theta_2)}{\theta_1}$$

The maximum efficiency of an ideal (Carnot) cycle (E_{max}) can be defined as the ratio between the work (W) and the high temperature heat (H_{in}); whether that be temperature change to deliver work, in the case of a heat engine, or in reverse for work undertaken to deliver a temperature change, as in a heat pump (Sumner, 1948).

2.6.2 Coefficient of performance

Efficiency of a heat pump system can be measured by the Coefficient Of Performance (COP), that is, the ratio of work undertaken to the heat energy output. Considering the reverse of Carnot's ideal heat engine, the theoretical maximum efficiency or COP can be expressed by Equation 2.5.

$$(2.5) \text{ COP}_{carnot} = \frac{\theta_1}{\theta_1 - \theta_2}$$

Where θ_1 is the low temperature feed, and θ_2 is the heat output, in degrees Kelvin, K (Banks, 2008).

As an example, a low temperature ground water sourced feed of 5°C (278K) is used to provide an output of 50°C (328K) for a conventional domestic heating system:

$$(2.6) \frac{278}{323 - 278} = 6.2$$

As explained by Equation 2.6, an input of 1 joule of energy (work) in the heat pump can theoretically produce 6.2 joules of energy (heat) from a low temperature source, where 1 joule of the output comes from the work undertaken. By reducing the target temperature, θ_2 , or by increasing the source temperature θ_1 , a higher theoretical COP is achievable.

In reality, however, the Carnot Cycle model provides an upper limit COP that is not normally achieved in practice (Banks, 2008). Most commonly, heat pumps employ a vapour-compression system, known as a 'Rankine Cycle' which has a lower efficiency than the ideal Carnot Cycle but can be employed in the real world. (Banks, 2008).

Table 2.4 provides a summary of heat pump performance based on EN14511 testing of a range of commercial heat pumps.

Table 2.4 Heat pump performance (COP) data (Heat Pump Test Centre WPZ Switzerland, 2012)

	35°C output			50°C output		
Source °C	5	0	-5	5	0	-5
COP min	4.5	4.0	3.4	3.1	2.7	2.3
COP mean	5.1	4.4	3.8	3.5	3.0	2.6
COP max	5.9	5.0	4.3	4.1	3.5	3.1

Compared to the calculated ideal Carnot Cycle COP of 6.2, it can be seen that the highest COP achieved by the Swiss Heat Pump Test Centre is just 4.1, with an average of 3.5. It is also clear to see that, as stated by the COP equation, higher source temperatures and lower output temperatures both increase the COP. Consequently, heat pump systems are designed to operate at a minimal temperature differential (ΔT) in order to maximise the COP.

2.6.3 Mechanics of a Rankine cycle heat pump

Conventional heat pumps utilise the Rankine cycle, comprising a condensation-evaporation cycle of a fluid with a suitably low boiling point.

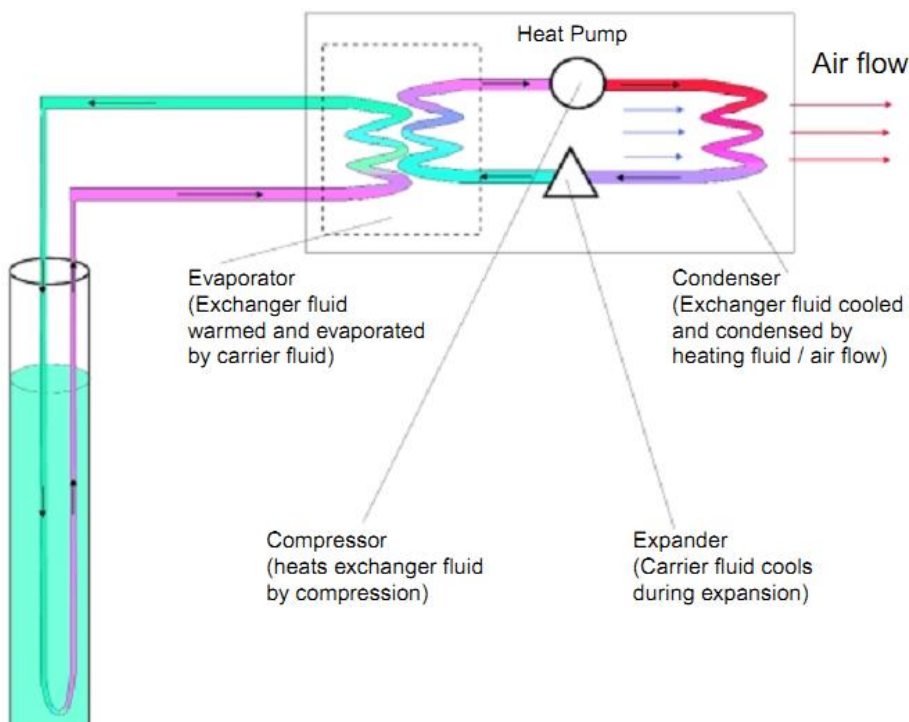


Figure 2.9 Ground sourced heat pump schematic (Banks and Robins, 2002)

A compressor forces the fluid to condense, giving up heat energy as it changes state. The now condensed fluid flows through an expansion valve, before collecting heat energy in the evaporator (a heat exchanger interfaced with the heat source). This vapour now passes back into the compressor to complete the cycle, as depicted in Figure 2.9 (Banks and Robins, 2002). In effect, low grade heat energy from the ground source is ‘pumped’ up-gradient in order to provide thermal energy at a useable temperature.

2.6.4 Applications of heat pumps in mine water environments

Mine waters are typified by poor water quality, where pH can be suppressed, and supersaturation with metals and other species. Concerns of corrosion of heat pump components, accretion and blockage of heat exchangers with precipitates may be reasons why installations fall from favour (Watzlaf and Ackman, 2006; Banks et al., 2003). A specific concern for mine waters rich in hydrogen sulphide is the corrosion of copper and cupro-nickel heat exchangers, where concentrations over 0.25mg/L can cause premature failure (Rafferty, 2003). Geochemical modelling can be undertaken in order to assess the risk of scaling within heat exchanger units (Rafferty, 1999), and was undertaken by Banks et al. (2009) for the two Scottish open-loop mine water sourced heat pump installations, where it was identified that exclusion of atmospheric oxygen was crucial to prevent the formation of troublesome precipitates. It may be possible to use closed-loop systems at mine water treatment systems, installing large heat exchangers within treatment systems. For example, units such as ‘blade’ type as shown in Figure 2.10, to recover heat flowing through the system while minimising the impacts of poor water quality (*pers comm.*, Prof. P. L. Younger, Glasgow University, 2015).



Figure 2.10 Installation of a 'blade' type heat exchanger at Caphouse coal mine water treatment system, Yorkshire, UK (photograph courtesy of Prof. Paul Younger). Note black lines which circulate glycol heat carrier to and from a heat pump.

Generally, however, there is a paucity of investigations in the literature which consider the impacts of mine water quality on heat pump installations. This poor quality might, however, be a resource in itself, in particular if the metals present could be recovered.

2.7 The metal content of metal mine waters in England and Wales

Mayes et al. (2013) provide an inventory of problematic metal fluxes through river basins in England and Wales, resulting from discharges from (typically long) abandoned non-coal (largely metal) mines. Given the typical length of time since mine abandonment, and the fact that just two treatment systems have been installed since the study at the time of writing, it is considered that these figures are still relevant.

Table 2.5 documents average flows and metal concentrations in the top 15 point source discharges in England and Wales ranked by zinc load, plus data for the two case studies investigated in this thesis: Nenthead and Force Crag (unpublished data courtesy of Dr H. A. B. Potter, Environment Agency, 2015).

Chapter 2. Assessment of the resource potential of metal mine waters

Table 2.5 High ranking polluting metal mines in England and Wales, ordered by zinc load (unpublished Environment Agency data, (2015) after Mayes et al. (2013); Jarvis et al. (2010a))

Rank by Zn load	Discharge name	Grid reference			Metal concentrations (mg/L)							Load (t/year)
		Easting	Northing	Flow (L/s)	Cd	Cu	Fe	Mn	Ni	Pb	Zn	Zn
1	County Adit	176199	041875	454	0.004	0.06	9.8	0.77	0.08	0.005	2.4	33.9
2	Parys Mountain Joint Level	243807	391218	10	0.17	43.1	599	19.42	0.19	0.04	71.4	22.5
3	Hayle Adit (mid 1)	159398	032416	644	0.002	0.39	3.8			0.02	0.91	18.5
4	Frongoch Adit	271237	274259	60						6.25	5.6	10.5
5	Nant y Mwyn Lower Boat Adit	278234	243796	30	0.03					0.09	10.6	10.1
6	Pughs Adit	280109	274407	13	0.03	0.007	0.9			0.58	22.4	9.2
7	Hayle Adit (lower)	155692	033128	213	0.002	0.22	0.40			0.002	1.3	8.5
8	Meerbrook Sough	429250	354350	740	0.002	0.0009	0			0.02	0.36	8.4
9	Bridford mine adit	283035	086504	20	0.04	0.019	57.2			2.7	12.3	7.8
10	Woodend Low Level	332514	526142	5.5	0.08	0.006	4.2	3.93	0.27	0.44	36.7	6.4
11	Collacombe Down Adit	243017	077032	35	0.01	0.08	29			0.01	5.0	5.5
12	Kingside Adit	280400	274500	18	0.03	0.006				0.74	9.2	5.2
13	Cwm Rheidol Adit 6	273022	278330	10	0.04		9.6			0.78	14.6	4.6
14	Dolcoath Adit	164850	041880	150	0.002	0.0001	8.0	2.25	0.02	0.002	0.9	4.3
15	Yatestooop Sough	426400	362600	172	0.008				0.007	0.02	0.71	3.9
27	Rampgill Horse Level, Nenthead	378120	543500	17	0.006	0.001	0.64	0.1	0.01	0.07	4.3	2.3
33	Force Crag Mine Level 1*	319921	521632	16	0.02	0.007	0.66	0.52	0.016	0.05	3.1	1.5

*Load now reduced by treatment system installation (Jarvis et al., 2015)

Out of ~180 of the most polluting metal mine waters in England and Wales, the total load discharged per annum for several key metals has been summarised in Table 2.6, alongside the 2015 market value of the respective metals based upon values available from the London Metal Exchange (LME, 2015).

Table 2.6 Summary of combined metal fluxes in England and Wales from abandoned metal mines, and indicative market value of some metals

Metal	Load (t/annum) from point mine water discharges (unpublished Environment Agency data 2015)	Market value for native metal (£/t) (*London Metal Exchange, www.lme.com 29/9/15 (exchange rate of \$0.65US to £1)	Potential aggregate value of metals (£)
Nickel	1.8	6,766.50*	12,179.70
Lead	21.2	1,086.82*	23,040.58
Zinc	252.9	1,061.32*	268,407.83
Copper	38.6	3,321.90*	128,225.34

It has been noted that a significant proportion of this national flux is concentrated in a relatively small number of discharges; e.g. 67% zinc is attributable to the 10 most polluting discharges (Mayes et al., 2010). The majority of these sites (6/10) are located in Western Wales (Mayes et al., 2010).

Data for non-coal mine water pollutant fluxes within Scotland has received little recent attention in the published literature, despite large areas of abandoned base-metal mines, such as Leadhills in the Scottish Borders (Rowan et al., 1995). Specifically, the Glengonnar Water and Wanlock Water in this mining area suffer chronic EQS failures for zinc, lead and cadmium but loadings from individual sources have yet to be characterised in detail (SEPA, 2011).

2.8 Mine water treatment systems

Metals contained within waters discharging from abandoned metal mines can cause widespread pollution (Mayes et al., 2009a). As a consequence, in Great Britain, there have been efforts to install treatment systems to remove metals from mine waters before they discharge into the environment (Moorhouse et al., 2015; Hamilton et al., 1999).

By design, metals accumulate within substrates or form waste sludge which requires management (Gray et al., 2012; Zinck, 2005). By understanding treatment process, the opportunities for recovering metals from these wastes might be assessed.

Mine water treatment technology is separated into two sections, ferruginous waters, where iron is a major contaminant targeted for removal, and metalliferous, where other metals are the foci of remediation.

2.8.1 Treatment of ferruginous mine drainage

Treatment systems vary along a scale in terms of operational input, from fully active (high energy, chemical process based systems) to fully passive (gravity-fed systems relying upon natural process for treatment) (Younger et al., 2002). The method of treatment adopted at any given site has implications on the physical and chemical properties of wastes and substrates produced by the system.

Aerobic treatment systems (both active and passive) oxidise and hydrolyse dissolved ferrous iron to form a hydrous ferric oxide precipitate that can settle out from solution within the treatment system (Hedin et al., 1994a). Figure 2.11 shows a passive mine water treatment system at Saltburn, treating water from the Cleveland Ironstone Orefield, England relying upon passive processes to oxidise and settle iron precipitates (NGR 467370, 519835). Pumped water at Saltburn is net alkaline (pH 6.7) with total iron concentrations of 125mg/L (unpublished Coal Authority data, 2014). At other sites where the alkalinity of the mine water is insufficient to buffer hydrolysis reactions, alkali addition can be made during treatment to raise pH (Hedin et al., 1994b).



Figure 2.11 Saltburn passive treatment system tackling ferruginous mine water from ironstone workings (photograph courtesy of The Coal Authority)

Less commonly, sulphate reduction processes are employed to remove iron as a sulphide (Younger, 2000; Tuttle et al., 1969), a process by which acidity is consumed rather than produced. Just a few examples exist in Britain, notably Tan-y-Garn in Carmarthenshire, and Bowden Close in Northumberland (Geroni and Sapsford, 2011; Matthies et al., 2010).

2.8.2 Ferruginous drainage treatment waste

Aerobic treatment systems removing iron produce large volumes of predominantly Hydrous Ferric Oxide (HFO) sludge. Approximately 4,500 tonnes of HFO is produced annually in treatment systems operated by The Coal Authority in Great Britain (Sapsford et al., 2015).

Dudeney et al. (2003) reported that the former British Coal Corporation (pre 1997) had established a market for mine water treatment HFO as a pigment within the brick and concrete industry, although to-date this is the only known successful commercial venture for the material in Britain. Bailey et al. (2013a) concluded that while a spectrum of possible uses exists, restrictive legislation and cheap alternatives provide obstacles to full-scale applications. More recently, studies have investigated the use of HFO in the development of phosphorous adsorbing buffer strips in agricultural land (Habibiandehkordi et al., 2014), development of a pre-catalyst for the cracking of

methane (Alharthi et al., 2014) and for the removal of phosphorus and zinc from waste water streams (Sapsford et al., 2015).

2.8.3 Treatment of metalliferous mine drainage

Understandably, the clean-up of pollution is often the focus of metal removal from mine waters. Due to the nature of metal pollutants, in that they do not degrade like many organic compounds, remediation strategies focus on immobilisation of metals within treatment systems (Gray et al., 2012). A wide range of approaches have been developed in order to achieve metal retention, each of which may be more or less amenable to metal recovery. The following sections provide an outline of the main treatment technologies available, and include examples from pilot and laboratory scale treatment trials as well as full-scale systems. Distinction is made between active and passive systems where active, in this case, implies that input of power and/or chemical reagents is required. A critical review of treatment approaches is provided in this section in order to evaluate the performance of passive systems harnessing bacterial sulphate reduction (which are investigated in this thesis) against alternatives.

2.8.4 Active treatment

Active treatment using the ‘ODAS’ (Oxidation, Dosing with Alkali and Settlement) approach effectively removes metals as solid hydroxide species (Younger et al., 2002). Although given the hydroxide solubility products of most pollutant metals (including lead, zinc, cadmium, nickel, copper, manganese) a higher pH and therefore requirement for alkali would be required for their removal, compared to iron (Jarvis et al., 2012b).

Desalination technologies such as electro-dialysis and reverse osmosis offer an alternative active treatment approach, as they represent a highly effective method of removing solutes from solution (Turek, 2004; Harries, 1985). Indeed high quality potable waters can be recovered from polluted mine waters using reverse osmosis, and consequently this approach may be favourable in water stressed areas (Holman, 2009). Clarke (1995) (after Younger et al., 2002) reports on the economic extraction of salt from saline mine waters in Katowice, Poland using reverse osmosis. Generally, however, the cost of membranes and power to generate high hydrostatic pressures rule out reverse osmosis when considering treatment options at most sites (Younger et al., 2002). In a global study of treatment systems, Zinck and Griffith (2013) found that

membrane based desalination technologies were the most expensive treatment technology, with passive treatment offering the lowest cost alternative.

Active sulfidogenic bioreactors can allow selective removal of metals from mine drainage, by dosing with sulphide and controlling pH. Off-line systems are often adopted, where the hydrogen sulphide is generated by sulphate reducing bacteria in a vessel isolated from the mine water (Johnson et al., 2009; Johnson and Hallberg, 2005a; Boonstra et al., 1999). Active 'on-line' bioreactors incorporating different populations of acidophilic, acid tolerant sulphate reducing bacteria to facilitate selective removal of metals in-stream from mine drainage has been proposed by Johnson et al. (2004). Laboratory trials by Jameson et al. (2010) showed that selective precipitation of copper from a copper-zinc synthetic acid mine water occurred through an online bioreactor system, demonstrating potential for the technology. Examples of active sulphate reducing bioreactors deploying the Thiopaq™ process (www.paques.nl) have been used for the economic recovery of metals: Boonstra et al. (1999) presents case studies of zinc recovery from a contaminated acid groundwater (Budelco Zinc Refinery, Netherlands) and copper recovery at a copper mine in Utah, USA.

Johnson et al. (2006) argue that active systems employing sulphate reduction are favourable over ODAS approaches or passive compost-based systems, due to the ability to recover metals for resale. Younger et al. (2005), on the other hand, determine that even at Wheal Jane (probably the most severe of all metal mine waters in the Great Britain) ODAS offers a more economically attractive package than biochemical sulphide precipitation with recovery of metals for resale. Paques Ltd suggest that the metal concentrations required to make the prospect of economic metal recovery attractive are between 50 – 5,000mg/L (Paques, 2015), far higher than seen in the majority of polluting mine waters in England and Wales (see Table 2.5). On this basis, the adoption of passive treatment systems in Britain probably offer a lower cost and lower impact approach to treatment, where sufficient land areas permit (Jarvis et al., 2006; PIRAMID Consortium, 2003; Hedin et al., 1994a).

2.8.5 Passive treatment systems

Passive treatment offers an alternative approach to remediation and can be defined as:

'...the improvement of water quality using only naturally-available energy sources, in gravity-flow treatment systems (such as wetlands or subsurface-flow bioreactors) which are designed to require only infrequent (albeit regular) maintenance to operate successfully over their design lives.' (PIRAMID Consortium, 2003)

As these systems typically offer low-impact and low-cost methods of treating mine drainage, they are normally preferred over active treatment methods where feasible (Ziemkiewicz et al., 2003; Younger, 2000). Life-cycle assessment by Hengen et al. (2014) demonstrated that passive treatment using locally source materials offered the lowest impact approach, compared to six alternative treatment scenarios which included active treatment with powdered limestone and hydrated lime.

Nuttall and Younger (2000) present data from laboratory and field trials of a Closed-Bed Limestone (CBL) reactor designed to remove zinc from hard circum-neutral mine waters by elevating alkalinity, and increasing pH to approx. 8.5. This was achieved by a closed loop design that prevented atmospheric CO₂ entering the system and lowering pH. This ensured the pH remained high, causing zinc to precipitate as a carbonate, smithsonite (Nuttall and Younger, 2000). Removal efficiencies of up to 50%, for an influent concentration of 5.5mg/L zinc, and 22% for an influent concentration of 7.3mg/L zinc, in the laboratory and field were achieved, respectively for a 14 hour residence time (Nuttall and Younger, 2000). Alternative approaches have been trialled where Dispersed Alkaline Substrates (DAS) are used as an alternative to limestone gravel/blocks (Rötting et al., 2008; 2007). By using a fine grained 'dispersed' alkali, within a larger particle size matrix to generate porosity, complete dissolution can occur before the alkali is armoured by precipitates (Rötting et al., 2008). In preference to calcite, magnesium hydroxide can generate sufficient alkalinity to buffer pH to 8.5-10, at which point the solubility of divalent metals is typically low (Rotting et al., 2007; Rötting et al., 2006). Throughout a 12 month laboratory trial, zinc concentrations were reduced from 300mg/L influent, to below generic ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) detection limits in the effluent (Rotting et al., 2007). Field scale trials, however, yielded far lower removal rates (5% reduction in zinc over a minimum residence time of 24 hours (Rötting et al., 2008)), potentially

explicable due to the use of calcite over magnesium hydroxide, although the importance of scale in this instance (field vs. lab) is difficult to ascertain. None of these authors make reference to the amenability of waste substrate to metal recovery or decontamination (Rötting et al., 2008; Rotting et al., 2007; Rötting et al., 2006).

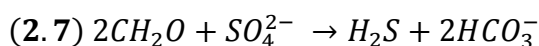
A study by Motsi et al. (2009) employed natural zeolite to remove metals from synthetic mine drainage containing metal concentrations of 400, 120, 20 and 20mg/L of iron, zinc, copper and manganese, respectively. Removal rates achieved a 67.8% reduction in dissolved zinc over the 6 hour trial, most of which was removed during the first 40 minutes (Motsi et al., 2009). It was noted that adsorption to the zeolite surface was not the sole removal mechanism, as the precipitation of metal hydroxides within the reaction vessel occurred. This was thought to result from H^+ ion sorption, allowing pH to rise (Motsi et al., 2009). Zeolites could well provide effective metal removal from metalliferous waters, particularly those which are zinc rich due to preferential sorption of this metal compared to others (Motsi et al., 2009). Competing H^+ ions and iron are often documented as problematic in sorption based systems (Wingenfelder et al., 2005). Deorkar and Tavlarides (1998) present data from lab-scale trials of Inorganically Chemically Active Adsorbents (ICAAs) for the selective removal of iron, copper, zinc, cadmium and lead from mine waters. ICAAs are formed from chelating agents immobilised on a ceramic support that provided stable adsorption for 20 cycles and could subsequently be stripped with sulphuric acid, which would allow recovery of metals (Deorkar and Tavlarides, 1998). Almost full selective removal of individual metals was seen for a 7 – 8 minute residence time, although the size of system was not presented (Deorkar and Tavlarides, 1998).

Hydrous Ferric Oxide (HFO), a waste product from coal mine water treatment, was formed into pellets and trialled as a sorbent for the removal of zinc from hard-circum neutral mine waters (Mayes et al., 2009b). Removal efficiencies in the pilot unit were relatively high (32%) for an influent concentration of 1.5mg/L zinc, considering the low residence time of the field based system of 49 minutes (Mayes et al., 2009b).

Unfortunately, however, an effluent pH of up to 11.8 was seen due to dissolution of the portlandite cement binder that released hydroxide ions. The formation of calcite crusts on the pellets and the inside of the tank (as a product of portlandite dissolution) and algae growth provided additional removal mechanisms for zinc; however, upon die-back of the algae in autumn, the system became a net-exporter of zinc (Mayes et al.,

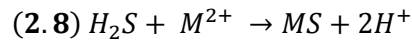
2009b). Further investigations into coupled metal removal from mine waters and bio-oil production has been investigated by Raikova et al. (2016), albeit that the cited article focuses on the process of oil recovery, rather than mine water treatment (Raikova et al., 2016). Another sorption approach using HFO has been investigated in a pilot scale study by Cui et al. (2012). A stirred tank reactor with settling tank and sand filter was successfully employed to remove metals from aqueous solutions, achieving removal rates of 99.8% zinc over 60 days (Cui et al., 2012). While high removal rates were also seen (~45g/m³/d for zinc), the mechanisation of the process places this system within the active treatment category (Cui et al., 2012). Furthermore, substrate life-time was just 70 days, meaning that frequent substrate replenishment and disposal of wastes is likely to be required (Cui et al., 2012).

Bacterial oxidation processes are somewhat ineffective at removing many metals at circum-neutral pH (Kleinmann, 1990), yet bacterially mediated sulphate reduction is a well cited removal mechanism within passive compost treatment systems (Jarvis et al., 2006; Hallberg and Johnson, 2005; Younger et al., 2003; Chang et al., 2000a; Hamilton et al., 1999; Hedin et al., 1994a). Furthermore, its application in the management of mine water pollution is not a new concept and was first explored more than four decades ago (Tuttle et al., 1969). Bacterial sulphate reduction is commonly harnessed by compost based treatment systems in Vertical Flow Pond (VFP) configurations, where compost substrates are submerged to maintain anaerobic conditions essential for sulphate reducing bacteria (Jarvis et al., 2015; Cheong et al., 2012; Rose, 2006; Gusek, 2002). Both alkalinity generation and sulphide production within compost systems are critical microbially mediated processes in the treatment of acidic and metalliferous mine drainage (Johnson and Hallberg, 2005a; 2005b). Sulphate Reducing Bacteria (SRB) oxidise short chain organic molecules, derived from the microbial breakdown of organic matter within the substrate, in a dissimilatory process reducing sulphate to sulphide (Postgate, 1979). Consequently, the availability of a suitable organic carbon source and sulphate are key rate limiting factors (Kleinmann, 1990). In the simplified Equation 2.7 after Hedin et al. (1994a), sulphates are reduced to hydrogen sulphide:



Organic matter + Sulphate → Hydrogen sulphide + Bicarbonate

Hydrogen sulphide then rapidly reacts with dissolved metals by Equation 2.8:



Activity of SRB occurs below an E_h of -100mV and therefore exclusion of oxygen is insufficient: reducing conditions must be achieved and maintained within the system (Postgate, 1979). Removal is consistent with metal sulphide solubility products, with copper, lead zinc, and cadmium removed first (in order) over nickel, iron and manganese. Table 2.7 provides solubility products after Hedin et al. (1994a):

Table 2.7 Solubility products of metal sulphides (from Hedin et al., 1994)

CuS	4×10^{-38}	< Removed first
PbS	1×10^{-29}	
ZnS	4.5×10^{-24}	
CdS	1.4×10^{-23}	
NiS	3×10^{-21}	
FeS	1×10^{-19}	
MnS	5.6×10^{-16}	< Removed last

Mayes et al. (2011) present data from a laboratory scale trial of a low-residence bioreactor, that includes methanol dosing as a supplementary carbon source. A net-acid synthetic mine water with a zinc concentration of 15mg/L was passed through a treatment column with a 12-14 hour residence time, for a period of 422 days (Mayes et al., 2011). For the first 4 months the system removed 99% of the dissolved zinc and, for the duration of the trial, >99% of the copper and lead were removed (Mayes et al., 2011). It was found by this study and others that metals were associated with non-sulphide bearing phases, suggesting that additional removal mechanisms such as adsorption and carbonate formation are important (Mayes et al., 2011; Matthies et al., 2009; Neculita et al., 2008b). There has been some discussion of the amenability of wastes from compost bioreactors to metal recovery (Gusek et al., 2006; Gusek and Clarke-Whistler, 2005) but, other than very preliminary work undertaken by Jarvis et al. (2014), there is no evidence of this having been investigated experimentally.

Pilot scale compost bioreactors installed under the MAGIC Research Project in 2010 have shown significant success in removing zinc in the field (Jarvis et al., 2014). The

pilot units were installed at two sites in Great Britain using Vertical Flow Pond (VFP) configurations. Mean removal efficiencies were 68% and 63% total zinc at Nenthead, England and Cwm Rheidol, Wales, respectively (Jarvis et al., 2014). Residence times were designed to be 19 hours at Nenthead and 14 hours at Cwm Rheidol, although tracer tests and variable flow rate caused substantial variability at the latter site in particular (Jarvis et al., 2014). Gandy and Jarvis (2012) use data from the system at Nenthead to demonstrate the importance of engineering scale when assessing removal rates, where lab-scale columns far outperform larger field based versions. It was suggested that preferential flow rates may have played a significant part in the lower performance of the pilot system compared to the laboratory scale column (Gandy and Jarvis, 2012). Subsequently, a full-scale system utilising compost bioreactors in a VFP configuration were installed at the Force Crag Mine in Cumbria, England based upon empirical data gathered at Nenthead (Jarvis et al., 2014). A detailed assessment of treatment performance at Force Crag is provided in Chapter 5.

2.8.6 Summary of treatment technology and potential for metal recovery

From the review of the literature, active treatment of mine waters using sulphate reduction to form a metal sulphide product is the only process effectively demonstrating metal recovery (although other technologies may be amenable). Yet active sulphide treatment plants require a substantial investment both for construction and operation (Younger et al., 2005). Consequently, such systems are best suited to discharges with very high metal loadings and flows which would mean passive treatment systems would be too large (Younger, 2000). Furthermore, there are a lack of mineral processing facilities in Britain which would be able to deal with a stream of metal sulphides recovered by active sulphide plants (Gray et al., 2012). Passive treatment, therefore, appears to be better suited to sites where metal loads are relatively modest and funds for remediation limited, such as is the case in Britain. Table 2.8 provides a summary of passive metal mine water treatment technologies which have been discussed, noting specifically their performance for zinc removal and information on substrates and zinc accumulation. Where volumetric removal rates and metal accumulation rates are not shown in the literature, they have been calculated where sufficient data are available.

Chapter 2. Assessment of the resource potential of metal mine waters

Table 2.8 Performance for a range of experimental metal mine water treatment systems tackling zinc

System name/loci	Removal mechanism:	Zinc Vol. removal rate (g/m ³ /d)	Efficiency (%)	Monitoring period (months) / scale*	Zinc accumulation details.
Nenthead, England, CBL (Nuttall and Younger, 2000; Nuttall, 1999)	Zinc carbonate precipitation	0.9	22	3 P	Smithsonite precipitation in tank (0.01% w/w calc.)
DAS (SW Spain) (Rötting et al., 2008)	Fine grained alkali within larger porous matrix	968	5	12 P	6.8kg Zn retained in 1.8m ³ substrate (0.05% v/v calc.)
Natural zeolite (Motsi et al., 2009)	Zeolite mineral within column for sorption	325 (equivalent)	67.8	L (Batch – 6 hr exposure)	Various metals Retained on zeolite
ICAA (Deorkar and Tavlarides, 1998)	Immobilised ligands on ceramic supports providing selective sorption sites	??	~100	L (7 – 8 min residence time)	Selectively sorbed metals can be stripped with H ₂ SO ₄
Pelletized HFO, Scraithole, England (Mayes et al., 2009b)	Sorption to hydrous ferric oxide	8.1	32	10 P	Algae and secondary minerals a significant sink (0.23% w/w)
Bioreactors (Mayes et al., 2011)	Bioreactors with shells/limestone and methanol dosing	9.9 – 11.4	90 - 99	13 L	~0.1 – 0.8% measured in substrate; largely Fe-Mn oxide bound
Nenthead VFP, England (Jarvis et al., 2014)	Sulphate reduction	0.89	67	7.5 – 14 P	Metal sulphides in substrate (<0.67% w/w measured)
Constructed wetland (Song et al., 2001)	Various suggested	0.01	72	10 L	Metals retained in substrate
Dealginated seaweed, mid Wales (Hartley, 2009; Pearce et al., 2007)	Seaweed matrix in tank for sorption	705	97 (for first 12hrs; Zn export after 5 days)	1 P	Metals sorbed to seaweed (up to 3.2%w/w; 1.3%w/w average)

*L = Lab; P = Pilot; F = Full

Closed bed limestone and DAS systems show relatively poor removal efficiencies, accumulating relatively low concentrations of zinc over experimental periods and with no discussion in respective papers of the amenability of wastes to metal recovery (Rötting et al., 2008; Nuttall and Younger, 2000). Data from lab-scale trials of zeolites

and ICAs suggest that techniques adopting adsorption mechanics could potentially provide both high efficiencies and removal rates (several orders of magnitude higher than alternatives) but the long-term effectiveness (sorption capacity) of these materials are undemonstrated in the field (Motsi et al., 2009; Deorkar and Tavlarides, 1998). However, acid washing may offer a mechanism of recovering metal salts from sorbents (Deorkar and Tavlarides, 1998). Longer term field trials by Mayes et al. (2009b) using recovered HFO from coal mine discharges suffered a series of problems, relating to a cement binder and algae growth in the pilot unit. Alternative methods for sorption media are presented by Perkins et al. (2007); Vaclav and Gulikova (2007); Warrender and Pearce (2007) showing proof of principle tests conducted at laboratory scale which demonstrate high removal rates and accumulations of significant levels of zinc in substrates over short duration studies. Over longer time periods, however, sorption capacity can be readily reached within short retention time systems (Warrender et al., 2011). Furthermore, Gandy and Jarvis (2012) demonstrate that system scale has a significant bearing upon performance, with significantly lower removal rates seen in parallel pilot scale systems compared to laboratory columns operated in the field. It was suggested that the formation of preferential flow paths in the pilot unit reduced the effective residence time, and consequently the removal efficiency, compared to the laboratory scale version (Gandy and Jarvis, 2012). Passive treatment using compost bioreactors is demonstrably effective at treatment (Jarvis et al., 2014; Mayes et al., 2011), and has shown great potential for wider implementation to treat metalliferous mine waters due to combined high volumetric removal rates and efficiencies coupled with long duration field trials. It was for these reasons, among others, that this treatment technology was selected for implementation at the Force Crag Mine in Cumbria, which is a case study investigated in this thesis (Jarvis et al., 2015; Moorhouse et al., 2015).

2.9 Passive treatment system lifetime

Passive treatment systems constructed from earthworks and minor engineered structures, such as capture chambers and transfer pipelines, require little regular maintenance; only occasional intervention is required, for example to keep channels clear and control vegetation (PIRAMID Consortium, 2003). Regardless, over time accumulation of metals either within settlement lagoons or within substrates reaches a point at which the system is no longer operating effectively and major intervention is

required to deal with wastes generated (Gray et al., 2012; Jarvis et al., 2007). Reducing the frequency of this activity by extending system lifetime offers a mechanism to offset the costs of treatment.

Given the absence of published long-term monitoring data, forecasting compost bioreactor treatment system life times is a challenging task. The limitations on system longevity are complex and may relate to a range of site specific factors. Whilst a notional 10 year life-time has been assigned to the Force Crag case study system by its operator (The Coal Authority, 2014), there is little certainty around this figure.

2.9.1 Database of known systems tackling zinc

During the course of this research, a database was compiled for all known passive bioreactor type treatment systems which tackle zinc as a major contaminant. This database was produced using data sourced from scientific articles where available, but also grey literature such as conference presentations and government documents (e.g. ITRC, 2013). Passive treatment systems based around the compost bioreactor approach (typically in VFP configurations) are not uncommon, and are typically employed to remove aggressive acidity and metals such as iron and aluminium (numerous examples from Korea and USA in: Cheong et al., 2012; Rose, 2006 respectively). Systems for removal of metals such as zinc are, however, less common; the database produced here includes all known field-scale systems, although some pertinent laboratory scale examples are also included. 13 full-scale systems have been identified along with a further 12 pilot units. 5 laboratory-scale systems are also included, although more are documented in the literature. The database is included in full as Appendix A and was developed to understand rates of accumulation of metals across a range of sites. This will help to contextualise the Force Crag system in terms of performance and suggest factors which may limit system lifetimes.

2.9.2 Limits on system lifetime and estimates from the literature

Treatment system failure can be characterised by a breakthrough event which, for the purposes of this thesis, means where sustained treatment performance ends and metal loadings in effluents increase significantly and permanently, independent from external factors such as influent water quality (for examples, see Song et al., 2012; Mayes et al., 2011; Warrender and Pearce, 2007; Cortina et al., 2003; Dvorak et al., 1992).

Breakthrough may occur due to any number of factors causing the treatment process to

fail, but there is a significant lack of long-term monitoring data characterising these events, or analyses of failed systems. This is particularly the case for systems dealing with divalent metals such as zinc in circum-neutral waters, perhaps largely due to the low number in existence. Nevertheless, given the relatively high abundance of VFPs tackling acidic waters rich in iron and aluminium, these systems still offer some useful lessons.

Rose (2006) discusses a review of 40 VFP treatment systems (apparently located in Pennsylvania, USA). Approximately half of these systems were more than 7 years old, with the oldest having been operating for 14 years (as of 2006). System operating life is assumed to be around 20 years by Rose (2006). Frequent system failure within this period was documented, however, with significant issues revolving around iron oxy-hydroxide precipitation on substrate surfaces and aluminium precipitates plugging/armouring limestone drainage layers (Rose, 2006). Considering the high loads of contaminants (for example, 23mg/L aluminium in the Jennings system which failed after 7 years) it is perhaps no surprise that a catastrophic build-up of oxy-hydroxide precipitates occurred. Rose (2006) notes that higher contaminant loadings are more difficult to treat and blockage due to iron and manganese oxy-hydroxide precipitates are the leading causes of system failure. Neculita et al. (2008a) finds that hydraulic residence time also has a significant bearing on substrate porosity and permeability, decreasing significantly with higher residence times in laboratory scale tests (10d compared to 7.3d). Interestingly, VFP performance has been successfully restored by thorough mixing of the substrate, which is believed to have increased its permeability (Rose, 2006) although the effects on effluent quality were not reported. Nordwick et al. (2006) document the use of a geotextile to form a cellular structure in a compost bioreactor substrate (horizontal flow) preventing settlement of organic matter and regulating flow across the system cross-section. It is also suggested that increasing substrate (labile) organic matter may act to decrease permeability, a problem of substrates with high organic matter content from sources such as manure (Nordwick et al., 2006; Amos and Younger, 2003).

In a study by Cheong et al. (2012) of VFPs operating in Korea, organic carbon and nutrients (phosphate, nitrate) were measured in treatment system substrates comprising mushroom compost. The 15 systems investigated were between 3 and 8 years old, treating low flows of acid mine drainage (Cheong et al., 2012). Data relating to water

quality are inherently lacking although digestions undertaken on substrates report data for aluminium, manganese and iron, suggesting that these might be key metal contaminants (Cheong et al., 2012). Data indicate that significant (if variable) decreases in total organic carbon occurs in VFP systems over time. Projections by Cheong et al. (2012) based upon statistical analysis of data presented conclude that typical system life-times may be between 15 and 20 years, which agrees with estimates by Rose (2006).

Bench scale microbiological investigations by Logan et al. (2005) identified that downstream bacterial communities were reliant upon products of cellulose hydrolysis (recalcitrant element of substrate), and consequently this represents a long-term limiting factor on the performance of communities within sulphate reducing bioreactors. To overcome this, pre-treatment of substrates to reduce cellulose crystallinity, particle size or lignification is suggested (Logan et al., 2005). Additionally, the study found that lactate is a preferable supplement to sulphate reducing bacteria over alternatives such as acetate, which it was suggested may be responsible for promoting other competing microorganisms (Logan et al., 2005). Typically, systems which perform well over long periods contain a mixture of recalcitrant material and more labile carbon sources (Neculita et al., 2007).

Neculita et al. (2008a) assessed the impacts of hydraulic retention time on laboratory scale compost bioreactors, finding that increased retention times resulted in a loss of porosity and permeability. This suggests that higher mine water through-put may act to counteract reductions in system permeability which might otherwise occur over time. But even in a low-residence pilot scale bioreactor, Jarvis et al. (2014) found that substrate porosity decreased from 62% at the time of commissioning to 40% and 32% in upper and lower substrate layers, respectively, after 2 years. These studies suggest that compaction of substrates is unavoidable but might be lessened in systems with lower residence times. Additional factors relating to metal accumulation and inhibition have been investigated by Utgikar et al. (2002). Serum bottle and batch reactor experiments found that, after 50 hours, sulphate reduction rates had decreased significantly, attributable to metal sulphide formation providing a physical barrier between the bacterial cell/enzyme and the electron donor-acceptor pair (Utgikar et al., 2002). Scanning electron microscopy provided further evidence, confirming that the formation of metal sulphides in the close vicinity of sulphate reducing bacteria can act to hinder

the sulphate reduction process (Utgikar et al., 2002). These findings imply that, over time, the accumulation of metal sulphides within treatment system substrates may act to inhibit sulphate reduction, thereby leading to loss of system performance.

Since commencement of this review, monitoring at the Force Crag treatment system by this Author and others identified that water levels had risen in the VFP units, attributed to loss of permeability of the substrate. Investigations identified a jelly-like algae layer several millimetres thick which had developed on the substrate surface, impeding infiltration of mine water (*pers comm.*, J. Byrom, The Coal Authority 2015). This was manually removed and normal flow was restored.

To summarise, system failure has been known to result from:

- Plugging due to iron and aluminium precipitates.
- Loss of porosity and permeability due to compaction over time or due to high residence times, or due to algae growth on substrate surfaces.
- High cellulose crystallinity limiting microbial hydrolysis of recalcitrant fractions.
- Physical hindrance of SRB by metal sulphide formation.

2.10 Possibilities for extending passive treatment system life-times

Overcoming the modes of failure described above may offer a way to extend system life-times, prolonging the duration between costly refurbishments and waste disposal. The activities discussed in this section may offer means of restoring system operation without entailing substantial cost.

2.10.1 *Increasing labile carbon*

Findings by Logan et al. (2005) show that crystalline cellulose may limit bacterial sulphate reduction over time. One possible mechanism to overcome this may be by dosing with enzymes to target and break down some of the highly recalcitrant cellulose material. This may be conducted later in the system's life, when labile carbon fractions such as sugars are depleted but cellulose remains. There are a vast range of cellulosic enzymes available used in bio-technological processes to break cellulose down into simple sugars (Teeri, 1997). This approach would need to be tested.

Alternatively, labile carbon sources may be added later in system life by dosing with a liquid carbon source. Mayes et al. (2011) and Costa et al. (2009) demonstrated at lab-scale the effectiveness of methanol and ethanol, respectively (the latter in the form of wine waste), in driving microbially mediated bacterial sulphate reduction for treatment of mine waters. Sodium lactate and biodiesel waste (64% glycerol) have also been successfully employed by other authors (Zamzow et al., 2007; Jong and Parry, 2003). By using waste materials as a nutrient source, costs of restoring treatment performance may be very low. Further investigations by Jarvis et al. (2014) with brewery waste as a carbon source had little success in achieving improved zinc removal rates in a pilot-scale bioreactor, although why this was the case is not clear (Jarvis et al., 2014). At the time of writing, further investigations are underway at Newcastle University trialling untreated sewage, propionic acid, methanol and glycerol as carbon sources to improve treatment performance of aged substrates.

In an alternative approach, Su et al. (2012) demonstrated that, under controlled laboratory conditions, microbial catalysed sulphate reduction can be achieved using a polarised electrode as the sole electron donor. 72% coulombic efficiency was achieved, indicating very efficient use of electrical charge by bacteria (Su et al., 2012). While demonstrating proof of principle, it is unknown whether this approach might be successful in stimulating sulphate reducing bacteria in somewhat more complex compost based treatment systems.

2.10.2 Selective harvesting and replenishment of substrates

Where metal accumulation is identified as a factor restricting system performance, selective removal may be used to restore the treatment process, given that metals preferentially accumulate in substrate layers closer to inlets (e.g. Rötting et al., 2008; Knox et al., 2006; Gibert et al., 2003). However, a detailed analysis of a down-flow pilot-scale column identified that while zinc, nickel and cadmium preferentially increased to very high levels in upper substrate layers, the inverse was the case for manganese and iron which was measured at greatest concentrations in lower layers (Neculita et al., 2008b).

2.10.3 Overcoming reduction in porosity and permeability

Several factors have been identified which, over time, will act to decrease the porosity and permeability of substrates themselves. Realistically, the only means of restoring

these properties would involve disturbing the substrate. Rose (2006) documents the successful restoration of treatment performance in a VFP system, which was achieved by excavation/mixing of the substrate. Any temporary impact upon the effluent of the treatment system is, however, not discussed.

It is evident that there are many mechanisms for system failure, but also potential for overcoming these to some degree to extend system life-times. There will, however, come a time at which treatment performance cannot be restored by minor interventions, and thus a full refurbishment is required to remove and replace the substrate (Gusek and Clarke-Whistler, 2005).

2.11 Management of spent passive treatment system wastes

2.11.1 Landfill disposal

European waste classification and waste acceptance criteria testing (a leach test used for assessment of waste classification (BSI, 2002)) of samples from the Nenthead pilot-scale compost bioreactor determined that the substrates were a hazardous waste (NRW et al., 2015; ESG, 2013). Furthermore, due to a high organic content, pre-treatment by high temperature incineration was deemed necessary before disposal (Atkins, 2014b). Assuming spent substrates from the full scale system at Force Crag would be similarly classified (they have the same specification as those from Nenthead and are also used for zinc removal), Atkins (2014b) has determined the cost of disposal to be between £580,250 and £1,846,250 from three waste management company quotations. This equates to £400 - £1,750 per tonne, which is substantially greater than the disposal cost of HFO produced by aerobic treatment of ferruginous waters, which has been quoted as £79 - £129 per tonne (Sapsford et al., 2015). On the basis of financial considerations alone, there is a strong case for exploring decontamination and re-cycling of this material.

2.11.2 Micro-fertiliser applications

Zinc deficient soils limit crop yields in many parts of the world, and can lead to severe health impacts upon humans where zinc intake is limited (Cakmak, 2008; Hacisalihoglu and Kochian, 2003; Salgueiro et al., 2000). Whysner et al. (2012) suggests that where zinc deficiency exists in agricultural soils, wastes from mine water treatment may be used as a low-cost nutrient source, provided that other potentially harmful substances

are at sufficiently low concentrations. Industrial waste products such as these may be used to improve zinc deficient soils; however, potentially toxic elements such as arsenic and cadmium contained in wastes may be problematic if not minimised (Alloway, 2008). Assuming mine water treatment wastes have a favourable composition, fertiliser applications in zinc deficient areas may offer a beneficial disposal route for these materials (Whysner et al., 2012); albeit that the likely markets for such a material would be overseas from Great Britain, given the global distribution of soil types associated with zinc deficiency (Figure 2.12).

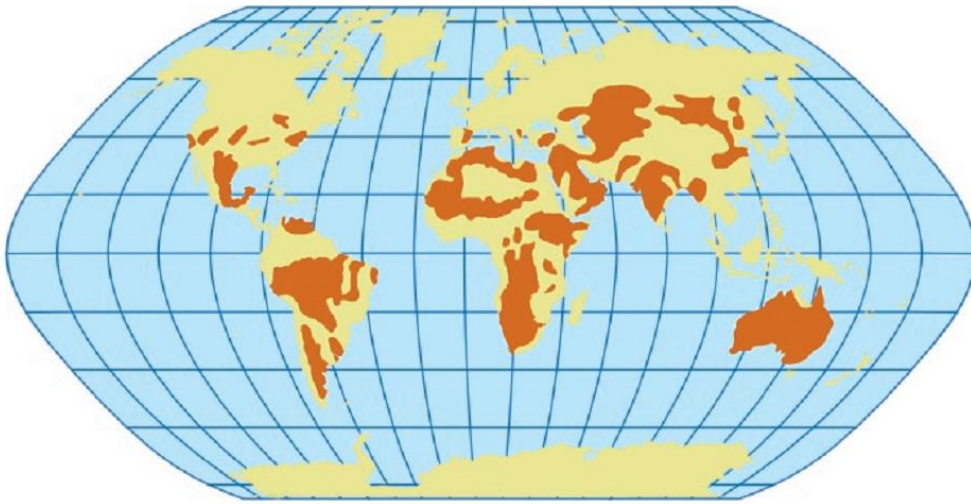


Figure 2.12 Soil types associated with zinc deficiency, shaded brown (Alloway, 2008)

2.11.3 Recovery of metals from passive treatment wastes

It may be that metals could be recovered from treatment system wastes for use in metallurgical applications, as a substitute for mined ores. Typical ore cut-off grades for zinc and lead of <1% are suggested by Gray et al. (2012). While this figure will clearly differ between facilities, dictated by economic and other factors, it provides a useful yardstick for the typical volumes dealt with by the mineral processing industry. Davenport et al. (2002) suggest that for copper, typical cut-off grades of between <0.5 – 2% are applicable for financially viable extraction from open pit to deep mines, respectively. This corroborates broadly with Rosenqvist (2004, p.178) who suggests that copper cut-off grades are often of the order >0.5% due to modern processing techniques. Nevertheless, there are a multitude of variables, such as commodity price, processing cost and capacity which affect cut-off grades (Asad, 2007). To complicate matters further, cut-off grades require careful calculation where multiple minerals are to be extracted (e.g. Ataei and Osanloo, 2004; Osanloo and Ataei, 2003), or where ore

bearing rocks may have other useful applications (Rosenqvist, 2004). Before the ore can be exported to smelting facilities, processing is required (normally involving crushing and flotation processes on-site) to increase the metal concentrate to 20 – 30% (Rosenqvist, 2004).

Sampling data by Jarvis et al. (2012b); Hartley et al. (2007); Pearce et al. (2007), indicate that metals in some parts of pilot units accumulate to levels close to and in excess of ore cut-off grades, respectively (Table 2.8). Field scale trials of de-alginated seaweed as a sorbent demonstrated very high volumetric removal rates and efficiencies (Hartley, 2009; Hartley et al., 2007; Pearce et al., 2007; Perkins et al., 2007). Analysis of substrates found that zinc concentrations up to 2.4% dry w/w accumulated within de-alginated seaweed (Hartley et al., 2007). At these concentrations, the substrate product is above typical ore cut-off grades. The principal problem with this pilot unit was, however, that sorption capacity for zinc and cadmium was rapidly reached and the treatment system efficiency had dramatically decreased after a period of several days (Pearce et al., 2007). Clearly the short-term performance of the system shows great promise, but if rudimentary scaling were to be applied to increase the longevity of a system operating at high efficiency for a period of say 5 years, then a system volume of 144m^3 (48m^3 substrate) would be required to deal with zinc within the experimental flow rate. This, in effect, decreases the volumetric removal rate to $0.19\text{g}/\text{m}^3/\text{d}$ for the whole system (compared to $0.89\text{g}/\text{m}^3/\text{d}$ from long-term operation of a pilot compost bioreactor at Nenthead, Cumbria (Jarvis et al., 2014). Nonetheless, with the high levels of metal accumulation reported by Hartley et al. (2007), the outlook for metal recovery from passive systems is rather positive.

2.11.4 Characterisation of mine water treatment wastes

Zinck (2005) suggests that one of the most significant knowledge gaps in the management of mine water treatment waste is accurate characterisation. In Britain, some efforts have been made to characterise sludge from coal mine water treatment systems in some detail (Hancock, 2005; Dudeney et al., 2003). At the time of writing, there are no mature compost-based metal mine water treatment systems within Britain requiring disposal of wastes. Consequently, it is somewhat difficult to accurately characterise the wastes generated by this type of system, although it is likely that this situation will change in the future. Costa et al. (2009) provide an example of an analysis of material from a laboratory scale treatment system which employed

bacterially mediated sulphate reduction to remove metals. No crystalline sulphide minerals were identified, but sulphides were present as amorphous phases in addition to the presence of carbonate and hydroxide metal precipitates (Costa et al., 2009). Other examples of uncertainty over metal retention mechanisms can be cited within the literature, particularly where biological processes are involved (Mayes et al., 2009b; Rötting et al., 2008; Hamilton et al., 1999). This can be attributed to heterogeneity within passive treatment systems resulting in a range of removal processes, and therefore a range of different solid metal phases consequently impacting upon designation of materials for disposal (Gray et al., 2012).

2.12 Methods for metal recovery from passive treatment substrates

Accurate characterisation of substrates or wastes for effective metal extraction will undoubtedly be necessary prior to design and implementation of any recovery system. It has been previously reported that no metal recovery or decontamination processes have been applied to wastes from passive metal mine water treatment systems (Gray et al., 2012; Gusek and Clarke-Whistler, 2005); this apparently continues to be the case from in-depth review of the literature undertaken during this study and discussions with industry specialists (*pers comm.*, J. Gusek, Sovereign Consulting 2015). A preliminary overview of techniques available for metal recovery from other wastes is provided in the following sections and which may be applicable to passive treatment system wastes.

2.12.1 Physical separation

Separation of materials on the basis of physical characteristics is a fundamental principle adopted by the mining and minerals industry. Mineral processing activities require the separation of ores from gangue (non-ore minerals). This process, known as ‘ore dressing’, involves an initial phase of crushing and grinding to liberate individual grains. The following processes, detailed by Rosenqvist (2004) and Wills (2006), separate the valuable ore grains from the gangue which is discarded.

Following crushing and grinding of the ore to typically <0.1mm by a series of machines, the fine grained material is screened from larger particles, which are re-circulated or given special grinding treatment. A technique known as classification can also be used, where the settling velocity of the particles determines if they are retained in the classifier or taken away in the flow of fluid (often water) (Wills, 2006;

Rosenqvist, 2004). Classification separates mineral grains on both particle size and density.

Concentration of the ore separates the ore mineral from the gangue, to produce a high grade concentrate. A number of techniques can be adopted at the concentration stage after Wills (2006) and Rosenqvist (2004):

- Sorting; either manual or computerised selection of ore from other rock on a conveyor.
- Gravity separation; this can handle a large particle size distribution and operates more effectively when there is a wide density range between mineral particles.
- Flotation; where air bubbles are passed through a tank of water containing the mineral grains, the hydrophobic nature of sulphide minerals allow them to be lifted by the air where they can be skimmed off the surface. The addition of ‘frothers’ helps to generate bubbles on the surface to aid recovery. Complex sulphide minerals can be selectively separated by the phased use of various additives.

Finally, the wet concentrate is separated by thickening (settling and flocculation) and/or filtration (Wills, 2006; Rosenqvist, 2004).

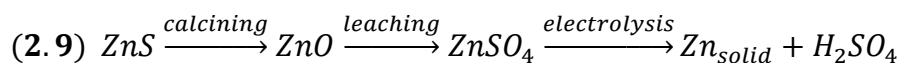
Pressure for the remediation of contaminated land has led to the development of industry specific pollutant recovery technologies (CL:AIRE, 2007). Largely based upon methods used by the mining industry, remediation equipment may be particularly applicable to the recovery of metals from mine water treatment substrates, considering, for example, the broad physical similarity of compost materials used by bioreactors to some soils. For example, it has been suggested that given the nature of VFP substrates, crushing and grinding processes would not be required to reduce mineral size fractions or liberate the ore from the substrate although classification processes may be useful (Gusek et al., 2006). Such methods include hydrocyclones, fluid bed separation and flotation allow smaller, typically more contaminated soil particles to be separated from larger, cleaner particles (Mulligan et al., 2001). A list of techniques is provided in Table 2.9.

Table 2.9 A range of techniques used by the contaminated land industry for soil washing adapted from CL:AIRE (2007)

Exploitable feature	Process Equipment
Size	Vibratory screens (sieves), sieve bends, trommel (rotary) screens
Hydraulic size (settling velocity)	Classifiers, hydrosizers, hydrocyclones, specific gravity jigs, sluices
Dense media separators	Spirals, shaking tables
Surface chemistry	Froth flotation systems
Magnetic susceptibility	Low intensity magnetic drums, induced magnetic separators, high intensity magnetic separators

2.12.2 Pyrometallurgy

Upon recovery of zinc concentrate from an ore, for example, the following processes are commonly adopted to convert this into a pure metal product. Sphalerite (ZnS) dissolution in acid is relatively slow (Rosenqvist, 2004): pyrometallurgical processes of calcining of the ore to convert ZnS to zinc oxide (ZnO) are undertaken before acid leaching. The leach liquor concentrate is then subject to electrolysis, converting the dissolved zinc to zinc metal (Zn) and sulphuric acid (H₂SO₄) according to Equation 2.9 after Rosenqvist (2004).



Drying and calcining processes involve the liberation of physically and chemically bound substances, respectively from the ore (Rosenqvist, 2004). Drying is typically a low temperature activity to achieve evaporation of water, whereas decomposition of some hydrated minerals can be more excessive, such as Al₂O₃ which requires over 1,000°C to remove the last traces of chemically bound water (Rosenqvist, 2004). At this temperature, combustion of organic matter would also occur.

Combustion of mine water treatment substrates with high organic matter content may be a suitable mechanism for concentrating materials, and may take the form of the ‘roasting’ step in conventional metallurgy (Gusek et al., 2006). Other authors have, however, suggested that incineration of wastes with low metal content, to provide drying and loss of organic matter by burning, may increase the subsequent success of hydrometallurgical extraction of metals from the bottom ash (e.g. Gray et al., 2012;

Morper, 1986) Alternatively, if metal concentrations are sufficiently elevated in the bottom ash, it may be exported directly to a smelter (Gusek and Clarke-Whistler, 2005). On face value, these approaches appear to offer an effective way of dealing with waste materials from passive metal mine water treatment systems; the difficulty being that the material would require transport to a specialised processing facility, and large quantities of energy would be used in the recovery process. Lower impact techniques, which might be feasibly undertaken at the treatment site, would therefore be preferable.

2.12.3 *Hydrometallurgy and soil washing*

The use of chemical processes in the extraction of metals is a well-established practice covering a wide range of approaches, including those which can be applied to low grade ores and wastes. Low-grade mined metalliferous ores are commonly in the form of metal sulphide minerals, principally excepting gold ores that occur as native metal in very small grains within host rock (Gribble and Hall, 1992). Metal sulphide minerals may well be present in waste materials from sulphate reducing bioreactors (Jong and Parry, 2004). In the case of industrial mineral processing applications, the following steps normally follow, after Rosenqvist (2004):

- Leaching (acid, caustic or complex forming solvent to form pregnant solution)
- Purification (either precipitation or solvent extraction of unwanted products)
- Precipitation of wanted product (chemical or electrochemical methods)

Alternatively, approaches used by the contaminated land industry may be suitable for recovering metals from mine water treatment wastes. Table 2.10 outlines a range of lixivants used for metal recovery from contaminated soils.

Chapter 2. Assessment of the resource potential of metal mine waters

Table 2.10 Metal removal efficiencies from contaminated soils by soil washing.

Soil	Washing method	Agents	Metal	Concentration (mg/kg)	Removal (%)	Reference
Artificially contaminated	Column	Na ₂ S ₂ O ₅	Pb Zn	204 79	61 94	(Abumaizar and Khan, 1996)
Artificially contaminated	Column	HCl EDTA CaCl ₂	Pb	500–600	85 100 78	(Reed et al., 1996)
Contaminated soil	Batch	EDTA, NTA and citric acid plus reducing reagents: sodium borohydride, Na ₂ S ₂ O ₅ and thiourea dioxide	Pb Cu Zn	21,560 1241 3729	99 99 97	(Peters et al., 1989)
Artificially contaminated	Column	NaOCl Diethylenetriamine pentaacetic acid (ADTPA) Tetrasodium EDTA	Zn	4450	38–81	(Davis and Singh, 1993)
Contaminated soil	Batch	S-carboxymethyl-cysteine (SCMC) N-2-acetamidomindiacetic acid (ADA) Pyridine-2,6-dicarboxylic acid (PDA)	Cd Cu Pb Ni Zn	2 5 100 6 290	80–100 (for all metals)	(Chen et al., 1995)
Bank sediment	Batch	Na ₂ EDTA	Cu Zn	970 2500	55 32	(Yu and Klarup, 1994)
Contaminated soil	Batch	EDTA	Pb	350	95	(Allen and Chen, 1993)
Contaminated soil	Batch	HCl EDTA	Pb	1000	90	(Cline et al., 1993)
Spiked soils	Batch	Saponin biosurfactant	Cu Cd Zn	50-1000	39-62 (silty clay), 82-90 (loamy sand), 67-88 (loam)	(Gusiatin and Klimiuk, 2012)
Mining contaminated soils	Batch, stirred	HCl HNO ₃ H ₂ SO ₄ EDTA	Cu Zn Mn Pb	4100 55900 6500 64195	10-46 38-97 42-93 6-83	(Moutsatsou et al., 2006)
Contaminated soil	Batch	Dissolved Organic Carbon	Zn	992	36 (pH3) 44 (pH2)	(Chiang et al., 2016)

Generally, the data presented show high extraction efficiencies for a range of contaminated materials, using a number of different lixiviants in predominantly batch experiments. Abumaizar and Smith (1999) found that a lixiviant solution comprising a combination of EDTA (ethylenediaminetetraacetic acid – 0.01 molar) and $\text{Na}_2\text{S}_2\text{O}_5$ (sodium metabisulphite - 0.1 molar) was highly effective at recovering zinc. It was suggested that the reducing agent ($\text{Na}_2\text{S}_2\text{O}_5$) served to weaken the soil-metal bond, making the metal more amenable to complexation with the ligand (EDTA). It was noted, however, that the effectiveness of the lixiviants was markedly reduced in column experiments over batch (Abumaizar and Smith, 1999), an issue also encountered by Jarvis et al. (2014) when conducting preliminary leaching of a mine water treatment substrate.

Metal recovery tests from a mining contaminated soil undertaken by Moutsatsou et al. (2006) found both hydrochloric acid and sulphuric acid were the most effective reagents for zinc recovery, achieving $\geq 78\%$ recovery. Tichy et al. (1996) provide an additional example demonstrating the potential for extraction of zinc from contaminated soil using sulphuric acid. Zinc solubilisation was shown to peak above pH 3, however aluminium solubilisation only increased substantially below this pH (Tichy et al., 1996). Consequently, careful optimisation of pH during acid extractions can recover zinc but minimise damage to key aluminium soil forming minerals (Tichy et al., 1996).

In practice, acid leaching of metal sulphides is often driven by microbially-mediated reactions and can be an unwanted process, such as in the generation of polluting acid mine or rock drainage (Keith and Vaughan, 2000). This process can be harnessed to extract metals from low grade ore in a method known as biomining or bioleaching, which falls under the heading of hydrometallurgical techniques (Johnson, 2013). This practice is relatively well established in the metals industry (Johnson, 2013; Renman et al., 2006; Lizama, 2001) often undertaken within rudimentary heaps (heap leaching) or occasionally stirred tank reactors (Morin et al., 2006; Brierley and Brierley, 2001)

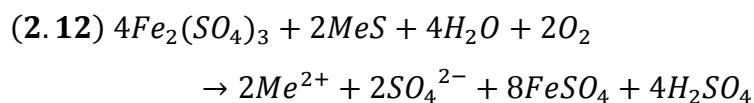
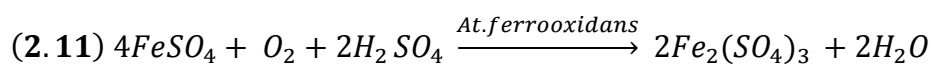
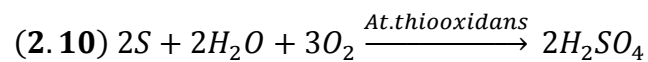
2.12.4 Biohydrometallurgy

Biomining might be used where it is either technically infeasible or prohibitively expensive to utilise chemical or pyrometallurgical processes (Brierley and Brierley, 2001). Heap leaching is a commonly adopted biomining process used by the mining industry due to the volumes of material dealt with (Johnson, 2013), although the same

biotechnology can be applied to industrial wastes and contaminated residues for both decontamination and economic recovery of metals (Morin et al., 2006). Here, studies are also discussed that operate, or simulate, bioleaching within stirred tank reactors.

Three organisms are widely cited in bioleaching studies: Autotrophic bacteria (e.g. *Acidithiobacilli* spp); heterotrophic bacteria (e.g. *Pseudomonas* spp., *Bacillus* spp) and heterotrophic fungi (e.g. *Aspergillus* spp., *Penicillium* spp) (Wu and Ting, 2006). Pathak et al. (2009b) suggested that *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* are the most widely used organisms in heap leaching due to their ability to survive in acidic environments and oxidise insoluble iron and sulphur compounds. It has been claimed that direct bioleaching processes solubilise sulphides such as ZnS; NiS; CuS during cellular contact with micro-organisms (Pathak et al., 2009b; Liu et al., 2008). However, there is evidence to suggest that only indirect mechanisms are at work (Sand et al., 2001).

During indirect bacterial leaching, sulphur oxidising bacteria convert elemental sulphur or reduced sulphur compounds into sulphuric acid by oxidation. This is expressed as follows for *At. thiooxidans* (Equation 2.10) and *At. ferrooxidans* (Equation 2.11), respectively, where Me represents a metal. (Pathak et al., 2009b; Waksman and Joffe, 1922)



The reduction in pH caused by sulphuric acid formation can then cause further leaching of metals. A positive feedback mechanism generates further acidity and metal solubilisation (Equation 2.12).

Modelling undertaken by Petersen and Dixon (2007) found that key constraints on heap leaching methods for zinc recovery included liquid/gas phase mixing, availability of sulphuric acid for ferrous oxidation, and the generation of excessive heat in certain areas of the heap limiting the spatial viability of microbes. Alternatively, it has been shown

that the rate limiting factor in sphalerite oxidative dissolution arises from presence of accessory minerals which restrict diffusion (da Silva, 2004). Villar and Garcia (2002) determined that zinc and nickel solubilised at a pH of 6 – 6.5 (near 100% extraction demonstrated) compared to copper and chromium required a pH of 2 – 3 to initiate solubilisation, catalysed by sulphur oxidising bacteria. Sand et al. (2001) note that sphalerite (ZnS) is acid-soluble and dissolution increases as pH decreases, indicating optimum reaction rates will occur at lower pH. In addition to a favourable pH and reduced iron compounds, temperatures of 28 - 30°C, a supply of oxygen and carbon dioxide by aeration and micronutrients such as ammonia, phosphate and magnesium are required for growth of *At. ferrooxidans*, one of the key species involved in biomining processes (Bosecker, 1997). A morphologically similar species in the same genus first documented by Waksman and Joffe (1922); *At. thiooxidans*, oxidises sulphur to sulphuric acid at a faster rate than *At. ferrooxidans* (Bosecker, 1997).

Applications for bioleaching have been tested for a number of different waste materials. Henry and Prasad (2006) presented a bespoke bioleaching process for the production of compost from sewage sludge within a laboratory scale reactor. Autotrophic bacteria were employed, using elemental sulphur added to drive the process. Zinc concentrations of typically 1,738mg/kg were reduced to between 180mg/kg and 15mg/kg over periods of between 8 and 20 days. Overall, metal solubilisation efficiencies were of the order of Zn (98%) > Cu (96%) > Cr (93%) > Cd (90%) > Pb (67%).

Extraction of zinc and aluminium from industrial waste sludge has been demonstrated by Solisio et al. (2002), using an *At. ferrooxidans* culture sourced from an acid mine discharge. Extraction efficiencies in the range 72 – 78% were achieved. However, by increasing the sludge concentration, the aqueous concentrations of metals were thought to begin to restrict microbial growth and thus reduce extraction efficiencies (Solisio et al., 2002). Similarly, Wu and Ting (2006) found that the aqueous concentrations of metals inhibited fungal growth when employing fungal bioleaching (*Aspergillus niger*) to incinerator fly ash. The extraction efficiencies in this study were also in favour of zinc, which was extracted more effectively by bioleaching than parallel chemical leaching tests using a range of 0.1 and 0.5 molar acids. The general order of extraction efficiencies was as follows: Al = Zn = Mn > Cu = Pb > Fe. Wu and Ting (2006) claim that their findings were in good agreement with those by Siegel et al. (1983). High

recovery efficiencies for zinc suggests that biohydrometallurgical techniques may be suitable for decontamination and metal recovery of passive mine water treatment substrates. Furthermore, it may be feasible to conduct 'heap leach' activities at abandoned mine sites, thereby reducing the cost of transporting bulk wastes to specialist processing facilities.

2.13 Removal of metals from pregnant leach solutions

Following extraction of metals using hydrometallurgical methods, a pregnant solution typically rich in numerous metals must be dealt with. In the minerals industry, sequences of processes are often adopted to recover individual concentrated metal products. Common methods of metal separation and concentration from pregnant leach solution include hydroxide precipitation, sulphide precipitation, ion exchange and solvent extraction (Zhang and Cheng, 2007)

2.13.1 Direct precipitation methods

Hydroxide precipitation of metals from pregnant leach solutions is achievable by the introduction of alkali to raise pH (Rosenqvist, 2004). Where solutions are acidic, for example, the generation of secondary precipitates such as gypsum consume large amounts of alkali (Baltpurvins et al., 1997). Furthermore, process difficulties can be encountered with the carrying over of metal colloids (Baltpurvins et al., 1997). Kongolo et al. (2003) document the successful sequential removal of iron, zinc and cobalt from solutions. Calcium carbonate dosing and filtration removed iron as hydroxide precipitates, with cobalt and zinc losses of 5% and 3% respectively (Kongolo et al., 2003). After iron precipitation, solvent extraction was used to remove cobalt and zinc simultaneously, before separation by selective stripping with sulphuric acid solutions of different strengths. More than 90% cobalt and 90% zinc were recovered (Kongolo et al., 2003).

Turan et al. (2004) suggest a process in which zinc is recovered from primary acid leach solutions by electrowinning. Lead is simultaneously recovered from a secondary sodium chloride leach solution by addition of sodium sulphide (Turan et al., 2004).

2.13.2 Solvent extraction

Selective recovery of metals from a pregnant leach solution is often undertaken using solvent extraction methods by liquid-liquid extraction (Rosenqvist, 2004). Most commonly, Di-2-ethylhexyl phosphoric acid (D2EHPA) dissolved in an organic solution such as kerosene is employed for zinc extraction (Qin et al., 2007; Ortiz et al., 2001; Forrest and Hughes, 1978). Silva et al. (2005) found that D2EHPA was successful in the extraction of a pregnant sulphuric acid solution of 2,000mg/L zinc and 10,000mg/L nickel. When alkyl phosphoric acids such as D2EHPA are used in conjunction with an ammonium chloride lixiviant, neutralisation of H⁺ ions within pregnant solutions is achieved (Amer et al., 1995). In a process context, this negates the need for external neutralisers which complicate and add cost to the process (Amer et al., 1995). Organic phase chelating compounds can allow for extraction of specific metals from an acidic 'pregnant solution', relating to the configuration of the atoms that allows preferential binding to certain species (Burkin, 1976). Often, combinations of extractants can be used to extract different metals: Gouvea and Morais (2010) investigated organophosphorus reagents for selective zinc removal while using chelating extractants for selective recovery of copper. The application of solvent extraction techniques is well suited where concentrations of target metals in leach solutions are relatively low (Ritcey and Ashbrook, 1984.). Yet, it has been reported that solvent extraction becomes unsuitable where metals such as lead and copper are below 1,000mg/L (Valenzuela et al., 1999).

2.13.3 Electrowinning

Once a solvent solution containing metals is obtained, a series of washing processes are often required in order to remove chlorides, before electrowinning to obtain a solid metal product (Amer et al., 1995). The presence of other substances can lower the efficiency and purity of the electrowon product although addition of certain additives can improve electrical efficiency and surface morphology (Das et al., 1997).

Vegliò et al. (2003) demonstrated high removal efficiencies of copper and nickel from waste water treatment sludge, generated from sodium hydroxide dosing of an industrial effluent. Sulphuric acid was used to leach metals from the sludge before the liquor was passed through an electrochemical cell with variable pH to achieve selectivity. Metal recovery efficiencies of 94 – 99% were achieved using this approach (Vegliò et al.,

2003). Some attention has been given to the use of electrowinning in the primary treatment of waste waters: the development of carbon fibre electrodes with very high surface areas has proven to reduce copper concentrations of 400mg/L to <2mg/L (Dinardo et al., 1991). In this context, this technology may be directed to combined treatment and recovery systems for particularly polluted metal mine waters.

2.14 Active treatment and combined treatment and recovery systems

Combined treatment and recovery systems are likely to be active, given that passive treatment systems generally produce complex wastes with heterogeneous metal distribution (Gray et al., 2012). There are very few examples of combined treatment and recovery systems for the treatment of non-ferruginous mine drainage or similar effluents, and these generally use sulphate reduction processes (Bratty et al., 2006; Huisman et al., 2006). An example of a modest system operating in Colorado, treating up to a 9.5L/s flow from an abandoned silver-zinc mine, reduces zinc concentrations from 135mg/L to <67µg/L using sulphide precipitation (Kratochvil et al., 2015). The system is claimed to produce a saleable zinc-cadmium product (11.3 tonnes in 2010) that offsets the cost of treatment. It is also claimed that the cost of the plant was 33% less than the alternative lime dosing unit (BioteQ, no date), however other authors suggest that the technique is actually the more costly option (e.g. Kuyucak, 2006; Younger et al., 2005). BioteQ Ltd. has also developed the technique for the recovery of copper from a pregnant leach solution draining a low grade tailings dump (Lawrence et al., 2005). Mosher (1994) documents an example of resource recovery from a lime dosing mine water treatment plant, where waste sludge is incorporated as a feedstock to a lead smelting operation as a lime replacement. Incidental metals such as lead and copper are recovered as part of the smelting operation (Mosher, 1994). Morin et al. (2006) suggests that mine water discharges could potentially be ideal candidates for biological metal recovery, turning a problem into a resource. Morin et al. (2008) presents an example of acid mine/rock drainage containing 500mg/L copper, but this is much higher than copper concentrations found in mine water discharges in England and Wales. Indeed the relatively modest mine water discharge tackled by BioteQ (no date) has a zinc loading similar only to the worst discharges in England and Wales, as outlined in Table 2.11. Additionally, flow rates from discharges in England and Wales are proportionately far higher relative to metal loadings. This means any system would

need to be designed to accommodate high flows, which is likely to increase the capital and operational costs of this type of treatment.

Table 2.11 Top 10 mine water discharges in England and Wales ranked by zinc loading, compared to zinc load treated at an active sulphate reducing bioreactor at a site in the USA (BioteQ, no date; unpublished data courtesy of the Environment Agency, 2015);

Wellington Oro, Colorado BioteQ plant		Flow (L/s)	Zinc (t/annum)
Capacity		9.5	39
Actual treated average flow in 2010		2.3	11.3
UK Top 10 Discharges			
1	County Adit	454	33.9
2	Dyffryn Adda Adit	10	22.5
3	Hayle Adit (mid 1)	644	18.5
4	Frongoch Adit	60	10.5
5	Nant y Mwyn Lower Boat Adit	30.12	10.1
6	Pughs Adit	13	9.2
7	Hayle Adit (lower)	213	8.5
8	Meerbrook Sough	740	8.4
9	Bridford mine adit	20	7.8
10	Woodend Low Level	5.55	6.4

2.15 Passive treatment vs. active and combined treatment recovery systems

Metal sulphides are generally more stable and of a greater density than hydroxides (Peters et al., 1985). The products of active sulphide reduction plants have reportedly been of commercial value and consequently entail less of a management challenge than those of conventional alkali dosed voluminous hydroxide sludges, which would normally require landfilling (Kratochvil et al., 2015).

Passive treatment can be cost effective to implement, operate, and have a low impact on immediate natural environments (Parker, 2003; PIRAMID Consortium, 2003; Hedin et al., 1994a) but wastes can be voluminous and require disposal at significant cost where metals are elevated (Atkins, 2014b). Active combined treatment/recovery systems are,

by their nature high cost, high impact units that require close control and inputs of energy and chemicals (Mayes and Jarvis, 2011; Johnson and Hallberg, 2005a). While on face value, units of this nature may not be immediately favourable, waste volumes may be low or non-existent in the case of high density sludge (Coulton et al., 2003) or sulphide precipitation plants (Kratochvil et al., 2015) respectively. Thus, consideration of the whole life cost of active vs. passive and potential for metal recovery should be evaluated for any specific site, taking into consideration the constraints present. The key knowledge gap, and thus the obstacle in allowing this assessment to be conducted, is the technical feasibility of recovering metals from passive substrates in an economic and environmentally sound manner.

2.16 Conclusion to Chapter 2

This chapter addresses objective 1 of the thesis:

- Review the resource potential of metal mine waters nationally and identify ways in which resources can be recovered.

Accordingly, this concluding section provides a summary of the resource potential of metal mine waters, which might be used to enhance or offset costs of mine water treatment systems and their amenability to recovery. Gaps in the literature are then specified, the most pertinent of which have been investigated experimentally, as described in Chapters 3, 4 and 5 of this thesis.

2.16.1 Energy

Potential exists to harness water that discharges from mine workings and flows through pipes and channels within mine water treatment systems. Hydropower systems may offer a mechanism to harness this valuable resource, recovering energy otherwise lost at a treatment site, or provide power at remote 'off grid' treatment sites. Additionally, energy might be recovered from iron oxidation or the mixing of saline and fresh waters, although at present technology to harness this geochemical potential is only emerging (Skilhagen et al., 2008; Cheng et al., 2007; Aaberg, 2003).

Large volumes of water within the mine void lend themselves to providing or receiving heat from heating or cooling schemes. Manual data from seven mine discharges find average temperatures typically in the range of 7.3 – 14.3°C. Considering a heating

application that extracts 4°C from the mine water (ΔT), two flows yield in excess of 300kW_{thermal} power. Regular monitoring suggests that mine water temperatures are perennially stable and thus might be suitable for the extraction or dumping of heat (Banks et al., 2003). This would be easily achievable using commercially available heat-pump apparatus although there remains some uncertainty surrounding the impact of metal mine water quality on heat exchanger systems.

Table 2.12 provides a summary of energy resources associated with mine water discharges, the features that they are associated with and the power that may be recoverable.

Table 2.12 Energy resources associated with mine waters at sites in England and Wales identified from review of the literature and unpublished data

Resource	Feature	Power
Potential energy	Flowing water from mines	0.1 – 2.6kW (data from 5 metal mine water discharges)
Thermal energy	Heat contained within mine waters	35 – 324kW _{thermal} (out of 7 metal mine water discharges)

2.16.2 *Mine water treatment and potential for metal recovery*

Significant amounts of metal are discharged from abandoned metal mines in England and Wales: estimates made in this review suggest approx. £430,000 of metal (Zn; Ni; Pb & Cu) is lost to the environment per annum causing widespread pollution. Table 2.13 provides a summary of metals discharging from abandoned metal mines in England and Wales, although it must be noted that this load is spread over many geographically discrete discharges.

Table 2.13 Metals in metal mine waters cumulatively discharged throughout England and Wales (unpublished Environment Agency data, 2015)

Metal	Quantity (t/annum)
Nickel	1.8
Lead	21.2
Zinc	252.9
Copper	38.6

Where remediation is planned, passive treatment offers a low cost and low impact option, with sulphate reducing bioreactors offering both high removal efficiencies and removal rates for sustained periods, compared to alternatives (see section 2.8). A range of mechanisms have also been identified which may extend system lifetimes further, such as dosing with waste carbon (e.g. Costa et al., 2009). Over time, however, metals accumulate within treatment system substrates which will eventually need replenishing, probably after 10 or 20 years (Cheong et al., 2012; Gray et al., 2012; Rose, 2006). There have to-date been no attempts to characterise in detail passive metal mine treatment system wastes from large scale VFP systems, or in-depth investigations to recover the metals from them. Yet, it is an understanding of exactly these factors which is needed to effectively manage the wastes generated by these systems.

Technology exists to recover metals from both low-grade ores and waste materials; some of which are broadly comparable to passive mine water treatment system wastes. The processes vary in complexity, but evidence suggests that leaching might be an effective mechanism to recover metals from treatment system wastes, using either chemical reagents or biologically mediated processes (see section 2.12). These hydrometallurgical techniques are known to be deployed on waste rock heaps at mine sites (Renman et al., 2006) or from contaminated soils at development sites (CL:AIRE, 2007). As a result, metal recovery might be achievable at mine water treatment sites, without the need to transport waste materials significant distances to specialist facilities.

2.16.3 Resource recovery impacts on life-cycle costs

Several resource recovery themes have been identified by this review which might be used to reduce the costs of passive mine water treatment. Yet, there is no evidence in the literature assessing how resource recovery might be used to this effect. In particular, several authors (Kratochvil et al., 2015; Johnson et al., 2006; Johnson and Hallberg, 2005a) claim that active sulphidogenic treatment technology is the only viable mechanism of economically recovering metals but have neglected to consider whether metal recovery might be achievable from passive treatment system substrates. Due to the lower cost of passive treatment systems, it may be that even with the addition of ad-hoc metal recovery waste processing, the whole-life costs might remain lower than active alternatives. This is explored further in Chapter 5, using the Force Crag treatment system as a case study.

2.16.4 Gaps in literature

This review of the literature has identified several knowledge gaps which are significant in terms of optimising passive treatment system life-times and offsetting their life-cycle costs by resource recovery. The following areas have been identified which are explored further in this thesis:

- Detailed characterisation of substrates from passive metal mine water treatment systems operating in the field.
- Attempts to recover metals from passive metal mine water treatment substrates using chemical and biological methods.
- Studies to assess quantitatively how recovery of resources may be used to offset the life-cycle cost of passive metal mine water treatment.

Substrate characterisation and metal recovery are investigated using material from the Nenthead pilot treatment system, which is detailed in Chapters 3 (methods) and 4 (results and discussion). Force Crag is then investigated to assess its performance, metal recovery potential and life-cycle cost scenarios with, and without, resource recovery: Chapters 3 (methods) and 5 (results and discussion). These cost scenarios are then compared against the costs of active treatment (Chapter 5).

Chapter 3. Methods

3.1 Introduction and chapter contents

Laboratory and field methods are presented in this chapter. Two case studies are investigated: the Nenthead pilot scale treatment system and the Force Crag full scale treatment system, both dealing with circum-neutral mine waters with elevated zinc concentrations. The methods detailed are relevant to research objectives 2 – 5 described in Chapter 1 (the first objective was addressed by Chapter 2). A bespoke experimental design was produced, based upon a campaign of sampling, experimentation and analysis to address the research objectives. Where appropriate, standard methods were adopted which ensured production of robust datasets.

3.2 Nenthead pilot treatment system decommissioning

Laboratory investigations were undertaken to characterise and to recover metals from the Nenthead mine water treatment system substrate. Details of the treatment system can be found in section 1.5. The following section details the collection and preparation of substrate samples.

3.2.1 *Substrate sample collection*

Treatment of the Rampgill mine water with a pilot scale system took place for two years at the Nenthead site, before it was decommissioned in August 2012 (Jarvis et al., 2014). At this time, a bespoke sampling method devised by Newcastle University was deployed to collect substrate samples. This Author was not involved with either the design, operation or decommissioning of the Nenthead treatment system. Figure 3.1 shows the substrate sample positions within the treatment tank, in plan, and the following details were provided in 2012 by P. H. A. Orme of Newcastle University, who was involved with the decommissioning. The system was uncoupled from the mine water feed, and allowed to partially drain, although the substrate remained submerged. Substrate samples were collected from 2 layers: an upper layer (approximately 0 – 230mm depth below substrate surface) and a lower layer (approximately 230 – 460mm, the base of the substrate) (also summarised in Jarvis et al., 2014).

The tank was subdivided into 5 rows along its length (A-E), and 4 along its width (no's.1 – 4), forming a grid pattern of 20 subdivisions, over an upper and lower horizon (A and B respectively). Samples were named following this convention, e.g. A1A and so on. After removing the first row of samples it was observed by the Newcastle University staff undertaking the work that the substrate near to the surface (top 25-50mm) was brown in colour, while beneath this surface layer the substrate was black. The substrate at the influent end of the system appeared 'blackier' than that at the effluent end. Samples (approximately 1 kg) were immediately placed into sealed polythene bags before being stored at -20°C at Newcastle University within 24 hours of collection for preservation purposes.

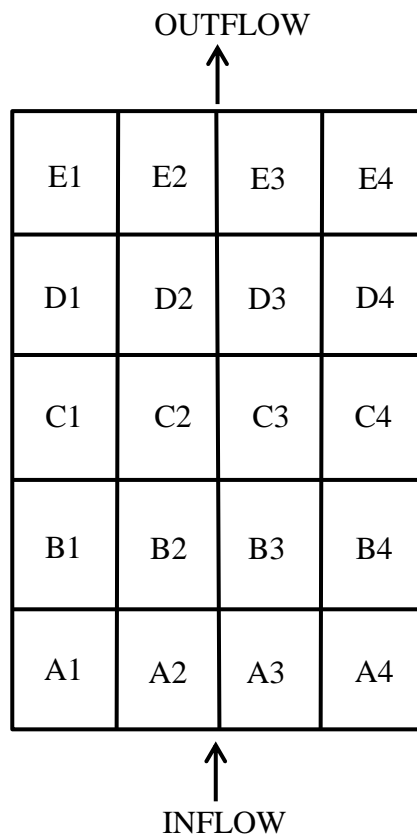


Figure 3.1 Sample plan of Nenthead pilot treatment tank (diagram courtesy of P. H. A. Orme, Newcastle University)

3.2.2 Sample preparation

Substrate samples were removed from frozen storage the day prior to use in laboratory investigations, and allowed to defrost within their airtight sample bags at room temperature. In order to reduce sample sizes to suitable amounts for sieving and sequential extractions, subsampling by a quartering method was adopted (BSI, 2006).

The procedure was repeated until approximately 12.5% (1/8th) of the bulk sample remained. De-frosted bulk samples were held for several days in a refrigerator during the procedures and remaining sample that was not used was re-frozen at -20°C.

3.3 Laboratory investigations – Nenthead substrate characterisation

3.3.1 Investigating metal content in relation to particle size

Metals are generally known to be associated with fine grained soils and sediments, given their higher surface area to volume ratio, compared to larger grained material (Mulligan et al., 2001; Singh et al., 1999). This pattern is also found in waste materials (German and Svensson, 2002; Chang et al., 2000b), although there are some cases where larger particles are coated with sorbents such as Fe/Mn oxides, which can lead to metals accumulating in larger particle size fractions (Singh et al., 1999). More recently, investigations of road sweepings by Gunawardana et al. (2014) identified that the mineralogical content of particles had a significant bearing on sorption, with clay forming minerals (<150µm) acting as important sorbents (Gunawardana et al., 2014). However, no investigations have been undertaken to assess the distribution of metals in mine water treatment system substrates according to particle size. Much of the literature investigating waste materials uses particle size separation to separate specific components of the waste, such as components from crushed batteries (Nan et al., 2006; Shin et al., 2005). As a consequence, it was necessary to design a method specifically for this work. Standard sieve sizes were chosen according to ISO1377:2 (BSI, 1990) in order to assess the relationship between metals and particle size within the Nenthead mine water treatment substrate.

Preliminary sieving using standard sieve sizes was conducted to determine the appropriate aperture for the substrate characterisation, as documented in Appendix B: ‘Trial sieving of Nenthead treatment system substrate samples’ January 2013. Sieves of 2mm and 212µm were selected, as these gave a relatively even split in terms of masses between particle sizes during preliminary sieving of a test sample: C1B³.

According to the British Standard method (ISO 1377:2), dry sieving is only applicable to soils with an insignificant quantity of silt or clay (i.e. particles <63µm) (BSI, 1990),

³ This sample was chosen, as it was considered to be of relatively low importance for spatial investigations, which follow.

however, the preliminary wet sieving of substrate sample C1B showed that 9.4% of the mass was associated with these fractions. On the other hand, it was thought that wet sieving may re-mobilise or re-distribute metals within the substrate. Therefore, in order to assess the impact (if any) of the use of a deionised water flush by wet sieving, compared to dry sieving of a sample, both approaches were conducted on sample C4B (as with sample C1B, this sampling location was chosen because the sample was not required for subsequent spatial investigations). The method adopted is outlined below:

- i. Quarter 1 was placed in an acid washed crucible and dried in a 105°C oven overnight, before being dry sieved using 2mm and 212µm sieves.
- ii. Quarters 2 and 3 were not sieved, but oven dried in acid washed crucibles and ground using a pestle and mortar and laboratory blender (Waring Commercial™). Liquid nitrogen pulverisation (Spex™ Freezer/Mill 6750) was used in addition to the laboratory blender to break down fractions of the substrate with high content of woody material, as shown in Figure 3.2. The procedure involved inserting the sample into a cylinder containing a magnetic rod, and placing in the machine. Liquid nitrogen bathed the sample for 1 minute before an oscillating electromagnet caused the magnetic bar to pulverise the sample. Between each sample, the cylinder and magnet was washed and rinsed with 18.2MΩ/cm deionised water. This was conducted until the entire sample passed the 212µm sieve.
- iii. Quarter 4 (undried) was wet sieved using 2mm and 212µm sieves with 250mL of deionised water (18.2MΩ/cm). A 20ml filtered (to <0.1µm with Pall Acrodisc Supor Membrane™ syringe filter) sample of deionised water was taken from the wash bottle, and another sample from the wash fluid once it had passed both sieves and been allowed to settle, for metals analysis. The three fractions of quarter 4 (the final including the residual wash fluid) were placed within acid washed crucibles and oven dried at 105°C overnight.
- iv. The two fractions retained on the 2mm and 212µm sieve from the dry sieving of quarter 1, and the same two fractions from the wet sieving/drying of quarter 4, were then ground using liquid nitrogen pulverisation (Spex™ Freezer/Mill 6750) and a laboratory blender (Waring Commercial™) to pass the 212µm sieve. The particles in the fraction which passed the 212µm sieve during the wet sieving had adhered together during the drying process, and so were broken up with a pestle and mortar before being passed through the 212µm sieve again.



Figure 3.2 Spex™ liquid nitrogen pulveriser, inset showing pulverised substrate sample

In total, there were 8 samples, all passing the 212 μ m sieve, as shown in Figure 3.3, where red boxes indicate samples for further analysis by sequential extraction.

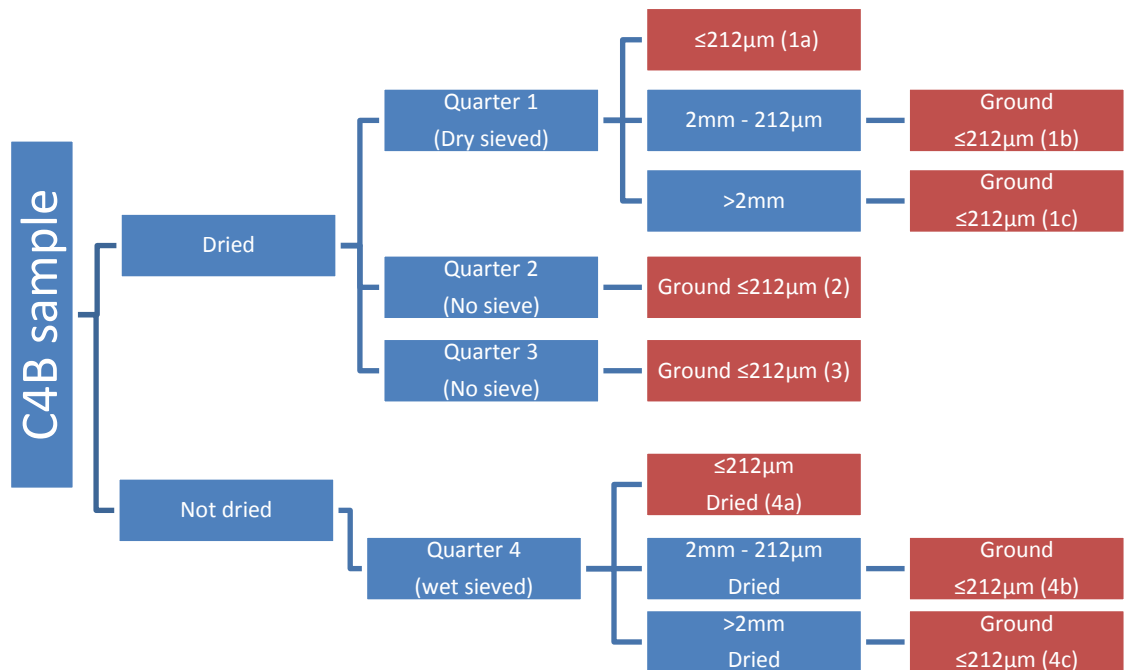


Figure 3.3 Flow chart showing sample C4B preparation using wet and dry sieving techniques

3.3.2 Investigating metal content in different locations

In addition to determination of the metal distribution in relation to particle size (and the impact of sieving methods on results), further investigation was conducted in February 2013 to assess the distribution of metals throughout the Nenthead treatment system. The following 12 samples were investigated, at both upper and lower levels, as shown on Figure 3.1: **A2A, A2B, A3A, A3B, C2A, Blank, C3A, C3B, E2A, E2B, E3A, E3B** (where the last letter of the sample reference refers to the upper 0-230mm (A) or lower 230-460mm (B) layer). Sample C2B in the sequence was substituted for a blank (substrate which had not been exposed to mine water) as a control. 12 samples were chosen due to this being the number of spaces on the centrifuge, and thus the practical limit for one sample round of sequential extractions. Identical sequential extraction procedures were undertaken on all samples.

3.3.3 Sequential extraction procedure

The 5 step method of Tessier et al. (1979) and the EC Standards Measurements and Testing Programme (BCR) method (Ure et al., 1995) are amongst the most widely applied sequential extraction procedures. The standardised procedure, developed by the Standards, Measurements and Testing Programme of the European Commission has seen improvements which have been commonly adopted to improve repeatability (e.g. Rauret et al., 1999). This method has been applied to a substrate from a permeable reactive barrier treating mine drainage (Gibert et al., 2003). However, in the case of Gibert et al. (2003) and similar studies discussed below, no investigations have been conducted on substrate samples separated by particle size.

Individual extraction steps are often classified by function, such as ‘exchangeable’ or ‘bound to Fe / Mn oxides’. However, in practice, the reagents used for these operationally defined steps can be poorly selective and species can suffer re-distribution by earlier steps (Gleyzes et al., 2002). In an addendum to the method of Tessier et al. (1979), Rapin et al. (1986) noted the significance of sample storage and preparation. It is concluded, in part, that contact of sample with atmospheric oxygen prior to and during the extraction procedure will compromise results. Sample preparation under nitrogen has been adopted by some: Jong and Parry (2004) apply this technique in the analysis of a substrate from a metal mine water treatment substrate. The substrate used in their study comprised commercial pool filter sand. In the current study, the compost

substrate contained large wood chips (up to ~100mm) which required sub-sampling, drying and pulverising/grinding to obtain a homogenous sample. This requirement for sample preparation would have been impractical under nitrogen. Several studies applying sequential extractions have been previously conducted on composts (Paradelo et al., 2011; Greenway and Song, 2002), including one using a modified Tessier (1979) procedure (Neculita et al., 2008b), but in none of these cases is there reference to extractions being conducted under nitrogen, or any other means of excluding oxygen.

Furthermore, the standard sequential extraction procedures have been developed for analysis of fluvial sediments (Tessier et al., 1979; Ure et al., 1995), which differ considerably in composition to the substrates used in compost bioreactors treating metal mine drainage (e.g. Jarvis et al., 2014; Song et al., 2012; Neculita et al., 2011). These issues are of lesser concern for the objectives of this investigation, which is to assess how tightly metals are bound within substrates, and therefore how amenable they might be to recovery. On this basis, the Tessier et al. (1979) method is preferable to the Standards Measurements and Testing method (Ure et al., 1995) as it is a 5 step procedure, rather than 3, and thus results will provide a higher resolution. To reflect the limitations of the procedure, the step number of the extraction sequence is used for data interpretation in Chapter 4. Details of the extraction steps are included in Table 3.1.

In this study, sequential extractions using procedures developed by Tessier et al. (1979) were performed on 1.00g of homogenised sample, sieved to 212 μ m. Solutions were recovered following each step by centrifugation (Sorvall Instruments™ RC5C) for 30 minutes at 10,000rpm and removed using a glass pipette. Between the 5 steps, samples were washed with 8mL of deionised water (18.2M Ω /cm), agitated and separated within the centrifuge for 30 minutes. The wash fluid was then discarded. Because of the high organic content of the material (TOC \geq 20%), there was concern that incomplete oxidation of organic matter by hydrogen peroxide may occur in the oxidising step (4) (see: Gleyzes et al., 2002). Accordingly, extra hydrogen peroxide was added to a single vile of both sets of triplicate samples at step 4 (oxidising agent) to assess whether, in the case of these compost samples, the reagent volume was limiting extraction during this step.

Chapter 3. Methods

Table 3.1 Sequential extraction procedure, after Tessier et al. (1979)

Step	Reagent	Treatment	Special amendments
1	1M MgCl (pH 7), 8mL.	Continuous agitation on rolling table for 1hr, room temp.	
2	1M NaOAc, adjusted to pH5 with HOAc, 8mL.	Continuous agitation on rolling table for 5hrs, room temp.	
3	0.04M NH ₂ OH-HCl in 25% (v/v) HOAc, 20mL.	Occasional agitation for 6hrs (shaken at 30min intervals), 96°C temp maintained using oven.	
4	a. 0.02M HNO ₃ (3mL) and 30% H ₂ O ₂ adjusted to pH 2 with HNO ₃ , 5mL. b. Additional 3mL of 30% H ₂ O ₂ added after first 3 hours c. 3.2M NH ₄ OAc in 20% HNO ₃ , 5mL added to cooled samples. 4mL deionised water then added to make solutions up to 20mL.	Occasional agitation 3hrs (shaken at 30 minute intervals), 85°C temp maintained using oven. Further occasional agitation for 3hrs at 85°C. Cooling of samples in cold room for 30mins. Following addition of reagents, continuous agitation for 30mins.	5mL extra H ₂ O ₂ added to triplicate vials (2iii; 3iii) – total volume at end of step 4: 25mL.
5	a. HClO ₄ , 2mL; HF, 10mL; added to sample. b. HClO ₄ , 1mL; HF, 10mL; added to sample. c. 1mL of HClO ₄ added until the appearance of white fumes. d. Conc. HCl, 5mL added to dissolve residue.	Residue from step 4 placed in Teflon crucibles. After first addition, samples heated on 130°C hotplate for 30 mins until almost dry. Samples heated on 130°C hotplate for 30 mins until almost dry. Solution transferred to 25mL volumetric flasks and made up using deionised water.	

All reagents were made up either from analytical grade salts or concentrated solutions, diluted with 18.2M Ω /cm deionised water, using acid washed glassware. Samples from step 1 were acidified with 2 drops of nitric acid to lower pH <2 thereby halting most bacterial growth, preventing oxidisation of metals and precipitation or sorption to container surfaces (Appelo and Postma, 2010).

3.3.4 Analysis of sequential extraction solutions

Metals analysis of extraction solutions was undertaken using a Varian Vista MPX Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) according to the British Standard Method ISO11885 (BSI, 2009). The following metals were investigated, as per Tessier et al. (1979) with their respective detection limits:

- Iron <0.01mg/L
- Manganese <0.01mg/L
- Lead <0.05mg/L
- Zinc <0.01mg/L
- Cadmium <0.01mg/L
- Copper <0.01mg/L
- Cobalt <0.01mg/L
- Nickel <0.01mg/L

Detection limits were calculated by running a blank 7 times on the ICP-OES and calculating 3x the standard deviation, which is improved over the BSI method which specifies that at least 3 outlier free readings are taken (BSI, 2009).

Calibration standards were made up to cover the anticipated range of element concentrations within the samples (Table 3.2). In total, 3 calibration standards, plus a blank, were made up in all 5 extraction matrices. By using the extraction solution as a base for the standards, any interference that this gives is considered within the calibration (BSI, 2009). Where analytes were reported in excess of the highest calibration standard, dilution of the samples was undertaken to bring them within range. Base solutions were used for dilutions, which were made up as ten-fold and twenty-fold as necessary.

Table 3.2 ICP-OES calibration standards for Tessier Extraction

	Calibration solution concentrations, mg/L (three standards per element)				
	Step 1 (Tessier matrix)	Step 2 (Tessier matrix)	Step 3 (Tessier matrix)	Step 4 (Tessier matrix)	Step 5 (Tessier matrix)
Cd, Co, Cu, Ni	0.2; 0.4; 0.6	0.2; 0.4; 0.6	0.2; 0.4; 0.6	0.2; 0.4; 0.6	0.2; 0.4; 0.6
Pb, Zn	2; 4; 6	5; 10; 15	5; 10; 20	5; 10; 15	2; 4; 6
Fe	5; 10; 15	5; 10; 15	10; 20; 30	10; 20; 30	10; 20; 30
Mn	5; 10; 15	5; 10; 15	5; 10; 15	2; 4; 6	2; 4; 6

Calibration standards were run at the start of every analysis sequence, and blanks (normally second standard) were run periodically (every 12 sample runs for convenience) in order to check that the calibration remained correct.

Samples were manually injected into the ICP-OES (rather than use of an autosampler device). This was in part due to the relatively low sample number per round (12 samples per run, over 5 runs: corresponding to each extraction step), but also to allow ease of data review and re-running of samples during analysis. Between individual samples, a 1% nitric acid wash solution was passed through the machine to remove residues from the preceding samples (APHA, 2005). In most cases, the plasma could be observed changing colour, as the salt from the sample base was flushed through.

3.4 Laboratory investigations – Nenthead chemical leaching tests

In order to assess the potential for metal recovery under low pH conditions, such as those which might be generated either by bio-oxidation of sulphide minerals or by conventional acid-leaching processes, proof-of-principle experimentation was conducted using laboratory grade sulphuric acid. The aim of these investigations, conducted between July and December 2014, was to understand the relationships between acid concentration, pulp density (i.e. lixiviant:solid ratio) and leach times on metal recovery from a mine water treatment substrate.

3.4.1 Leach test procedure

A method was designed for the chemical leach testing, as there is no defined method to assess the recoverability of metals from mine water treatment wastes. The experimental design was, however, informed by a number of studies in which broadly analogous investigations were conducted, and these are cited where relevant.

Bulk samples from an even distribution across the upper layer of the Nenthead pilot treatment system substrate were combined to form a composite (**A2A, A3A, C2A, C3A, E2A, E3A** – see Figure 3.1). The composite was oven dried at 105°C for >48 hours and sieved to <2mm to remove large fragments. This composite was then subsampled using the quartering method (BSI, 2006) and weighed to ± 0.01 g.

Composite subsamples were then placed within 2,000mL acid washed High-Density PolyEthylene (HDPE) flasks and subjected to contact with dilute sulphuric acid solutions at room temperature for 100 hours under aerated conditions. Collection of samples and manual measurements (temperature, Eh, pH, conductivity), using a calibrated⁴ Myron 6P Ultrameter, were taken at specific intervals following commencement of the experiments, as outlined below:

- 0 hours (start of experiment)
- 1 hour
- 3 hours
- 6 hours
- Daily for the following 4 days

Simultaneously, filtered water samples were collected, using 0.45 μ m Pall Acrodisc Supor Membrane™ syringe filters to remove suspended debris from pulp. Note that vessels were not topped up as minimal sample volumes of ~15mL had been collected for analysis, and any topping up would have diluted leach solutions.

All bottles were aerated using a simple air injection configuration as shown in Figure 3.4. This was to ensure that conditions were oxygenated, facilitating oxidation reactions which are responsible for metal solubilisation, in addition to providing agitation to the substrate-acid pulp in place of mechanical stirring. Tests were conducted within a fume

⁴ Calibration of the Myron 6P Ultrameter was undertaken periodically using a three point method (with pH 4, 7, 10 buffers), and conductivity using a 1413 μ S/cm solution.

cupboard, to provide containment/venting in case of any spills of acid or liberation of fumes.

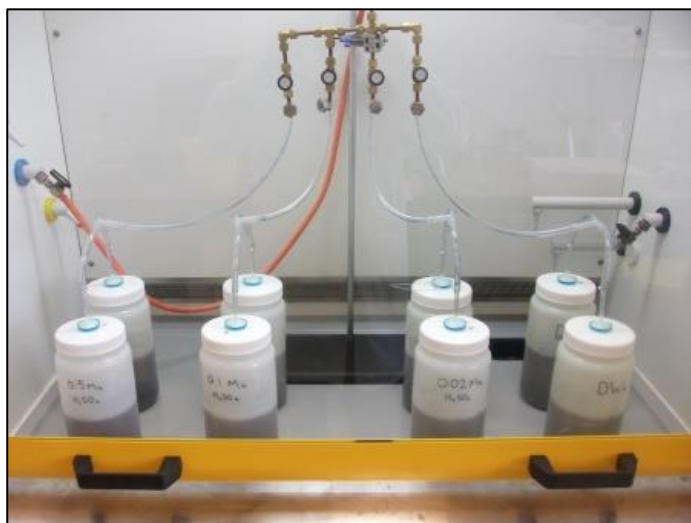


Figure 3.4 Leach test experimental configuration

Samples collected were stored below 5°C and analysed by ICP-OES. Upon completion of the leach test, the compost/lixiviant pulp was filtered through 8µm pass, 150mm no.40 Whatman™ filter papers to separate the pregnant leach solution from the solids fraction. This size filter paper was chosen because it is identical to those used for subsequent aqua regia digests of leached substrates (section 3.4.6).

3.4.2 Leach test variables

A range of acid concentration and pulp-density variables were investigated in order to determine the optimum leaching conditions, as outlined in the following sections. All batch leach tests were conducted in duplicate rather than triplicate due to restrictions on fume cupboard space.

3.4.3 Acid concentration

Three different dilutions of sulphuric acid were compared, against a distilled water control. Solutions were made up from concentrated laboratory grade sulphuric acid and distilled water, up to 1,200mL in the following dilutions: 0.02, 0.1 and 0.5 molar. These dilutions were selected as they covered a wide range: from more concentrated acids, comparable to those successfully used by other researchers, to very dilute acid; thereby testing the limit of acid concentration on metal extraction. For example, Souza et al. (2007) determined in excess of 70% zinc extraction from a zinc silicate calcine

with 5 acid concentrations between 0.2 and 1.0 molar, over a 10 minute extraction. Wu and Ting (2006) achieved >48% zinc recovery with 0.1 and 0.5 molar sulphuric acid, from a 1% pulp of fly ash containing 6,288mg/kg of the metal. For brevity, the symbol M is used in this thesis to denote molarity.

Each acid solution was added to 22.5g of compost within the 2,000mL flasks to provide a pulp density of 1.875% (solid/liquid), which is comparable to pulp-densities used by other researchers (Bayat and Sari, 2010; Henry and Prasad, 2006; Ishigaki et al., 2005). Further experimentation to assess the effect of different pulp density was undertaken subsequently, as detailed in section 3.4.4.

3.4.4 Pulp density

Determination of extraction recoveries over a series of increasing pulp density increments was conducted: 1.875%, 3.75%; 7.5% and 15%, measured as the ratio of substrate mass (g) to liquid volume (mL), plus a reagent blank. 0.1M acid was selected for the pulp density experiments since this provided a balance between high zinc and cadmium recovery while minimising acid concentration, as determined by preceding tests (see leach test data in Chapter 4, section 4.3.1). The '1.875% pulp' density test was a repeat of the '0.1M' acid concentration test in the preceding round of experiments, since both these combinations used 0.1M acid and had a 1.875% pulp density. This allowed direct comparison of repeatability between the variable acid concentration and variable pulp density tests.

Experimental conditions were identical to the previous tests using variable acid concentrations. Initially, however, acid volume was varied in order to increase the pulp densities, and consequently it was necessary to vary flask size proportionately to the acid volume. Varying the acid volume and retaining the 22.5g compost volume allowed use of the same batch of compost used in the preceding experiments for consistency purposes. Additionally, this maintained the same pulp surface:air ratio, in case this would have had any bearing upon reaction rates (i.e. smaller containers reduced the cross-sectional surface area of the pulp for smaller leach volumes). Unfortunately, during the pulp test experimentation, it became evident that the substrate had absorbed a substantial amount of the acid in the highest density flasks (the substrate had been oven dried beforehand). Thus, collection of small but frequent samples (8 x ~15mL) caused a gradual but observable increase in the pulp density, effectively meaning that there was

little circulation of acid as the pulp turned into more of a thick sludge. This was most notable in the 15% pulp experiment, where there was just 150mL of acid to start with.

As a result, the pulp-density tests were re-run, using 1,200mL of 0.1M acid in the 2,000mL flasks, but increasing the masses of compost to achieve the variation in pulp density. This larger quantity of acid meant that sample collection had little bearing on final volumes (in total 120mL was taken from a starting volume of 1,200mL), albeit data have been corrected to account for these sampling events. It is these data which are presented in Chapter 4 (Nenthead Results and Discussion). Due to the requirement for larger amounts of substrate, an additional composite was produced from Nenthead tank substrate samples, also from the upper layer as with the preceding experiments, but from locations between the original samples (**A1A, A4A, B1A, B2A, B3A, B4A, C1A, C4A, D1A, D2A, D3A, D4A, E1A & E4A**; see Figure 3.1). Additional aqua regia digests were undertaken on this new composite to accurately calculate metal recovery efficiencies.

3.4.5 Metal recovery from pregnant leach solutions

Solutions recovered from the pulp-density tests were subjected to alkali dosing in order to raise pH and cause precipitation of metals. This study has focussed largely upon zinc, which is not only the most prolific pollutant in metal mine waters of England and Wales (Mayes et al., 2013) but also when present in treatment system substrates deems them hazardous waste due to its ecotoxicity (NRW et al., 2015; ESG, 2013). Therefore, as the key metal of concern, pH adjustment of pregnant solutions was trialled to remove zinc as a solid precipitate. As Figure 3.5 shows, the optimum pH range for zinc hydroxide formation is between 8.5 and 11.5. On this basis, a target pH of 9.5 was chosen, and achieved by drop-wise addition of 6M (24%) NaOH solution. Given other metals have lower solubility at this pH, it was expected that many of these would also have formed insoluble hydroxides (see Figure 3.5). pH measurement was undertaken with a pre-calibrated Fisherbrand Hydrus 300 pH probe during mixing with a magnetic stirrer to achieve pH of 9.5 (± 0.1). Solutions were then allowed to rest for 3 days to allow settlement of precipitates. Periodic measurements identified that the pH of the pregnant solutions had dropped, below 9 in most cases, following 1 day of settlement. To correct for this, 1mL of 6M NaOH was added to each of the 8 pregnant solutions; mixing and re-measurement confirmed pH had increased to, and stabilised at, between 9

and 10 in all flasks which has previously been shown as an effective pH for metal removal from leach solutions (Seidel et al., 2004).

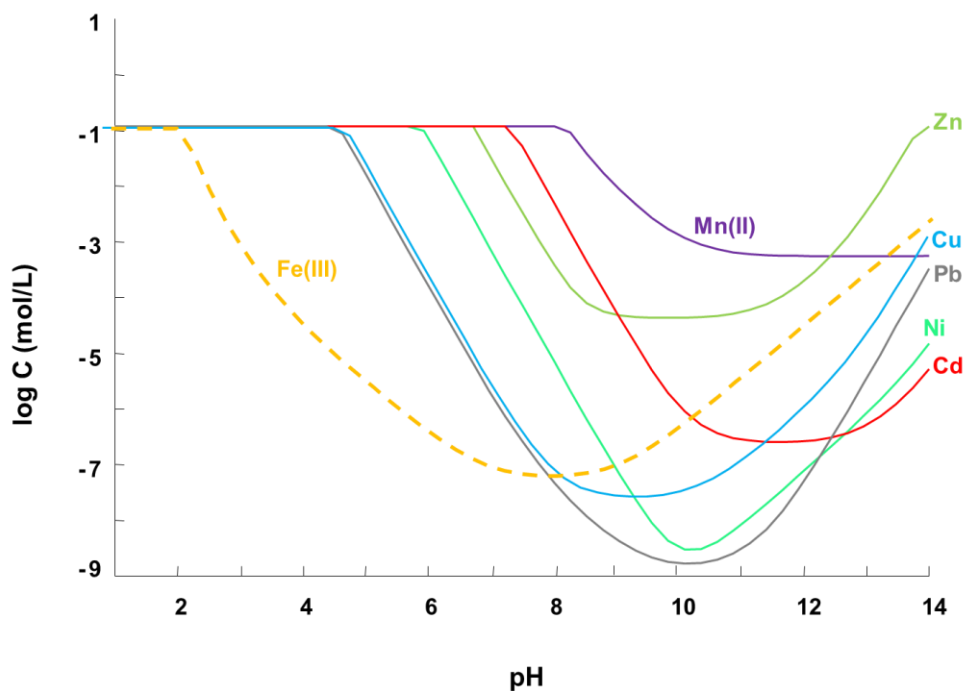


Figure 3.5 Hydroxide solubility of Mn(II), Zn, Cd, Cu, Pb, Ni, Fe(III) as a function of pH, redrawn after Cortina et al. (2003)

Following pH correction, samples were filtered through 8 μ m pore size filter papers (no.40 Whatman™), using a vacuum pump to recover the precipitate. This filter pore-size was chosen on the basis that it is the same as that used in the digest procedure described in the following section, and also that used for the separation of substrate from pregnant solutions in the leach test. Thus, any recovered solids would have formed after the addition of sodium hydroxide and settlement period. Recovered solids were dried and weighed before aqua regia digestion. The filtrate was sampled and the samples re-acidified to pH<2 using concentrated nitric acid as per normal practice and analysed by ICP-OES for metals. Un-acidified samples were also taken and analysed for sulphate as detailed in section 3.4.8.

3.4.6 Aqua regia digests

Digestion of the composite substrate was undertaken before leach-testing in order to determine initial metals concentration and thus allow mass-balance calculation of recovery efficiencies. The aqua regia digest procedure, according to the British Standard was conducted in triplicate (BSI, 1995b). Due to elevated Total Organic Carbon (TOC) concentrations in the samples, an additional 2.5mL of nitric acid was

added to accommodate up to 25% organic carbon (BSI, 1995b). Organic carbon was determined by analysis of triplicate substrate samples by P. Green, Technician in Chemical and Biological Laboratories at Newcastle University, according to BSI (1995a).

Additional aqua regia digests were undertaken on the precipitates recovered from the pregnant leach solutions. The standard digest method requires a 3g sample; although due to the small mass of recovered precipitate, just 0.5g of sample was used for digest in this case (i.e. 1/6). Accordingly, the volume of aqua regia used was scaled down (i.e. 1/6 volume of aqua regia compared to BSI method). In an effort to improve repeatability, the sample was ground to <106 μ m (i.e. finer than 150 μ m which is required by the standard method (BSI, 1995b)) before analysis.

3.4.7 Metals analysis of leach and digest solutions

ICP-OES analysis of metals and digests from acid leach testing was conducted on a Varian Vista MPX in accordance with the British Standard Method ISO11885 (BSI, 2009). The following metals were investigated: iron, manganese, lead, zinc, cadmium, copper and nickel; these are both prevalent in mine drainage responsible for polluted waters in England and Wales (Mayes et al., 2013), and were investigated by the Tessier sequential extraction detailed in section 3.3.

Additionally, the leach solutions and residues following metal removal by hydroxide precipitation were investigated for major elements of sodium, potassium, calcium, magnesium and aluminium by ICP-OES, in addition to filtrate analysis for sulphate by ion chromatography (see section 3.4.8 for method). The detection limits for the major elements, as determined using the method specified in 3.3.4, are as follows:

- Sodium <0.1mg/L
- Potassium <1mg/L
- Calcium <0.02mg/L
- Magnesium <0.02mg/L
- Aluminium <0.5mg/L

Calibration standards were made up to cover the anticipated range of element concentrations within the samples (Table 3.3). In total, 3 calibration standards, plus a blank, were made up for all 3 acid concentrations and the distilled water control. By

using the acid leach solution as a base for the standards, any interference that this gives is considered within the calibration (BSI, 2009). Where analytes were reported in excess of the highest calibration standard, the samples were diluted to bring them within range. Base solutions were used for dilutions which were factored as necessary.

Table 3.3 ICP-OES calibration standards for acid leach tests

	Calibration solution concentrations, mg/L (three standards per element plus blank)	
	Leach test calibration solutions (matrices: distilled water; 0.02M; 0.1M; 0.5M H ₂ SO ₄)	Aqua regia digest calibration solutions (matrix of aqua regia)
Cd, Cu, Ni, Pb	1; 2; 3	1; 2; 3
Zn, Mn	4; 8; 12	6; 12; 18
Fe	10; 20; 30	10; 20; 30
Na*	5; 10; 15	5; 10; 15
Ca*	30; 50; 100	30; 60; 90
K*	10; 20; 30	30; 60; 90
Mg*	10; 20; 30	15; 30; 45

*Only investigated in leach solution precipitates and filtrate after NaOH dosing for metal removal

Calibration standards were run at the start of every analysis sequence, and blanks (second standard) were run periodically (every 16 samples for convenience) in order to check that the calibration remained correct.

Samples were manually injected into the ICP-OES, as in the Tessier extraction investigations, to allow ease of data review and re-running of samples during analysis. Between individual samples, a 1% nitric acid wash solution was passed through the machine to flush through and remove residues from the preceding samples (APHA, 2005).

3.4.8 Leach solution filtrate analysis for sulphate

Following recovery of solids from pregnant leach solutions, the sulphate content in the filtrate was determined using a Dionex IC25 ion chromatograph according to the standard method: 4110B Ion Chromatography with Chemical Suppression of Eluent

Conductivity (APHA, 2005). Given that up to 0.5M sulphuric acid was used for the leach test, the sulphate readings were expected to be very high:

H_2SO_4 molar mass = ~98 g/M (SO_4 ion molar mass ~96g/M)

Therefore a solution of 0.5M (moles per litre) H_2SO_4 contains 48g/L; or 48,000 mg/L SO_4^{2-} .

To account for this using a normal calibration solution of 20mg/L SO_4 , and to prevent measurements exceeding the machine's calibration and normal working limit of 100mg/L, 1,000 fold dilutions were conducted on the leach solutions prior to running (i.e. bringing the maximum anticipated sulphate concentration to 48mg/L). This is still well above the 0.5mg/L detection limit used for this method. As just 8 samples were analysed, the calibration solution was re-run at the end of the analysis to ensure the machine remained in calibration.

3.5 Laboratory investigations – Nenthead bioleaching tests

Bioleaching, the principles of which are discussed in Chapter 2, offers a means of metal leaching by microbial processes, thereby reducing or removing the requirement for industrially produced acids. This approach was explored using an acid mine water as both a leach solution and microbial inoculum for the recovery of metals from the Nenthead substrate.

The role of sulphur and iron oxidising bacteria in the genesis of polluting mine drainage is well documented (Aplin et al., 2008; Baker and Banfield, 2003; Younger et al., 2002) and the presence of *At. Thiooxidans* and *At./L. Ferrooxidans* has been recorded at several UK mine waters (Johnson, 2003; Johnson and Hallberg, 2003). It is exactly these bacteria which have been cited previously as important species in bioleaching applications (see Chapter 2, section 2.12.4). In fact, some authors have actually used cultured mine water sourced bacterial colonies to inoculate metal recovery experiments (Bayat and Sari, 2010; Solisio et al., 2002). Alternatives involve the use of pure cultures (Wu and Ting, 2006; Ishigaki et al., 2005) and indigenous strains (i.e. no inoculum) (Liu et al., 2008; Villar and Garcia, 2002). Reduced iron and sulphur (sulphides) within the treatment system substrate might therefore be amenable to oxidative dissolution, catalysed by iron and sulphur oxidising bacteria which are

commonly present in mine waters. Further discussion of bio-hydrometallurgy is provided in Chapter 2, section 2.12.4.

3.5.1 Leach solution and inoculum

Mine water to provide microbial inoculum and leach solution was collected from the Woodend Level mine water discharge at the abandoned Threlkeld Mine in Cumbria on 18 September 2015 (NY32506 26109 – also known as Gate Gill). It was collected in an acid-washed 25L carboy, before transport to Newcastle University and storage below 5°C until required (less than 1 week). Threlkeld Mine was considered a suitable site as the water is net-acidic with a low pH (~4), and contains elevated zinc concentrations (40mg/L). Therefore any active micro-organisms were likely to be acid and zinc tolerant and therefore better adapted to the bio-leaching application. Use of mine drainage as a source of inoculum has the benefit of being both low or no-cost, and convenient, in that there are inevitably sources of mine drainage waters near to mine water treatment systems.

3.5.2 Bioleach test procedure

Biological leaching was conducted in the laboratory between September and November 2015. Nenthead substrate was used for bioleaching tests, which consisted of the composite of samples **A1A, A4A, B1A, B2A, B3A, B4A, C1A, C4A, D1A, D2A, D3A, D4A, E1A & E4A** which had been sieved to <2mm; identical to the composite used in the variable pulp density acid leach tests (section 3.4.4). As a consequence, initial metal content of the substrate was known from previous aqua regia digests.

The configuration, conditions and sampling regime of these bioleaching experiments mirrors that undertaken for the acid leaching tests, but includes additional measures to ensure sterility of vessels and sampling equipment. Experimental vessels were acid washed before being autoclaved at 121°C for 20 minutes to ensure that they were both chemically and biologically clean (APHA, 2005). Nenthead substrate for leaching was oven dried at 105°C overnight, which is believed to be sufficient to kill all vegetative bacteria (*pers comm.*, Dr A. Sherry, Newcastle University 2015). This was chosen, in preference to autoclaving, because exposure to high temperature steam might have impacted upon the properties of the substrate and thus the metal recoverability. Additionally, it is unlikely that autoclaving would be practical for full-scale substrate decontamination activities.

Experiments were conducted in 2,000mL polyethylene flasks, with aeration and agitation provided by injection of compressed air at a rate of approximately 1L/min. This was to ensure oxygen and carbon dioxide required by bacteria is provided (Bosecker, 1997). Air was subject to 0.2µm filtration (Pall Acrodisc Supor Membrane™) to remove any foreign bacteria or other debris in the supply (again selected over autoclaving to minimise impact upon chemistry). Sampling was conducted using sterile syringes/bottles and 0.45µm Pall Acrodisc Supor Membrane™ syringe filters to remove debris; sample bottles were stored below 5°C prior to analysis to preserve inorganic species (APHA, 2005). Key parameters of Eh, pH, conductivity and temperature were determined with a calibrated Myron 6P Ultrameter⁵. These factors were identical to those used in the preceding acid leach tests. Also, for comparative purposes, the same pulp-density was adopted as the variable acid concentration round of leach tests, where 22.5g of substrate to 1,200mL of lixiviant was used. This provided a pulp density of 1.875%. Experimental flasks were graduated at 30mL increments, in order to provide a reliable measurement ($\pm 2.5\%$) of the pulp volume at the time of sampling. This was an improvement over the preceding acid leach tests where the lixiviant volume was assumed to be reduced by the volume of samples taken; however, over the longer leach period used in the biological leaching tests, volume reduction by evaporation was also significant. This was observed during preliminary biological leach tests (not presented in this thesis).

Experiments were conducted with sulphur (S_0) addition to stimulate sulphur oxidising microbial populations such as *At. thiooxidans*. Seidel et al. (2004) achieved 80% zinc extraction from a sediment enriched with 2% zero valent sulphur using a fixed-bed configuration (Seidel et al., 2004). Similar success for zinc recovery was achieved using 0.4% and 0.5% sulphur enrichment during experimentation on sewage sludge (Henry and Prasad, 2006; Villar and Garcia, 2002 respectively). Liu et al. (2008) found that optimum metal recovery from a Pb-Zn-Cu mine tailings occurred with sulphur additions of between 0.5% and 2%. Based upon previous studies, 5g zero-valent sulphur was added to experimental flasks to provide ~0.4% enrichment. Assuming that all added sulphur converts to sulphuric acid, a 0.127M H_2SO_4 solution would be

⁵ Calibration of Myron 6P Ultrameter was undertaken using a three point method (with pH 4, 7, 10 buffers), and conductivity using a 1413µS/cm solution

generated⁶, which is comparable to the optimum acid leach concentration of 0.1M determined by the preceding tests.

Some studies have shown success in bioleaching with neutral or alkaline starting pH: pH 9 (Brombacher et al., 1998); pH 11 (Wu and Ting, 2006); pH 7.1 (Henry and Prasad, 2006);. Other investigators have adjusted substrates to generate acidic conditions favourable to bacteria. For example, Bayat et al. (2009) adjusted an alkaline metal plating sludge to pH 2.5-3 with sulphuric acid, and Solisio et al. (2002) used the same reagent to reduce the pH of an industrial waste sludge to 4. It was anticipated, based upon acid-leaching tests, that the buffering capacity of the Nenthead substrate was likely to raise pH of the Threlkeld mine water lixiviant. Bioleach tests in this study were conducted using pH adjusted substrates, in order that they were comparable to the mine drainage leach solution. It is believed that this would reduce the risk of harm to bacteria brought about by rapid pH change (*pers comm.* Dr A. Sherry, Newcastle University 2015). pH adjustment was made with dropwise addition of sulphuric acid to substrates in a minimum volume of mine water (200mL) before addition of the remaining mine water. Approx. 0.3mL of concentrated sulphuric acid was required to adjust pH to 4(± 0.1), which was established after stirring continuously for 15 minutes.

3.5.3 Bioleach test variables

All variables described were trialled in duplicate to assess repeatability, although it is acknowledged that, if budgets had allowed, triplicate analysis would have produced more statistically robust data. Bioleach tests were conducted in tandem with a sterilised replicate, consisting of mine water which has been filtered using 0.2 μ m syringe filter (Pall Acrodisc Supor MembraneTM) to remove bacterial cells (APHA, 2005). This was to test the influence of micro-organisms present within mine water to inoculate the metal recovery process. In addition, replicates were undertaken to assess the impact of stirring and, separately, heating upon the rate of bio-oxidation and metal recovery (the latter since optimised temperatures of $\sim 30^{\circ}\text{C}$ have been successfully used by other authors (Henry and Prasad, 2006; Wu and Ting, 2006; Seidel et al., 2004)). Stirring of beakers was achieved using Fischer ScientificTM magnetic stirrers at rates at which the pulp surface was broken (180rpm), which is comparable to speeds used by Henry and Prasad (2006) and Solisio et al. (2002). Stirring was intended to improve the suspension of pulp over flasks where agitation was only provided by a stream of

⁶ Based upon the molecular weight of sulphur being 32.8g/mol

compressed air. Stirrers were frequently checked and replaced when showing any signs of wear of their Teflon sheaths. Heating was achieved by immersion of flasks in a water bath (Fisher Bioblock Scientific™) which was set to 30°C. Occasional re-filling of the water bath was required in order that the water level remained above the pulp level within the flasks. Table 3.4 describes the variables for the bioleaching tests.

Table 3.4 Variables for bioleaching experiments

Leach test (shown in duplicate)								
	1a	1b	2a	2b	3a	3b	4a	4b
Substrate	22.5g Nenthead substrate <2mm, pH adjusted		22.5g Nenthead substrate <2mm, pH adjusted		22.5g Nenthead substrate <2mm, pH adjusted		22.5g Nenthead substrate <2mm, pH adjusted	
Leach solution	1.2L mine water		1.2L mine water		1.2L mine water		1.2L sterile filtered mine water	
Nutrient source	5g S ⁰ (0.4%v/v)		5g S ⁰ (0.4%v/v)		5g S ⁰ (0.4%v/v)		5g S ⁰ (0.4%v/v)	
Special treatment	Heated 30°C		Stirred 180RPM					

3.5.4 Chemical analysis of bioleach solutions

Samples were collected on a less frequent basis than the acid leaching test, given that bioleaching processes generally require significant time periods for microbial communities to become established (Johnson, 2013). Samples were collected at the following intervals after commencement of the experiments:

- 0 hours (start of experiment)
- 6 hours
- 24 hours
- 96 hours
- Periodically over the following 9 weeks until the experiments were terminated

Vessels were topped up with sterile filtered distilled water at regular intervals, to compensate for evaporative losses. Metals analysis (Fe, Mn, Pb, Zn, Cd, Cu & Ni) was conducted using ICP-OES and sulphate analysis was conducted using ion chromatography, using apparatus and methods previously described in the chemical leaching procedure (section 3.4). ICP-OES calibration standards conformed to those used for the Force Crag water sample analysis, as detailed in Table 3.7 (section 3.6.3).

3.5.5 *Microbial analysis*

At the outset, consideration was given to detailed molecular methods of microbial analysis to identify community profiles, although, due to the limits upon time and resources, this was not undertaken. Regardless, samples were taken in case it was decided that this course of investigation was appropriate in the future. In place of molecular methods, Most Probable Number (MPN) cell counts were conducted in order to identify the presence and abundance of cells within a sample of the Threlkeld Mine water. Note that the sample used for cell counts was collected on the 20 January 2015, whereas the mine water used for the bioleach tests was collected on 18 September 2015. The protocol adopted by the Newcastle University Geomicrobiology team was used (Brown 2008⁷) which involves use of a SYBR[®] Gold nucleic acid gel stain and manual cell counts under an optical microscope (Olympus BX40 Epi-fluorescence), a method based loosely upon that documented by APHA (2005). A photograph of the stained microbial cells under the microscope is shown as Figure 3.6.

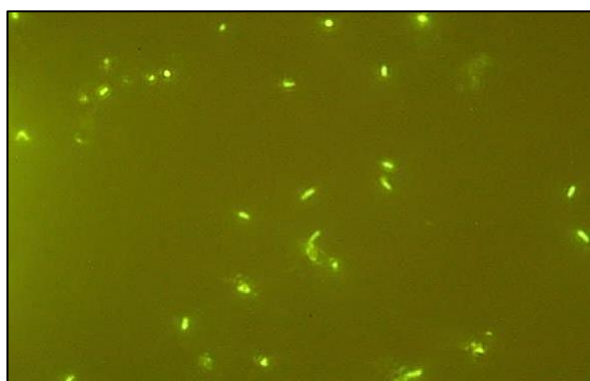


Figure 3.6 Stained cells in the Threlkeld Mine drainage under 100x magnification with oil immersion

It was determined that there were 5×10^3 cells within the Threlkeld Mine water, thought to be chemolithotrophic bacteria, given their source (for example, see Johnson, 2003). This number is at the lower end of the spectrum when compared to other studies. Given that this sample of Threlkeld Mine water was collected in January 2015, low cell numbers may be due to seasonal effects reducing cell numbers during the winter (McGuinness and Johnson, 1993; Walton and Johnson, 1992). If this is the case, the water used for the bioleach tests (collected separately in September 2015) might have had a greater abundance of cells.

⁷ Cell count protocol included as Appendix C.

3.6 Field based investigations – Force Crag

Commissioning of the Force Crag mine water treatment system took place in April 2014. The system removes zinc from a circum-neutral mine water entirely by passive means (Jarvis et al., 2015). In the context of this study, the Force Crag system offers a timely and pertinent case study, allowing investigations into metal removal and consequently accumulation rates within system substrates. Additionally, the site allowed a detailed study of other resource potential, and a review of life cycle costs with and without resource recovery.

3.6.1 Water sampling and field analysis

Sampling visits took place twice a week for the first 2 weeks of operation of the Force Crag mine water treatment system (1, 3, 8 & 10 April 2014). Visits were then reduced to weekly for the remainder of the year (until 31 March 2015), occasionally less frequently when staff availability was limited. During sample visits, water was collected for metals (cation) and anion analysis, and manual field conditions were measured as a minimum in order to assess system performance and metal accumulation rates. Table 3.5 provides a summary of the sampling and monitoring parameters relevant to this study.

Calibration of the Myron 6P Ultrameter used in the study was undertaken using a three point method (with pH 4, 7, 10 buffers), and conductivity using a 1,413 μ S/cm solution before each sampling visit. A YSI field oxygen probe was also calibrated prior to use, which involved re-setting the device while the sensor was in a controlled atmosphere.

Table 3.5 Force Crag field samples and measurements

Parameter	Equipment/vessel	Rationale
Inorganics samples (for laboratory analysis)	25mL universal sample containers (unamended: inorganics; acidified: metals; filtered and acidified: dissolved metals)	To determine metals and sulphate concentrations throughout treatment system (and consequently its performance with respect to metals removal)
Eh ⁸	Myron 6P Ultrameter™	To determine oxidation/reduction potential of water (Appelo and Postma, 2010)
pH	Myron 6P Ultrameter™	Key geochemical parameter indicative of hydrogen ion activity (Appelo and Postma, 2010)
Conductivity	Myron 6P Ultrameter™	Solutions with high inorganic content generally have higher electrical conductivity (APHA, 2005)
Temperature	Myron 6P Ultrameter™	To determine if heat extraction from mine water might be feasible
Dissolved oxygen ²⁵	YSI field oxygen probe	Measurement of oxygen content of water in mg/L to determine if conditions are oxic or anoxic (APHA, 2005)
Alkalinity	Hach digital field titrator with bromcresol-green methyl-red indicator	Acid neutralising potential, titration to pH 4.5 (Appelo and Postma, 2010)
Sulphide	Merck MColorstest™	Colorimetric field method to determine presence of S ²⁻ generated by sulphate reduction (APHA, 2005)

Samples were taken from the Vertical Flow Pond (VFP) inlets and outlets in order to determine the performance of the system and the rates of metal accumulation within substrates. Additionally, samples were taken from the final effluent, which was a combination of the effluents from VFPs 1 and 2 which had then passed through a small aerobic wetland. Inlet and outlet sample and flow measurement locations are shown either side of the VFPs in Figure 3.7.

⁸ All manual parameters were measured, and samples taken, from a 5L sampling jug; this is excepting Eh and DO measurements, which were taken either in-stream or in buckets used for sample collection from the VFP outlets. This was to minimise exposure of samples to atmospheric oxygen which might have influenced Eh or DO.

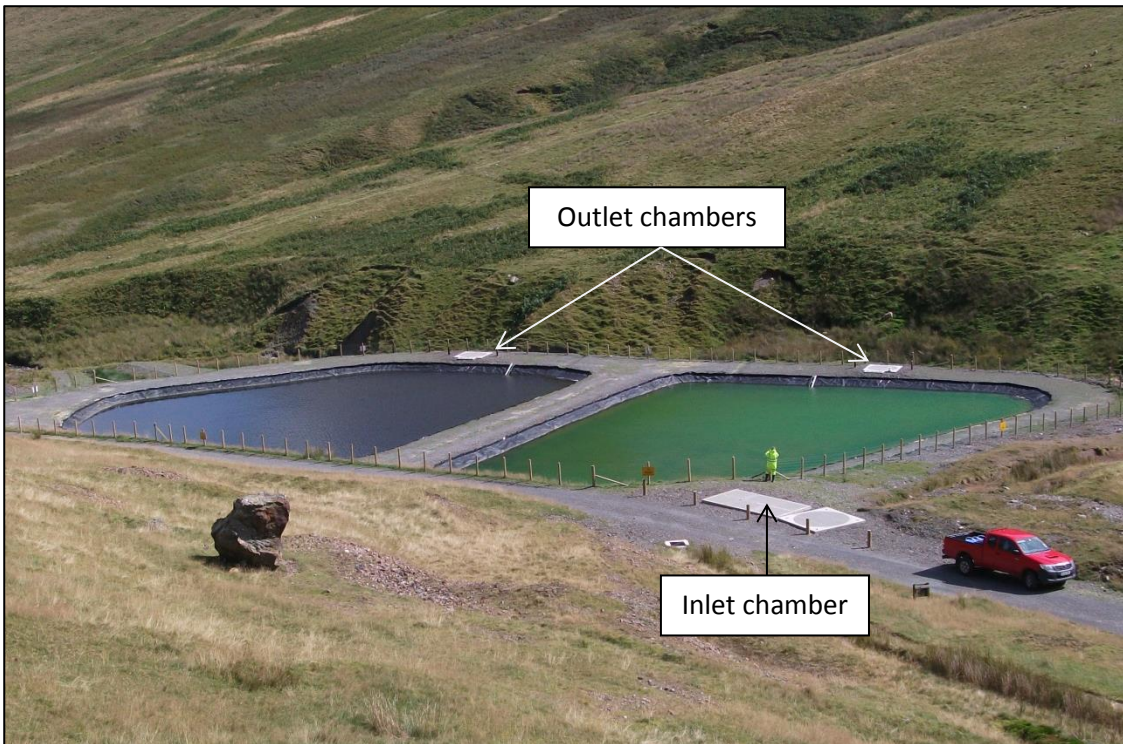


Figure 3.7 Photograph of Force Crag mine water treatment system VFPs (note that at the time of the photograph, a fluorescein tracer test was being conducted on the right hand VFP)

3.6.2 Flow measurements

20° v-notch thin-plate weirs facilitated influent flow measurements into the VFPs. Due to the swan-neck configuration of the outlet pipes, a manual bucket and stopwatch method was adopted for effluent flow measurements instead. The principle of v-notch flow measurement is based upon a relationship between the upstream head on the weir, the geometry of the weir and the channel leading up to it, and the fluid properties of water (ISO 1438:2008). Flows are calculated using the height of water behind the v-notch and an experimentally determined coefficient (see: ISO 1438:2008). Flow data was principally collected by pressure transducer type loggers (Schlumberger Water Services Diver™) which were placed behind weirs and determine water level by changes in pressure. These devices operate in pairs, with an atmospheric diver correcting for barometric pressure changes (Schlumberger Water Services, 2014). The loggers were set to 15 minute intervals and downloaded periodically. Manual readings were taken during site visits to check logger data.

At the VFP outlets, manual bucket (6.5L) and stopwatch readings were taken. As the outlets were located in a deep manhole chamber, the bucket was lowered from the surface by means of a short length of rope before being allowed to fill, to avoid entry

into the confined space. Regardless of non-entry, personal gas alarms were worn during fieldwork as a precaution against the risk of hydrogen sulphide which is generated by the system. Bucket and stopwatch flow measurements were repeated 3 times and averages taken to calculate the flow in L/s (Younger et al., 2002).

3.6.3 Analysis of water samples

Analysis of collected samples was undertaken by technical staff at Newcastle University, rather than this author, as this data was also being collected for purposes outside this research. Table 3.6 provides a summary of the parameters determined.

Table 3.6 Analytical parameters adopted for Force Crag water sampling analysis

Parameter	Method
Total and dissolved (filtered to <0.1µm and <0.45 µm) elements (Mg, Na, K, Ca, Zn, Cd, Pb, Cu, Ni, Fe, Mn, Al, Si)	ICP-OES (Varian Vista MPX) according to standard method ISO 11885 (BSI, 2009)
Anions (SO ₄ ²⁻)	Ion chromatograph (Dionex IC25)

0.45µm syringe filters are used widely to separate dissolved species from total; however, it has been shown that fine metal oxy-hydroxides pass through 0.45µm pores, and therefore 0.1µm (Pall Acrodisc Supor Membrane™) syringe filters were also used (Appelo and Postma, 2010). ICP-OES Standards used for metals analysis are presented in Table 3.7. Note that samples were acidified using ~0.1mL of concentrated HNO₃ (69%) to preserve metals in solution. This approximates sample acid concentration of ~0.3% in a 25mL sample container, which is comparable to the calibration standards, in case of any interference caused by the acid (BSI, 2009). 3 standards plus a blank were used for all elements, other than zinc, which had a 5 point calibration to improve accuracy. Calibration checks were made using a certified reference material sourced from a local government chemist (LGC 6019) and blanks and standards run every 8 test samples.

Chapter 3. Methods

Table 3.7 ICP-OES calibration standards for Force Crag mine water metals analysis

Calibration solution concentrations, mg/L (three standards per element plus blank)	
Leach test calibration solutions (~0.3% HNO ₃ matrix)	
Cu, Ni	0.2; 0.5; 1
Zn; Fe	2; 4; 6 (+10; 20 Zn only)
Mn; Pb	1; 2; 3
Cd	0.1; 0.2; 0.3

Sulphate analysis was conducted by ion chromatography (Dionex IC25) and was calibrated using a 20mg/L standard. The standard was also run every 5 samples to check for analytical accuracy. The detection limit of the ion chromatograph for sulphate is 0.5mg/L, as determined by the 4110B method (APHA, 2005).

Chapter 4. Results and Discussion – Nenthead Substrate Characterisation and Metal Recovery

4.1 Introduction and chapter contents

This chapter presents results and discussion of detailed geochemical analyses and metal recovery experiments on substrate taken from the Nenthead pilot scale treatment system at the time of its decommissioning in August 2012 (refer to section 1.5). This is to fulfil objectives 2 and 3 of this Thesis as described in Chapter 1, to:

- Characterise the distribution of metals within passive metal mine water treatment system substrates (objective 2).
- Assess the options for metal recovery from passive treatment system substrates and undertake lab-scale proof-of-principle metal recovery tests (objective 3).

The geochemical analysis investigates the nature and distribution of metals within the compost substrate, in order to understand the wastes generated by systems of this type. Sequential extractions according to the method developed by Tessier et al. (1979) were undertaken and are detailed in section 3.3.3 (herein referred to as ‘Tessier extraction’ for convenience). Variation in metal extractability in relation to particle size was investigated, as was the spatial distribution of metals within the treatment system. To achieve this, sieving of substrate was conducted, along with analysis of samples taken in three dimensions from across the treatment tank.

In addition, data are presented and discussed relating to the recovery of metals from the Nenthead substrate. Reducing metal concentrations within contaminated mine water treatment system substrates is a fundamental objective of this research, as a key element of identifying ways to recover resources and reduce whole life costs of compost-based passive treatment systems. The intention of reducing the metal content of the compost is so that it no longer represents a hazardous waste but can either:

- a. be re-used as a major substrate component in the treatment system from which it came; or,
- b. be re-used in an alternative application either on or off-site.

Metal recovery tests have been conducted using laboratory grade sulphuric acid and biological leaching to determine if these common strategies were effective at recovering metals from organic substrates. Additionally, recovery of a metal-rich solid was trialled by dosing pregnant leach solutions with a strong alkali followed by filtration. The focus of investigations was to attempt metal recovery from passive treatment system substrate samples to establish whether, in principle, they could be decontaminated, generating a concentrated low-volume metal product which might be suitable for further metal recovery by commercial recycling operations. Although it is acknowledged that if recycling of the waste concentrate is not realised, disposal to landfill would still offer substantial savings due to mass reduction of hazardous waste.

4.2 Characterisation of treatment system substrates

Presented in this section are sequential extraction data for zinc in samples which have been sieved, and copper, lead, zinc, cadmium, nickel, iron and manganese within samples taken from three dimensions within the treatment system. Substrate characterisation data are included as Appendix D.

4.2.1 Particle size characterisation

Physical separation has been identified as a key method for separating metal rich components from other materials in mining and contaminated land remediation industries (CL:AIRE, 2007; Wills, 2006). It has also been suggested that this technique may be suitable for metal recovery operations from VFP substrates (Gusek et al., 2006). Preliminary sieving was therefore conducted, using both wet and dry procedures outlined in the British Standard method for soil classification in order to determine which technique yielded better results (BSI, 1990).

Sieving was conducted on two quartiles of the Nenthead substrate using wet and dry methods (see section 3.3.1 for details of sample and procedure). By separating the substrate by particle size, this also allowed the metal content of different fractions to be determined. It was found that the mass of the wet sieved sample had a more even distribution across the three particle sizes, compared to dry sieving where a greater mass was associated with the larger size fraction. It is thought that this is due to aggregation of dried substrate which was observed during the procedure; whereas wet sieving can cause disintegration of aggregates which has been seen by other authors (e.g. Sainju,

2006; Beauchamp and Seech, 1990). The masses of the sieved fractions (quarter 1 and 4) for each sample are shown in Table 4.1.

Table 4.1 Masses of compost following sieving of quarters 1 and 4 of sample C4B (quarters 2 and 3 were not sieved)

Ref	Sample	Mass (g)
1a	≤0.212mm dry sieved	1.17
1b	2mm - 0.212mm dry sieved	4.58
1c	>2mm dry sieved	7.04
	<i>Quarter 1 total</i>	<i>12.79</i>
4a	≤0.212mm wet sieved	4.56
4b	2mm - 0.212mm wet sieved	3.05
4c	>2mm wet sieved	5.11
	<i>Quarter 4 total</i>	<i>12.72</i>

4.2.2 Sequential extraction procedure

There has been much conjecture surrounding the interpretation of sequential extraction data (for review, see: Gleyzes et al., 2002) and, consequently, an alternative approach to classification of extraction steps has been suggested, based upon the operational definition of the extraction step rather than the assumed nature of solid phase metals (Tessier et al., 1979).

Data from studies of the Nenthead treatment system by Jarvis et al. (2014) suggests that, during operation, zinc sulphide solid formation under reducing conditions is an important removal mechanism, which agrees with other studies (Johnson and Hallberg, 2005b; Jong and Parry, 2004). It might therefore be expected that, during sequential extractions of arising substrates, metals associated with sulphides would consequently be removed by oxidisation (e.g. step 4 of a Tessier extraction) (Clark et al., 2000). However, studies by Peltier et al. (2004) and Burton et al. (2006) found that there is little evidence of this during multi-method investigations. The majority of Acid Volatile Sulphide (AVS) associated metals were extracted during step 3 of the Tessier

procedure (Burton et al., 2006; Peltier et al., 2004). The Tessier method actually defines step 3 as ‘bound to iron and manganese oxides’ which, if used for interpretation of data, could lead to mischaracterisation of sulphides. On the other hand, when considering the ‘reducible’ interpretation made by Gleyzes et al. (2002) for the third extraction step, it is implied that metals are amenable to further reduction. In the case of sulphate reducing bioreactors, it would be assumed that metals would already be in reduced forms, yet large quantities of metal have been found to be associated with this third step in several other studies (Mayes et al., 2011; Neculita et al., 2008b). For the purposes of this thesis, therefore, the extraction step sequence number is used for simplicity and to avoid any mischaracterisation surrounding described phases. This approach provides an adequate indication of the recoverability of different metals within the substrate according to particle size and spatially within the treatment system.

4.2.3 Zinc data for sieved samples

Sequential extractions according to the Tessier et al. (1979) method were performed on 1g of each sieved fraction. Triplicate extractions were conducted on the two remaining un-sieved quarters of the substrate sample (quarters 2 and 3 of sample C4B – see Chapter 3, Figure 3.1 for location) in order to test the reproducibility of the procedure which is detailed in section 4.2.6. Zinc data as concentrations in mg/kg are presented as this was the key metal removed by the Nenthead treatment system (Jarvis et al., 2014).

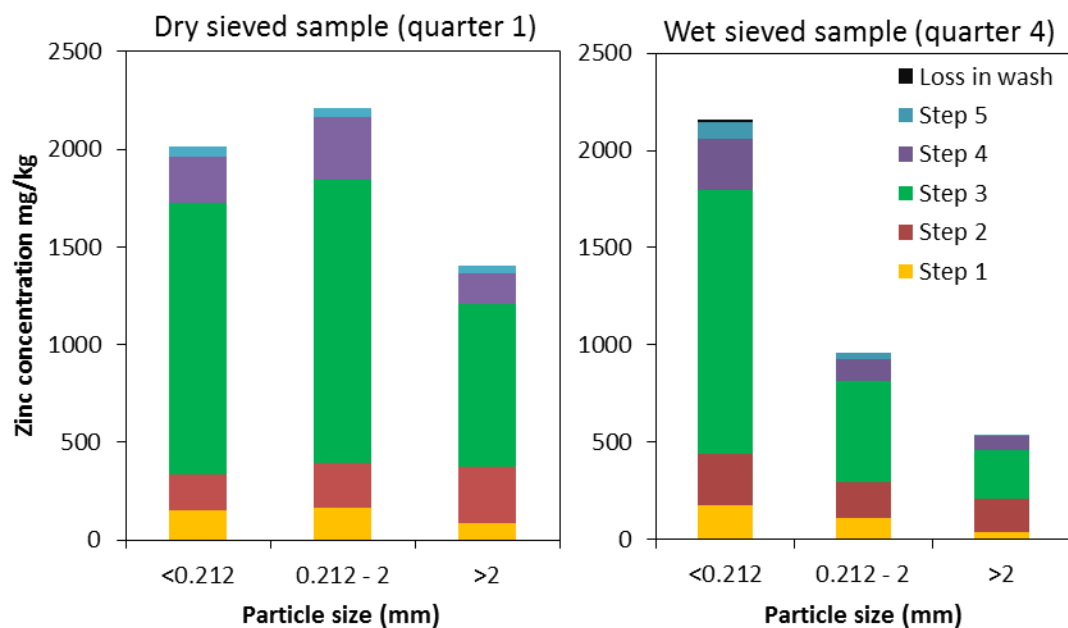


Figure 4.1 Zinc content of wet and dry sieved substrate

Figure 4.1 shows results from dry sieved and wet sieved fractions (quarters 1 and 4 of sample C4B, respectively). In addition to a breakdown of the zinc concentration in each of the 5 extraction steps, the amount of zinc lost from the wash solution used for the wet sieving (included in 4a: $<212\mu\text{m}$ fraction) is depicted on this bar as 'Loss in wash'.

A clear pattern was apparent within the wet sieved sample: the greater the particle size, the lower the zinc concentration. The wet sieved fraction $\leq 212\mu\text{m}$ contained 2,158mg/kg of zinc, in contrast to the $>2\text{mm}$ fraction that contained just over a quarter of this amount (541mg/kg). This pattern was also observed for iron, manganese, lead and cadmium (data not presented). Such behaviour may be attributable to the function of increased surface area for sorption or precipitation of metals in materials with finer grains, yet previous studies indicate that specific sorbents may also accumulate in smaller particle fractions. Soares et al. (1999) determined a similar pattern in contaminated river sediment, that finer grained material contained the greatest metal concentration: the $<150\mu\text{m}$ fraction contained 12,167mg/kg zinc, compared to the $>150\mu\text{m}$ fraction which contained 9,015mg/kg. This behaviour might be explained by higher clay forming mineral content found in solids $<150\mu\text{m}$ (Gunawardana et al., 2014). An alternative explanation might be that it is due to increasing organic matter content with decreasing particle size: 39% in $<150\mu\text{m}$ fraction, vs. 21% in $>150\mu\text{m}$ fraction of contaminated river sediments (Soares et al., 1999). Both clay forming minerals and organic matter are important sorbents; Soares et al. (1999) identified that organic matter sorption occurred in the following order: $\text{Cu}>\text{Zn}>\text{Pb}>\text{Cr}>\text{Ni}>\text{Cd}$. Organic matter or clay mineral fractionation between different particle sizes was not investigated during experimentation with the Nenthead substrate, so it is unclear how this may impact upon metal partitioning. In terms of metal partitioning according to the sequential extraction, wet sieving shows an inverse relationship between particle size and zinc concentration across all extraction steps, excepting step 2 (Figure 4.1).

Dry sieving, however, did not yield such a clear pattern, with the $\leq 212\mu\text{m}$ fraction containing 2,014mg/kg of zinc, in comparison to $>2\text{mm}$ fraction which had 1,403mg/kg, but the intermediate dry sieved size fraction ($212\mu\text{m}$ - 2mm) contained the greatest amount 2,214mg/kg, albeit by a small margin (Figure 4.1). Such a distinct contrast between sieving methods is potentially explicable by the behaviour of materials within the sieves: dry sieved compost, pre-dried to remove moisture, comprised loosely cemented fragments bound together with fine grained material. These findings are

consistent with those following investigations by other authors using wet and dry methods for soils analysis (Sainju, 2006; Beauchamp and Seech, 1990). Sieving only showed some success in separating these fragments, evidenced in part by the recovery rate of fine grained material (see Table 4.1): just 1.17g passing $\leq 212\mu\text{m}$, compared to 7.04g of material retained on the 2mm sieve. In contrast, 4.56g of material passed the 212 μm sieve and 5.11g was retained on the 2mm sieve during the wet sieving operation. From observations during the sieving process, the deionised water wash solution aided the separation of compost fragments to achieve a more accurate representation of particle distribution.

It was not unexpected that wet sieving would assist the separation of particles during sieving, but it was recognised that the deionised water wash has the potential to both dissolve metals and, potentially facilitate geochemical reactions which might alter speciation. Unfortunately, on the basis of the data presented (and the issues discussed with dry sieving discussed in section 4.2.1) it has not been possible to demonstrate that the latter concern is not the case. Nevertheless, a sample of the deionised water wash solution was analysed by ICP-OES (in parallel with a blank), which showed that just 13.76mg/kg equivalent of zinc was leached from the compost (see ‘Loss in wash’ in Figure 4.1 for relative significance). This demonstrates that there was very minimal dissolution of zinc in the wash solution.

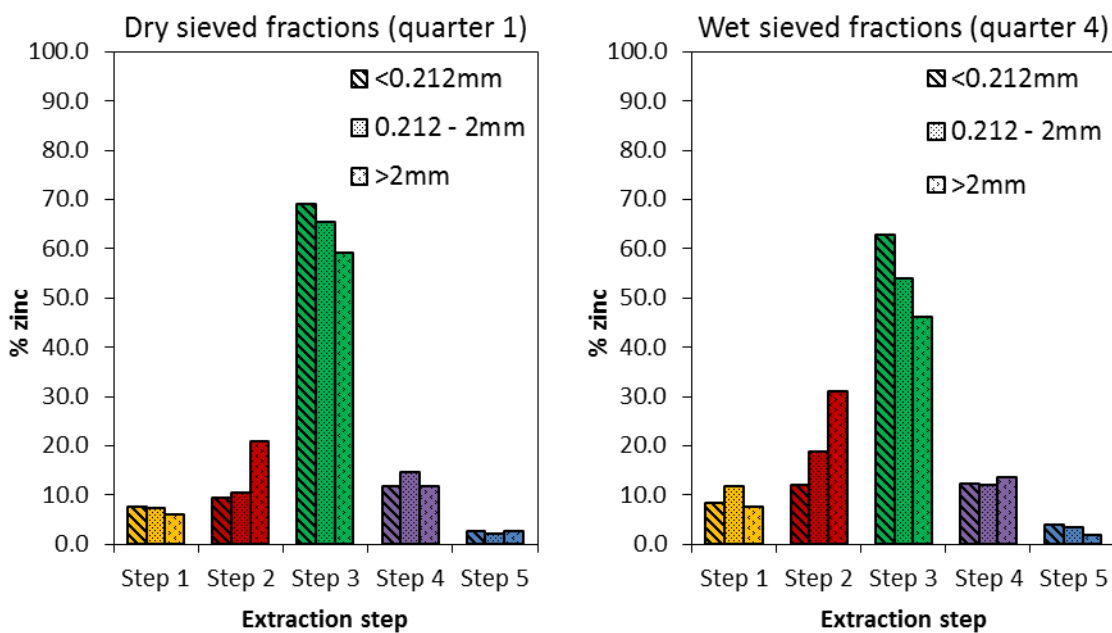


Figure 4.2 Comparison of zinc partitioning according to particle size (as % of total determined by Tessier extraction), showing data for wet and dry sieved substrate samples

It can be seen from Figure 4.2 that step 3 of the Tessier procedure yielded greatest zinc concentrations, with more than 50% of the total extracted during this step for both wet and dry sieved samples. Additionally, there appears to be similar patterns between the sequential extraction profiles across all particle size fractions. However, for both wet and dry sieved samples, more zinc is extracted during step 2 as particle size increases and, less zinc is extracted during step 3 as particle size increases. This suggests that the fraction of zinc extracted by step 2 may be more associated with coarse grained material, whereas the fraction extracted by step 3 is more associated with fine grained material. There is, however, a paucity of published investigations into particle size coupled sequential extraction investigations of organic wastes which means it is difficult to corroborate this data. Furthermore, due to the limited sample number in this preliminary study (just one wet and one dry sieved sample) and the inherent variability between replicate samples (see section 4.2.6), further investigation would be required before any firm conclusions on metal partitioning in different size fractions of contaminated substrates can be drawn.

4.2.4 Metal distribution in samples from different locations

The significance of spatial variation was investigated in a second round of sequential extractions using the Tessier method detailed in section 3.3. Particle size separation was not undertaken as part of these tests, as they were conducted to assess the variation (if any) between metal species throughout different parts of the Nenthead treatment system. 11 bulk samples in total were analysed, plus a substrate blank. A fuller analysis is presented covering copper, lead, zinc, cadmium, nickel, iron and manganese, as it has previously shown that different metals accumulate in different parts of sulphate reducing bioreactor systems (Neculita et al., 2008b). Cobalt is also investigated in the standard Tessier sequential extraction (Tessier et al., 1979), but is not considered in this analysis as it is not a major pollutant from abandoned mines (e.g. Mayes et al., 2009a).

Table 4.2 provides details of the Rampgill mine water prior to treatment at the Nenthead site for reference, and Figures 4.3 - 4.12 depict the metal concentrations and the steps by which they were extracted for the different sample locations, including the blank substrate.

Table 4.2 Rampgill Horse Level water quality, after Jarvis et al. (2014); Gandy and Jarvis (2012)

Parameter	Unit	Mean	Range
pH	pH units	7.74	6.88-8.62
Temperature	°C	8.89	5.8-12.5
Conductivity	µS/cm	589.5	389-681.4
Eh	mV	139	28-276
Alkalinity	mg/L CaCO ₃	156	103-238
Sulphate	mg/L	134	87-164
Copper	mg/L	<0.01	-
Lead	mg/L	<0.05	-
Zinc	mg/L	2.32	1.69-4.5
Cadmium	mg/L	<0.01	-
Nickel	mg/L	<0.01	-
Iron	mg/L	0.33	0.1-2.72
Manganese	mg/L	0.15	0.08-0.56

Data are discussed in the context of existing literature and sulphide solubility products of metals, given that this is a primary removal mechanism in anaerobic compost based systems (e.g. Neculita et al., 2007). Please refer to Table 2.7 (Chapter 2) after Hedin et al. (1994a) which provides a summary of metal sulphide solubility products.

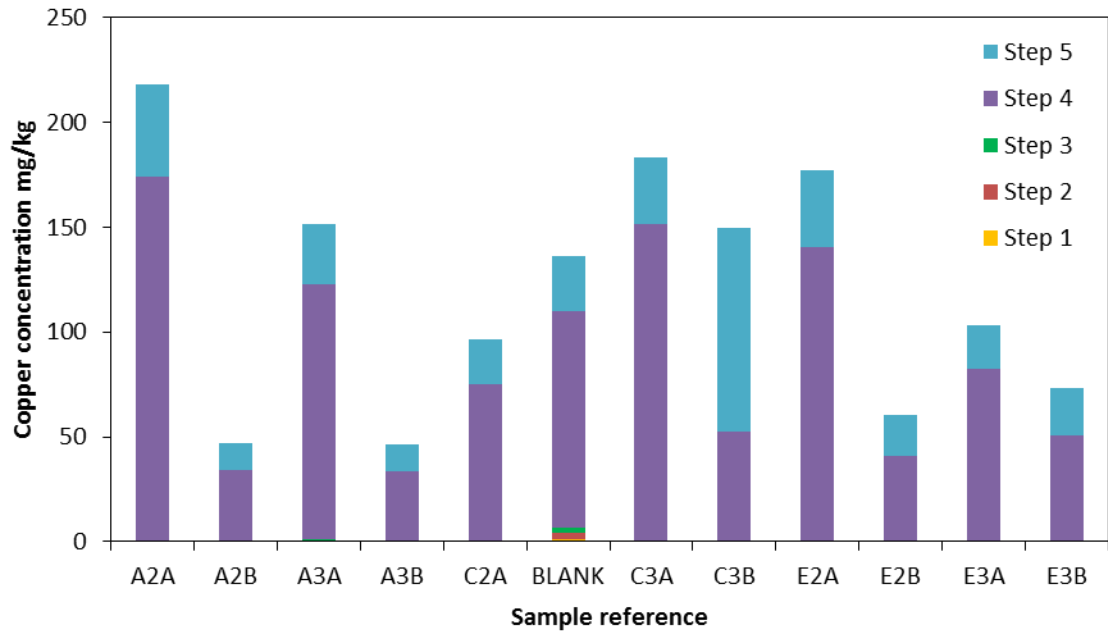


Figure 4.3 Copper partitioning in different sample locations

Copper concentrations in the blank sample equal 136mg/kg, a slightly greater amount than the mean copper concentration of all samples taken from the pilot system after operation, which equal 119mg/kg. It appears unlikely that net copper removal occurred in the treatment system, probably due to its low concentration in influent mine water: below 0.1mg/L detection limits in both influent and effluent samples (Gandy and Jarvis, 2012). However, under reducing conditions, copper is the first element to form a sulphide due to its low K_{sp} , and consequently is also likely to be the last metal sulphide to be solubilised during a sequential extraction. This might explain why copper is almost entirely associated with steps 4 and 5 of the sequential extraction procedure (>99.5%), a pattern also found by Jong and Parry (2004) who found that, in their investigations into a pilot scale sulphate reducing bioreactor, >98.5% of copper was associated with the last two steps of a modified Tessier analysis, with step 4 yielding 86.7%. This finding is also in agreement with Mayes et al. (2011) who found 96-98% of copper associated with the 4th step of a Tessier analysis investigated column bioreactors. Mayes et al. (2011) concludes that the high copper association with step 4 of the Tessier extraction is likely to be copper sulphide, because sulphides are commonly associated with this step of the extraction, and copper's low sulphide solubility product increases the likelihood of sulphide formation compared to other metals.

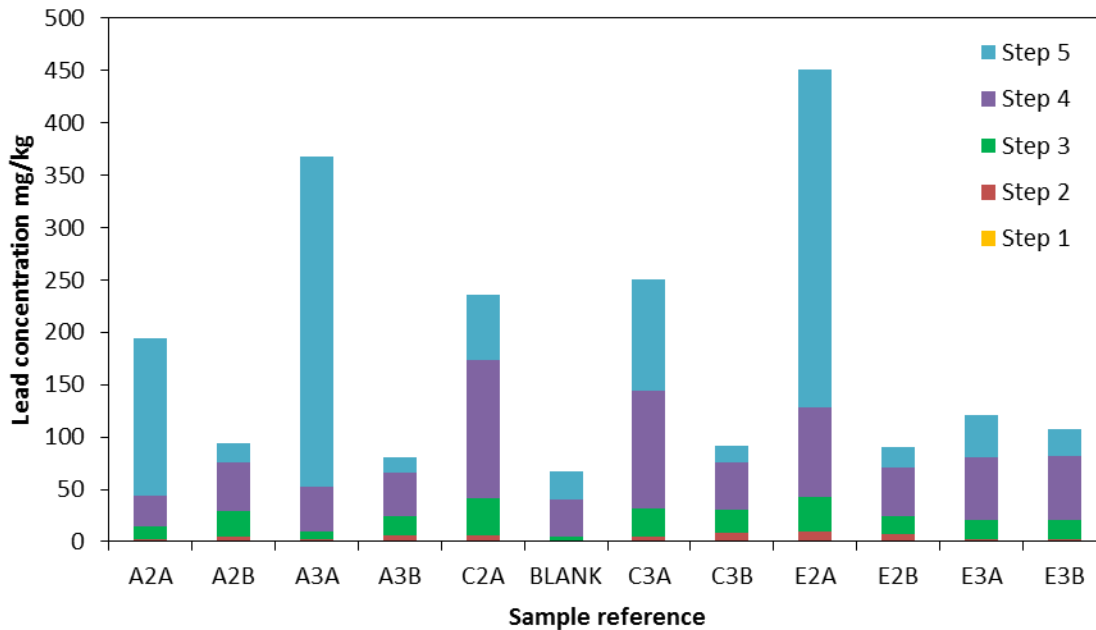


Figure 4.4 Lead partitioning in different sample locations

More lead has accumulated in upper substrate layers compared to lower layers across each sample location. Generally, step 4 and 5 fractions dominate for lead, where concentrations on average are 64mg/kg and 99mg/kg, respectively, with other fractions representing just 27mg/kg in total. Mayes et al. (2011) on the other hand identifies that, in Tessier analysis of laboratory scale sulphate reducing bioreactor substrates, most lead is associated with step 2. These laboratory-scale systems contain 50% limestone or shells, therefore increasing the likelihood of metal association with acid-soluble carbonate fractions typically targeted by the second extraction step (Mayes et al., 2011). This is in comparison to the Nenthead pilot unit which contained just 10% limestone by weight, which was removed before analysis (Gandy and Jarvis, 2012). Given that lead has a relatively low solubility product, it is more likely to form a sulphide compared to other metals (excepting copper). Sequential extraction data is, to some degree, in agreement with this, given that significant quantities of metal are seen in step 4, which has been attributed to the step at which sulphides are generally extracted (Mayes et al., 2011).

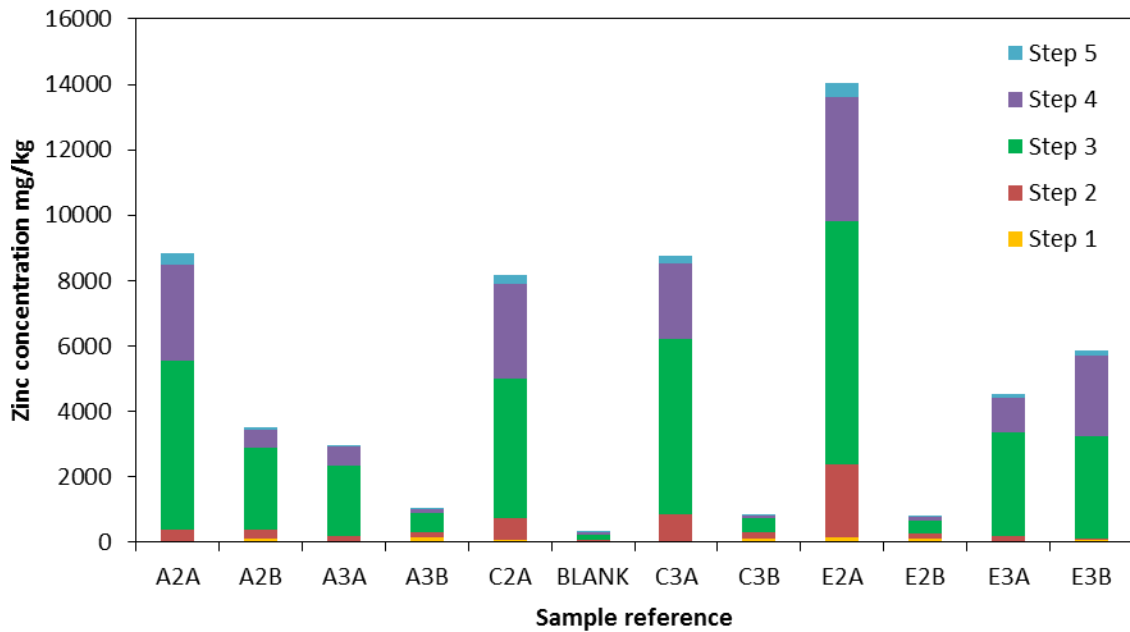


Figure 4.5 Zinc partitioning in different sample locations

In all but one case (samples E3A/B), substrate from the upper layer contains substantially more zinc than samples taken from the respective lower layer. Greatest total zinc concentrations were seen in sample E2A (14,050mg/kg), with the lowest seen in the corresponding lower layer sample E2B (808mg/kg). 340mg/kg zinc was measured in the blank substrate. To facilitate comparison between zinc fractions, the target metal of the Nenthead treatment system, a series of pie charts have been plotted on a sketch of the treatment tank sampling grid. These are displayed in Figure 4.6 and Figure 4.7, where each pie chart position corresponds to the location from which that sample was taken.

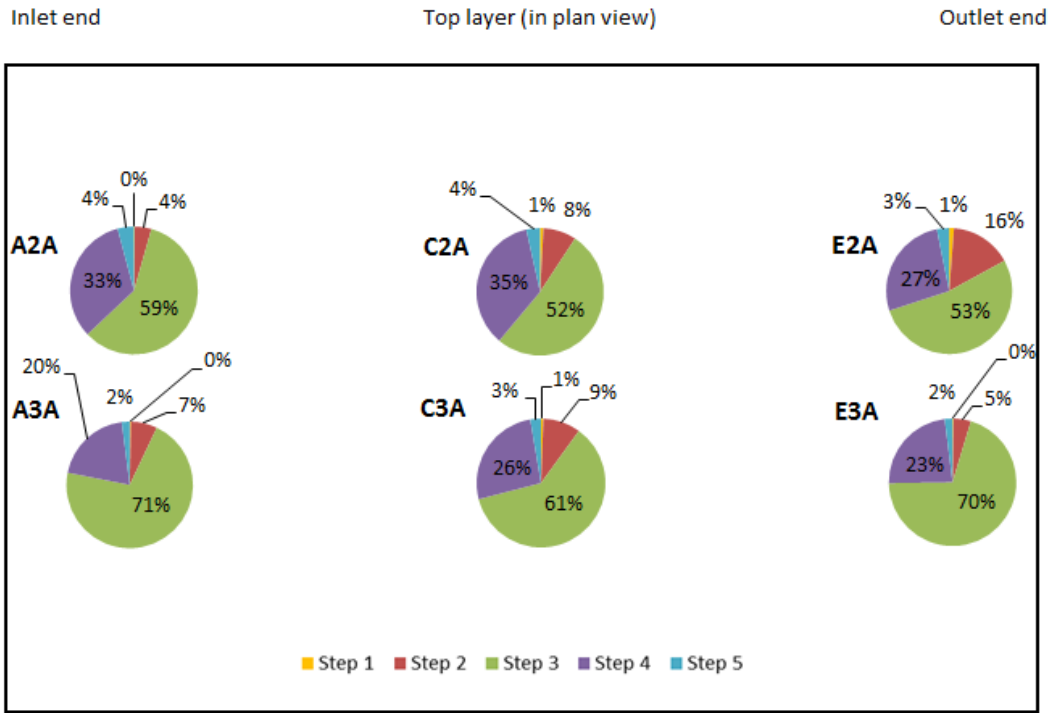


Figure 4.6 Zinc partitioning in upper 0 – 23cm compost layer: pie charts positioned approximately at sample locations

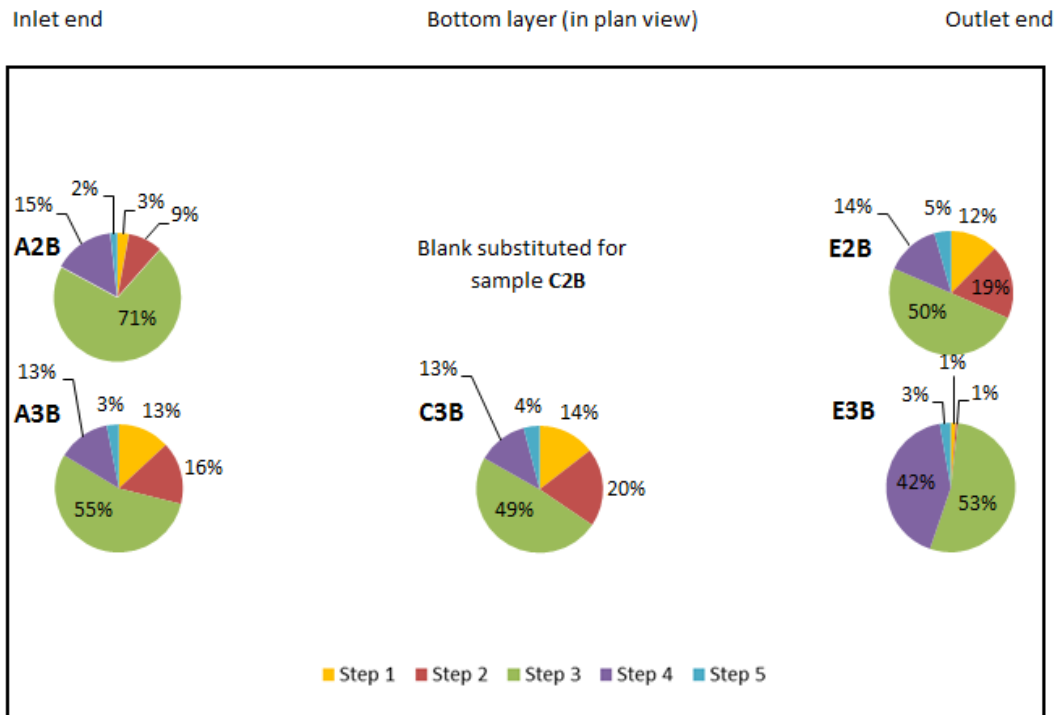


Figure 4.7 Zinc partitioning in lower 23 - 46cm compost layer: pie charts positioned approximately at sample locations

Step 1 of the sequential extraction provided perhaps the clearest pattern in variation between metal concentrations in upper and lower levels, as significant zinc associated with this step was only shown at depth. E3B did not show this clear pattern, but this sample was an outlier for total metal concentrations also, compared to other sample locations. In the upper layer, zinc was largely extracted by step 3 and step 4 (3,139mg/kg and 1,536mg/kg, respectively), with very small concentrations of zinc associated with steps 1 and 2 - 80mg/kg and 485mg/kg, respectively. Step 5, however, extracted a relative small fraction of zinc at Nenthead: 3.1% on average. Data for the blank sample showed a similar pattern; almost half (46%) zinc attributed to the 3rd step, with significant amounts also associated with steps 2 and 4, and a lesser amount (5%) step 1 (Figure 4.8).

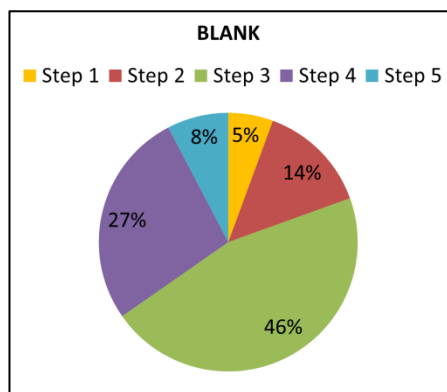


Figure 4.8 Zinc distribution for blank compost sample

Tessier analysis of sewage sludge by Perez-Cid et al. (1996) identified zinc fractions were dominantly extracted by step 3 (37.3%) and 4 (20%); which is comparable to the blank Nenthead substrate; however step 5 of the sewage sludge also contained a substantial fraction of zinc (26.7%) whereas this was significantly lower in the Nenthead blank substrate (8%). While zinc extracted by step 5 in the blank is still proportionally higher than every sample from the treatment system, it was less in absolute terms than all other substrate samples. Several samples (A2A, C2A, E2A) had in excess of 10 times the concentration of zinc extracted in this final step, compared to the blank (Figure 4.5).

In a modified Tessier extraction on a column bioreactor with a 7.3 day residence time, Neculita et al. (2008b) found the greatest zinc fraction (37 – 50%) was associated with step 3, which is comparable with Nenthead data. In contrast, substantial zinc concentrations were also associated with the 4th and 5th steps: specifically 4th in the top

layers (36 – 46%) and 5th in the lower (28 – 36%) (Neculita et al., 2008b). What is of significance here is that substantial amounts of zinc appear more tightly bound (i.e. latter sequential extraction steps) in the study by Neculita et al. (2008b), specifically at depth. Yet, while data from the Nenthead tank shows typically very low zinc extracted by step 1 in the surface layer, Neculita et al. (2008b) found that this is where most of this readily extractable zinc occurs (8 – 12%). A second duplicate set of columns were investigated, with an increased hydraulic residence time of 10 days (Neculita et al., 2008b). These columns yielded similar results, although one possible trend was an increase in zinc extracted by step 5 in the bottom layers of the columns: 33 - 41% (Neculita et al., 2008b). Increased zinc attributable to the final sequential extraction step found in lower parts of the treatment system appears to be associated with increasing residence times as follows, where * denotes investigations by Neculita et al. (2008b):

Nenthead pilot (19hr – 2.7%) < Columns* (7.3d – 32%) < Columns* (10d – 37%)

The inverse is the case for residence time to exchangeable and acido-soluble zinc (steps 1 and 2):

Nenthead pilot (19hr – 11%) > Columns* (7.3d – 8%) > Columns* (10d – 3%)

This pattern suggests that increasing residence time may lead to more tightly bound zinc phases deep in the treatment system. One possible explanation is that increased sulphide formation is known to occur in systems with higher residency times (Chang et al., 2000a), although further investigation would be required to confirm that this is the case. In particular, to rule out the wide range of variables which differ between the Nenthead system which was installed in the field in northern England (Gandy and Jarvis, 2012), and the laboratory scale columns operated by Neculita et al. (2008b). For instance, it is thought that the seasonal temperature fluctuations at Nenthead had a significant effect on zinc removal, compared to parallel laboratory experiments which took place under controlled conditions (Gandy and Jarvis, 2012).

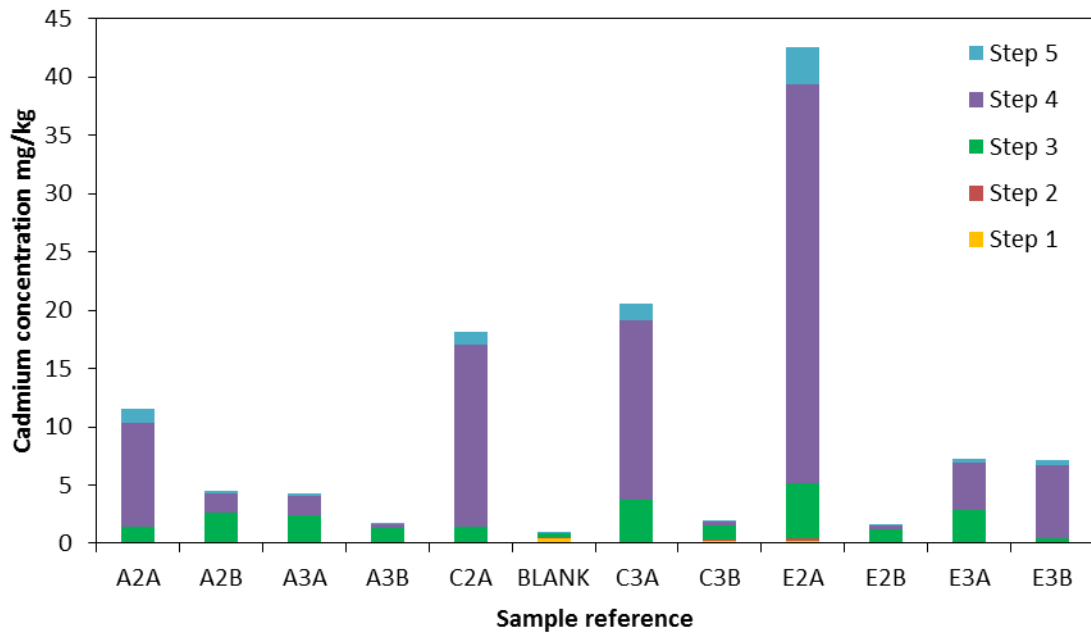


Figure 4.9 Cadmium partitioning in different sample locations

Cadmium concentrations across all substrate samples were elevated compared to the blank, although concentrations were still low compared to other metals studied (i.e. Figures 4.3 – 4.12). In particular, it appears that substantially more cadmium accumulated in surface layers⁹. Given that the treatment system operated in a down-flow configuration, this suggests that rapid removal of cadmium was occurring before the water reached lower layers of the system. Most cadmium was extracted during step 4, with a lesser amount in steps 3 and 5. These data are in agreement with findings by Neculita et al. (2008b), who find that 72-97% of cadmium is concentrated in step 4 across 7 of 8 samples (the eighth shows 77% of cadmium associated with step 5). It might be expected that cadmium would have a similar extraction pattern to zinc, given their similar sulphide solubility products, but this is not the case. The key variable between the two metals at Nenthead is concentration, which is far higher for zinc in the mine water (2.32mg/L zinc, <0.01mg/L cadmium) and the substrate (mean metal content 5,404mg/kg zinc, 11mg/kg cadmium). It is likely that metal concentration therefore has some bearing upon removal mechanisms.

⁹ Where the last letter of the sample reference is A, samples are from an upper layer of the treatment system, which differentiates samples from a lower layer of the system which are denoted B.

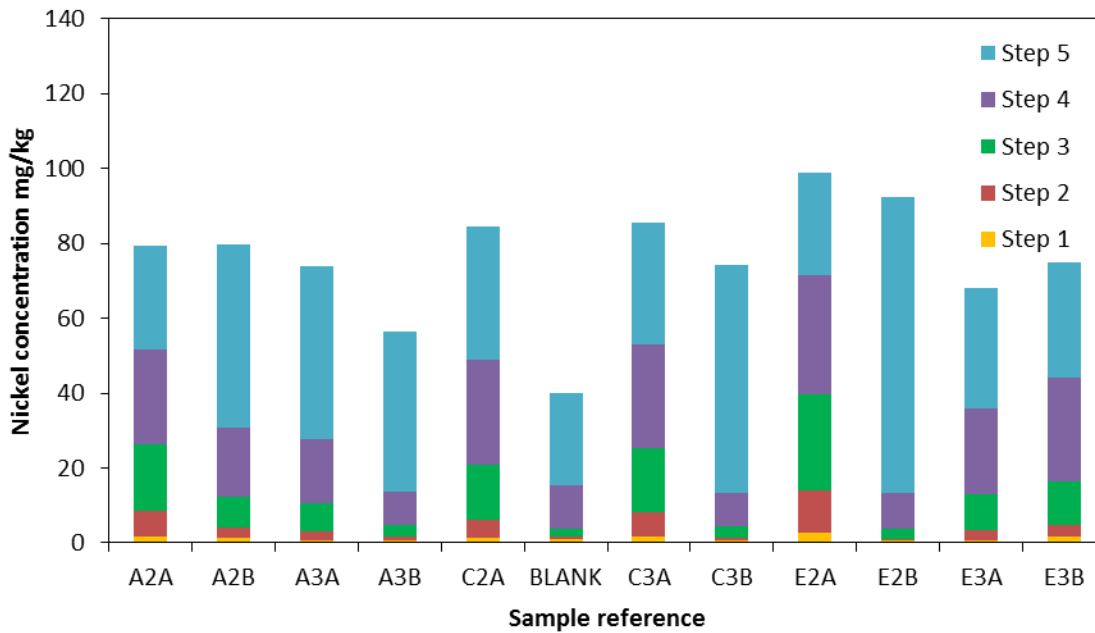


Figure 4.10 Nickel partitioning in different sample locations

Nickel was moderately elevated across all substrate samples in comparison to the blank. Unlike cadmium, there was a far less pronounced difference between concentrations in the upper and lower layers. Considering its relatively high K_{sp} , nickel would be expected to form a sulphide after cadmium, zinc, lead and copper; and therefore had a greater chance of accumulating in lower parts of the treatment system. Nickel was most associated with step 5 of the sequential extraction (46mg/kg on average) with lesser amounts associated with steps 3 (11mg/kg) and 4 (21mg/kg). Jong and Parry (2004), however, determine that most nickel was associated with steps 2 and 4 in their investigations¹⁰, yet this is in contradiction to Neculita et al. (2008b) who find nickel most concentrated in steps 3 and 5. It should be noted that both of the Tessier methods used by these authors had been modified and, that the treatment system configurations differed from this study, all of which may have had a bearing on the results. In particular, Jong and Parry (2004) used a method which excludes oxygen in order to prevent reaction of metal sulphides with atmospheric oxygen. This was undertaken to minimise mischaracterisation of sulphides during the sequential extraction procedure (Jong and Parry, 2004).

¹⁰ Note Jong and Parry (2004) use an additional first-step 'step 0' in their modified Tessier analysis which is not referred to in this discussion. All other numbered steps (i.e. 1-5) are functionally comparable to the standard method.

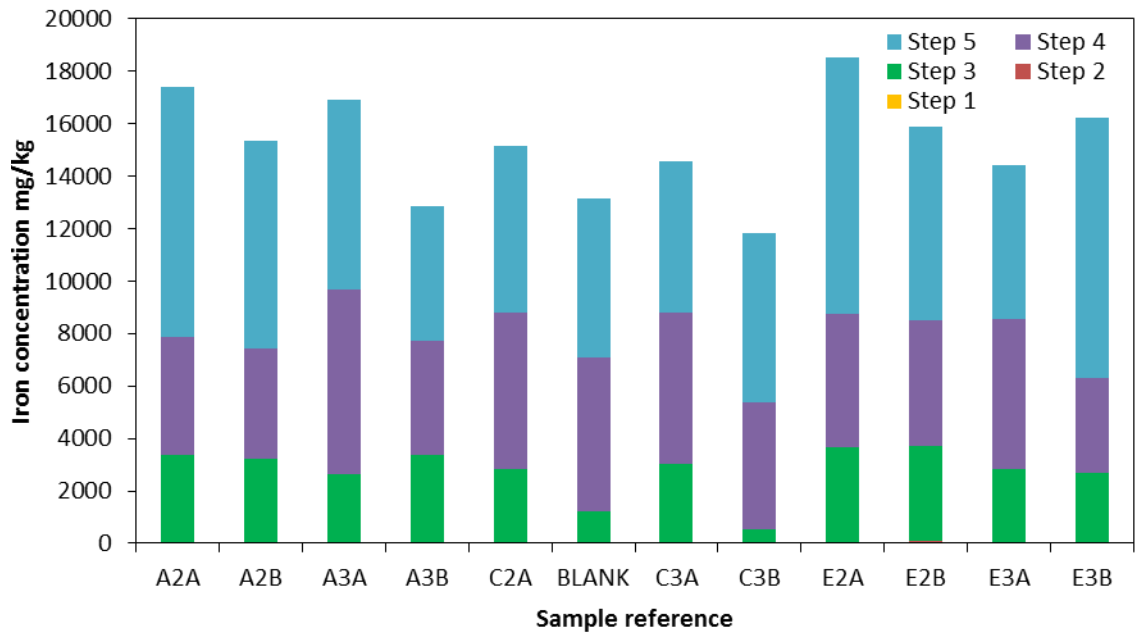


Figure 4.11 Iron partitioning in different sample locations

Iron exhibited very high concentrations in the pilot treatment system substrate and the blank, with similar partitioning across all samples. Iron concentrations in the blank were 13,128mg/kg, slightly lower than the average concentration in the samples taken from the treatment system: 15,376mg/kg. It is thought unlikely that there was any iron accumulation in the substrate due to the low concentrations in the mine water. In fact, influent mine water concentrations were 0.2mg/L, yet over the first year of operation, the average concentrations of the treatment system effluent were 0.6mg/L (Gandy and Jarvis, 2012). This suggests iron was exported from the system during this period. It may be that the lower than average concentrations in the blank sample could be explained by sample heterogeneity; yet without further sampling of the blank, this cannot be confirmed.

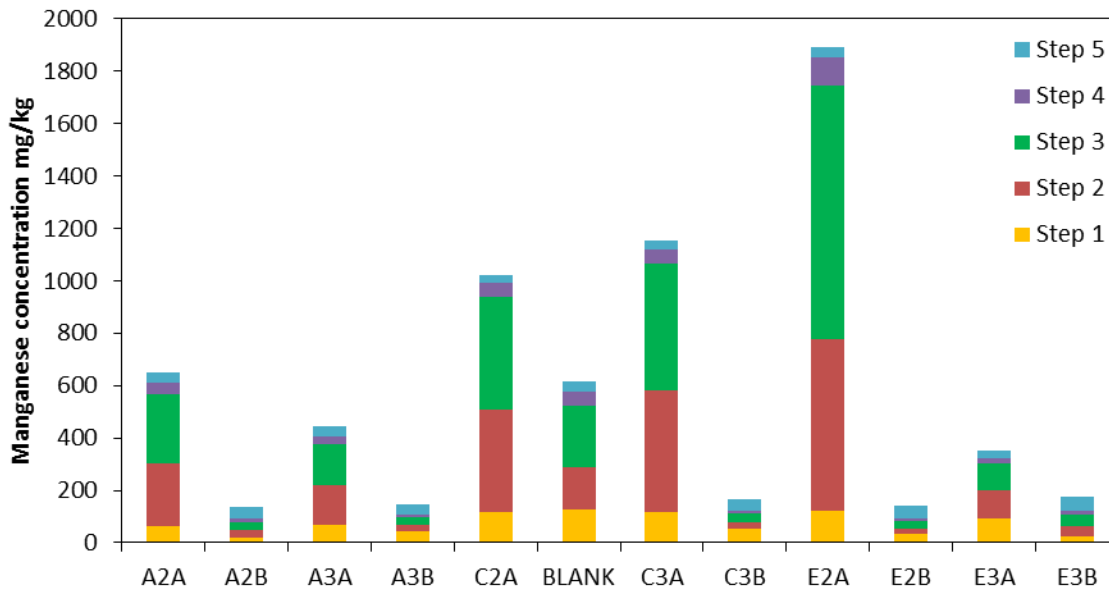


Figure 4.12 Manganese partitioning in different sample locations

Manganese, at the opposite end of the K_{sp} scale to copper for sulphide formation, showed the greatest proportion of readily extractable fractions: step 1, and step 2, as it is easily dissolved into solution compared to the other metals investigated, which agrees with data obtained in a similar studies by Mayes et al. (2011) and Dufresne et al. (2015). Yet, more metal is still seen in upper layers even though the K_{sp} would indicate that this metal forms a sulphide last. This may be due to the relatively low concentration in the mine water (0.1mg/L) meaning that little had actually been removed (only 4 of 11 samples show higher concentrations than the blank). In fact, Appelo and Postma (2010) suggests that manganese sulphide is extremely rare in recent environments, due to its greater solubility, over elements such as iron. Mayes et al. (2011) suggests that one possible explanation, where similar observations were made, is that manganese recovered during step 2 is associated oxalic limestone surfaces contained in the treatment system. Additionally, according to Irving and Williams (1953); manganese has low complex stability compared to a range of other metals ($Mn < Fe < Ni < Cu > Zn$) and, as a consequence, it would be more amenable to extraction by weaker reagents when in sorbed phases (i.e. first steps of a sequential extraction).

It is notable that, across all elements investigated, metal concentrations in the blank sample were elevated. The source of these metals must have been from the constituents of the substrate, such as the PAS100 compost or digested sewage sludge. When comparing total concentrations of cadmium, copper, lead, nickel and zinc in the blank substrate, they are all below limits set out by the PAS 100 standard (BSI, 2011).

4.2.5 Partitioning of metals

Data for the spatial investigations was aggregated and averages taken to provide an overview of the metal partitioning determined by the sequential extraction procedure. Fractions associated with each extraction step are shown for the range of metals investigated in Figure 4.13. The pie charts are ordered according to their sulphide solubility products, which are noted on each chart for reference.

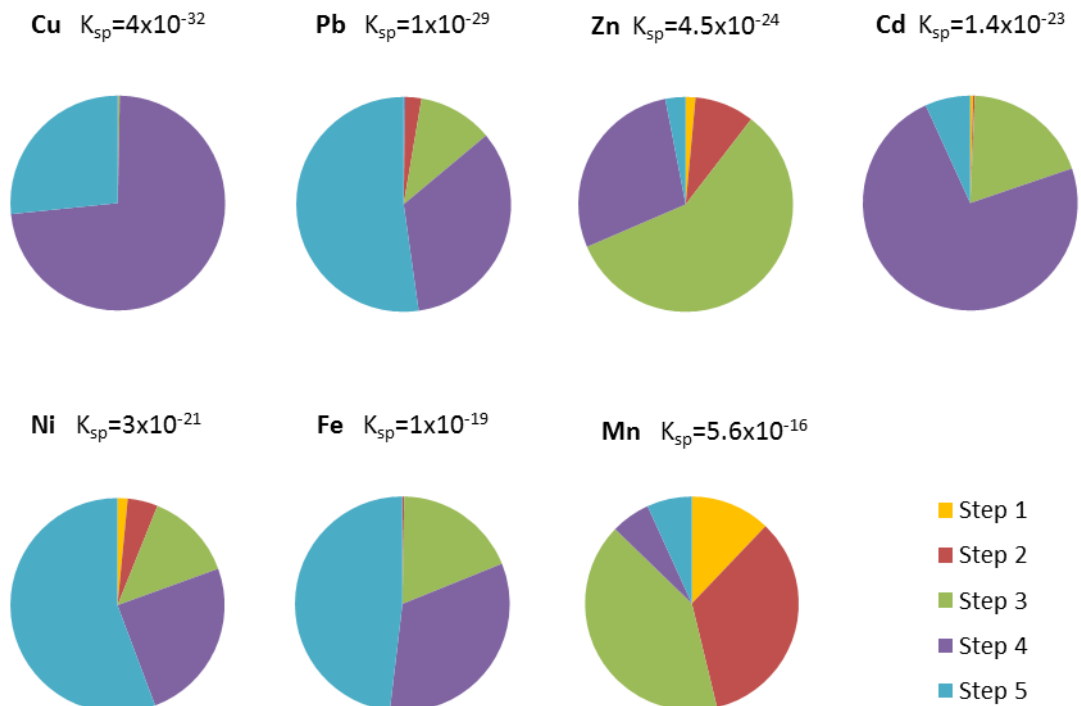


Figure 4.13 Metal partitioning using aggregated data, ordered in terms of sulphide solubility products for metal sulphides.

From the data presented in Figure 4.13, it is clear that there was distinct variability between the sequences in which the metals were extracted. Comparatively little was extracted during step 1 and 2 for all metals, other than manganese which has been shown to form weakly sorbed phases (Irving and Williams, 1953). Additionally, manganese occurs as its Mn^{2+} aqueous species over a range of Eh conditions when pH is below 6 (e.g. Appelo and Postma, 2010, p. 436). Lead, copper, cadmium, nickel and iron were all characterised by strongly bound phases, with in excess of 75% of their mass being extracted only by steps 4 and 5. Most zinc was extracted during step 3 (58%), which differs substantially from cadmium which was largely extracted by step 4 (73%), even though zinc and cadmium would be expected to both form sulphides at similar times according to their similar solubility products. In addition to the difference in concentrations between zinc and cadmium previously discussed, there is evidence

that cadmium forms a strongly bound organic complex which is not affected by acid. This may also explain its preferential partitioning in oxidisable and residual steps 4 and 5 of the Tessier extraction, compared to zinc (Neculita et al., 2008b; Palágyi et al., 2006).

Despite some patterns seen between increasing sulphide solubility products and metal partitioning seen by Tessier analyses, the sequence does not correspond exactly. This implies that other factors may be impacting upon metal partitioning, such as non-sulphide metal phases. It has been suggested that other metal removal mechanisms are at work in sulphate reducing systems such as complexation with organic matter and sorption to oxyhydroxide minerals (Matthies et al., 2009; McCauley et al., 2009; Neculita et al., 2008b). While it has not been possible to identify the metal species present, data suggest that metals accumulate preferentially within upper layers of the treatment system; and that different metals exhibit selectivity to different steps of the sequential extraction. Specifically, manganese shows greatest recovery during steps 1 and 2 of the procedure (46%) out of all metals investigated, whereas lead and copper show greatest selectivity to steps 4 and 5 of the procedure (>86%). 69% of zinc is recovered between steps 1 – 3 of the extraction (58% by step 3), which is substantially higher than all other metals, except manganese. On this basis, it may be possible to selectively recover the main contaminant, zinc, along with manganese, while leaving the majority of other metals within the substrate. But, given that manganese is likely to be recovered simultaneously to zinc, selective recovery of just zinc may be difficult.

When considering influent metal concentrations, copper, lead, cadmium and nickel are all below laboratory detection limits and, out of these metals, only cadmium appears to show significant enrichment in used substrates compared to the blank. Zinc, on the other hand, has the highest concentrations of all metals in the treatment system influent (2.32mg/L) and accumulates in substrates to concentrations of typically well in excess of an order of magnitude greater than the blank. The greatest substrate concentration of zinc was 14,050mg/kg, compared to the greatest cadmium concentration which was just 43mg/kg. Geochemically, zinc and cadmium are similar with comparable sulphide solubility products 4.5×10^{-24} and 1.4×10^{-23} respectively (Hedin et al., 1994a). It might therefore be assumed that in a sulphide producing treatment system, these metals would form sulphides in a similar way and consequently show similar geochemical profiles when extracted sequentially. Yet this is not seen, as zinc exhibits association with

earlier steps in the sequential extraction process. One explanation for this is that the nature of metal sequestration in bioreactor systems varies depending upon influent concentration. This will have a knock-on effect for metal recoverability from these materials, and would therefore warrant further investigation to assess metal removal mechanisms as a function of influent metal concentration.

4.2.6 Sequential extraction reproducibility

In order to demonstrate reproducibility, triplicate samples were run for the remaining two quarters of sample C4B (those which were not sieved: quarters 2 and 3). Presented in Figure 4.14 are the results of these replicates for zinc.

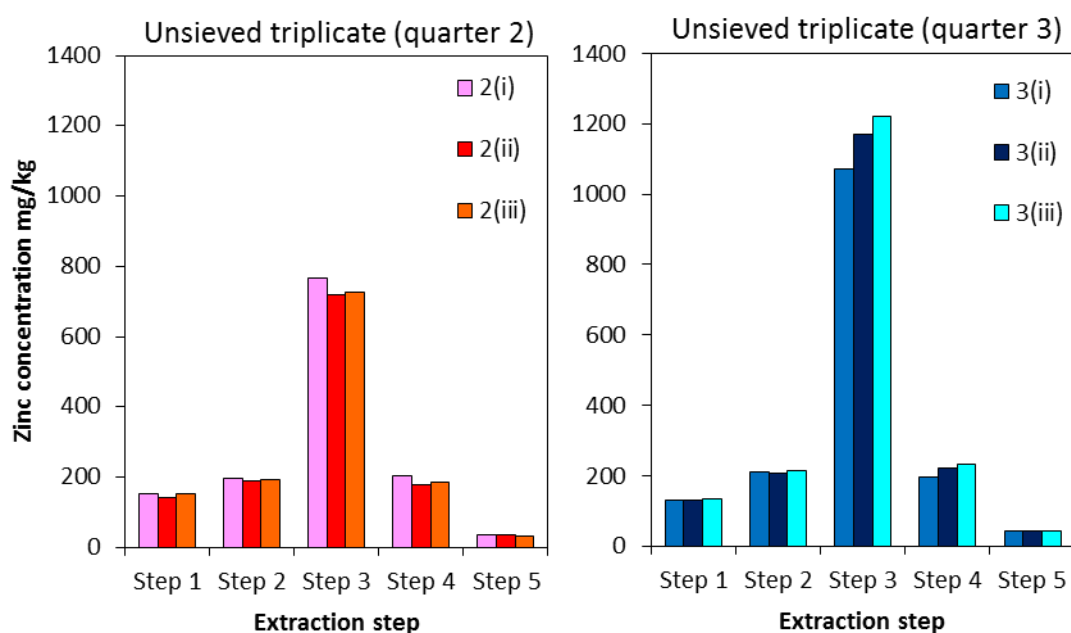


Figure 4.14 Zinc concentrations in triplicate samples of two unsieved replicates as determined by Tessier extraction (additional 5mL H₂O₂ added to triplicates 2(iii) and 3(iii) in step 4)

A minimal variance between both sets of triplicates was seen: statistically this is at most 8.5% of the mean value (within quarter 3, step 4) and is less for all other steps in both quarters. This variation might be partly due to additional hydrogen peroxide being used in samples 2(iii) and 3(iii) in step 4 of the extraction, leading to greater recovery in these replicates (see section 3.3.3, Chapter 3). On the other hand, there is only very modest variation between fractions mirrored between numerous steps: for example, zinc concentrations in 2(i) are frequently greater than 2(ii) where experimental conditions were identical. Although this pattern is not entirely consistent, it does suggest that the experimental error of the relative fractions is less significant than the experimental error between samples. Yet, when two apparently identical quarters of the same bulk sample

are compared visually (i.e. Figure 4.14) the significance of heterogeneity within the larger substrate sample is clear to see. Total metals were substantially higher in quarter 3, compared to quarter 2. In particular, far more zinc appears to be recovered during step 3 in quarter 3. A similar observation can be made when comparing the sum of the zinc concentrations of dry sieved sample to the wet sieved sample of the other two quarters (1 and 4).

4.3 Metal recovery from treatment system substrates: Chemical leaching

Chemical leaching with a range of sulphuric acid concentrations and solid:liquid ratios (pulp densities) was undertaken as described in section 3.4. Raw data from the chemical leaching tests are included as Appendix E. Data are presented as percentage metal recovery, which is calculated as the efficiency of metal extracted from the substrate by leaching, compared to the metal content of the unleached substrate determined by aqua regia digest. Correction is made to account for metal removal from the experiment by preceding sampling events. Metal quantities (as mg) are used to calculate efficiencies and correct for sampling, as expressed in Equation 4.1.

$$(4.1) \quad e = \left[\frac{s_l + s_s}{s_t} \right] 100$$

Where:

- e** efficiency of leaching, %
- s_l** quantity of metal leached from substrate, mg
- s_s** quantity of metal removed by sampling, cumulative, mg
- s_t** quantity of metal in unleached substrate, mg

4.3.1 Leaching with variable acid concentrations

Across all metals, significant recovery occurs at the very start of the leach process so that the first sample taken at the very start of the tests typically has substantial metal concentrations. This sample was collected immediately after addition of the acid to the substrate, indicating that very rapid solubilisation of metals can occur under these conditions. To a much lesser degree, the same pattern is shown for the deionised water control which suggests that very weakly bound metal phases are quick to dissolve in deionised water.

Aqua regia digest data, summarised in Table 4.3, are presented for triplicate samples taken from the composite substrate before leaching (samples from locations A2A, A3A, C2A, C3A, E2A, E3A - see Figure 3.1). There is good similarity between metal concentrations in the replicates, except for iron, where there is substantially more within replicate 3. This is considered to be due to sample heterogeneity. Averages of the aqua regia triplicates were used to calculate percentage metal recovery in the leach tests. Extraction efficiencies, as percentages, are presented in Figure 4.15. This shows the

percentage of metal leached after 100 hours in relation to metal extracted from the un-leached substrate by aqua regia digestion.

Table 4.3 Metal content of mine water treatment substrate used for variable acid concentration tests

[mg/kg]	Fe	Ni	Cu	Cd	Mn	Pb	Zn
<i>Replicate 1</i>	16564.9	54.1	135.7	17.1	907.8	224.3	8200.0
<i>Replicate 2</i>	17093.7	56.2	139.9	17.6	992.8	235.0	8437.6
<i>Replicate 3</i>	29536.8	54.1	138.2	17.0	984.0	218.5	8158.4
Mean	21065.1	54.8	137.9	17.2	961.5	225.9	8265.3
Std. deviation	220.2	0.04	0.06	0.01	1.4	0.25	4.5

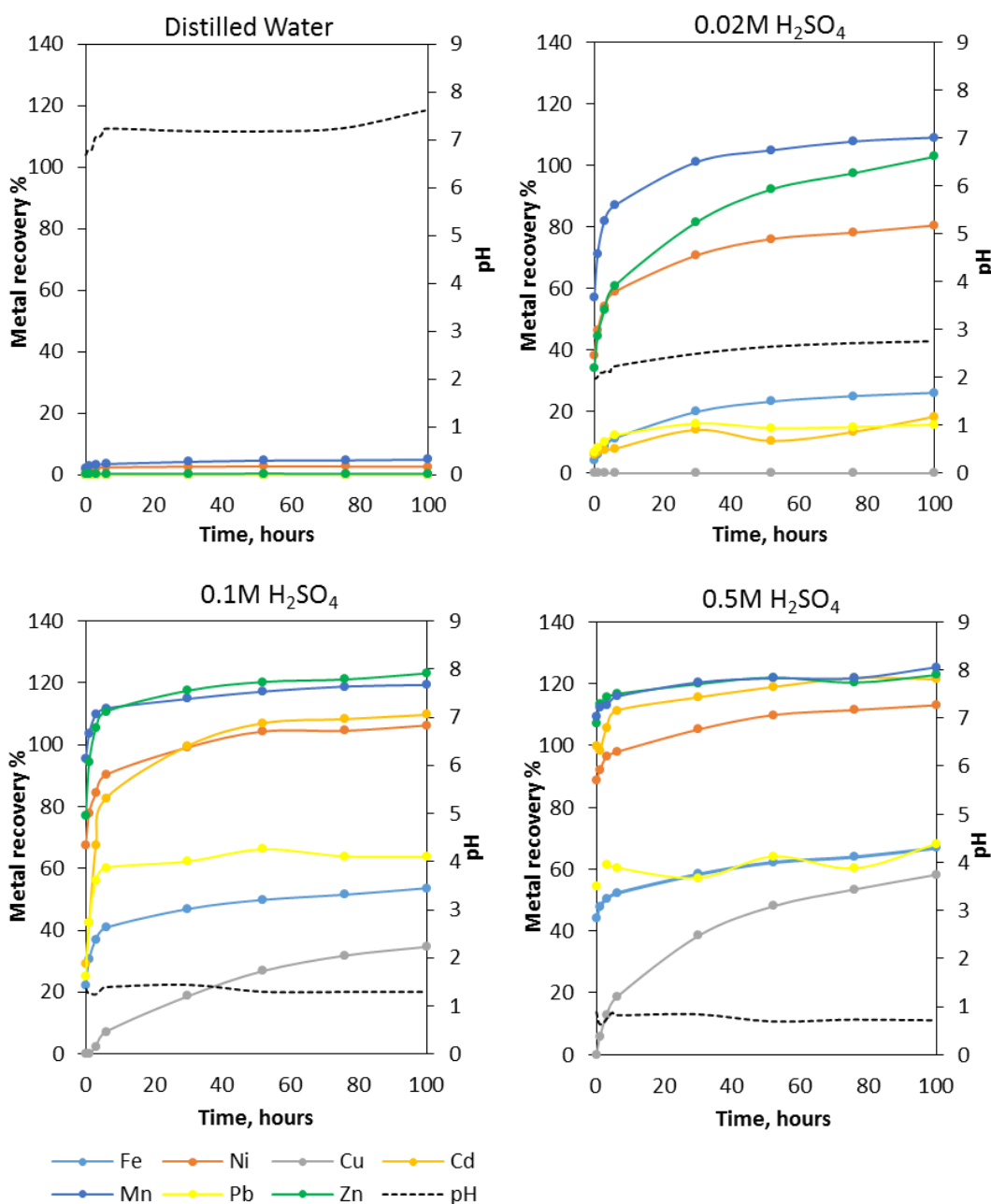


Figure 4.15 Metal extraction efficiencies during leach-test where acid concentration was varied, compared to metals extracted by aqua regia digest (mean values of duplicates)

It is initially evident for zinc, manganese, cadmium and nickel, that in excess of 100% was extracted during 2 of the 4 leach-tests, with in excess of 100% of zinc and manganese also extracted during the 0.02M leach test. This means that greater amounts of these metals were removed using dilute sulphuric acids over 5 days than achieved by aqua regia digest. Although the aqua regia comprises a mixture of concentrated nitric and hydrochloric acids (BSI, 1995b), there may be tightly bound fractions of metal which are not extracted by the process. It has been shown by Chen and Ma (2001) that conducting aqua regia digest on a hotplate (standard method adopted in this research, see section 3.4.6) can have relatively poor metal recovery efficiencies, compared to

more aggressive methods such as microwave aqua regia and microwave aqua regia with hydrofluoric acid. In their investigations, average total metal recovery from certified soils using the hotplate method was 74%; with 85% recovery for manganese and 93% for zinc (Chen and Ma, 2001). This has been confirmed by additional aqua regia digestion of the substrates after leaching, which shows <100% extraction across all metals and all acid dilutions. It may, therefore, be the case that due to the long exposure time of substrate to acids during the leaching procedure, a greater amount of metal was leached when compared to the short-exposure aqua regia digests. This would explain the >100% recovery observed for some metals during the acid leach process.

Extraction efficiencies for iron were 26% to 68% (depending upon acid concentration) when compared to total iron content as determined aqua regia digests. This suggests that the majority of zinc can be solubilised with dilute acid, but more concentrated acids are required to have the same effect on iron. Similar findings have been made by Oliver and Carey (1976), who determined that in a waste ash, iron showed lower solubilisation than zinc, copper and cadmium in dilute sulphuric acid (~10% v/v) whereas more concentrated acid (<75%) increased the recovery of iron over these elements. When considering the sulphide solubility of these elements, iron would be expected to dissolve preferentially to zinc when present as sulphides, given that it has a higher solubility product. Yet, this is not seen, which suggests that these metals may not be retained in substrates in the same sulphide form.

Solubilisation appears to be consistently very rapid for manganese, with the greatest percentage (109%) of all elements extracted upon test completion during exposure to the most dilute acid, 0.02M. This is consistent with both its high sulphide solubility product ($K_{sp} = 5 \times 10^{-16}$) and the Irving-Williams order of complex stability, where manganese features the lowest stability in the sequence ($Mn < Fe < Ni < Cu > Zn$) (Hedin et al., 1994a; Irving and Williams, 1953). On this basis, it would be expected that manganese both in sulphide and complex form would be released rapidly when compared to other metals. Significant lead recovery was only observed in the 0.1M and 0.5M tests (64% and 68%, respectively). Copper shows the poorest extraction efficiencies of all elements, although time of exposure to acid has a pronounced bearing on copper extraction when compared to other metals (Figure 4.15). Copper extraction efficiencies are greatest at the end of the 0.5M test at 58%. Both lead and copper have low sulphide solubility products (4×10^{-32} and 1×10^{-29} , respectively) and, as a

consequence, lead and copper sulphides would dissolve last out of the metals studied. Additionally, copper is known to form a highly stable complex with a range of substances (Irving and Williams, 1953). However, other studies find high leach efficiencies for copper when using sulphuric acid leaching: between 53 and 100% across a range of experimental variables (Bayat and Sari, 2010; Wu and Ting, 2006; Brombacher et al., 1998). This high copper recovery might be explained by the nature of the wastes being treated: incinerator fly ash as opposed to an organic substrate which has been under anoxic conditions. High temperatures involved with incineration would both substantially reduce organic carbon (to which copper may be bound) and oxidise any metals in sulphide form to oxides (Jha et al., 2001); a common approach used in mineral processing to improve the recovery of copper from sulphide ores (Davenport et al., 2002). Cadmium and nickel both show high extraction efficiencies in the more concentrated acids (>105% in 0.1M and 0.5M acids) albeit slightly lower than manganese and zinc (>120%). In the case of this substrate, however, starting concentrations of nickel and cadmium were low at <60mg/kg, more than two orders of magnitude lower than zinc and iron.

Generally, the most soluble metal sulphide, manganese, is most readily extracted and copper, the least soluble, most conserved in the substrate, showing agreement with the sulphide solubility products for these elements and the Tessier extraction data. Yet there is less agreement with other metals: zinc, in particular, shows high extraction efficiencies, second only to manganese on average, but it is the fifth most soluble out of the elements investigated. When considering Tessier extraction data, more zinc was associated with acido-soluble and reducible fractions compared to other metals (in particular cadmium, nickel and iron which have higher sulphide solubility products). This may be explained by other zinc species being present in the substrate which could be more amenable to solubilisation (Neculita et al., 2011).

4.3.2 Leaching with variable pulp densities

Pulp density was investigated using 0.1M sulphuric acid leaching across a range of solid:liquid ratios. Data are presented in Figure 4.16 for percentage metal recovery compared to aqua regia digest of the unleached substrate. Digestion data for the composite substrate used in pulp-density tests is summarised in Table 4.4, although note that this substrate was taken from slightly different positions compared to that used in the variable acid concentration tests (A1A; A4A; B1A; B2A; B3A; B4A; C1A; C4A;

D1A; D2A; D3A; D4A; E1A & E4A). There is marginally greater variation between these digest triplicates compared to the digests used in the previous tests, which is considered to be due to heterogeneity of the compost substrate (Table 4.3).

Substantially larger amounts of substrate were used in the leach tests: 22.5g versus 3g used in aqua regia digests as dictated by the standard digest method and, on this basis, the heterogeneity will have had a greater bearing on the aqua regia than the leach tests where individual sample size was smaller. Averages of the triplicates were used to calculate percentage metal recovery in the leach tests to account for this heterogeneity.

Table 4.4 Metal content of mine water treatment substrate used for variable pulp density acid leaching tests and biological leaching tests

[mg/kg]	Fe	Ni	Cu	Cd	Mn	Pb	Zn
<i>Replicate 1</i>	18744.1	53.4	191.4	13.9	996.3	205.2	7405.9
<i>Replicate 2</i>	19681.2	52.3	204.6	13.6	980.8	197.2	7290.7
<i>Replicate 3</i>	14875.1	52.4	154.1	13.3	786.3	192.1	5977.2
Mean	17766.8	52.7	183.4	13.6	921.1	198.1	6891.2
Std. deviation	2547	0.61	26.2	0.3	117	6.6	794

Additionally, there was significant variation between the two composite substrates (i.e. that represented in Table 4.4 used for the pulp-density tests and that used in the variable acid concentration tests, Table 4.3). For example, average iron concentrations were 17,767mg/kg and 21,065mg/kg between the two composites, respectively. Similarly, zinc was lower in the pulp density test substrate compared to the variable acid concentration test substrate: 6,891mg/kg vs. 8,265mg/kg, and a similar pattern was seen across all other metals; suggesting that sample heterogeneity affects all metals. This is explored further in the leach test, where the 1.875% pulp density is a repeat of that conducted during the 0.1M variable acid concentration leach tests (both conducted using 0.1M sulphuric acid and 1.875% pulp densities), but differing in the composite substrate used. Across the flasks with 1.875 – 7.5% pulp densities shown in Figure 4.16, the pH shows an initial spike after 1 hour, although it is unclear why this has occurred.

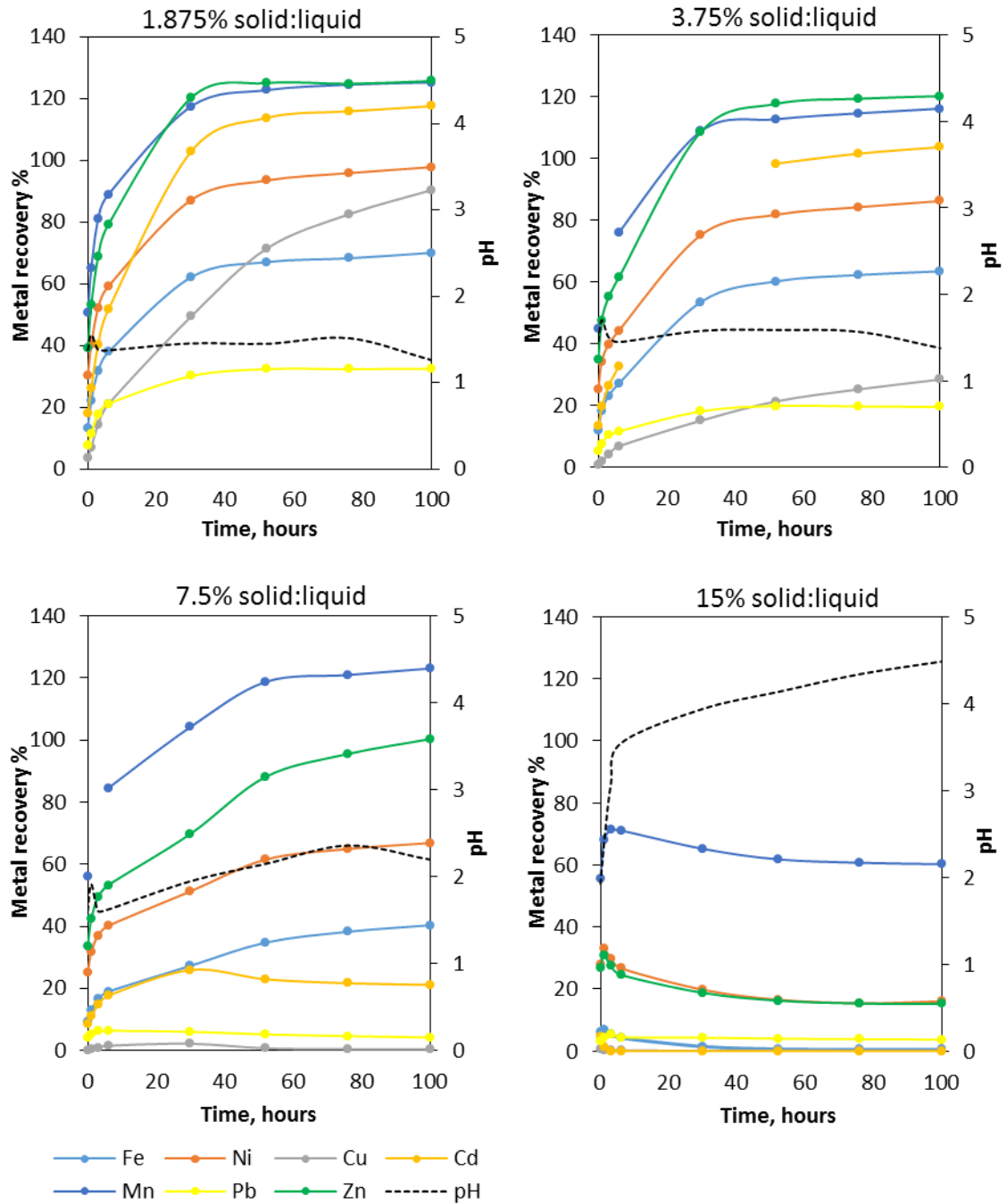


Figure 4.16 Metal extraction efficiencies across a range of solid: liquid ratios compared to metals extracted by aqua regia digest (mean values of duplicates)

Significant variability in recovery was seen between metals, indicating that sulphuric acid was far more effective at recovering some metals compared to others. For example, at a 1.875% pulp density, just 33% of lead was recovered after 100 hours, yet in excess of 120% of both zinc and manganese were recovered, compared to the aqua regia. As pulp density increases from 1.875% to 3.75% little substantive change was seen in terms of extraction efficiency, excepting copper, which decreased from 90% extraction to 28%. In the 7.5% pulp density flasks lead and copper recovery was 4%

and 0.4% respectively, whereas other elements showed greater than 20% extraction over the experimental period. Indeed, at this increased pulp density, in excess of 100% extraction was seen for both zinc and manganese. However, at the greatest pulp density, 15%, far less metal was extracted for all elements. In fact, over the 100 hour experimental duration, the concentration of most metals in solution started to decrease, perhaps as metals became less soluble due to an increasing pH. The following extraction orders have been derived from the average extraction efficiencies during the leach tests across the four pulp densities:

1.875%: Mn > Zn > Cd > Ni > Fe > Cu > Pb

3.75%: Mn > Zn > Ni > Cd > Fe > Pb > Cu

7.5%: Mn > Zn > Ni > Fe > Cd > Pb > Cu

15%: Mn > Ni > Zn > Pb > Fe > Cd > Cu

As with the variable acid concentration tests, manganese had the greatest solubility across all pulp density tests, and copper or lead the least, which is consistent with their sulphide solubility product and the Irving-Williams order of complex solubility (Hedin et al., 1994a; Irving and Williams, 1953). Similarly, zinc also exhibited high extraction rates, second to manganese in 3 out of the 4 experiments, yet this does not correspond to its sulphide solubility product which suggests that iron, nickel and cadmium should have greater solubilities. It is not clear why this was the case, but may be due to factors associated with the high levels of zinc which have recently accumulated in the substrate during its exposure to mine water. If zinc and iron (also at high concentrations in the substrate) are removed from the sequence, the orders of the remaining metals correspond exactly to the sulphide solubility product order for the 3.75% and 7.5% pulp density tests. This might be explained by the high zinc concentrations being attenuated as non-sulphide phases such as sorption within the treatment system. Binding of metals to sorption sites can be time dependent, with less metal being desorbed from sorbents such as ferrihydrite over longer ageing processes (Appelo and Postma, 2010). Therefore, metals recently removed from mine water by sorption processes may be more amenable to recovery than those which have been sorbed for some time.

While it was evident that there is a decreasing pattern of metal solubilisation as the ratio of solid to liquid (pulp density) increases, there appears to be a threshold between 7.5% and 15% solids where metal recovery becomes ineffective. These findings are in broad

agreement with a study by Bayat and Sari (2010), who found a substantial drop in metal recovery between a similar pulp density change during bioleaching of a metal plating sludge. For example, nickel recovery from the Nenthead substrate was 67% for 7.5% pulp density and 16% for 15% pulp density, compared to 68% recovery for 8% pulp density and 41% for 14% pulp density in the metal plating sludge study (Bayat and Sari, 2010). Observing the pH throughout the experiment sheds some light upon the findings at Nenthead, where pH in the 1.875%, 3.75% and 7.5% pulp experiments remained steady between 1.2 and 2.4 (mean 1.6); except in the 15% pulp experiment where pH gradually rose, reaching 4.5 by the end of the experiment. It is suspected that the buffering capacity of the compost in the latter neutralised the acid, allowing the pH to rise and therefore the solubility of metals to decrease, a conclusion also drawn by Bayat and Sari (2010).

In the context of the current investigation, zinc and cadmium were of particular concern in terms of recovery from substrates, due to their prevalence in the Rampgill mine water (and consequently Nenthead treatment system substrate) and mine waters more widely (Mayes et al., 2013; Gandy and Jarvis, 2012). Additionally, high zinc concentrations have classified the Nenthead substrate as a hazardous waste (ESG, 2013), and cadmium has a high toxicity and is of specific concern for regulators in soil and water environments (Environment Agency, 2009a; ECC, 2000). Further accumulation of cadmium in treatment system substrates, for example, where they are exposed to mine water for longer durations, may pose particular problems with substrate disposal or re-use. Sulphuric acid leaching has demonstrated effectiveness at recovering both these elements across a range of conditions over 100 hours, summarised in Table 4.5.

Table 4.5 Zinc and cadmium recovery efficiencies for acid leaching after 100 hours

	Variable acid concentration (fixed 1.875% pulp density)			Variable pulp density (fixed 0.1M sulphuric acid concentration)			
	0.02M	0.1M	0.5M	1.875%	3.75%	7.5%	15%
Zn recovery (%)	102.9	123.1	122.9	125.8	120.3	100.4	15.2
Cd recovery (%)	18.4	109.6	121.4	117.6	103.73	20.2	>0.6

On the basis of combined high cadmium and zinc recoveries, 0.1M sulphuric acid concentration appears to be the most dilute acid suitable for high recovery rates, as this

demonstrated >100% recovery of both zinc and cadmium. Cadmium recovery efficiencies for the 0.02M test were poor at just 18.4%. Leaching with 0.1M acid at an increased pulp density of 3.75% yielded $\geq 100\%$ recovery rates for both zinc and cadmium which suggests that this combination would offer an optimum compromise between recovery efficiency and quantity of substrate leached. Further increases in pulp density caused substantial decreases in total cadmium recovery (7.5% pulp), and then zinc and cadmium recovery (15% pulp).

4.3.3 Leach test reproducibility and controls

Chemical leach data showed good replication and typically duplicate tests were well within 10% of the mean values. Where replicate measurements deviate more than 10% from mean values, they were discarded. Distilled water recovered very little metal over the 100 hour experimental period (<5% for all metals) with many much lower, such as zinc (<0.5% recovery). Control flasks containing no substrate were simultaneously operated using 0.1M acid and metal concentrations in samples taken were below detection limits ($n=103$) or very close to them ($n=9$). This confirms that metals data were not affected by contamination during the experimental procedure.

The 1.875% pulp density test flasks are an identical repeat of the 0.1M variable acid concentration test flasks (bottom left Figure 4.15 and top left Figure 4.16). Both these experiments had a 1.875% pulp density and used 0.1M sulphuric acid, although data obtained indicate notably different recovery rates and efficiencies. More copper is recovered from the substrate in the 1.875% flasks, however, when compared to lead in the 0.1M repeat; all other metals following a similar order of extractability. Rates of recovery differ considerably between the two repeated experiments: the rate of recovery is considerably greater in the 0.1M test. This may be explicable upon observation of the average pH between the two: 1.32 in the 0.1M flasks, compared to 1.42 in the 1.875% flasks. Given that conditions were identical, the substrate in the 1.875% test appears to have had a greater buffering capacity, causing the pH to rise, compared to that used in the 0.1M test.

4.3.4 Metal removal from substrate

Digest of residues from the 0.1M, 1.875% pulp density sulphuric acid leach test determined metal concentrations as summarised in Table 4.6¹¹. Comparison is made between the contaminated substrate used in the leach tests, and the substrate before it was exposed to mine water, known as the blank. Immediately, it was evident that zinc and cadmium concentrations in the used substrate were reduced to levels comparable to the blank. Lead and copper concentrations were largely unaffected, given that sulphuric acid is a poor lixiviant for these elements (Sadegh Safarzadeh et al., 2007). Iron, nickel and manganese concentrations were all reduced to below concentrations in the blank. The figures presented for the leached substrate are conservative: the substrate was not rinsed following leaching, thus it is likely that some of the metal-containing leach solution was retained within the compost during the drying and digestion procedure. Therefore, it may be possible to reduce metal contents of the substrate further by rinsing after the leach procedure. Regardless, the data presented in Table 4.6 suggests that zinc and cadmium, in particular, can be effectively removed from the compost substrate, down to concentrations comparable to the blank compost.

Table 4.6 Average metal content of (1) contaminated Nenthead substrate, (2) substrate after leaching with 0.1M acid and (3) blank substrate which was used in the mine water treatment system, as determined by aqua regia digests

Metals (mg/kg)	Fe	Ni	Cu	Cd	Mn	Pb	Zn
(1) Substrate pre-leach (Composite 2) (n=3)	21,065.1	54.8	137.9	17.2	961.4	225.9	8,265.3
(2) 0.1M; 1.875% pulp leach residue average metal conc. (n=4)	8,999.6	17.3	118.7	1.6	77.4	211.4	650.5
(3) Blank substrate sample* (n=3)	19,344	81.2	234	1.5	851	88.8	634

*Newcastle University unpublished data for blank substrate used in Nenthead pilot treatment system

In comparison with the Nenthead study, acid leaching of a sewage sludge by Oliver and Carey (1976) was generally less effective at removing metals from solids, reducing zinc

¹¹Digests of leached substrate were only undertaken for the variable acid concentration tests due to limitations on time and resources.

concentrations from 5,100mg/kg to 1,500mg/kg; cadmium from 57mg/kg to 27mg/kg; and copper from 2,500mg/kg to 2,050mg/kg. Like the Nenthead study, sulphuric acid was used and pH maintained at 1.5 (Oliver and Carey, 1976), which is not vastly dissimilar to the 0.1M Nenthead test which had an average pH of 1.3. Substantially shorter leach times of just 1 hour may explain this relatively poor removal (Oliver and Carey, 1976). Iron, however, showed high rates of removal, being reduced by 68% in the solid from 29,000mg/kg to 9,280mg/kg (Oliver and Carey, 1976). This is comparable to the 100 hour long leach test of the Nenthead substrate using 0.1M acid and 1.875% pulp, where 70% of the iron was recovered (Figure 4.16).

4.3.5 Separation of solids from pregnant leach solutions

Dosing with 6M (24% w/w) sodium hydroxide was undertaken to adjust pH to ~9.5 in order to achieve precipitation of metals from pregnant leach solutions. Final pH values at the time of filtration are provided in Table 4.7, indicating a slight drop in pH during the intervening two days between final pH adjustment and filtration. It is thought that this pH drop was as a result of oxidisation and hydrolysis of metals such as iron within the solution resulting in a net increase in hydrogen ions, as per Equations 4.2 and 4.3 (after Banks et al., 1997). Additional evidence to support this comes from visual observation of the pregnant solutions, which turned from green to a red-brown as shown in Figure 4.17, at least at the liquid-air interface, during settlement. This is characteristic of a change in iron valency from ferrous (II) to ferric (III).

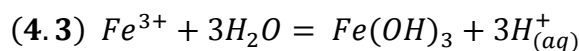
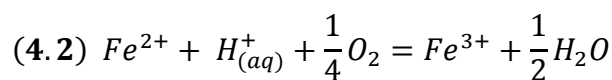


Table 4.7 Final pH of leach solutions from variable pulp density leach test, prior to filtration

Solution	1.875%a	1.875%b	3.75%a	3.75%b	7.5%a	7.5%b	15%a	15%b
pH	9.89	9.93	8.89	9.07	8.92	8.92	9.36	9.37

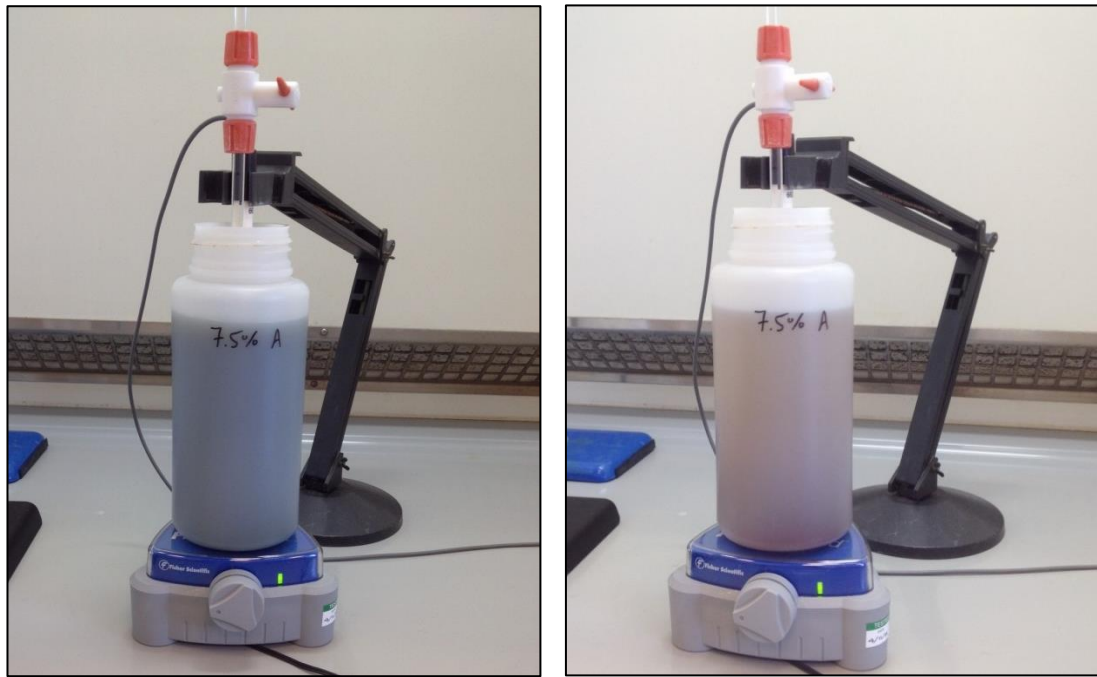


Figure 4.17 Dosing of pregnant leach solutions with sodium hydroxide (left – at time of dosing; right – one day after dosing)

Table 4.8 Metal content and pH of pregnant leach solutions after 5 day leach test

Leach-test pulp density	Fe mg/L	Ni mg/L	Cu mg/L	Cd mg/L	Mn mg/L	Pb mg/L	Zn mg/L	pH
1.875% a	248.31	1.02	3.36	0.32	22.63	1.22	171.92	1.36
1.875% b	224.67	0.93	3.09	0.29	20.65	1.21	154.65	1.42
3.75% a	428.36	1.72	1.92	0.54	39.86	1.50	313.41	1.82
3.75% b	432.25	1.73	2.15	0.54	40.59	1.42	314.11	1.59
7.5% a	557.20	2.69	0.05	0.23	85.60	0.60	532.50	2.43
7.5% b	540.45	2.65	0.05	0.20	84.52	0.60	518.93	2.43
15% a	2.88	2.69	0.05	0.23	80.80	1.09	150.69	4.21
15% b	3.39	2.65	0.05	0.20	79.84	1.06	139.33	4.26

Data showing replicate tests, a and b.

Table 4.9 Metal content and pH of leach solution after dosing with NaOH and filtration

Leach-test pulp density	Fe mg/L	Ni mg/L	Cu mg/L	Cd mg/L	Mn mg/L	Pb mg/L	Zn mg/L	pH*
1.875% a	0.58	0.03	0.05	<0.01	0.06	<0.05	0.40	9.93
1.875% b	0.30	0.03	0.04	<0.01	0.08	<0.05	0.28	9.89
3.75% a	0.28	0.12	0.02	<0.01	0.49	<0.05	0.24	9.07
3.75% b	0.39	0.12	0.03	<0.01	0.29	<0.05	0.33	8.89
7.5% a	0.25	0.19	<0.01	<0.01	0.54	<0.05	0.38	8.92
7.5% b	0.45	0.18	<0.01	<0.01	0.56	<0.05	0.73	8.92
15% a	0.02	0.42	0.02	<0.01	0.81	<0.05	0.33	9.36
15% b	0.02	0.46	<0.01	<0.01	0.68	<0.05	0.16	9.37

*pH measured in solutions after adjustment with NaOH, but before filtration. Data showing duplicate tests, a and b.

Table 4.8 and Table 4.9 present data for the leach solution after the 5 day leach test, and data for the leachate which had been dosed with sodium hydroxide and filtered, respectively.

It is evident that dosing with sodium hydroxide and filtration achieved very good recovery of metals from the low-pH pregnant leach solutions. >99.7% of the target contaminant zinc was removed from the leach solutions by this method, with >98.8% of manganese and >99.4% of iron also being removed across all eight experiments. Cadmium and lead were both removed to below detection limits, although starting concentrations were very low, and lead showed comparatively poor solubilisation into the leach solution from the compost substrate ($\leq 68\%$ in leach tests). Nickel was less effectively removed from solution, albeit >90% was achieved in all but the 15% pulp density solutions. Copper shows >98.5% removal in the two lower density leach solutions (1.875% and 3.75%) and was close to or below detection limits in the higher density solutions. These data suggest that dosing leach solutions with sodium hydroxide to a moderately high pH followed by filtration can reduce metals to very low concentrations.

Other than adjustment to a favourable pH, initial inspection of data suggests that discharge to the environment or re-use within the metal recovery process may be achievable with little or no further treatment. Further analysis for major elements, however, revealed substantial concentrations of sodium (from pH adjustment with sodium hydroxide) and sulphate (from sulphuric acid). Major element data are presented in Table 4.10 for the treated leach solution, and are compared to water quality data at 3 locations; the Rampgill mine discharge, its receiving watercourse the River Nent at the point of discharge, and a location approximately 8km downstream. The Nent is an upland water course in a metal mining area, presented as an example of a watercourse which might receive effluent from a metal recovery operation.

Table 4.10 Major species in leach solution after dosing with NaOH and filtration

	Na	K	Ca	Mg	SO₄	Al
1.875% a	4650	24.4	187	1.23	10169	9.95
1.875% b	3113	12.8	264	2.33	7376	6.98
3.75% a	3382	29.4	204	48.1	8311	0.73
3.75% b	3646	31.2	160	26.3	7959	1.22
7.5% a	2116	28.5	94.0	60.4	4966	0.59
7.5% b	2150	27.9	99.1	57.8	5073	0.83
15% a	549	25.4	500	210	2601	0.01
15% b	510	21.5	477	213	3047	0.01
Rampgill*	10.1 – 24.4	5	73 - 81	22.5 – 24.5	118 – 130	<0.01-0.02
Nent at Rampgill*	13.4 – 92.8	0.8 – 1.1	14 - 32	2.9 – 6.4	12 – 110	0.08 – 0.2
Nent at Alston*	32.4 - 49	1.6 – 2.5	32 - 58	4.8 – 9.5	28 – 63	0.06 – 0.7

*Data from catchment monitoring report (Atkins, 2010)

Greatest concentrations of sulphate and sodium were seen in solutions from lower pulp-densities. Sulphate would be present in the leach solutions, primarily from the sulphuric acid totalling 11,520mg/L calculated using molecular masses (96,000mg SO₄²⁻ per L 1M H₂SO₄ solution). Dosing with sodium hydroxide would add sodium to the leach

solutions, which varied depending upon how much was added to each flask (138mg per mL for 6M NaOH solution). Calculations based upon volumes added suggest that sodium values in the leach solution fit well with measured values in the leach solutions, for example: 35mL 6M NaOH added to flask 1.875a increasing its sodium concentration by 35mL x 138mg and bringing its total volume to 1,050mL; therefore, total added sodium is $(35 \times 138) \div 1,050 = 4.6\text{mg/mL}$ or 4,600mg/L, a figure very comparable to that in Table 4.10¹². Identical quantities of sulphate (11,520mg/L) were added to the flasks in the form of sulphuric acid, although these were reduced substantially in the higher pulp density solutions. The mechanism for sulphate attenuation is unclear and further investigation would be required to determine the cause.

Sodium concentrations were, on occasion, two orders of magnitude higher than those in the Nent, and sulphate concentrations significantly in excess of one order of magnitude greater¹³. Therefore discharge of significant volumes of a leach solution with this chemistry would cause substantial increases in salinity of a receiving watercourse like the River Nent, unless flow conditions provided adequate dilution. Yet this increase in salinity would only be on a temporary basis during the metal recovery operation.

A similar pattern of decreasing concentrations with higher pulp densities is seen for aluminium, although at far lower levels. Its presence in the pH adjusted leach solution may be explained by the amphoteric nature of aluminium hydroxide, which has a low solubility around pH6, but as pH increases above this value it increasingly forms an aqueous hydroxy-anion, $\text{Al}(\text{OH})_4^-$ (May et al., 1979). Aluminium could still be problematic if concentrations of the order seen in 1.875% solutions were to be discharged to small watercourses, as found by Jarvis and Younger (1999) from an aluminium-rich spoil tip discharge. Magnesium concentrations are more than an order of magnitude lower than sodium but increase with increasing pulp density. Potassium concentrations show little in the way of a clear trend with increasing pulp densities and average concentrations are relatively low. Calcium concentrations are also relatively low, except in solutions from the greatest pulp density, 15% where up to 500mg/L was measured.

¹² This assumes sodium concentrations in the leach solution were comparatively minimal before addition of sodium hydroxide, although this was not measured.

¹³ It should be noted that an over-titration of 1.875A with NaOH occurred, and was corrected with 4 drops of concentrated sulphuric acid, which accounts to some degree for the additional sodium and sulphate within this particular sample, compared to its duplicate.

4.3.6 *Metal content of leach solution residues*

Residues obtained on the filter papers from filtration of the alkali dosed pregnant leach solutions consisted of gelatinous green-brown solids. These residues were oven dried at 105°C and ground prior to analysis (Figure 4.18).



Figure 4.18 Filtration residue (left) and after drying and grinding (right)

Metal masses are determined by weighing dry precipitate and determining total metals by aqua regia digest (section 3.4.6). These data are presented in Table 4.11. It should be noted that there would have been some loss of metal mass during the leach process due to sampling of pregnant leach solutions. Additional factors during the recovery of solids from leach solutions may have also led to some loss of mass. These include unavoidable retention of some precipitate on sides of flasks and filtration apparatus, and fragments of dried residue being lost in the oven/desiccator or en-route to the balance for weighing. With these factors in mind, Figure 4.19 shows metal content of residues plotted against metal content of treatment substrate before leaching.

Table 4.11 Metal mass of residues obtained from leach solutions, determined as product of residue mass and total metals by aqua regia

	Residue mass	Fe	Ni	Cu	Cd	Mn	Pb	Zn	Na	K	Ca	Mg	S	Al
	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>
1.875% a	3139.20	208.75	0.67	1.05	0.23	17.27	0.87	139.79	232.48	1.30	296.76	54.28	191.94	95.06
1.875% b	1772.60	140.58	0.44	0.72	0.15	11.48	0.85	92.52	47.47	0.23	185.68	34.93	52.67	63.83
3.75% a	4565.10	392.59	1.24	1.36	0.43	35.54	1.23	274.05	215.87	2.49	298.17	72.66	170.60	208.55
3.75% b	5063.20	395.50	1.27	1.52	0.44	36.10	1.16	275.38	288.13	3.29	346.57	91.52	234.20	218.63
7.5% a	4842.80	412.95	1.69	0.03	0.14	57.22	0.43	388.03	158.52	3.87	325.35	142.12	147.29	196.37
7.5% b	5994.90	506.59	2.09	0.04	0.18	69.92	0.51	474.77	206.31	5.01	399.45	173.01	193.88	245.50
15% a	1165.30	2.48	0.26	0.01	0.00	45.04	0.01	83.08	6.42	0.51	122.69	68.77	27.03	2.91
15% b	1079.90	2.61	0.24	0.01	0.00	49.28	0.01	85.09	5.70	0.51	132.90	63.99	28.94	3.09

a and b are duplicates across the four pulp densities

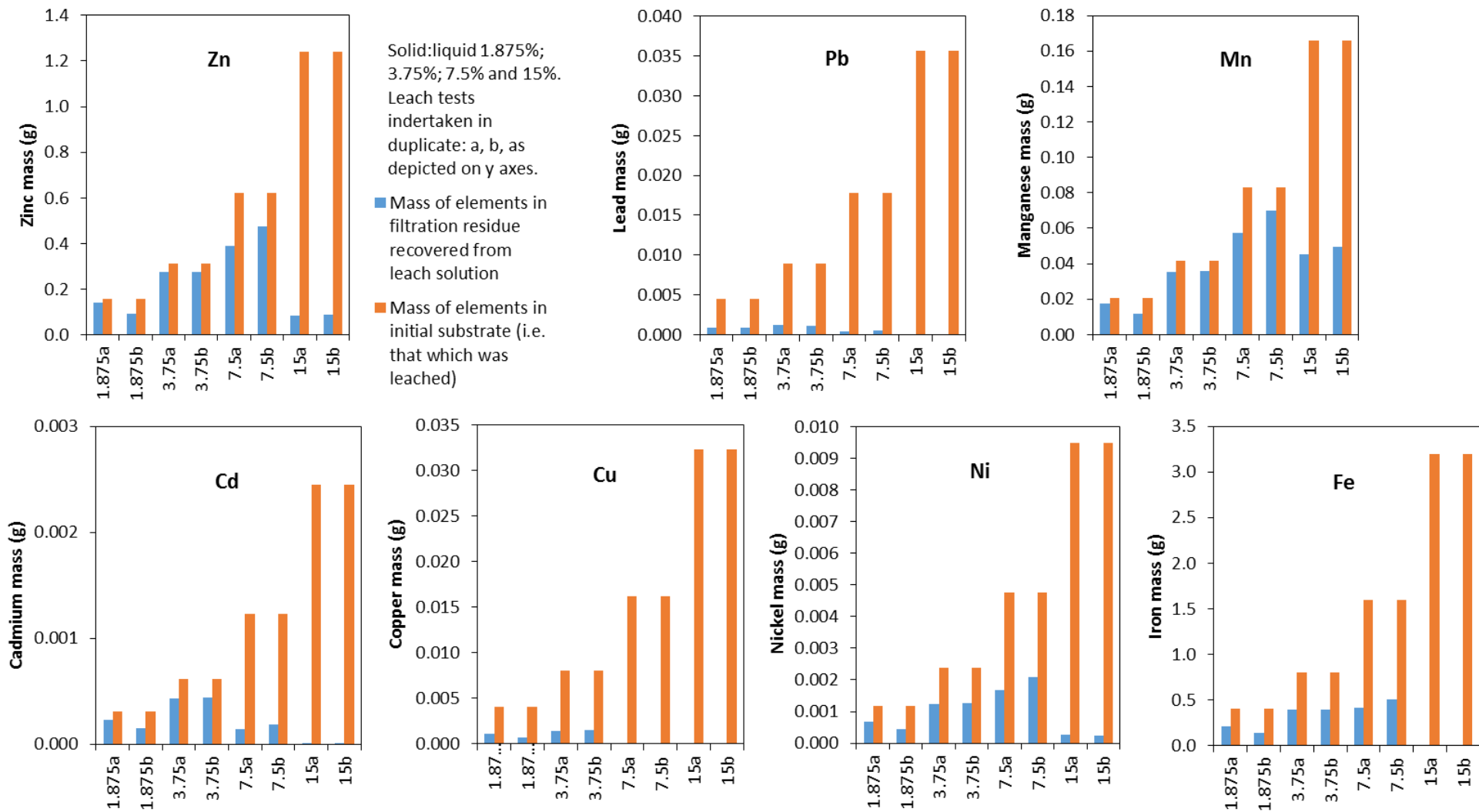


Figure 4.19 Metal mass in leach solution residues compared to metal mass in the unleached substrate

Iron, zinc and manganese, in descending order, were the most abundant of the measured metals within the Nenthead treatment system substrate. Less than 50% iron was recovered as a solid in all but one of the tests (1.875%a), with less than 0.1% of the element recovered in the highest density (15% pulp) leach tests. Manganese showed good recovery in the residue across all solutions: 54 – 84% in the 1.875, 3.75 and 7.5% pulp density tests and even 27-30% recovery in the 15% pulp density tests, the greatest of all metals investigated under these conditions. In excess of 60% zinc was recovered from the 1.875, 3.75 and 7.5% pulp density tests, with greater recovery shown in the lower density tests, excepting the 1.875%b residue. This appears to be an outlier across all metals except lead, where recoveries between 1.875a and 1.875b were 19.5% and 19.1% respectively. This is explicable when the mass of the residue is considered: just 1.77g compared to its replicate, 1.875%a, which was 3.14g as shown in Table 4.12. It is possible that a significant amount of the residue may have been inadvertently lost during the grinding and drying process: desiccated fragments of the residue were of low density and could easily have fallen from the petri-dish between the oven/ desiccator/ balance, although this was not actually witnessed during the analysis. A mass balance of the 1.875b leach test does, however, support this: 154.65mg/L zinc in final leach solution (~1.02L pregnant leach solution recovered), reduced to 0.28mg/L in filtrate means 157.7mg zinc must have been recovered in the filtration residue. Yet just 93mg zinc was measured in the 1.875b residue, compared to 139.8mg in the duplicate (1.875a) precipitate.

Nickel exhibits similar patterns to zinc when recovered as a solid across the range of pulp density leach tests, yet with lower efficiencies (36 – 56% in the 1.875, 3.75 and 7.5% leach tests), and very low efficiencies (2.6 - 2.7%) for the 15% test. Cadmium mass in the compost is extremely low, with recovery efficiency typically ~70% in the lower pulp density tests (i.e. 1.875 and 3.75%) and $\leq 15\%$ in the higher density tests, suggesting that for recovery of cadmium, pulp density of lixiviant to solid should be 3.75% or lower.

Table 4.12 Residue and substrate masses, and mass and efficiency of zinc recovered

Leach-test pulp density	substrate mass	Residue mass	Residue mass as percentage of substrate	Overall recovery efficiency of zinc from substrate
	g	g	%	%
1.875%a	22.5	3.14	13.95	90.16
1.875%b	22.5	1.77	7.88	59.67*
3.75%a	45	4.57	10.14	88.37
3.75%b	45	5.06	11.25	88.80
7.5%a	90	4.84	5.38	62.56
7.5%b	90	5.99	6.66	76.55
15%a	180	1.17	0.65	6.70
15%b	180	1.08	0.60	6.86

*outlier – see text for further details

Copper and lead both show very low recoveries as a solid: $\leq 26.1\%$ for copper and $\leq 19.5\%$ for lead across all tests. It is clear from both analysis of residues, and also leach efficiencies, that sulphuric acid leaching is not effective for the recovery of copper and lead. Both these elements have shown very poor recovery rates during leaching with sulphuric acid, requiring high acid concentrations and low pulp-densities to achieve significant recovery from substrates, which at least in part can be explained by their relatively low sulphide solubility products compared to the other metals investigated (Hedin et al., 1994a).

Where copper is present as a sulphide within these materials, highly oxidising conditions are required before it is dissolved (Davenport et al., 2002). Pacović (1980) (after Vračar et al., 2003) indicates that an electrochemical potential of +337mV is required for effective copper sulphide dissolution. Eh measurements conducted during the Nenthead leach tests indicated electropotentials were between 209mV in the 15% pulp solutions and up to 389mV in the 1.875% pulp solutions. Under the most oxidising conditions of the lower pulp densities it is possible that Cu^{2+} species may form; however, studies have shown that even where oxidising agents are added, sulphuric acid-leach procedures yield low copper solubilisation rates at $\leq 60^\circ\text{C}$ (Vračar et al., 2003; Oliver and Carey, 1976). This also explains the slow solubilisation of copper compared to other metals as seen during the leach tests (see, for example, Figure 4.15). Increasing temperature also has also been shown to have a dramatic effect on recovery (Vračar et al., 2003). Such behaviour has been attributed to the higher temperatures providing the activation energy required to oxidise copper in sulphuric

acid solutions (Vračar et al., 2003). Therefore, recovery of copper from substrates is likely to require increased temperatures and may also require additional oxidising agents within the leach solution or, alternatively, the use of a bacterial catalyst to obtain reasonable reaction rates (Davenport et al., 2002).

Upon exposure to low pH oxidising solutions, lead forms a sulphate (PbSO_4) where sulphur is present, such as in sulphuric acid leach solutions. PbSO_4 is known to be insoluble in aqueous solutions (Inoue, 2000; Mercier et al., 1996) which explains the very poor recovery seen during the leach tests conducted as part of this work. This is in addition to its low sulphide solubility product which means that it is less likely to dissolve compared to other metals when in sulphide form. Alternative lixivants such as hydrochloric acid or chelating compounds such as EDTA would therefore be required where lead recovery is an objective (Inoue, 2000; Cline et al., 1993).

4.4 Metal recovery from treatment system substrates: Bioleaching

Biological oxidisation of iron and sulphur offers a mechanism of recovering metals from waste materials (e.g. Bayat et al., 2009; Pathak et al., 2009a; Solisio et al., 2002). This approach avoids the need for handling large quantities of sulphuric acid as it is generated in-situ by microbially catalysed reactions (Rawlings, 2002). Experimentation has been conducted, using conditions to promote biological sulphur oxidation, to test if this approach is effective at metal recovery (see section 3.5 for details of approach. Raw data are included as Appendix F). This experimentation is preliminary only due to limitations on time and resources. As a result, no attempts have been made to identify microbiological communities which might have otherwise provided a fuller picture of the mechanisms at work.

Biological leaching of the Nenthead substrate used a configuration comparable to the acid-leach tests (sections 3.4 and 4.3) although using sterile apparatus and reagents, and substrates with 2% sulphur (S^0) enrichment as a microbial nutrient source, comparable to other studies (Liu et al., 2008; Seidel et al., 2004). A leach solution consisting of acidic mine water from the Woodend Low Level of the Threlkeld Mine, Cumbria (also known as Gate Gill), was selected to provide a microbial inoculum (refer to section 3.5). Static flasks at room temperature ($\sim 19^\circ\text{C}$ - 3a/b) were tested against a stirred (2a/b) and heated flask ($\sim 30^\circ\text{C}$ 1a/b) to test the influence of these variables on metal recovery rates (see section 3.5). In addition, a control replicate (4a/b) was operated which was

identical to the static flask (3a/b) but the Threlkeld mine water was sterile filtered (<0.2 μ m) to remove the inoculation. Table 4.13 shows the key parameters for the Threlkeld mine water.

Table 4.13 Chemical analyses of the Threlkeld Mine discharge used for bioleaching tests

Parameter	unit	<0.2 μ m filtered	total	Apparatus
Eh	mV	503	465	Myron 6P Ultrameter
pH		3.54	3.58	Myron 6P Ultrameter
Cond.	μ S/cm	472.0	474.4	Myron 6P Ultrameter
Zn	mg/L	43.27	43.35	ICP-OES
Pb	mg/L	0.41	0.40	ICP-OES
Cd	mg/L	0.08	0.08	ICP-OES
Ni	mg/L	0.32	0.31	ICP-OES
Fe	mg/L	1.27	1.49	ICP-OES
Mn	mg/L	4.33	4.33	ICP-OES
Cu	mg/L	<0.01	<0.01	ICP-OES
SO ₄	mg/L	220.8	235.2	IC

4.4.1 Key variables during bioleaching

Figure 4.20 provides variables of pH, sulphate, and temperature measured during the biological leaching test and also shows sulphate as a function of pH.

At the start of the biological leaching test, flasks were adjusted to pH 4 \pm 0.1 using concentrated sulphuric acid. After 6 hours, however, pH had risen to >5, and after 96 hours was >6 in all flasks but one (pH 5.9 in flask 4a – control). This rapid rise in pH at the start of the test is attributable to buffering by the substrate, which was observed over a similar period during the chemical leaching tests (Figure 4.16). After 216 hours, a rapid drop in pH to <5 (mean=4.39 for flasks 1a/b, 2a/b, 3a/b) was observed across all flasks excepting the control (4a/b) which remained pH >6. All inoculated flasks (i.e. 1a/b, 2a/b, 3a/b) continued to drop in pH, with mean pH for replicates as follows: 1a/b: 2.48, 2a/b: 2.14 and 3a/b: 2.83. pH in the control also dropped during the leach tests, but remained >4 (mean=4.12 upon test completion for flasks 4a/b).

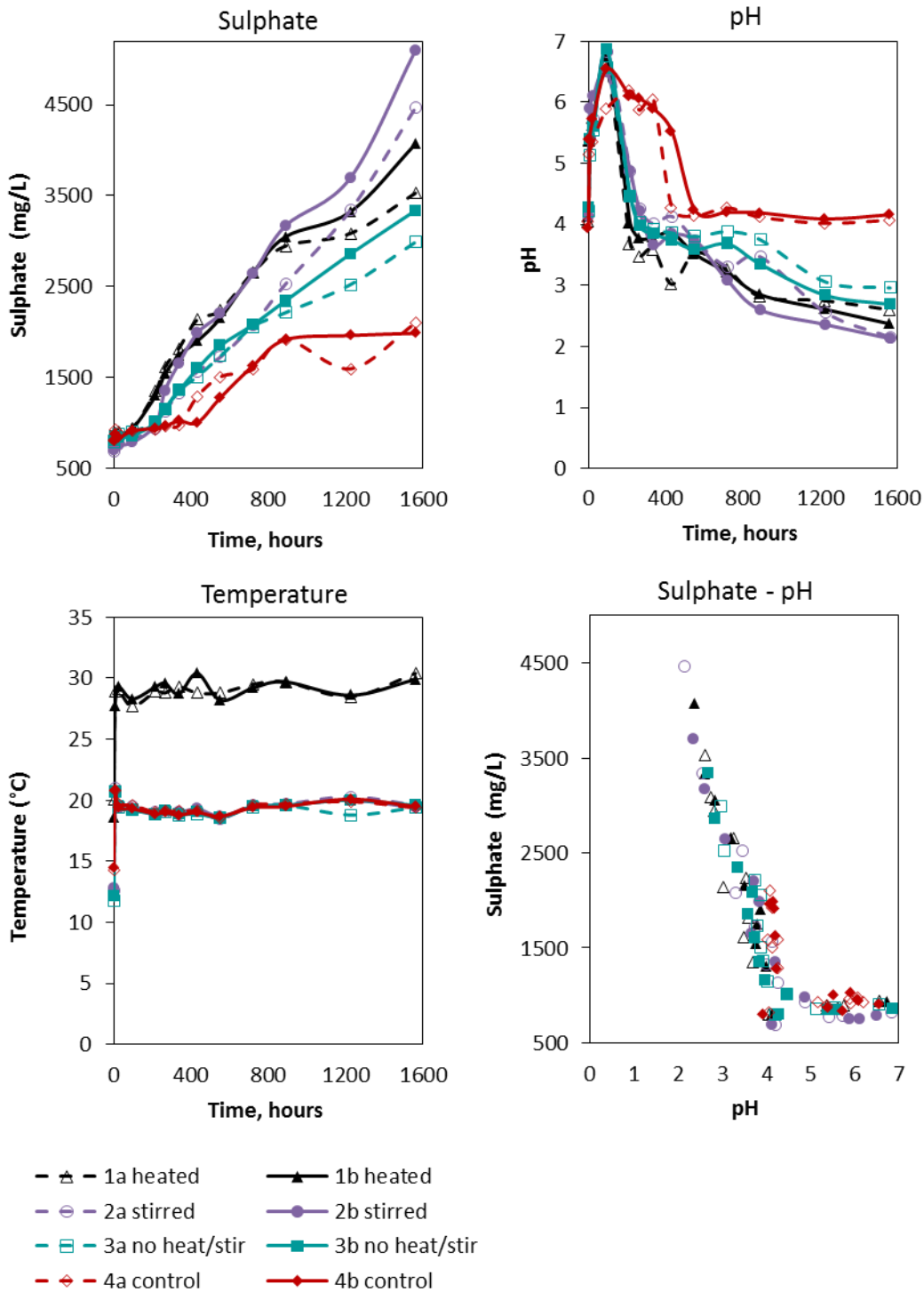
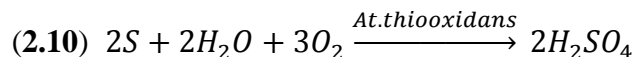


Figure 4.20 Plots showing sulphate, pH and temperature over time, and pH vs. sulphate during bioleaching experiments

Sulphate increased substantially in the inoculated flasks during the experimental period, from an average of 645mg/L at the start to 3,245mg/L in the heated flasks (1a/b), 4,085mg/L in the stirred flasks (2a/b), and 2,702mg/L in the static room temperature flasks (3a/b) by the end of the test. Sulphate in the control (4a/b) also increased, but to a lesser degree: 1,769mg/L. As shown in Figure 4.20 (sulphate-pH plot), there was an

inverse correlation between sulphate concentration and pH ($r_s = -0.91$ ¹⁴ across inoculated flasks), indicating that H_2SO_4 was being generated. Given that flasks were enriched with S^0 and there was a ready supply of O_2 (via aeration) and H_2O , this suggests the following reaction could be occurring, (Waksman and Joffe, 1922):



The key missing piece of evidence is the identification of specific micro-organisms such as *At. thiooxidans* which would confirm the mechanism for sulphur oxidation, although it is known that sulphur is chemically stable which implies that abiotic oxidation is unlikely (Rawlings et al., 2003). Acid mine drainage waters such those from Threlkeld Mine used as a leach solution in these experiments are toxic to the majority of micro-organisms, with a few extremophile taxa which are adapted to such hostile environments, in particular iron and sulphur oxidising autotrophs (Mendez-Garcia et al., 2015; Rawlings et al., 2003). It is suspected that the cells identified in the Threlkeld Mine water (used to inoculate replicates 1-3) were autotrophic iron/sulphur oxidisers, given the mine water was sourced from deep underground, was strongly acidic (pH<4) and contained significant quantities of toxic metals and sulphate (Table 4.13). In-fact, a number of studies have actually used acid mine drainage as a sources of bacteria to inoculate biological leaching experiments (Bayat and Sari, 2010; Liu et al., 2008; Renman et al., 2006; Solisio et al., 2002). It is less clear, however, why sulphur oxidation also appeared to have occurred (albeit to a lesser degree) within the control flasks (4a/b), in which mine water was sterile filtered to remove microbial cells. A possible explanation for this could be due to microbial contamination from the atmosphere, or spore-forming bacteria remaining within the substrate after oven drying. It is not uncommon for bacterial leaching to be conducted without inoculum but rather being operated in non-sterile environments allowing microbial communities to establish (Rawlings and Johnson, 2007; Seidel et al., 2004). While these experiments were undertaken in a relatively clean environment, there was potential for microbial contamination of control flasks from the atmosphere (i.e. during setting up and sampling). Generally, gram-negative sulphur oxidising bacteria such as *At thiooxidans* are non-spore forming (Waksman and Joffe, 1922) but spore-forming gram-positive acidophiles capable of sulphur oxidation have been identified, such as *Sulfobacillus* (Dufresne et al., 1996) and other *Firmicutes* (Rawlings and Johnson, 2007). More

¹⁴ d.f. = 76, P <0.001; Spearman rank order correlation

recently, gene sequencing technology has identified that the often quoted gram-negative bacteria, such as *Acidithiobacillus* and *Leptospirillum* genera, are actually less diverse than gram-positive strains in a range of acid-sulphide mine waste dumps (Schippers et al., 2010). This means that spore-forming sulphur oxidisers do exist and, may well have been part of a sulphur-cycling community present in the Nenthead treatment system substrate. If so, it is possible that these organisms could have survived storage and 105°C oven drying and been revived in the leach tests, giving rise to bio-oxidation of sulphur to sulphuric acid. This latter explanation seems most plausible because it is known that sulphur oxidising organisms both exist in mine drainage waters and are active in passive mine water treatment systems (Hallberg and Johnson, 2005; Johnson, 2003). Nevertheless, as shown in Table 4.14, sulphur oxidation was substantially higher within the inoculated flasks (1-3) when compared to the control (4).

Table 4.14 Sulphate and pH measurements upon completion of bioleaching experiments, showing replicates

Flask	Heated		Stirred		No heat/stir		Control	
	1a	1b	2a	2b	3a	3b	4a	4b
SO ₄	3,015	3,475	3,815	4,355	2,554	2,851	1,841	1,697
pH	2.60	2.37	2.15	2.13	2.96	2.69	4.07	4.16

Note that sterile filtering caused minimal change to geochemistry of mine water (Table 4.13) and, as a consequence, it is considered that the difference in sulphuric acid generation is due to the filterable fraction present in the mine water. Microbiological analysis would be required to confirm whether this filterable fraction contains sulphur oxidising bacteria. Greater increases in acid generation were seen in inoculated flasks which were stirred and heated, and were continuing to increase at the time the experiments were terminated. If completely oxidised, the added 5g/L of sulphur would form 12,192mg/L of sulphate¹⁵, far more than measured at the completion of the biological leaching experiments. Additionally, upon dismantling, significant quantities of what appeared to be raw sulphur were observed within the substrate. These factors imply that further oxidation of sulphur might have occurred if experiments were allowed to continue.

¹⁵ Sulphur molecular weight 32.8g/mol, sulphate molecular weight 96g/mol.

In addition to oxidation of added sulphur, there may have also been oxidation of reduced sulphur present in the substrate, such as metal sulphides. Metal removal in the Nenthead treatment system was thought to be, at least in part, due to sulphate reduction and formation of metal sulphides (Jarvis et al., 2014). Because no analyses have been conducted on the substrate to determine its sulphur content and oxidation state, the importance of this mechanism in the generation of sulphuric acid is unknown. However, given that the Rampgill mine water was poorly mineralised (particularly in respect to iron: 0.02mg/L (Gandy and Jarvis, 2012)), its treatment is unlikely to form significant quantities of acid generating minerals such as pyrite. Dissolution of zinc sulphide (and other di-valent metals sulphides such as NiS; PbS; CdS and CuS) on the other hand generate no acidity (Younger et al., 2002) and could therefore not be responsible for the observed drop in pH.

4.4.2 Metal recoveries during bioleaching

Data are presented for metal recovery efficiencies in Figure 4.21, calculated according to equation 4.1 (section 4.3). Because the same substrate was used for the bioleaching tests and the variable pulp density acid leach tests, the un-leached substrate metal concentration is the same as that shown in Table 4.4.

Manganese showed rapid and substantial recovery compared to other metals after a relatively short period in the heated flasks (72% after 336 hours) compared to 59% in the stirred flasks, 50% in the room temperature static flasks, and just 23% in the control flask. >100% manganese was recovered in the heated flasks after 720 hours and 888 hours in the stirred and static flasks at room temperature, with recovery reaching 96% in the control. Zinc, like manganese, also showed high recovery efficiencies, although initially recovery rates were negative, reflecting removal of zinc from the leach solution (refer to Table 4.13 for starting concentrations). Positive recovery was established after 336 hours in the heated and stirred flasks, 552 hours in the static, room temperature flasks and 720 hours in the control. Similarly to the chemical leaching tests, >100% recovery efficiencies were seen for zinc, with >100% being achieved by the end of all inoculated tests reflecting greater extraction than achieved by aqua regia digest of the substrate. Zinc recovery in the control reached 71% by the end of the experimental period. Nickel and cadmium both show good recoveries (71 – 92% across all inoculated experiments) albeit that these figures are lower than those for zinc. Re-examination of sequential extraction data show that both nickel and cadmium were

predominantly extracted by latter steps of the procedure (>75% associated with steps 4/5 – Figure 4.13). This implies that these metals were more tightly bound than zinc, which would explain their lower rates of recovery.

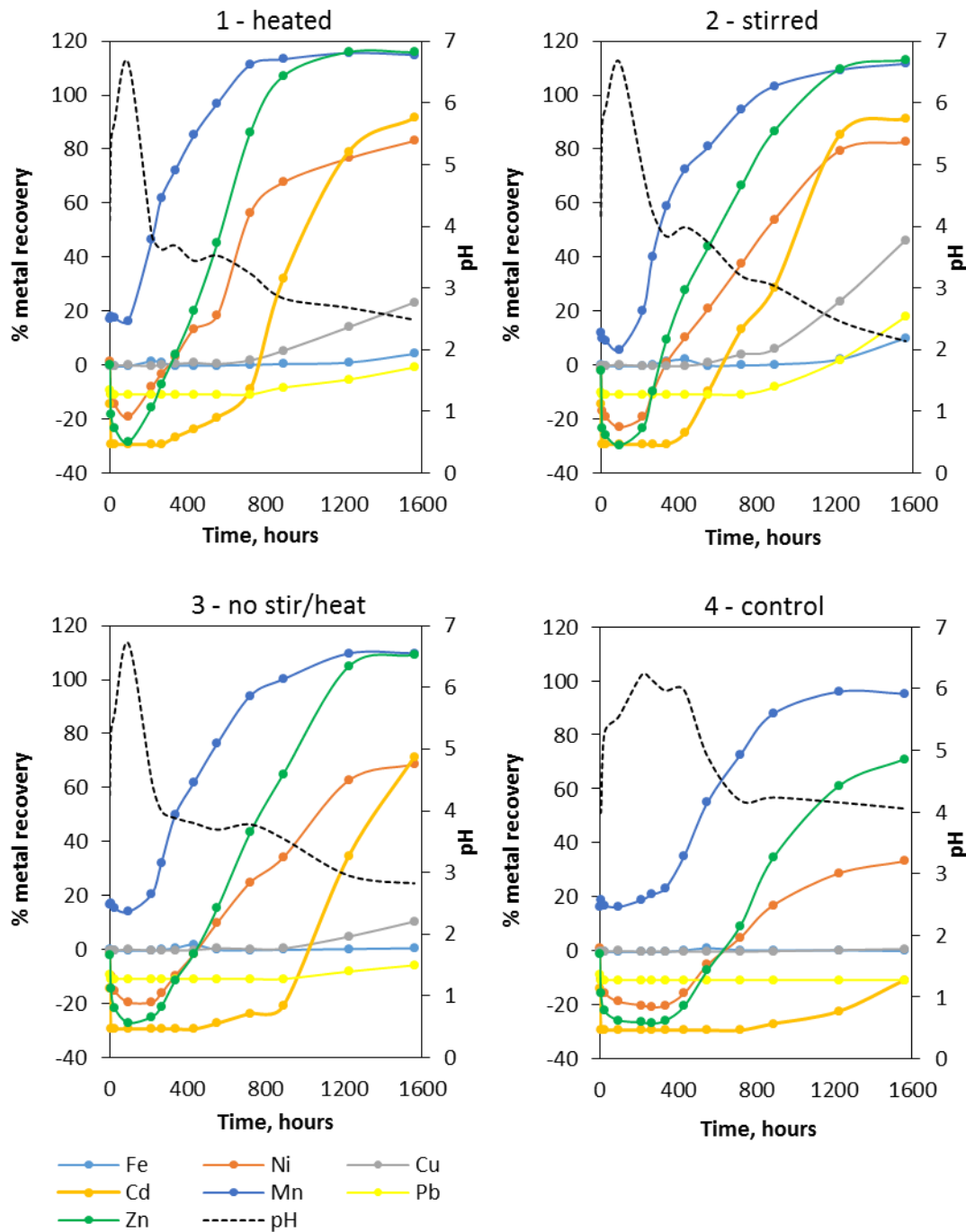


Figure 4.21 Metal recovery efficiencies and pH during bioleaching experiments

4.4.3 Reproducibility of bioleaching experiments

Replication of biological leaching tests was generally good, with the majority of replicate measurements being within 10% of the mean value ($n=342/364$). The majority

of replicates with poor repeatability (i.e. >10% deviation from mean, $n=18/22$) occurred within the stirred flasks (2a/b) as is evident from deviating recovery efficiencies as shown in Figure 4.22. It may have been that in one of the stirred replicates (2a/b) effective stirring may not have been achieved, compared to the other replicate. The fact that flask 2a shows very comparable zinc recovery rates as the unstirred flasks (3a/b) supports this theory. Further investigation using an improved stirring mechanism (such as top-mounted mechanical stirrers) would be required to determine the impacts of stirring on metal recovery rates.

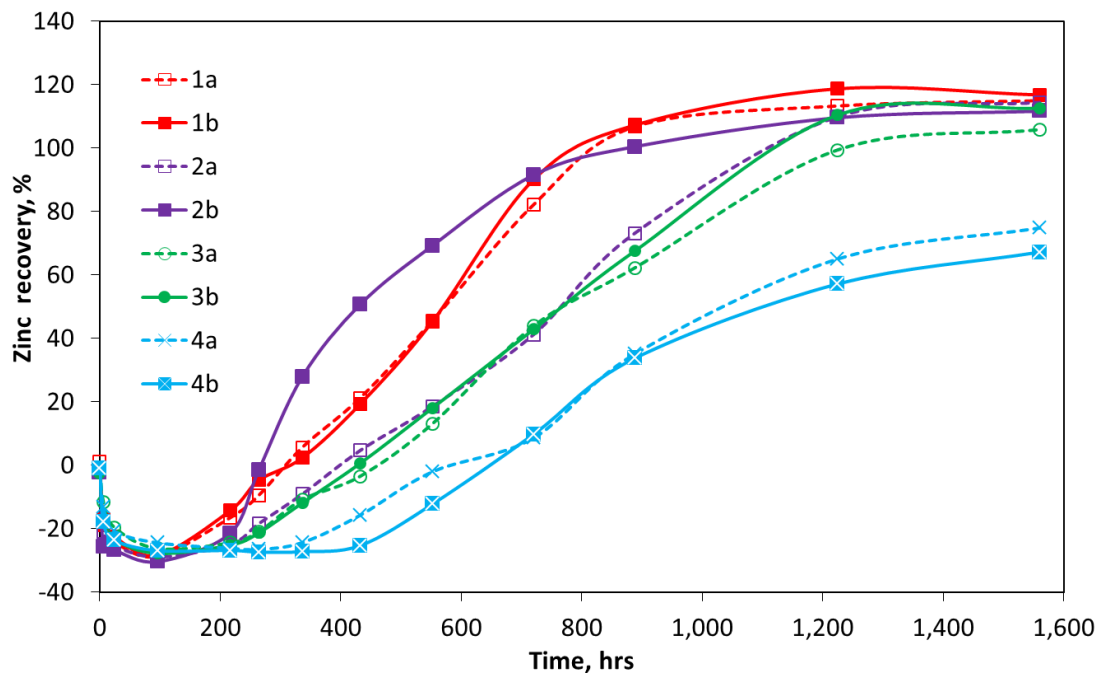


Figure 4.22 Zinc recovery from bioleaching tests showing replicates

Compared to other studies in the literature, recovery rates were relatively slow. For example, Bayat and Sari (2010) achieved 97% zinc removal from a metal plating sludge after 480 hours, whereas it took 720-888 hours to achieve the same efficiency in any of the tests in this study. Furthermore, after the same period, 96% copper and 84% lead recoveries were seen from the metal plating sludge (Bayat and Sari, 2010); whereas even after 1,560 hours, <50% of these elements were recovered from the Nenthead substrate. Brombacher et al. (1998) undertook a leach test over just 144 hours, demonstrating ~80% zinc recovery, ~90% copper recovery and ~100% cadmium recovery from fly ash after a three stage process (Brombacher et al., 1998). Variables and experimental configurations in these studies differ significantly from this study, making it difficult to draw meaningful comparisons. When inspecting the manuscripts, however, the microbial populations used have been pre-cultured to increase their

numbers before being used in the leaching tests. For example, cell counts were 10^9 in the stock leach solution used by Brombacher et al. (1998) and 10^6 in the 10% v/v inoculum used by Bayat and Sari (2010); whereas the cell count in this study was just of the order of 10^3 . This is just one variable which would warrant further investigation in order to optimise the bioleaching process.

It has been suggested that biogenic sulphuric acid leaching is effective at leaching metals bound to iron and manganese oxides (characterised by step 3 of a Tessier analysis), yet less effective when metals are bound to organic matter (step 4) (Karwowska et al., 2015). These findings are in agreement with data presented in this thesis: copper and lead are largely extracted during steps 4 (and 5 for Pb) of a Tessier sequential extraction, and show poor recovery efficiencies during biological (and chemical) leaching. However, zinc and manganese, dominated by steps 3 (and 2 for Mn) in the Tessier results show very high recovery efficiencies in the biological leaching tests. As explored throughout this chapter, these differences in extractability may be due to several factors, including sulphide solubility products and complex stabilities (Irving and Williams, 1953).

In terms of order of extraction of different metals, biological leaching exhibits a similar sequence to chemical leaching, perhaps unsurprising given sulphuric acid is involved with both approaches. Nevertheless, there is one notable difference in that very little iron is extracted in any of the bioleaching tests: a maximum of 13.4% measured in flask 2b (stirred). The static flask at room temperature (3a/b), while recovering 106/113% of the zinc, recovered just 0.3/0.8% of the iron by the end of the experimental period. Whereas, for instance, the 0.02M chemical leach test (Figure 4.15) recovered 102.9% zinc and 26.1% iron. Because there was no significant enrichment of iron in the substrate as a result of treating mine water, its source must be the substrate itself and, therefore, leaching is likely to result in change to the substrate composition which may impact its suitability for re-use. Furthermore, iron can be a nuisance component of leach solutions adding cost and complexity to downstream processing requirements (Amer et al., 1995; Rabah and El-Sayed, 1995).

While copper and lead recovery efficiencies remained very low or negative throughout the majority of the test, towards the end the rate of recovery started to increase in the inoculated flasks. In particular, greater recovery efficiencies were seen for lower pH (mean of replicates - stirred: pH 2.1, Cu 46%, Pb 17.9%; heated: pH 2.5, Cu 23.3%, Pb

-0.8%; static room temp: pH 2.8, Cu 10.4%, Pb -5.8%). The pattern for copper is in agreement with the chemical leaching tests and could be explained by the speciation of copper in the substrates (refer to Figure 4.3) and its low sulphide solubility. Lead recovery was particularly poor, explicable by its propensity to form a sulphate with low solubility (Mercier et al., 1996). However, as pH values were on a downward trajectory, it might be possible that significant increases in recovery of these metals might have occurred if experiments had been allowed to continue (Bayat and Sari, 2010; Brombacher et al., 1998).

4.5 Conclusions

4.5.1 Summary of investigations

Tessier sequential extractions were undertaken to characterise substrates from the Nenthead pilot treatment system after it had been decommissioned. The samples were subjected to both wet and dry sieving, and samples were analysed from different locations within the treatment system, to identify how metals had accumulated and how amenable they might be to recovery.

Leach tests were conducted on a mine water treatment substrate across a range of sulphuric acid concentrations (0.02M; 0.1M; 0.5M) and pulp densities (1.875%; 3.75%; 7.5%; 15%) in two separate sets of experimentation. Leach solutions for the variable pulp density tests were dosed with alkali and filtered to recover leached metals as a solid. Additionally, biological leaching was attempted in a third set of experiments, using an acidic mine water as a lixiviant and microbial inoculum. Recovery efficiencies were calculated against metals data from aqua regia digest of the unleached substrate.

4.5.2 Substrate characterisation

Wet sieving indicated that substantially more zinc was associated with the fine grained fraction of the Nenthead substrate. This pattern was not seen from dry sieving, where it is thought that the results are partially an artefact of the procedure (by cementing of compost fragments during drying). Sequential extraction procedures appear to be reproducible based upon triplicate samples, but differences between duplicate sub-samples was identified as an issue. This is attributed to bulk sample heterogeneity.

Average metal concentrations based upon 11 samples from across the treatment tank identified zinc and iron as the most abundant metals with average total concentrations of 5,404mg/kg and 15,374mg/kg, respectively. Zinc and iron concentrations were typically an order of magnitude greater or more than other metals investigated: manganese (570mg/kg), lead (189mg/kg), copper (119mg/kg), nickel (83mg/kg) and cadmium (11mg/kg). Substantially more zinc, cadmium and manganese were found in upper substrate layers compared to respective lower layers across most sample locations. This general pattern was seen for other metals, although to a lesser degree.

Copper appeared to be most tightly bound, associated with steps 4 and 5 of the sequential extraction, whereas manganese was least tightly bound, mostly associated with the first three steps. This is consistent with both their sulphide solubility products and Irving-Williams order of complex stability, which order copper and manganese as the least and most soluble, respectively (Hedin et al., 1994a; Irving and Williams, 1953). Generally, most zinc was associated with the 3rd extraction step. This is counter intuitive since zinc was expected to be largely present as a sulphide, commonly extracted in the 4th step (Mayes et al., 2011; Jong and Parry, 2004). This may be explained by issues with the sample collection and preparation for analysis which may have altered species (Rapin et al., 1986). Alternatively, the high concentrations of zinc compared to other metals may have led to differences in removal mechanisms within the treatment system, such as adsorption. On the basis of the most readily extractable fractions (steps 1-3 of the Tessier analysis), the metals investigated can be ordered in the following sequence of extractability:



These findings suggest that sieving may offer a means of concentrating the zinc rich fraction of the substrate. Separation of fine grained material by a wet-sieving process might be used to recover a zinc rich concentrate, leaving behind a material comprising larger, less contaminated particles. Selective removal of upper substrate layers may also offer a mechanism of separating more contaminated substrates from those which are less contaminated. Both these processes could be used to reduce volumes of contaminated material which require disposal off site, or processing for metal recovery; thereby reducing life-cycle costs of mine water treatment.

4.5.3 Acid leaching tests and metal recovery

More than 100% of the zinc was extracted after 100 hours across the three acid concentrations investigated, whereas it took more concentrated acids to achieve significant extraction efficiencies of other elements such as iron, copper, cadmium and lead. Manganese showed high extraction efficiencies, with in excess of 100% leached across all acids after just 30 hours. Nickel and cadmium also showed >100% extraction by the end of the leach tests in the two more concentrated acids (0.1M & 0.5M), although starting concentrations were low. Extraction efficiencies >100% are thought to have arisen due to incomplete recovery of metals by the aqua regia digest of the starting substrate, thereby providing an underestimate of the metal available for leaching (Chen and Ma, 2001). Extraction efficiencies for lead and copper were comparatively poor, reaching 68% and 58% for these metals in the most concentrated acid by the end of the test.

Pulp density tests were all conducted using 0.1M sulphuric acid, and experimental conditions were identical to the first round where acid concentration was varied. In excess of 100% of zinc and manganese was leached by the end of the 1.875%, 3.75% and 7.5% pulp leach tests. Yet <60% of manganese and <20% of zinc was leached in the 15% pulp density test, with all other metals showing leach efficiencies of <20%. pH measurements showed that values remain suppressed below 2.5 in all tests, other than the 15% pulp density test, where pH rose to above 4.5. It is thought that buffering of the lixiviant by the substrate has caused the pH rise, responsible for poor leaching efficiencies in this test. It appears that there is a threshold, between 7.5% and 15% pulp density where the recovery of the target metal zinc drops significantly. Higher pulp densities would offer a greater through-put of substrate for less lixiviant, assuming that a batch rather than a continuous process is operated.

It can therefore be concluded that 0.1M sulphuric acid offers an effective compromise between very high zinc and cadmium extraction efficiencies (>100%) yet only mobilising 50% of iron from the substrates. Optimum pulp densities for similarly high recovery of zinc and cadmium were 1.875% and 3.75%. The higher of the two pulp densities may be preferable in practical applications, given that this would allow a greater through-put of material for a given volume of leach solution.

In the 0.1M leach test (1.875% pulp density), both zinc and cadmium were reduced to levels comparable with the blank. With respect these two elements, therefore, it can be considered that the substrate was effectively de-contaminated by the acid-leaching process.

Precipitation of metals from pulp density test leach solutions was achieved by raising pH to >9 with sodium hydroxide, which resulted in precipitation of a solid, recoverable by filtration. Zinc, iron, manganese, nickel and copper were all below 1mg/L in the filtrate, and lead and cadmium were below detection limits. Sodium (from sodium hydroxide alkali), sulphate (from sulphuric acid) and aluminium remained elevated in the filtrate, which may cause problems for discharge in the case of spent leach solutions, although this would only be for the duration of the metal recovery process. Between 60% and 90% of the zinc was recovered as a solid, compared to starting concentrations in the substrate, across 1.875%, 3.75% and 7.5% pulp density leach tests. Metals were determined by aqua regia digest in both the substrate and the residue, although it was noted that some material was probably lost in the process of leaching and recovery and processing of solids from leach solutions, and thus true recovery efficiencies might have been higher.

Chemical leach and precipitation procedures investigated demonstrate a highly effective mechanism for the decontamination of passive compost based treatment system substrates and generation of a concentrated metal solid. This method of substrate decontamination may offer a mechanism of reducing treatment system life-cycle costs by reducing waste volumes and recovering metals. This is discussed in the context of a full-scale system in Chapter 5.

4.5.4 Bioleaching tests

Leaching was conducted, encouraging biological sulphur oxidation to form sulphuric acid within aerated leach test reactors in a similar configuration to the chemical leach tests. In order to provide conditions to facilitate biological sulphur oxidation, S^0 was added to the Nenthead substrate, along with raw acid mine drainage (Threlkeld Mine) to serve as a microbial inoculum. Additional variables were investigated: stirring, heating and control replicates. The control replicate received sterile filtered acid mine drainage from the Threlkeld Mine, in order to remove any inoculation that this might provide. Geochemically, the filtered water was comparable to that which was unfiltered,

meaning that any difference between the control and inoculated flasks arose due to the filterable fraction.

Sustained decreases in pH and increases in sulphate were observed which is indicative of microbial sulphur oxidation (Rawlings et al., 2003). Lower rates of sulphur oxidation were also observed in the control flasks, indicating that self-inoculation may have occurred, or sulphur oxidation may have occurred by another mechanism. Potentially, microbial contamination from either the atmosphere or the oven dried substrate could have given rise to self-inoculation of the substrate. Further investigation would be required, however, to determine the mechanisms of sulphur oxidation across all replicates. Nevertheless, data collected confirm that increased rates of sulphuric acid generation are achievable by the use of raw mine water, compared to the same water after sterile filtering.

At the start of the experiments, the pH rose from 4 to >6 across all flasks, attributable to buffering by the substrate. This rise in pH was accompanied by negative metal recoveries (for all metals excepting Mn) which reflected metal removal from the mine water leach solution. However, this pattern was observed to have started to reverse by 216 hours as pH dropped to <5 in all inoculated flasks.

Although biological leach tests operated for much longer periods than the chemical leaching (1,560 hours vs. 100 hours), metal recovery efficiencies were generally high. In particular, >100% recovery was seen for zinc and manganese for all the inoculated experiments; with 100% being reached between 552 and 888 hours in the heated flasks. High recovery efficiencies were also seen for nickel and cadmium, where 71-83% and 71-92% were achieved in respectively, across the inoculated flasks. Higher recovery efficiencies were seen in the stirred and heated flasks, compared to the static flasks at room temperature, although metal recovery efficiencies in the control were significantly lower. For example, at the end of the experiment just 31% nickel, 71% zinc and <0% cadmium had been recovered. Average pH measurements at the end of the tests were: 4.1 controls, 2.8 static room temperature flasks, 2.5 heated flasks and 2.1 stirred flasks.

Copper recovery rates were slow, however, and only started to increase towards the end of the test implying that, for this substrate, a longer leach period would be required. Lead recovery was very poor, with a maximum of 18% being recovered in the most successful leach (stirred reactors). This can be explained due to the low solubility of

lead sulphate in aqueous solutions (Mercier et al., 1996). Both these elements were at relatively low concentrations in the substrate.

Perhaps one of the most significant differences observed in biological leaching is that iron extraction was low, compared to chemical leaching, with an average of $\leq 10\%$ recovery in the most successful leach (stirred reactors) when $>100\%$ of zinc and manganese, and $>80\%$ nickel and cadmium were extracted. Because iron can be a nuisance when processing leach solutions (e.g. Amer et al., 1995), biological leaching yields a benefit over chemical leaching.

Chapter 5. Force Crag: Resource Recovery to Offset the Cost of Mine Water Treatment

5.1 Introduction and chapter contents

Review of the literature identified a research gap relating to how resource recovery might be used to reduce or offset the life-cycle costs of passive metal mine water treatment systems (see Chapter 2). To date, there have been no investigations of passive metal mine water treatment systems to either forecast life-cycle costs, or to assess how resource recovery might be used to reduce or offset these costs. In particular, for passive treatment systems, it appears that little consideration has been given to the rates of metal accumulation, which directly relate to the quantities of metal recoverable for a given operational period.

Commissioning of the first full-scale passive treatment system in England to tackle a zinc rich metal mine water took place in April 2014 at the Force Crag Mine, Cumbria. In the context of this research, this offered an ideal opportunity to closely study the possibilities for recovery of resources from a system of this type at full-scale. It may be that resources are available for recovery, which could offer potential to offset life cycle costs. Or, monitoring of system performance might identify possible limits to the length of time for which the system will operate effectively and which, if resolved, could extend system lifetime. To reiterate the objectives outlined in Chapter 1, the intention of studying the Force Crag treatment system was to:

- Monitor the performance of a passive treatment system to gain an understanding of the rates of metal accumulation and thereby forecast future metal concentrations in the substrate (Objective 4).
- Estimate life-cycle costs associated with an operational metal mine water treatment system and determine how resource recovery from the mine water might offer a mechanism for offsetting these costs (Objective 5).

This chapter firstly evaluates the performance of the Force Crag mine water treatment system. This is important to demonstrate the effectiveness of this technology for tackling pollution from abandoned metal mines. In addition, a break-down of costs for construction and operation are provided.

The water quality monitoring forms a larger body of externally funded research into system performance and, consequently, while this author has been significantly involved with the sample collection, there are some elements which have been entirely undertaken by others. In particular, laboratory analyses of water samples were completed by technical staff and analysed according to methods outlined in section 3.6.3, Chapter 3. Interpretation of data presented in this chapter has been made by this Author.

Whole life-cycle costs presented are based upon actual outturn for construction and forecast operational costs, without resource recovery. The possibility of reducing these life-cycle costs by resource recovery and waste reduction are then investigated. Data from preceding chapters and the literature will be contextualised and their implications discussed in the context of the full scale treatment system. Assessment is made of the rates of accumulation of the key metal, zinc, in the substrate in comparison to estimates and measurements from other examples in the literature. Evaluation of the cost implications of metal recovery from the substrate are investigated using estimates from industry specialists, Acumen Waste Ltd. As the first of its kind in Great Britain, the Force Crag system presents a new set of challenges relating to waste disposal, which have not previously been evaluated in any detail, either nationally or internationally. Renewable energy generation may offer a way to both generate revenue and improve the heritage facilities at the site, which, due to its location, does not have access to conventional energy supplies. Potential for hydropower and mine water-sourced heating are explored. Additionally, the life-cycle costs of the passive system with and without metal recovery are evaluated against costs of active treatment.

5.2 Treatment system performance

Data presented and discussed in this thesis are for the first year of operation of the treatment system (April 2014 – March 2015). The general focus is on performance of the two Vertical Flow Pond (VFP) units in the treatment system, rather than the treatment system as a whole (i.e. including the polishing wetland) since the latter component provides only an auxiliary function to reintroduce oxygen into the water before discharge to the Coledale Beck (see Jarvis et al., 2014). Raw data are included as Appendix G.

5.2.1 Metal removal over monitoring period

System performance over the first year of operation was carefully monitored; Table 5.1 provides a summary of metal removal over the first year of operation for both VFPs.

Table 5.1 VFP treatment performance showing mean values for April 2013 - March 2014, inclusive

	Influent	VFP1 out	VFP2 out	Efficiency	
	(Level 1)			VFP1	VFP2
	mg/L	mg/L	mg/L	% removal	% removal
Zn	3.26	0.04	0.16	98.68	95.17
Pb	≤0.053	≤0.051	≤0.051	-	-
Cd	≤0.017	<0.01	<0.01	-	-
Ni	0.018	≤0.012	≤0.012	-	-
Al	≤0.07	≤0.099	≤0.112	-	-
Fe	0.51	1.47	1.35	-186.02	-162.67
Mn	0.56	0.44	0.51	20.87	8.28
Cu	<0.01	≤0.013	≤0.013	-	-

Zinc removal of >95% was achieved across both VFPs as shown in Table 5.1. Because removal of zinc as a key pollutant was the overarching objective at Force Crag (Jarvis et al., 2014), this result signifies a major success of the treatment system. Further details relating to this main contaminant are provided in section 5.2.2. Aluminium, iron and copper were greater in the system effluents than influents when averaged over the first year of operation, indicating that the system was a net exporter of these metals. A rapid decline in concentration within effluents was seen, however, over the first few months of operation. Nickel and copper decreased to below the 0.01mg/L analytical detection limits after just 1 and 2 weeks, respectively. Copper was below detection limits in the system influents throughout the study period and nickel concentrations were only marginally elevated on occasion. Likewise, lead and cadmium concentrations were frequently below analytical detection limits and therefore further investigation is required to determine actual values before any firm conclusions can be drawn on removal of these metals.

Aluminium had a mean influent concentration of 0.07mg/L excepting occasional times when it was below 0.05mg/L analytical detection limits (*n* below detection: 3/43). Effluent aluminium concentrations decreased and remained below detection limits after

2 months in VFP1 (n below detection: 29/43), although it took 7 months before concentrations remained below detection limits in VFP2 (n below detection: 12/43). Due to limits of detection, removal efficiencies may have been higher than might be inferred from the data presented¹⁶. Iron concentrations in effluents did not reach detection limits during the experimental period, although they decreased to below 1mg/L after 6 months of operation. Removal mechanisms for iron and aluminium in passive treatment systems are dominated by (oxy)hydroxide formation (Uster et al., 2015; Younger et al., 2002). Ochreous precipitates were observed on the substrate surface indicative of iron removal by this process, which has been shown to dominate over sulphate reduction in similar systems elsewhere in the UK (Matthies et al., 2009; Watson et al., 2009). Manganese exhibits low removal efficiencies (8-21% removal) which might be explained by its high sulphide solubility product (5×10^{-15}) and low complex stability ($\text{Mn} < \text{Fe} < \text{Ni} < \text{Cu} > \text{Zn}$) (Hedin et al., 1994a; Irving and Williams, 1953). If manganese is to be removed as a sulphide, it has been shown that an excess of H_2S is required (Yoo et al., 2004), although other mechanisms such as carbonate (Uster et al., 2015; Zagury et al., 2006) and hydroxide (Bamforth et al., 2006) precipitation have also been shown to be important removal mechanisms elsewhere.

5.2.2 Zinc

The Force Crag treatment system was designed specifically to remove zinc as a key contaminant, and removal efficiencies for this metal were very high during the monitoring period. If considered on a quarterly basis, for the first two quarters of operation total zinc removal efficiency was 97%, for the third it had increased to 98% and by the final quarter of the year it was 99%. Such consistently high performance, particularly over the colder winter months, is encouraging for the longer term operation of this treatment system. Mean influent zinc concentrations were broadly comparable for total zinc: 3.26mg/L, <0.45 μm filtered: 3.20mg/L and <0.1 μm filtered: 3.07mg/L. Filtered zinc (<0.45 μm) shows marginally higher removal efficiencies compared to total zinc, with zinc removed to below 0.01mg/L detection limits in VFP1 on several occasions in the final quarter (Figure 5.1). However, throughout the duration of the monitoring period, zinc filtered to <0.1 μm was consistently below 0.01mg/L detection limits in both effluents (data not shown) compared to the total zinc concentrations of 0.04mg/L (VFP1) and 0.16mg/L (VFP2). This suggests that, while the majority of zinc

¹⁶ Analytical detection limits in mg/L for Pb, Al: 0.05; Cd, Cu, Ni: 0.01

in the system influent is dissolved (i.e. $<0.1\mu\text{m}$), very little is dissolved in system effluents ($<0.01\text{mg/L}$). It is worth noting, however, that classification of dissolved species is not clearly defined by particle size (Stumm and Morgan, 1996). Mechanisms for zinc removal are discussed further in section 5.2.4.

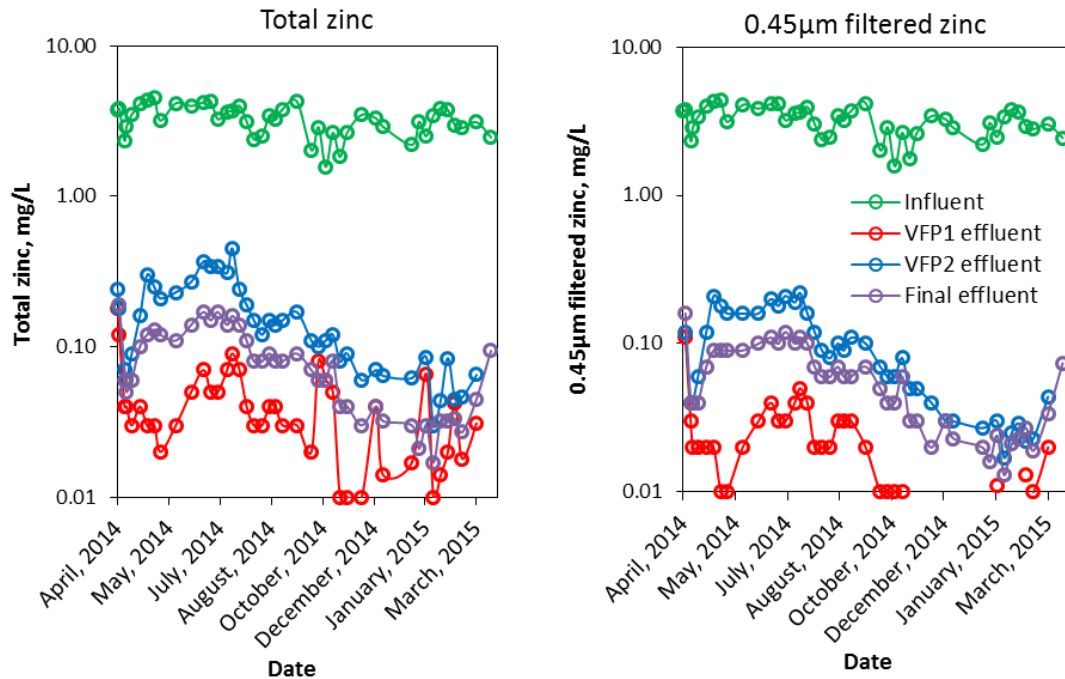


Figure 5.1 Zinc removal at Force Crag. Final effluent is a combined flow of VFPs 1 and 2 after having passed through a small aerobic wetland (note log scale)

Table 5.2 compares the performance of the Force Crag VFPs to some other passive pilot and full scale systems engineered to harness bacterial sulphate reduction for metals removal. However, mine water geochemistry and treatment system design vary between sites, which is likely to affect performance. These data are a short summary of removal metrics relating to total zinc, where efficiency is calculated as the percentage zinc removed between influent and effluent (%), and volume adjusted removal rate is the mass of metal removed per unit of treatment system volume per day ($\text{g/m}^3/\text{d}$). All data, including other variables, are available within the database in Appendix A.

Table 5.2 Comparative mean zinc removal rates and efficiencies from a range of bioreactor systems harnessing bacterial sulphate reduction

System name/ description, Reference	Location	Influent zinc	Flow	Study period	Efficiency and removal rate (zinc)	
		mg/L	L/s	d	%	g/m ³ /d
Nenthead, field based pilot bioreactor (Jarvis et al., 2014)	Cumbria, UK	2.2	0.018	730	68	0.9
Luttrell system, single cell bioreactor (ITRC, 2013; Hiibel et al., 2008)	Montana, USA	205	0.048	1,095	99	1.45
West Fork Unit, settling / anaerobic ponds active lead mine (Gusek et al., 1998)	Missouri, USA	0.36	75.8	180	80	0.63
Burleigh Mine, up-flow bioreactor (USEPA, 2002)	Colorado, USA	57	0.32	1,460	56	3.40
Burleigh Mine, down-flow bioreactor (USEPA, 2002)	Colorado, USA	57	0.32	1,460	65	3.93
Cadillac Molybdenite bioreactor / oxidation pond & ALD (Kuyucak, 2006)	Quebec, Canada	1.35	0.38	420	99	0.11
Cwm Rheidol field based pilot bioreactor. Unpublished data, Newcastle University	Wales, UK	12.75	0.060	750	63	2.07
Palmerton pilot unit, smelter drainage bioreactors (Dvorak et al., 1992)	Pennsylvania, USA	317	0.003	126	100	9.58
Dalsung Tungsten Mine pilot bioreactor (Cheong et al., 1998)	South Korea	11.4	0.001	118	84	2.40
Standard Mine superfund site, Biochemical reactor (Rutkowski, 2013; Reisman et al., 2008)	Colorado, USA	24.7	0.063	1,230	100	11.20
Haile Mine bioreactors (2no.) / wetland (ITRC, 2013)	S. Carolina, USA	1.8	0.38	1,643	95	0.02
Lady Leith bioreactor and wetland (ITRC, 2013)	Montana, USA	0.75	0.38	3 visits	72	0.54
Active coal mine site, pilot bioreactor (Trumm and Ball, 2014)	New Zealand	6.3	0.010	141	100	5.40
Galkeno adit, United Keno Hill Mines wetland (Infomine, 2015)	Yukon, Canada	25	0.3		72	0.64
Force Crag VFP1 bioreactor. Unpublished data, Newcastle University	Cumbria, UK	3.26	3.27	365	99	1.89
Force Crag VFP2 bioreactor. Unpublished data, Newcastle University	Cumbria, UK	3.26	2.94	365	95	1.90

Flow rates at Force Crag are greatest out of all systems studies, excepting the West Fork Unit system which was operating at an active mine site (Gusek et al., 1998). Performance indicators of zinc removal efficiency and volume adjusted removal rate show that the Force Crag system is a high performing compost bioreactor, outperforming 5 similar systems described in the literature across both these metrics, including the Nenthead system of the same design, albeit that this system suffered some operational problems which affected its performance (Gandy and Jarvis, 2012). A further 5 sites show broadly comparable performance to Force Crag when considering both removal rate and efficiency together (where efficiencies ranged between 56-99% and removal rates between 1.45 and 3.93g/m³/d). Three treatment systems cited, however, outperform the Force Crag VFPs by both rate and efficiency of zinc removal: Palmerton pilot system treating smelter drainage in Pennsylvania (Dvorak et al., 1992), Standard Mine bioreactor, Colorado (Rutkowski, 2013; Reisman et al., 2008) and a pilot bioreactor operating at an active coal mine site in New Zealand (Trumm and Ball, 2014). Looking more closely at the variables for these three systems, both the influent sulphate concentrations at the Palmerton and the New Zealand sites were in excess of 2,000mg/L (mean values). The Standard Mine site also had relatively high sulphate concentrations of 281mg/L (mean, $n=7$), more than an order of magnitude greater than those seen at Force Crag (mean: 26.7mg/L, $n=43$). Zinc concentrations were also very high in the Palmerton system at 317mg/L (mean, $n=26$). Given a sulphate to zinc stoichiometric ratio of 1:1 for ZnS formation, there is a comparative excess of sulphate (950%) to that at Force Crag (820%). While there appears to be little empirical evidence linking stoichiometric excess of sulphate to metal removal efficiencies, an excess of biogenic sulphide would prevent this factor from being a limit on treatment performance (Klein et al., 2013). Closer inspection of the system configuration, however, finds a residence time of 33 days at Palmerton, dictated by the unusually low flow, highly concentrated waters (Dvorak et al., 1992). Both the site in New Zealand and Standard Mine also have higher zinc concentrations than Force Crag (6.3mg/L and 24.7mg/L, respectively – mean values) yet retention times at both these sites are only slightly higher than at Force Crag (28 and 30 hours, respectively, compared to the 15-20 hours at Force Crag (Jarvis et al., 2015)). Given the relatively high metal accumulation rates of these systems, it would be of great interest to compare, in the long term, their life-times with that of the Force Crag VFPs.

5.2.3 Alkali and alkaline earth metals and secondary contamination

Considering firstly the four major alkali/ alkaline earth metals (calcium, magnesium, sodium and potassium), data shows that initial effluent concentrations were very high, followed by exponential decay. Within 4 months of operation, concentrations of magnesium, sodium and potassium had decreased to levels comparable with influent concentrations (potassium below detection limits of 1mg/L). Calcium concentrations do not exhibit the same exponential decay but a relatively linear decline over the monitoring period.

Effluent metal concentrations in excess of those measured in the system influent during the early phase of operation must have been sourced from within the treatment system, probably from leaching of the compost substrate. Jarvis et al. (2015) identifies that ammonium, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are also significantly elevated in the effluent shortly after commissioning at this site, also attributable to leaching of the substrate and resulting in secondary contamination of the receiving Coledale Beck (Jarvis et al., 2015). After 4 months, however, these parameters had decayed in the system effluent and concentrations in the Coledale Beck were back to acceptable levels (Jarvis et al., 2015).

5.2.4 pH, conductivity, sulphate and alkalinity

During the first month of operation, pH was, on average, 6.6 in system influent and 7.6 in system effluent, before decreasing slightly in the effluents to 6.9, on average, for the remaining 11 months. Conductivity was initially highly elevated in system effluents for the first week (typically >1,000 μ S/cm) before showing rapid decline to <500 μ S/cm after this period, decreasing to <200 μ S/cm after 6 months. This pattern is consistent with the major ion and organic contaminant data, reflecting initial leaching of the substrate. Influent conductivity measurements remained relatively stable for the monitoring period at 114 μ S/cm on average (SD 20.8, $n=42$).

Sustained removal of sulphate through the treatment system was seen during the first year of operation. Figure 5.2 shows that, during summer months, sulphate concentrations were <10mg/L in effluents, although they rose later in the year. It is too early to determine if this effect is seasonal and, although some studies have identified that low temperatures do not adversely affect bacterial sulphate reduction (Tsukamoto et

al., 2004; Zaluski et al., 2003; Fortin et al., 2000), others have observed that low temperatures can affect overall system performance (Gandy and Jarvis, 2012; Gusek, 2002). It might be that temperature affects other sulphate removal mechanisms such as adsorption and formation of sulphate rich phases (Leticariu et al., 2015). Alternatively, it could be that these mechanisms are particularly important for sulphate removal during the early phase of system operation which was during spring and summer months.

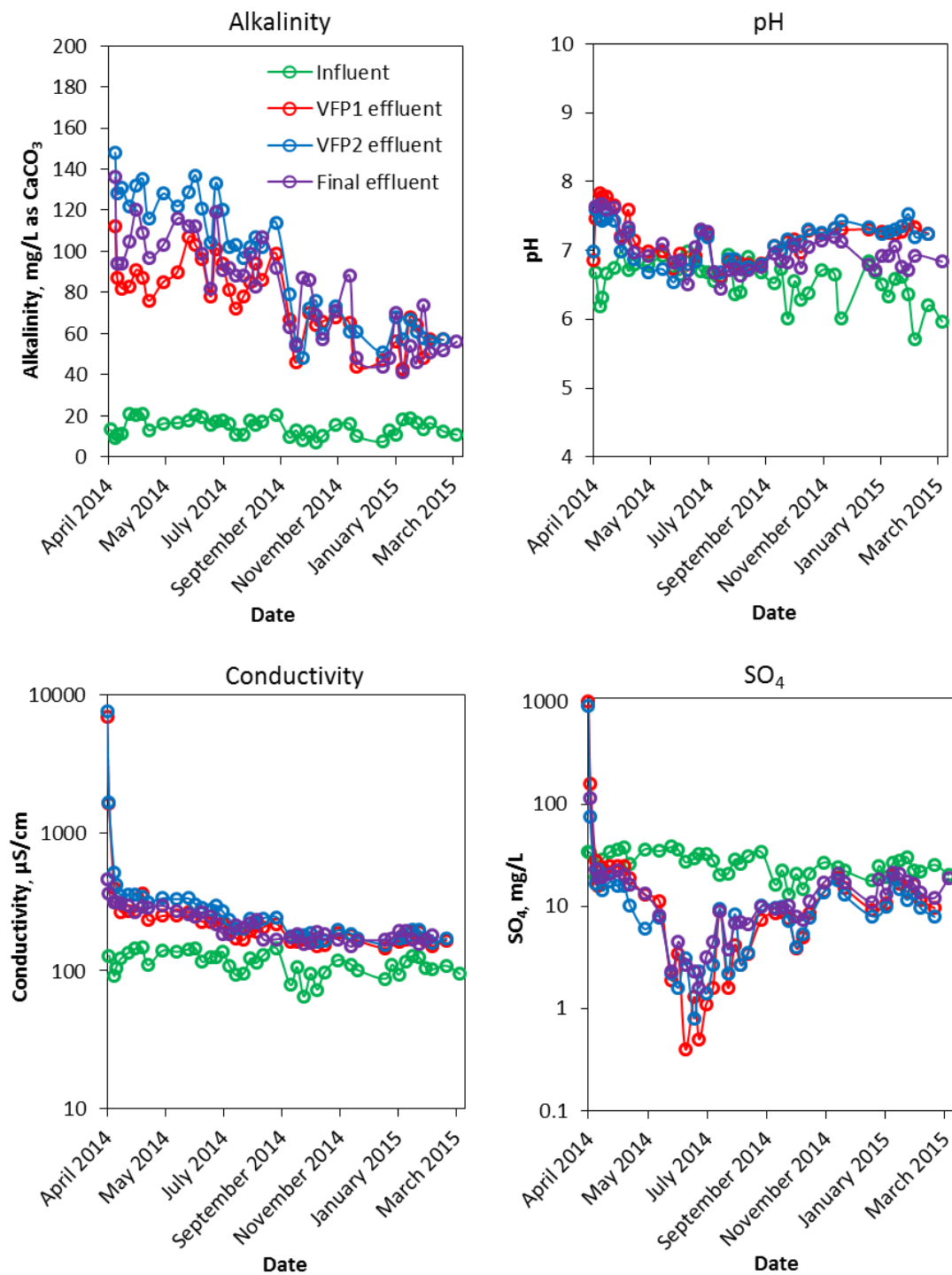
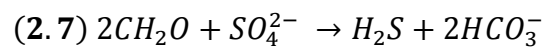
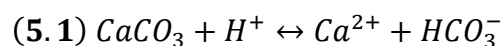


Figure 5.2 Alkalinity, pH, conductivity and sulphate at the Force Crag treatment system. Final effluent is a combined flow of VFPs 1 and 2 after having passed through a small aerobic wetland

Unlike sulphate, zinc removal does not peak during the summer, with the lowest concentration in the final effluent seen during the middle of winter (3/02/2015) while influent concentrations remain comparatively stable over the monitoring period (Figure 5.1). Data presented in Figure 5.2 indicate that, on average, sulphate concentrations are reduced by 12mg/L throughout the monitoring period. According to equation 2.7 from Chapter 2 (repeated below for convenience) two moles of alkalinity are generated for every one mole of sulphate reduced (Younger et al., 2002). Therefore, it would be expected that 24mg/L of bicarbonate alkalinity would be generated by sulphate reduction, on average, during the monitoring period. This assumes that all sulphate is removed by sulphate reduction.



Alkalinity measurements (as bicarbonate) increase by 68.4mg/L on average through the system. As seen in Figure 5.2, there is a progressive decline in alkalinity generation throughout the monitoring period (effluent - influent = 39.8mg/L as CaCO₃ over the last month of monitoring ($n=4$)). Over the same period the amount of bicarbonate produced, assuming that all influent sulphate was removed by sulphate reduction, was 15.4mg/L. These data suggest that while sulphate reduction may contribute significantly to the elevated alkalinity of the system effluent, there appear to be additional mechanisms of alkalinity generation at work, such as reduction of sulphate present in the substrate (Yim et al., 2015) or calcium carbonate dissolution associated with limestone (McCauley et al., 2009). Net increases in calcium concentrations, which might be expected to arise from calcium carbonate dissolution, are observed through the treatment system supporting the latter explanation. According to the measured calcium values during the last month of monitoring (8.8mg/L influent, 27.7mg/L effluent), 18.9mg/L of calcium was sourced from the treatment system. Equation 5.1 indicates that, equally, 18.9mg/L of bicarbonate alkalinity would have been generated if the increase in measured calcium concentrations through the system arose from calcite dissolution (Younger et al., 2002).



Combining the estimated alkalinity generated by calcite dissolution and sulphate reduction, a value of 34.3mg/L alkalinity is obtained, which is close to the measured value of 38.9mg/L. This implies that it is possible that these two mechanisms are

responsible for the generation of the majority of alkalinity in the system, although there may be other, less dominant, mechanisms at work. Sulphate to zinc removal at Force Crag had a stoichiometric ratio of 3.4:1 based upon mean data ($n=43$), with removal as metal sulphide solids under sulphate reducing conditions being cited as a key mechanism (Jarvis et al., 2015). It is unlikely, considering the chemistry of the Level 1 water, that there is much in the way of competing cations which might react with sulphide instead of zinc: both copper and lead which have higher sulphide solubility products than zinc (Hedin et al., 1994a) are below detection limits of 0.1mg/L and 0.5mg/L respectively. Given the stoichiometry ratio of zinc sulphide formation (1:1) and the absence of measured competing cations in the influent water, it is entirely plausible that zinc removal as a sulphide is the most important metal removal mechanism at this time. Nevertheless, it is known that hydrogen sulphide is highly reactive and volatile and can often be oxidised or liberated from bioreactors before reacting with metals (Jong and Parry, 2003; Johnson and Hallberg, 2002).

Sulphide (S^{2-}) concentrations were also measured from July 2014 using a field based indicator kit (Hach – see Table 3.5, Chapter 3). This method provides a useful indicator for the presence of sulphide within the treatment system (APHA, 2005). Sulphide concentrations measured within effluents were typically 0.1-0.7mg/L in VFP1 and 0.5-2.0mg/L in VFP2 effluents ($n=17$) showing that there was still unreacted sulphide in solution at the point it was leaving the VFPs. This, coupled with highly negative Eh values when taking measurements from VFP effluent pipes (-191, VFP1; -220, VFP2; $n=160$) and a notable hydrogen sulphide odour, indicates that sulphate reducing conditions were present in the treatment system.

While there is evidence to suggest that bacterial sulphate reduction is occurring within the treatment system, other processes such as adsorption and co-precipitation have also been cited as important removal mechanisms (Mayes et al., 2011; Matthies et al., 2009; Neculita et al., 2008b). These studies and others have been discussed in Chapter 2 and data from the Force Crag treatment system has not yet proven beyond doubt that bacterial sulphate reduction is the most important metal removal mechanism. Ongoing investigations, which include microbial community analysis, are hoped to address this (*pers comm.*, Dr C. J. Gandy, Newcastle University, 2015).

5.2.5 Electroneutrality

In addition to the accuracy checks undertaken during analysis of water samples, it is good practice to conduct a charge-balance of major ions, in order to provide additional data verification. The charge balance error is calculated for the Force Crag water analyses using Equation 5.2, with data expressed in meq/L (Appelo and Postma, 2010).

$$(5.2) \text{ Charge balance, \%} = \frac{\Sigma \text{cations} + \Sigma \text{anions}}{\Sigma \text{cations} - \Sigma \text{anions}} \times 100$$

Where full analytical suite are investigated (data not presented in this thesis¹⁷) the charge balance is typically within 5% ($n=46/60$) and all within 15%, excepting values from the very first monitoring event, which have consequently been discarded. While data with a charge balance of <5% is considered to be indicative of good accuracy, it is suggested that data with electroneutrality of 5-15% should be used with caution (Younger, 2009). These analytical errors are attributable to difficulties in conducting accurate colorimetric alkalinity titrations in the field, because of the murky colour of the effluent waters. This was particularly problematic during the early phase of system operation when waters had a deep brown colour. The electrical conductivity can be used as a quick check of analytical accuracy by the following expression (Equation 5.3 after Appelo and Postma (2010)):

$$(5.3) \Sigma \text{Cations} = \Sigma \text{Anions (meq/L)} \approx EC/100(\mu\text{S/cm})$$

Analytical data from shortly after start-up of the treatment system for turbid VFP and wetland effluents confirms that the anions are suspect, with total cation values comparable to EC/100: 13.16-13.47 meq/L and 16.3-16.6 $\mu\text{S/cm} \cdot 100$, respectively; whereas anions were somewhat lower at 6.39-8.45 meq/L. Good charge balance for the clear, poorly mineralised influent mine waters provides further reassurance of analytical accuracy, as all charge balances following the first sampling event were within 10%.

¹⁷ Species used in charge balance: cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Zn^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Al^{3+} , Fe^{2+} , Mn^{2+} , Mn^{2+} , Cu^{2+} ; anions: HCO_3^- , SO_4^{2-} , PO_4^{3-} , NO_3^- .

5.3 Life-cycle costs of mine water treatment

Throughout the process of design and construction, it has long been standard practice in the civil engineering industry for project costs to be carefully controlled and all opportunities for savings identified by value engineering to be explored (Miles, 1962). On this basis, and for the purposes of this study, it can be assumed that the construction cost of the Force Crag treatment system was as low as practicable. The figures presented in Table 5.3 are actual outturn figures obtained from The Coal Authority following completion of its construction. Normally, costs attributed to scoping/feasibility and outline design stages are not counted as part of the construction cost on the basis that, at this stage of the project, the decision has not yet been made to invest in the treatment scheme. Table 5.3, however, details all known expenditure in order to provide a full illustration of the costs associated with the project.

Table 5.3 Construction costs for Force Crag mine water treatment system (courtesy of The Coal Authority)

Construction item	Actual cost
Scoping and feasibility studies	£100,957.00
Outline design and planning	£54,322.18
Environment Agency permits and consents	£4,805.82
Land agent costs	£19,974.00
Project management (Coal Authority staff cost)	£117,132.47
Ground investigation	£86,600.00
Detail design	£53,993.32
Level 1 diversion and treatment system construction	£650,280.86
Archaeological watching brief	£10,444.00
Total	£1,098,509.65

Operational costs have been forecast by The Coal Authority and its consultants, based on experience of operating similar coal mine water treatment systems for over 20 years

(Table 5.4). Waste disposal costs are, however, different to most coal mine water treatment systems due both to the nature of the treatment substrate and the metals which accumulate within it. Therefore, quotations were received from waste carriers to determine the waste disposal cost (Atkins, 2014b). It is pertinent to mention that the substrate density used to calculate substrate tonnage has been assumed to be comparable to soils at 1.25 tonnes per m³ (Atkins, 2014b). Preliminary measurements of the blank substrate by Newcastle University indicate that the actual density is significantly lower: 0.61 (wet) – 0.32 (dry) (unpublished data, Newcastle University 2015). Yet these measurements were conducted on loose substrate in the laboratory and do not consider the effects of compaction of the substrate once within the VFPS.

Table 5.4 Operational costs (forecast) for the Force Crag mine water treatment system (courtesy of The Coal Authority)

Description	Forecast cost
<i>Annual costs</i>	
Routine inspection and maintenance	£6,000
Landscape maintenance	£1,000
Routine sampling and testing for regulatory compliance	£3,000
Total annual cost	£10,000
<i>One-off costs (10 year estimate)</i>	
Substrate excavation and haulage	£97,500
Substrate disposal*	£685,750
Substrate renewal	£29,200
Total one-off cost	£812,450

*Disposal cost based upon quotations received from hazardous waste carriers, assuming substrate has the same classification as the Nenthead pilot system wastes – lowest of 3 quotes considering combined cost of haulage and disposal

Assuming a life-cycle of 10 years (as estimated by The Coal Authority before the system performance drops and the substrate requires replenishment), the total cost of construction is £1.1m and operation £0.1m for routine sampling and monitoring. At the point at which the system starts to fail, it has been forecast by Atkins (2014b) that expenditure of more than 70% of the initial capital construction cost will be entailed by substrate disposal and replenishment. The life-cycle cost profile based upon these figures is graphically represented in Figure 5.3, in comparison to the monetised benefits as determined by a benefits assessment according to the National Water Environmental Benefits Survey (NWEBS) (RPA, 2013).

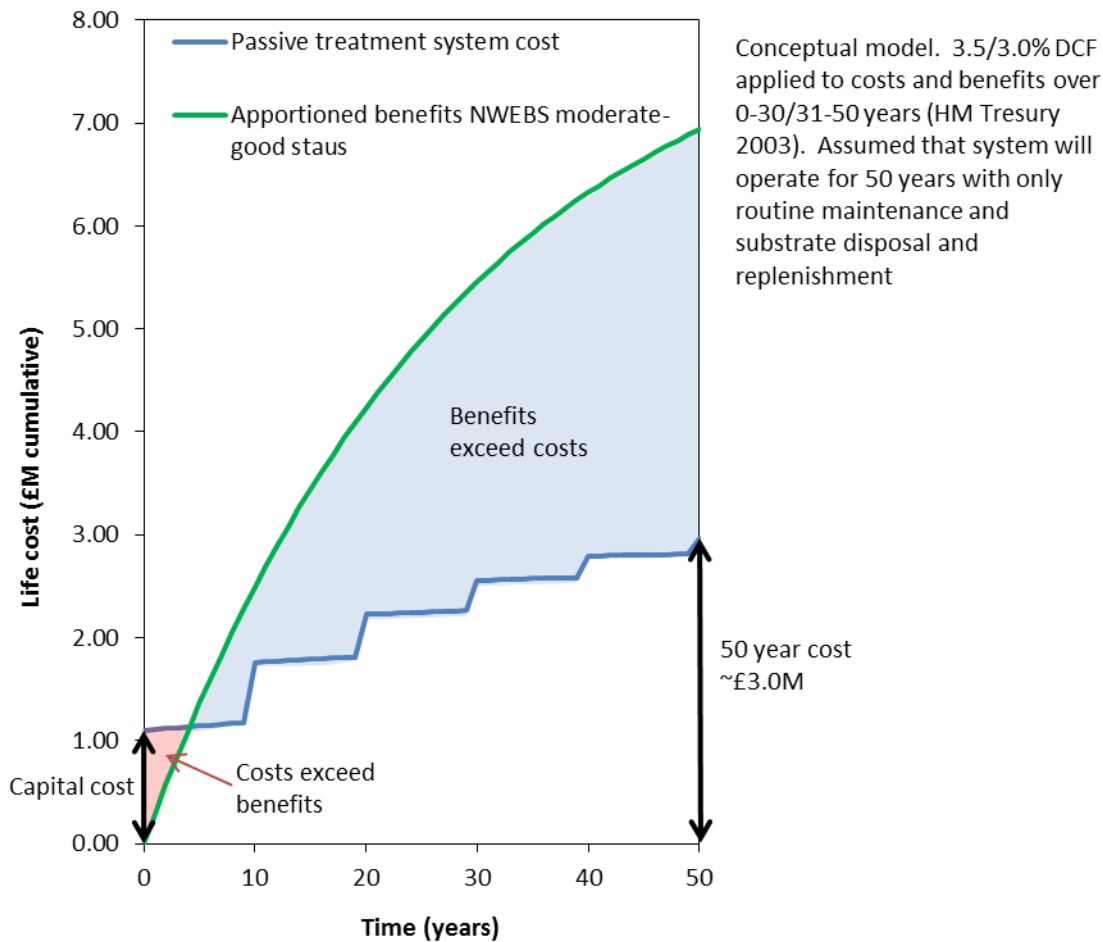


Figure 5.3 Force Crag treatment system cost in relation to monetised benefits (financial data used to produce conceptual model was supplied by The Coal Authority, see text for further explanation)

The NWEBS approach was designed to assess the non-market benefits to UK households of implementing measures to improve water quality to achieve Water Framework Directive objectives (Metcalf et al., 2012). Several methods were employed to derive these benefits figures, including discrete and dichotomous choice scenarios and willingness to pay surveys using focus groups (Metcalf et al., 2012). Values determined from the study by Metcalfe et al. (2012) were used to determine the benefits of improving the water quality of the Derwent Catchment which is impacted by mining pollution from sites at Force Crag and Threlkeld (RPA 2013). Financial benefits of remediating the mine water pollution at Force Crag, devised using the NWEBS assessment, are compared to predicted scheme life-cycle cost, providing financial justification for investment in the project (The Coal Authority, 2014). All figures have been discounted using a Discounted Cash Flow (DCF) factor of 3.5% over the first 30 years, and 3.0% thereafter according to Government guidance (HM Treasury, 2011). This DCF provides adjustment when forecasting future cash flows, considering that the value of an investment varies depending on when it is received

Chapter 5. Force Crag: Resource Recovery to Offset the Cost of Mine Water Treatment (HM Treasury, 2011). Calculations showing discounted life-cycle costs and NWEBS benefits are provided in Appendix H.

Financial forecasting reveals that, over 50 years, the cost of substrate disposal (assuming 5 disposal/replenishment events) equates to £1.6m, compared to all other maintenance costs which are just £0.24m. As the single greatest cost beyond value engineered construction, substrate disposal might offer the greatest area for potential saving in the whole-life cost of the treatment system. Two possible approaches to reducing this element of cost are:

1. Increasing substrate lifetime, thereby reducing the frequency of disposal.
2. Finding alternative (less costly) disposal routes for substrates, which may involve some degree of decontamination or processing for resource recovery.

These two approaches are discussed in the following two sections.

5.4 Force Crag substrate lifetime

Passive treatment systems, constructed from earthworks and minor engineered structures, such as capture chambers and transfer pipelines, require little regular maintenance (PIRAMID Consortium, 2003; Jarvis and Younger, 1999). Only occasional intervention is required, for example, to keep channels clear and control vegetation (PIRAMID Consortium, 2003). This approach has been adopted at the Force Crag site (Jarvis et al., 2015). Over time, however, accumulation of metals within a system may reach a point at which the system is no longer operating effectively and major intervention is required (Gray et al., 2012; PIRAMID Consortium, 2003). Excavation and disposal of treatment sludge and substrates is one of, if not the greatest operational costs of passive mine water treatment systems (PIRAMID Consortium, 2003). Reducing the frequency of this activity by extending system lifetime should therefore be a key objective at Force Crag and of system operators more widely.

5.4.1 Forecasting VFP substrate lifetime

Given the absence of published long-term monitoring data for analogous treatment systems, forecasting the life-cycle of the Force Crag treatment system is a challenging task. The limitations on system longevity are complex and may relate to a range of

factors, which are discussed in detail in section 2.9 (Chapter 2). While The Coal Authority has assigned a notional 10 year life-time to the Force Crag treatment system substrate, there is little certainty around this figure. If anything, 10 years appears to be conservative compared to estimates of VFP systems in the literature (Cheong et al., 2012; Rose, 2006). Furthermore, site specific factors will undeniably have a bearing upon life-times, such as cellulose concentration of substrates (Logan et al., 2005), and consequently there is likely to be variation between individual sites (refer to section 2.9). When system failure occurs, however, there may be ways in which the performance could be restored, without wholesale substrate removal and replacement as detailed in section 2.10.

5.4.2 Possibilities for extending substrate lifetime

Evidence from the literature evaluated in Chapter 2 (section 2.9) identified several common reasons for VFP system failure, including the blinding of substrate surfaces by hydroxide precipitates (Rose, 2006), loss of permeability due to compaction (Nordwick et al., 2006), drop in sulphate reduction due to crystalline carbon fractions and inhibition of SRB by high metal content of substrate (Logan et al., 2005; Utgikar et al., 2002). At Force Crag, there are relatively low concentrations of metals such as iron and aluminium which readily form hydroxide solids at circum-neutral pH, compared to other sites (e.g. ITRC, 2013). This means that one of the major modes of VFP system failure, blinding of substrate surfaces with hydroxide precipitates, is unlikely to apply at Force Crag. Nevertheless, other potential modes of failure relevant to Force Crag might be overcome by minimal intervention:

- Digging over of compacted substrates to restore permeability has been suggested (Rose, 2006); although the implications on effluent quality from changes in redox conditions and suspension of solids during excavation are unknown.
- Drops in sulphate reduction due to depletion of labile carbon might be counteracted by liquid carbon dosing. Various substances have been suggested for this including wine wastes (Costa et al., 2009); methanol (Mayes et al., 2011; Bilek, 2006); tannery effluent (Boshoff et al., 2004) and biodiesel waste (Zamzow et al., 2007).
- Metals accumulate in surface layers of substrates, according to this research (section 4.2.4). Therefore, where high metal content is inhibiting removal processes, upper substrate layers could be selectively replaced.

Detailed monitoring of the treatment system in the long-term would allow the reasons behind any decrease in system performance to be investigated, and thus facilitate targeted measures to counteract it.

5.5 Substrate re-use and metal recovery

Eventually, minor interventions will no longer be sufficient to restore system performance. At this point, it will be necessary to either dispose of the exhausted substrate, or identify ways in which it can be de-contaminated for re-use.

Decontamination processes might feasibly be coupled with recovery of metals for recycling.

5.5.1 Metal content of used substrates

The used substrate from the Nenthead pilot system has been deemed as hazardous waste due to its elevated zinc concentrations (ESG, 2013). Some degree of decontamination coupled with resource recovery might therefore offer a means of reducing otherwise very high disposal costs forecast for Force Crag (see section 5.3). Experimentation presented in Chapter 4 (section 4.3) has demonstrated at proof-of-principle scale that metals are recoverable from the Nenthead passive treatment system substrate, which is very similar to that used at Force Crag. Data show that, in acid leach tests, concentrations of zinc and cadmium are substantially reduced, resulting in residual concentrations very close to the blank, unused substrate in at least one of the leach configurations. Crucially, this indicates that the leaching process may completely decontaminate the substrate in respect of concentrations of these two key contaminant metals (see section 4.3.4). Copper and lead appear not to have been significantly recovered by leaching, although, similarly to Nenthead, their low concentrations in the water discharging from Force Crag Mine suggests that these metals are unlikely to be problematic: $<0.01\text{mg/L}$ and $\leq 0.053\text{mg/L}$ (mean values, $n=43$) for copper and lead in the Force Crag mine water, respectively (Table 5.1). At sites where copper and lead concentrations are significant, alternative lixivants may be required to decontaminate substrates (refer to section 4.3 for discussion). At Force Crag it is likely that zinc will have accumulated within substrates by the time the system fails, given that significant amounts are being removed by the treatment system. Figure 5.4 shows, based upon data presented for zinc removal at Force Crag, the average rate of accumulation in the substrate. Additionally, data points are plotted for a range of systems from the literature

where it has been possible to determine zinc accumulation from monitoring data. Note that, because zinc concentrations in the raw substrates have not been included, actual substrate zinc concentrations are likely to be higher than indicated in Figure 5.4. For these data refer to Appendix A.

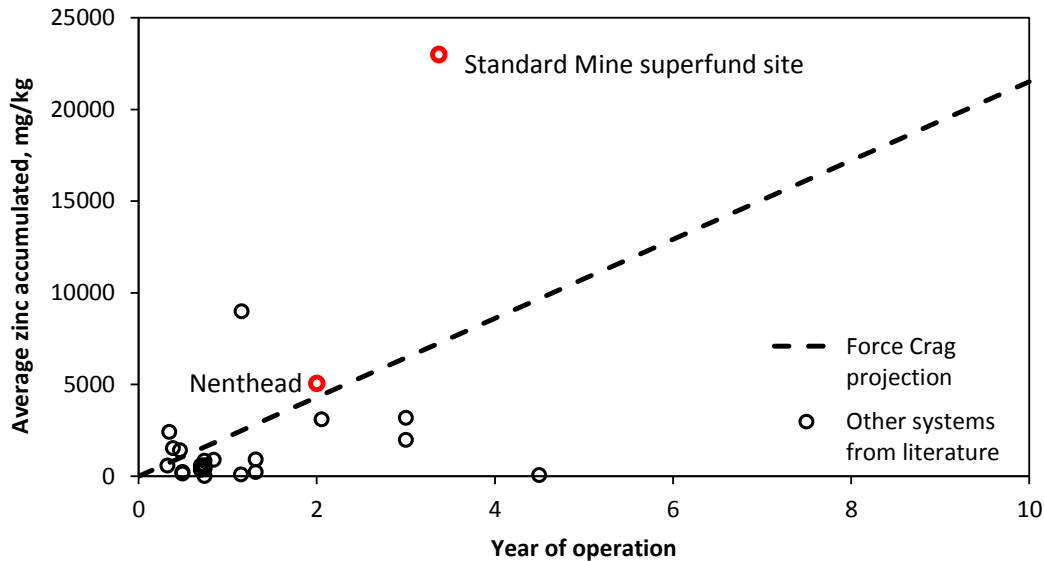


Figure 5.4 Zinc accumulated in treatment system substrates from cases in the literature¹⁸, and projected for Force Crag. Force Crag substrate zinc content as mg/kg dry weight (substrate density 0.32¹⁹). Nenthead and Standard Mine sites shown in red

On the basis of projections, the Force Crag treatment system will accumulate 4,304mg/kg of zinc within its substrate after 2 years, which is broadly comparable to the Nenthead substrate, where 4,724mg/kg had accumulated following 2 years of operation²⁰. Nevertheless, it has been shown by Rutkowski (2013) that sustained performance is likely to result in very high zinc concentrations within substrates of compost based treatment systems (22,940mg/kg calculated based upon performance data for the Standard Mine bioreactor, Colorado – refer to Table 5.2). After 3.4 years of operation, the passive bioreactor at Standard Mine was decommissioned, yet its performance had shown no noticeable decline by this time (Rutkowski, 2013). Zinc accumulation in the Standard Mine system was greater than forecast for Force Crag after 10 years of operation (20,954mg/kg), based upon calculations made by this Author. This implies that, after 10 years, the Force Crag system may still have not accumulated a quantity of zinc which might adversely affect its performance. The

¹⁸ Density of 0.5 assumed for substrates from case studies in literature where data do not exist, after Logan et al. (2005), for indicative purposes only.

¹⁹ Determined by weighing a known volume (500mL) of blank substrate.

²⁰ Average zinc content of 11 samples taken from the Nenthead pilot system, minus blank substrate zinc concentrations; see section 4.2, Chapter 2.

projections provided in Figure 5.4 are, however, heavily extrapolated from just a single year of monitoring data and are based upon a laboratory defined figure for substrate density. This density measure may not necessarily be representative of field conditions of aged substrates, which may have been affected by compaction, for example (Jarvis et al., 2014; Rose, 2006). Furthermore, the figure quoted for the Standard Mine site is based upon calculations from data extracted from grey literature sources, and has not been measured directly. It is therefore important that long term performance monitoring of these systems is undertaken, along with measurements of substrate density and metal content in order that the rates of metal accumulation can be accurately assessed.

Acid leaching has been shown to reduce metal content of the used Nenthead substrate to levels close to the blank (Chapter 4), although no evidence has been collected to indicate its suitability for re-use within the treatment system as this is out of the scope of this research. It is known that breakdown of cellulose occurs during operation of the system, and also to some degree by the application of sulphuric acid (Mukherjee and Woods, 1953). It is also noteworthy that key nutrients might be depleted by the exposure to sulphuric acid, a phenomenon which has been widely investigated in the wider environment as a result of atmospheric pollution and acid rain (e.g. Tomlinson, 2003; Pennanen et al., 1998; Haynes and Swift, 1986). Furthermore, Pennanen et al. (1998) discovered that soil acidification can have significant impacts upon microbial communities. Investigations are therefore required in order to assess the requirements for pH adjustment, nutrient replenishment and re-inoculation of leached substrates before re-use in a treatment system.

5.5.2 Alternative uses for used substrates

Alternative uses of leached substrates may exist, for example as clean-cover material at brownfield sites, or to achieve vegetation at abandoned mine sites where soils are typically poor (Neville, 2007). The latter application may, in fact, be the most environmentally sound, in that transport of leached substrates may not be required but might provide a beneficial alternative use at the mine site from which they came.

Younger and Mayes (2015) suggest a novel concept for carbon sinks in flooded open pit mine voids by infilling with organic sediments sequestering their carbon. Retention of organic matter under anaerobic conditions in the presence of sulphate causes methanogens to remain suppressed, thus atmospheric methane emissions from degradation would be prevented (Younger and Mayes, 2015). This approach might

have the added benefit of removing dissolved metals present within the flooded mine void and local water table as insoluble sulphides within the organic substrate (Younger and Mayes, 2015). This approach would require an open pit mine void to exist near to the passive treatment site to make this a practical solution.

Soils which may be contaminated must undergo environmental assessments before re-use or site development occurs, under guidance by UK regulators (DEFRA and Environment Agency, 2007). If treatment system substrates were to be re-used as soils for new developments, contamination assessments in line with this guidance would be required to assess risks of exposure to human health. This consists of a tiered approach, initially assessing soil quality against ‘soil guideline values’ where they exist. However, soil guideline values have only been produced for a handful of contaminants, and therefore where they do not exist, values produced must be generated by modelling using the Contaminated Land Exposure Assessment (CLEA) software by assessors (DEFRA and Environment Agency, 2007).

Considering Soil Guideline Values (SGV) exist for both nickel and cadmium, comparison is made in Table 5.5 between leached substrate values and soil guideline values for a range of land uses (Environment Agency, 2009a; Environment Agency, 2009b). Additional Generic Acceptance Criteria (GAC) values, produced by a third party (Amec, 2011), are provided where SGVs do not exist (for zinc, lead and copper). For context, PAS 100 thresholds are also included in Table 5.5.

Table 5.5 Comparison of pre- and post-leach substrate from the Nenthead pilot system with SGVs (Cd, Ni) or GAC (Zn, Pb, Cu) for human health exposure and PAS 100 threshold (see text for further details)

		Cd (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)
Substrate pre-leach		17.2	54.8	8,265.3	225.9	137.9
Substrate post-leach (0.1M H ₂ SO ₄ for 5 days).		1.6	17.3	650.5	211.4	118.7
SGV/ GAC according to Land use	Residential	10	130	40,000*	450*	5,200*
	Allotment	1.8	230	No data	No data	No data
	Commercial	230	1,800	No data	No data	No data
PAS100 compost specification (BSI 2011)		1.5	50	400	200	200

*Generic acceptance criteria for residential without plant uptake, as applied by Amec (2011) during tier 1 contamination assessment of Force Crag mine site.

Mean data from Nenthead substrate analysis, both pre and post-leach (with 0.1M sulphuric acid over 5 days) show that, against SGV/GAC levels of zinc, copper, nickel and lead are acceptable for use in residential developments. Projections suggest that for zinc at Force Crag (Figure 5.4) this key contaminant is still likely to be below residential GAC after 10 years in this full-scale system. Cadmium, on the other hand, has a stringent SGV and therefore restricts the un-leached Nenthead substrate to commercial land use, unless further site specific assessments are undertaken to evaluate whether risks are acceptable for residential or allotment sites (DEFRA and Environment Agency, 2007). Following leaching, all metals provided in Table 5.5 are at concentrations considered suitable for use in residential developments from a human health risk perspective. It is important to note, however, that a more detailed analysis (extending to organic contaminants, and risks of metal leaching to controlled waters, in particular) would be necessary before substrates could be certified as a suitable soil for use at a development site (DEFRA and Environment Agency, 2007). This is beyond the scope of investigation in this thesis, but such investigation would be highly advisable in case the substrates require little or no decontamination before re-use.

5.5.3 Metal recovery potential

Based upon performance data for the Force Crag treatment system and data collected during leach-testing of the Nenthead pilot treatment system substrate, it is possible to forecast the mass of metal recoverable from the substrates after a given time. It should be noted that the figures discussed below are based upon data extrapolation and therefore are only intended to provide an indication of likely quantities of metal concentrate recoverable from a full-scale system. Quantities of metal recoverable have been calculated by working out their removal rates from the Force Crag mine water over the first year of operation and then multiplying by the efficiency of recovery during the Nenthead leach test. Leach test data for the 0.1M sulphuric acid and a pulp density of 1.875% was used as these yielded the greatest extraction efficiency (see section 4.3) Recovery potential calculations are presented in Table 5.6.

Table 5.6 Metal recovery potential at Force Crag based upon current performance, showing metal accumulation rates and metal recovery potential, using Nenthead substrate leach efficiencies

	Fe	Ni	Cu	Cd	Mn	Pb	Zn
Influent concentration, mg/L	0.51	0.02	<0.01	≤0.017	0.56	≤0.053	3.26
VFP 1 effluent, mg/L	1.47	≤0.012	≤0.013	<0.01	0.44	≤0.051	0.04
VFP 2 effluent, mg/L	1.35	≤0.012	≤0.013	<0.01	0.51	≤0.051	0.16
VFP1 metals retained, kg/annum	-86.23	≥0.55	-	-	10.47	-	289.80
VFP2 metals retained, kg/annum	-78.57	≥0.58	-	-	4.33	-	291.22
Leach efficiency from Nenthead substrate, %	54	100	35	100	100	64	100
VFP 1 metal recovery potential, kg/annum	-46.56	≥0.55	-	-	10.47	-	289.80
VFP 2 metal recovery potential, kg/annum	-42.42	≥0.58	-	-	4.33	-	291.22

Initially, it is evident that for iron the recovery potential per annum is negative. This is due to a net export of this metal from the treatment system over the first year of operation, thought to be a component of secondary contamination of the treatment substrates over the first few months of operation (section 5.2). Copper, lead and cadmium are typically below analytical detection limits and, therefore, it is unclear how much metal, if any, might be recoverable. Likewise, while nickel is just above detection limits in influent, it is below in the effluent and, as a consequence, only a lower limit can be placed on masses recoverable. However, for the main contaminant, zinc, it is estimated that in excess of 500kg of metal in total is recoverable from the VFPs for each year of operation, based upon data for the first year of operation. If the system were to perform similarly for 10 years before substrates were removed and metals recovered by leaching, it may be expected that in excess of 5 tonnes of zinc metal would be recoverable.

When considering these materials as native metals, the theoretical value recoverable from the metal rich precipitate may be illustrated. Table 5.7 provides figures from the London Metal Exchange and compares them to the projected metal recovery rates for the Force Crag treatment system. It is clear that zinc is the only metal which might be

recovered in any significant quantity of any value, although it is important to point out that the efficiency and cost of metal processing has not been considered as this is out of scope of this research.

Table 5.7 Value of metals potentially recoverable from Force Crag based upon first year of operation

Metal	Projected mass over 10 years (t)	Market value for native metal (£/t)	Value as native metal recoverable after 10 years at Force Crag (£)
		(*London Metal Exchange, www.lme.com 29/9/15; • FOB Warehouse USA www.metalprices.com 19/9/15 (exchange rate of \$0.65US to 1GBP)	
Zn	5.81	*1,061.13	6,165.17
Mn	0.15	•1,806.06	270.10
Ni	>0.011	*6,766.50	74.43

5.5.4 Waste reduction potential

Disposal costs for the substrate from Force Crag are calculated based on their tonnage (Atkins, 2014b) and consequently, if it is possible to reduce the mass of waste by a significant factor, the costs of disposal are likely to be reduced proportionately. Evidence obtained from investigation with the Nenthead substrate indicates that this is achievable. Leaching with dilute sulphuric acid has been shown to effectively leach zinc, cadmium, nickel and manganese from contaminated substrate from the Nenthead pilot system as detailed in Chapter 4, section 4.3. These metals have then been successfully removed as a precipitate from pregnant leach solutions by pH adjustment with sodium hydroxide. Assuming that leached substrates can be re-used, either at site or elsewhere, the concentrated metal precipitate will represent a waste (probably classified as hazardous²¹), requiring disposal, or a metal rich material worthy of recycling. Assuming the former, the mass of this precipitate was determined as 6% - 11%²² of the mass of the initial (dried) substrate. This would substantially reduce Force Crag VFP waste disposal costs from £685,750 to between £40,000 and £75,000,

²¹ Waste classification testing would be required before the category of the waste can be confirmed

²² Mass of precipitate for 7.5% pulp density leach test (6% of initial substrate sample) and for 1.875% pulp density leach test (11% of initial substrate sample) as determined experimentally on Nenthead substrate

according to the cost/tonne figures in Atkins (2014b)²³. These values exclude the cost of substrate decontamination by recovering metals.

When considering the metal constituents (zinc, cadmium, copper, nickel, iron, lead and manganese) in the precipitate, they equate to just 13 – 16% of the total precipitate mass, 7 – 8% of which is iron and 5 – 8% of which is zinc²⁴. It should be noted that the Nenthead treatment system had not reached a point of failure, and as a consequence, the substrate characteristics are likely to be different for a full-scale decontamination activity. Specifically, metals such as zinc will have accumulated to higher levels in systems which have been operating for longer time periods (Figure 5.4).

5.5.5 Cost of metal recovery

Indicative costs of metal recovery to achieve substrate decontamination were kindly provided by an industry specialist Acumen Waste Services Limited (www.acumenwaste.co.uk). In order to gauge the practicalities and costs of large-scale decontamination, elements of research conducted for this thesis were discussed in confidence with a Director and Technical Specialist in hazardous and difficult wastes; Mr. Leon Kirk, between 9th and 10th March 2015. The details presented in the following paragraphs of this section were provided by Mr. Kirk in personal communications, unless otherwise stated.

Based upon the findings of particle size investigations and acid-leaching (Chapter 4), it was suggested that a bespoke mobile ‘soil washing’ type plant would be required for substrate decontamination. Acidification and lime dosing could also be incorporated to leach metals from substrate particles and precipitate them as a finer grained, more contaminated material. Soil washing and sieving would be expected to produce a decontaminated aggregate largely composed of wood-chip fragments (approximately 90% by mass) and a filter cake (<63µm) containing high concentrations of metals (approximately 10% by mass). This waste reduction factor is similar to that achieved by leach and precipitation tests conducted as part of this research. Given the atypical nature of the material (compared to typical contaminated soils which might have lower organic matter content) the requirement for a bespoke plant would entail significant capital cost. Assuming that the plant received reasonable use against this investment,

²³ Assume waste falls under worst-case classification of hazardous waste with high TOC content requiring high temperature incineration

²⁴ Data taken from 1.875% - 7.5% pulp density tests.

the cost per tonne is estimated as £25 - £45²⁵, exclusive of waste disposal costs. In addition, a one-off cost of mobilisation/demobilisation of plant would be required, of approximately £8,000. It is assumed that the de-contaminated material can be re-used within the treatment process with minor additions of carbon, such as sewage sludge or PAS100 compost, for example. The costs for substrate excavation, addition of carbon and replacement have not been forecast, but it is thought that these are likely to be relatively low-cost items. The costs for de-contaminating the Force Crag substrate is estimated in Table 5.8, assuming the greater per unit cost of £45/tonne and the same per tonne cost for waste disposal of the concentrated filter cake as estimated for the untreated substrate. This disposal cost is an upper limit, based upon high temperature incineration at a specialist waste facility before hazardous waste disposal (Atkins, 2014b).

Table 5.8 Costs of substrate decontamination

Item	Breakdown	Cost, £
Soil washing	1,055t substrate*; 45£/t assumed	47,475
Mobilisation/demobilisation	£4,000 mobilisation/demobilisation	8,000
Waste transport and disposal	105.5t residue; £650£/t	70,015
	Total	125,490

*Mass assumed by Atkins (2014)

Disposal of the concentrated filter-cake still represents a substantial cost, outweighing that of the cost of the washing process. However, after a 10 year period, zinc concentrations in a filter cake of 105.5t would be 5.5%, based upon projections in Table 5.6 and assuming the entire zinc content of substrate were concentrated in its fraction. Because this metal concentration is above typical ore cut-off grades, it may be economically viable to recover metals from the filter cake. There are, however, few facilities in Great Britain to take this type of material, although export for processing overseas is not uncommon (*pers comm.*, L. Kirk, Acumen Waste, 2015).

Regardless, these figures indicate that a substantial net saving may be achievable, based upon employing a soil-washing process to decontaminate substrates. It has been

²⁵ Cost per unit assumed to include labour, power, servicing and reagents

suggested that, prior to design and implementation of any decontamination equipment, recovery trials should be conducted with contaminated substrates from candidate treatment systems (*pers comm.*, L. Kirk, Acumen Waste, 2015).

5.6 Renewable energy

As discussed in Chapter 2, waste decontamination and recovery of metals from treatment systems are not the only resource recovery mechanism of reducing or offsetting operational costs at mine water treatment sites. Abandoned mine sites may also offer opportunities for recovery of renewable energy.

Situated within a steep valley of the English Lake District, the Force Crag Mine site is well positioned to harness the potential energy of cascading waters, both from mine entrances and within rivers and streams. Small-scale hydroelectric systems may offer a way of generating electricity which could be used in the treatment process, for example for telemetry systems to collect operational data, or within the mine buildings to enhance their utility as a visitor attraction.

5.6.1 Small scale hydropower

There are a number of practical considerations when assessing the suitability of mine drainage waters and surface waters for hydropower, both of which exist at Force Crag. Table 5.9 evaluates some of the pros and cons of hydropower installations at surface water streams and drainage from abandoned mines, although this is far from exhaustive.

Table 5.9 Factors affecting small hydropower installation in watercourses and mine discharges

	Hydropower system harnessing surface water stream or river	Hydropower system using drainage from abandoned mines
Ecological considerations	Fish passes around installed turbines may be required, adding to scheme cost (Environment Agency, 2013a).	No evidence of ecological sensitivities in mine drainage.
Land drainage	Surface waters provide land drainage and, therefore, in England Flood Defence Consent are required from the Local Authority or Environmental Agency depending upon size of watercourse (Environment-Agency, 2013).	Unlikely to require Flood Defence Consent unless works are located within, under, over or next to a watercourse (Environment Agency 2013).
Consenting implications	Additional consents for surface waters are likely to be required, such as abstraction and transfer licenses (https://www.gov.uk/environmental-management/water).	Consents likely to already in place where there is a treatment system and thus will only require amendment.
Wider stakeholders	Stakeholder interest may be significant such as impact upon local angling clubs and river trusts (Environment-Agency, 2013).	Mine explorers frequent abandoned mines in Great Britain and may require consultation (http://www.mineexplorer.org.uk/.)
Suitability of equipment for turbine use	Turbines widely designed specifically for use in small watercourses (Paish, 2002).	Mine waters are often characterised by poor quality. In particular, high dissolved solids content and acidity can lead to corrosion of turbine parts (Sharma et al., 2010).

Mine waters are subject to less permitting and other requirements due to their lower environmental sensitivity than streams and rivers. Additionally, monitoring data suggest that the upland streams at Force Crag (the Coledale and Pudding Beck) have highly variable flow rates which may pose difficulties for engineering of a hydropower system (Rose, 2015). This is particularly significant during periods of low flow when abstractions need to be reduced to maintain base flow in the rivers (Environment Agency, 2013b). Rose (2015) found that, because of this requirement, a system on the Pudding Beck would generate no power at all for 3 months of the year.

Mine water quality may be a problem though when compared to surface water courses: many discharges are characterised by acidity and high metal content, which may cause corrosion and blockage of turbine components (Sharma et al., 2010). At Force Crag, however, mine waters are circum-neutral and contain relatively low concentrations of metals. In particular, the iron concentration is low (typically 0.5mg/L), which is

important as it is known to cause blockages in renewable energy technologies (Bailey et al., 2013b). Nevertheless, geochemical modelling by Rose (2015) identified that iron minerals hematite and goethite are supersaturated in the Level 1 mine water at Force Crag, and may therefore form as precipitates in a hydropower installation (Rose, 2015). Small-scale hydroelectric systems are, however, designed for frequent servicing, and replacement parts are inexpensive and readily obtainable (*pers comm.*, G. Sharples, National Trust 2015). Weighing up these considerations, the main discharge at Force Crag Mine (Level 1) appears most suitable for a small scale hydropower system, assuming that a regular programme of maintenance can be incorporated.

The Level 1 discharge at Force Crag emanates from a mine portal in the hillside of Grisedale Pike, before being transferred via a gravity pipeline to a distribution chamber where the flow is split (see Figure 5.5).

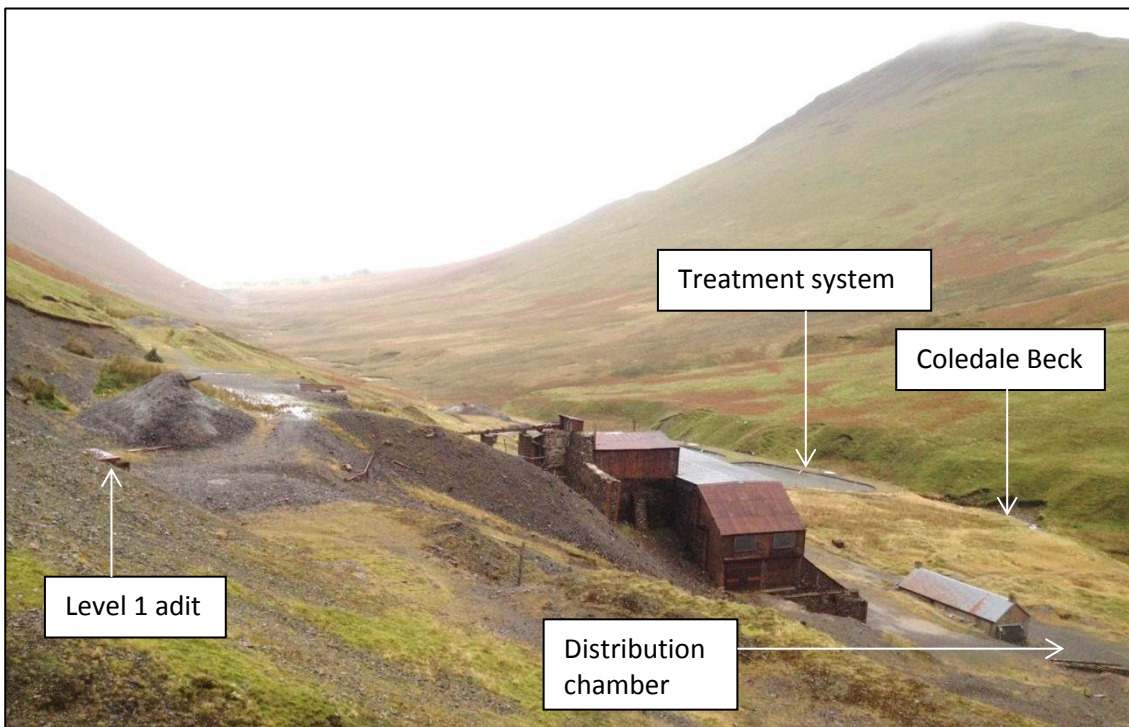


Figure 5.5 Elevation of Level 1 discharge compared to mine water distribution chamber and treatment system, note location of former mine office building near the distribution chamber at base of Grisedale Pike

Approximately 6 L/s is diverted to the mine water treatment system, with the remainder being discharged untreated to the Coledale Beck (Atkins, 2014a). Flow rates from Level 1 are presented in Figure 5.6, which indicates the minimum flow is 8.5L/s and mean flow 12.3L/s.

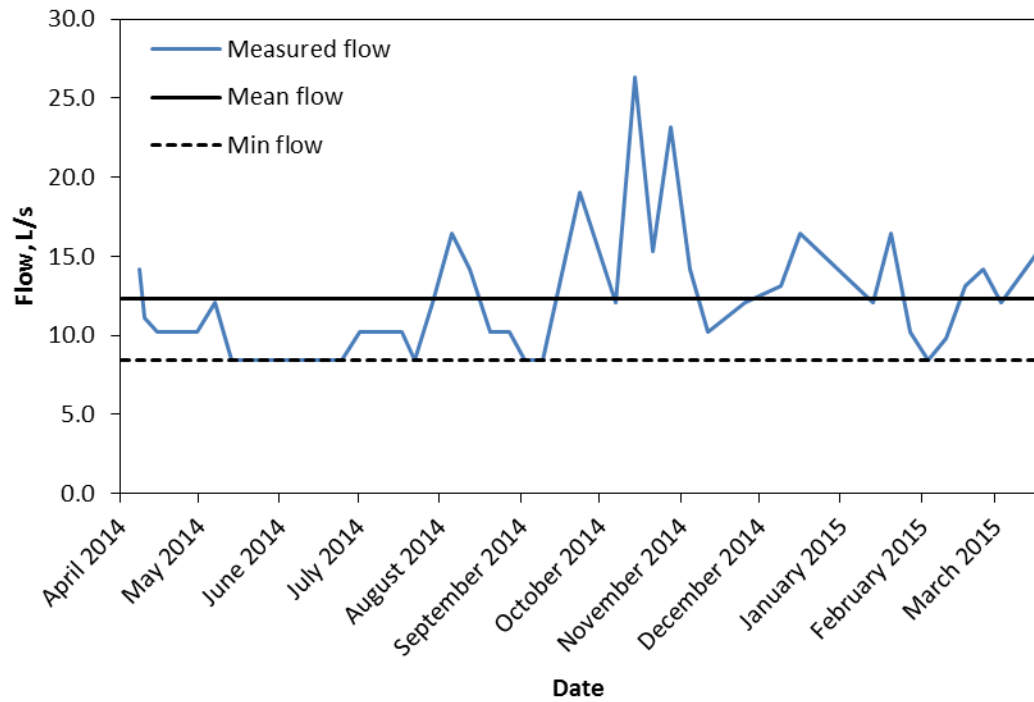


Figure 5.6 Level 1 flow rates at Force Crag Mine measured from April 2014 to March 2015, inclusive

In order to optimise the potential energy available from the Level 1 mine water discharge, it is necessary to harness the maximum available head and flow (see section 2.3). Installation of a penstock arrangement at the mouth of the Level 1 portal and a tailrace connected to the distribution chamber would allow use of the full flow. Between these two locations, there is also a significant drop in elevation: 19.09m according to the general arrangement as-built drawing of the treatment system (Atkins, 2014a). The minimum flow of 8.5L/s measured between April 2014 and March 2015 (inclusive) has been assumed for the purposes of this investigation, although it is noted that higher flows were available for the majority of the year. According to equations 5.4 and 5.5 (rearranged from equation 2.1, Chapter 2) the following power is available:

$$(5.4) \rho Qgh = P$$

$$(5.5) 1 \times 8.5 \times 9.8 \times 19.09 = 1,590W$$

Where P = power in watts (W); ρ = density of water (1 kg/L); Q = flow in L/s; g = gravitational acceleration (9.8m/s^2) and h = hydraulic head in m (Harvey et al., 1993).

Based upon the hydraulic head/flow characteristics, impulse turbines such as crossflow or pelton wheels are suitable for this site (Paish, 2002). System efficiency must be calculated in order to consider all the potential losses within both the hydraulic, mechanical and electrical components (Harvey et al., 1993). Therefore, whilst a system

design would be required prior to determination of power generating efficiency, there are similar ‘rules of thumb’ in the literature: 50% (Harvey et al., 1993); 53% (US Department of Energy, 2001); 51% (Meier and Baumer, 1985). Taking a conservative 50% system efficiency estimate, the electrical power generation potential based upon the minimum Level 1 flow measured between April 2014 and March 2015 at Force Crag would be 795W. During periods of higher flow rate in autumn and winter, this value would be higher, and consequently it would be beneficial if a hydropower system was designed to operate across a range of flows.

5.6.2 Mine water heat recovery

Temperature monitoring of Level 1 flow between April 2014 and March 2015 reveal that the temperature of the mine water showed little seasonal variation, remaining above 8°C year round (Figure 5.7).

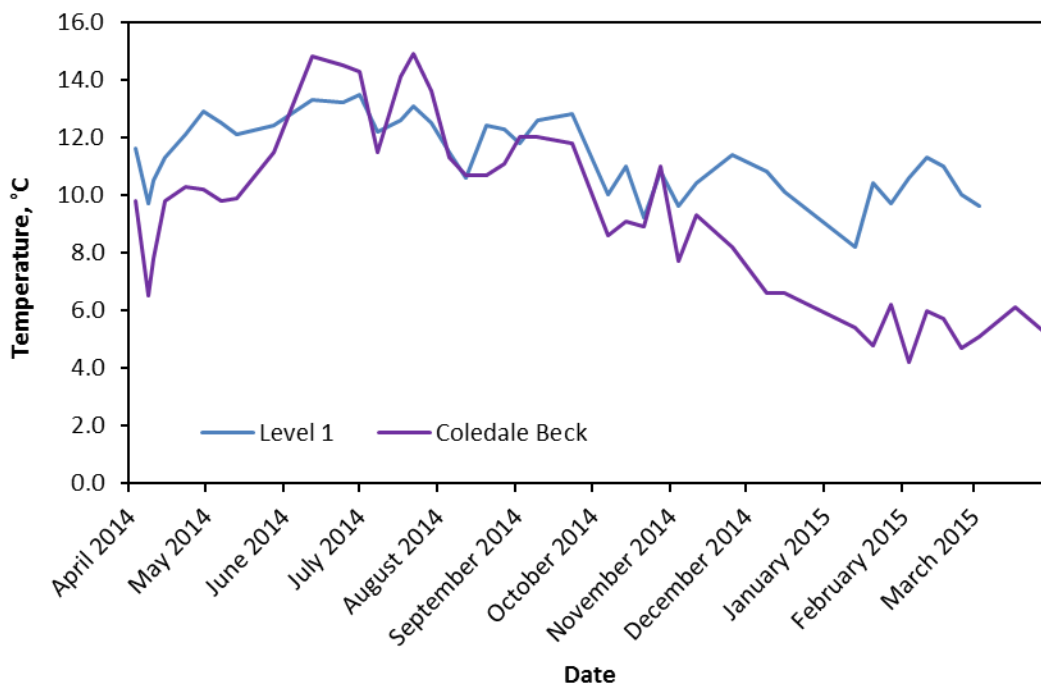


Figure 5.7 Force Crag Level 1 and Coledale Beck temperatures April 2014 - March 2015

In contrast, measurements of the Coledale Beck show peaks of >16°C in the summer (June-August) decreasing to ≥4°C in the winter (January-March). Given that any space heating demand is likely to be greatest in the winter, a source which retains higher temperatures during these months is likely to offer greater efficiency when coupled to a heat-pump system (see equation 2.5, Chapter 2).

As an example, a 6kW system, typical of small residential units (e.g. Kensa Heat Pumps, 2016) may be suitable for heating a small space within the abandoned mine buildings. Assuming the heat pump was operating at capacity with a Coefficient Of Performance (COP) of 3.5 (Heat Pump Test Centre WPZ Switzerland, 2012), 4.3kW of heat would be provided by the mine water source, with the remaining 1.7kW provided by electrical energy supplied to the heat pump. Approximately 1L/s of mine water was used in a successful 12kW heat pump installation at the Dawdon site in Co. Durham (Bailey et al., 2013b); suggesting that for a 6kW system, 0.5L/s might be a suitable flow. Applying the simple power calculation (equations 5.6 and 5.7) provided by Banks et al. (2003) allows us to calculate the temperature change of a 0.5L/s flow of mine water for this power output:

$$(5.6) \Delta T = \frac{P}{Qc}$$

Where ΔT = temperature change of source in °C; Q = flow in litres per second; c = specific heat capacity in KJ/litre/°C (assumed as 4.2) and P = power is in kW.

$$(5.7) \Delta T = \frac{6}{0.5 \times 4.2} = 2.86$$

For the 0.5L/s flow of Level 1 mine water passed through a 6kW heat pump to provide hot water at space heating, the temperature of the mine water would be reduced by just 2.86°C. In reality, system inefficiencies may increase this temperature drop slightly; however, due to the elevated mine water temperature (11.3°C annual average), it is likely that the COP efficiency would be greater than 3.5 (a figure based upon a 5°C source) as the temperature increase would be lower (Banks, 2008). A higher COP efficiency would produce the same amount of heat output for a lower electrical power input. At full power, the electrical demand for the 6kW heat pump operating at a COP of 4.0, for example, would be 1.5kW, albeit this would be on a 'peak demand' basis. Due to the remote nature of this site, this electrical demand would need to be met by an on-site power source, such as a hydroelectric turbine. Calculations suggest, however, that a micro-hydro turbine would generate just 0.795kW of power, assuming the minimum Level 1 flow. To achieve the peak demand of a heat pump system, batteries charged by the hydropower system could be used to boost power (Davis, 2003).

Additional consideration must be given to ensure any system operates in a way which excludes oxygen from the source water, to minimise precipitation of (oxy)hydroxide

minerals such as ferrihydrite. Precipitation of these minerals from mine waters have been known to cause blockage of heat pump systems (Bailey et al., 2013b; Banks et al., 2009), although iron concentrations are relatively low at Force Crag.

5.6.3 Energy recovery to offset operational costs

Small scale micro-hydro power capturing potential energy from the Level 1 discharge may provide 795W of electrical power, assuming low flow conditions (see equation 5.4, assuming 50% efficiency). The cost of this system has been estimated at £10,180 during a parallel study by Rose (2015) although the power generated would be of unique value to this site, given its remote location and lack of grid connection. Power generated could be used at the mine site to enhance its value as a visitor facility, for example, by providing lighting and power to a heat pump system for space heating (e.g. REALL, 2007). Government incentives currently apply for micro-hydro schemes in England under the Feed In Tariff (FIT) scheme. The generation tariff (which is applicable to off-grid systems) pays 15.45p/kWh for systems below 15kW at the time of writing (Ofgem, 2016). Therefore, assuming the turbine at Force Crag operates continuously, 6,934kWh per annum would be generated, which would be eligible for a generation tariff of £1,071. Decreases in the tariff have been made over successive years, and therefore, it is not possible to forecast the long term income stream based upon these incentives (see: www.ofgem.gov.uk). Nonetheless, it has been suggested that use of power by a field classroom (one possible option for the old mine buildings at Force Crag) may generate a revenue stream which could offset the cost of a hydropower turbine (Rose, 2015).

Development of the small former mine office at the site as a visitor facility (field classroom or café, for example) would demand space heating during colder months. To provide this, a small 6kW domestic-type heat pump might be suitable (given the ~55m² footprint is comparable to a small domestic dwelling – quoted as 60m² by the EST (2015)). This heat source would offer an alternative to oil-fired heating, which is one of the few realistic alternatives at such a remote site. Savings calculated by the EST (2015) suggest that domestic sized ground-sourced heat pumps may offer savings of between £475 and £725 per annum over oil alternatives, although typical system installation costs are normally between £11,000 and £15,000 (EST, 2015)²⁶. Given the

²⁶ Figures based upon electrical power for the heat pump supplied by a grid connection rather than by hydropower.

relative small size of the old mine office and, consequently, its proportionately modest heating requirement, the smaller figure might be most applicable to this study but it is worth noting that the building is a simple structure, likely to be of poor energy efficiency, which would increase its heating demand²⁷. Over a 25 year life-cycle, a conservative estimate of £8,103²⁸ of operational savings might be achieved by use of a heat-pump over oil fired space heating. By providing electrical power for the heat pump from an un-metered source at site, such as a hydroelectric turbine, this cost saving would be greater. In addition, government subsidies such as the Renewable Heat Incentive (RHI) may apply.

For systems installed on or after 1 October 2015, the RHI applies a subsidy of 8.84p/kW/hr of energy generated by a heat pump (Ofgem, 2015). For a 6kW unit, operating for 7.2 hours a day during the coldest 6 months of the year, 7,884kW/hrs of renewable heat would be produced. This would generate a subsidy income stream of £697 per annum. Over 20 years (duration of the incentive) the discounted RHI income would be £10,252. Nevertheless, it should be noted that changes in Government policy may affect the eligibility and rate of any subsidies for a renewable heating system.

5.7 Financial assessment of active vs. passive treatment

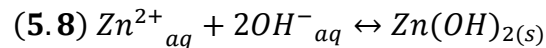
Passive mine water treatment system construction costs are known in detail for the Force Crag installation, yet ongoing operational costs have to be estimated based upon current knowledge (Atkins, 2012). Forecasting of these operational costs has identified disposal of spent substrates as a substantial expense which will be entailed at the end of a passive treatment system life-cycle. On this basis, it seems pertinent to compare the possible life-cycle costs of an active treatment system (engineered to produce a low-volume waste) to the passive system. In order to undertake this assessment, a costed design was kindly provided by an experienced chemical engineer, Mr. Hein Schade of Helix Projects Ltd. All information pertaining to the active treatment design in this section is sourced from the report by Schade (2015), unless otherwise stated.

²⁷ A full energy performance assessment would be required for any building, prior to design and costing of a space heating system. The figures provided here are for indicative purposes only.

²⁸ 3.5% DCF applied HM Treasury (2011)

5.7.1 Hypothetical active mine water treatment system design

Several active treatment techniques are suitable for the removal of zinc from the Force Crag mine water. However, given the proven effectiveness of hydroxide precipitation (e.g. Younger et al., 2002), this technology was selected for the process design. This involves raising the pH to 9.8 with hydrated lime to achieve rapid precipitation of zinc hydroxide according to the following reaction (equation 5.8) (Schade, 2015):



Aluminium sulphate is used as a coagulant, along with an organic polymer flocculent which acts to increase settlement rates and generate sludge with a high density. Separation of the precipitate is achieved with a lamellar clarifier and the sludge is de-watered using a filter press to increase its density from 3 to 37% solids. Predictions made suggest that 210kg of sludge would be produced per day (37% solids), with a zinc concentration of 4% (as dry solids) which would be disposed of as a hazardous waste (Schade, 2015).

The chemical process plant would be housed within an industrial unit with associated office/welfare/laboratory and chemical store. The footprint of this unit would be 30m x 45m with a roof height of 8m (Schade, 2015).

5.7.2 Comparison of active vs. passive life-cycle costs

The costs associated with active and passive treatment (with and without substrate washing) are shown in Table 5.10. Active treatment system cost breakdown has not included peripheral items, such as ground investigation, archaeological investigations and Coal Authority staff costs for administration of the project. Because of uncertainties associated with these elements, comparison will be made solely upon the treatment systems' capital and operational costs, although it is acknowledged that this falls short of full-life cycle costs.

Table 5.10 Construction and operational costs of active and passive treatment and passive treatment with substrate washing for the Force Crag site

Operational and ad-hoc costs	Active (Schade, 2015)	Passive (Atkins, 2012)	Passive with substrate washing
Annual operational costs (labour/power/maintenance)	£108,360.00	£10,000.00	£10,000.00
Sludge disposal (annual average)	£10,680.00	£78,325.00	£12,549.00*
Substrate replenishment (annual average)	n/a	£2,920.00	£2,920.00
Chemical reagent cost (annual average)	£20,448.00	n/a	n/a
<i>Average annual operational cost</i>	<i>£139,488.00</i>	<i>£91,245.00</i>	<i>£25,469.00</i>
25 year operational cost, 3.5% DCF	£2,298,973.51	£1,537,147.60	£429,060.36
Capital cost	£1,550,000.00	£704,274.18**	£704,274.18**
25 year life cycle cost	£3,848,973.51	£2,241,421.78	£1,133,334.54

*Budget based upon costs for soil washing obtained from Acumen Waste Ltd, assuming a 10 year life-time of substrates and cost of disposal of filter cake.

**Passive capital cost only considers treatment system design and construction to be in line with active comparison.

It is evident, based upon the figures in Table 5.10, that active treatment is far more expensive than passive treatment, both for capital costs and over system lifetimes (calculations included in Appendix H). Although waste disposal costs from passive treatment are predicted to be substantially greater than active treatment, the overall operation of an active system including waste disposal is greater than passive treatment. Decontamination of passive system substrates by soil washing has the potential to reduce waste volumes considerably. As a result, 25 year whole life costs may be almost halved from £2.24m to £1.13m for the passive system (Table 5.10).

These figures assume that the Force Crag VFP substrate has a 10 year life. If this life was, in practice, just 5 years, the cost of passive treatment without substrate decontamination would be comparable to active treatment over 50 years (see Figure 5.8). Yet, if VFP system substrates were decontaminated, passive treatment would still offer a more cost effective solution, even if decontamination was required every 5 years.

In fact, the cost over a 50 year period would be less than half of the active and passive (without substrate decontamination) alternatives (see Appendix H for calculations).

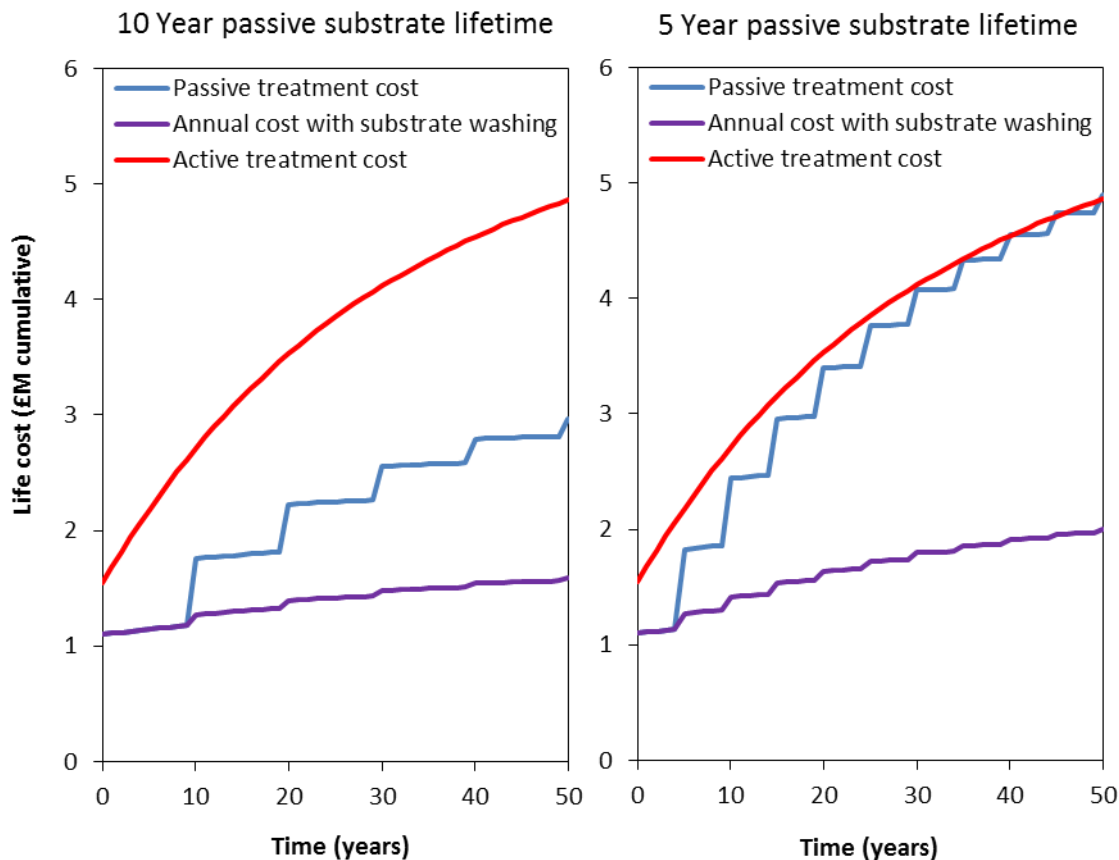


Figure 5.8 Whole life costs for different treatment scenarios, assuming passive treatment substrate life of 10 years (left) and 5 years (right). Note capital build costs only include system design and construction for comparison purposes.

5.7.3 Composition of wastes

Active treatment produces a high density sludge with a water content of ~37% (Schade, 2015), which requires disposal to landfill as a hazardous waste or recycling via a metal recovery process (Zinck, 2005). Given that the process design undertaken by Schade (2015) was intended for zinc removal, it is perhaps no surprise that zinc is predicted to be a major constituent of active treatment sludge at 4% by dry weight (Figure 5.9). This is a significantly greater zinc content than in the passive treatment substrate taken from the geochemically similar Nenthead site²⁹, which contains approximately 0.5% (see Figure 5.4). Yet, acid leaching of the Nenthead substrate and recovery of a solid concentrate has been demonstrated in the laboratory (section 4.3). The concentrate

²⁹ Data presented from 1.875% pulp density leach tests using 0.1M sulphuric acid, followed by precipitation of metals with sodium hydroxide.

obtained from the 2 year old Nenthead substrate had zinc concentrations of 4.5 – 8.0%, which is greater than concentrations in sludge from the hypothetical active treatment system (Figure 5.9). Because of this, a smaller mass of metal concentrate would need to be processed to recover the same amount of zinc compared to a given mass of high density sludge from active treatment.

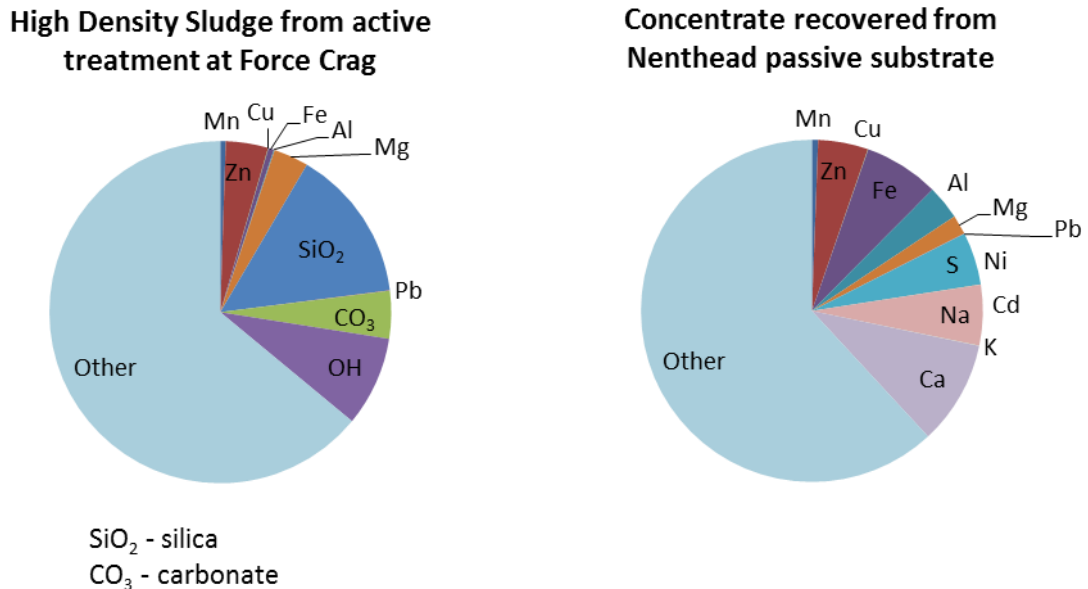


Figure 5.9 Left - predicted composition of active treatment sludge (Schade, 2015). Right - metal concentrate recovered from acid leaching of the Nenthead passive system substrate with 0.1M H₂SO₄ and 1.875% pulp density.

5.8 Conclusions

This chapter investigated the performance of the Force Crag mine water treatment system over the first year of operation, focussing on the rates of metal accumulation and potential for metal recovery, comparing it to a database of systems from around the world. Additionally, the life-cycle costs of passive treatment have been forecast, considering options for resource recovery which might be used to offset or reduce these costs. These scenarios were then compared against a life-cycle cost estimate for a common type of active treatment system.

5.8.1 Treatment system performance and metal accumulation

The Force Crag treatment system has been monitored in detail from commissioning in April 2014 until the end of March 2015. Data indicate that treatment performance has been good: on average 95% to 99% removal of zinc across VFPs 1 and 2, respectively.

Given the loading and system size, this equates to 1.89g/m³/d and 1.90g/m³/d of zinc removal for VFPs 1 and 2, respectively. These metrics situate the system within the upper-middle of a ranking of the known systems of this kind globally (Table 5.2). Secondary contamination during early operation resulted in a net export of some metals less abundant in the mine water, as well as initially elevated concentrations of some organic components (Jarvis et al., 2015). Nonetheless, the period of secondary contamination was short lived. Projection of zinc removal rates suggest that 2,152mg/kg of zinc are accumulating in the substrate per annum. Yet, a study from overseas (Standard Mine Superfund Site) indicates that zinc might accumulate to 23,000mg/kg in VFP systems without affecting treatment performance (Rutkowski, 2013; Reisman et al., 2008). This suggests that, if zinc concentrations in the substrate is the limiting factor on system longevity, the Force Crag system might expect to perform well for in excess of 10 years. On the other hand, it is known that there are other factors which limit system life-times, such as depletion of carbon sources (Cheong et al., 2012). Long-term monitoring of the Force Crag system will be of great value in understanding the limits on VFP system life-times.

5.8.2 Life cycle cost estimates

Life-cycle costs for the passive treatment system at Force Crag are calculated as £2.2m over 25 years, and £3.0m over 50 years, based upon data obtained from The Coal Authority and using current discounting rates (HM Treasury, 2011). While the greatest single cost is scheme development and construction (£1.1m), the removal, disposal and replenishment of substrates over 50 years has been estimated at £1.6m, assuming a 10 year interval. These figures have been discounted though, and therefore the actual substrate management costs may be far higher. Regardless, the discounted figures highlight that, over 50 years, the costs of substrate management are substantial and cumulatively outweigh the initial development and construction costs. This reinforces the need to identify sustainable ways of reducing or offsetting substrate disposal costs.

5.8.3 Resource recovery to offset operational costs

One mechanism of reducing substrate disposal costs is by extending system lifetime to increase the disposal interval. This might be achievable at a low cost by dosing with waste carbon sources (Costa et al., 2009; Zamzow et al., 2007; Boshoff et al., 2004), digging over substrates to restore permeability (Rose, 2006) or selective removal and

replenishment of more contaminated substrate layers at system surfaces. There will, however, be a point at which minor interventions are unable to maintain system performance and substrates will then require disposal.

Evidence suggests that alternative routes to landfill disposal do exist for used substrates. Contaminated land screening values indicate that, for human health risks of key metals, the substrate from the Nenthead system (after 2 years of operation) might be suitable for industrial land use applications. After acid leaching (0.1M H₂SO₄; 1.875% pulp density; 100 hour leach) the substrate is suitable for use in the more stringent residential and allotment applications (in respect of risks to human health). Further investigation to assess the risks to human health posed by other contaminants would be required, in addition to assessment of risk to other receptors such as controlled waters, before this material could be considered for use as a cover material (DEFRA and Environment Agency, 2007).

Leaching of the Nenthead substrate and precipitation of metals from leach solutions reduces the contaminated waste material to 6-11% of the mass of the starting substrate. In terms of costs of waste disposal, this would reduce from £685,750 to £40,000-£75,000, assuming the same disposal route was applicable (see: Atkins, 2014b). This volume reduction may be achievable by the implementation of soil washing equipment. Independent specialist advice suggests that a volume reduction of 90% might be achievable, with a waste disposal cost of £70,015. This waste reduction factor is in very good agreement with that developed by this author by laboratory scale tests. The cost of soil washing at the Force Crag site is estimated to be £55,475, excluding waste disposal. On this basis, a substantial saving over wholesale substrate disposal might be achieved by employing soil washing, to allow re-use of the de-contaminated substrate and disposal of the low-volume filter cake, ideally for further processing to recover metals.

Renewable energy generation at the Force Crag treatment system appears feasible and is an exciting prospect, in part because the system is entirely passive and would be a net source of energy. In addition, the site has significant heritage value which may benefit from the energy generated. There is significant interest in the use of such renewable energy by the National Trust which owns the site and operates tours around the historic mine buildings. Located within a remote area, the site is ideally placed for off-grid energy generation and use to heat/light mine buildings, which would enhance their

value as a visitor facility. Specific energy potential exists in the cascading mine waters (from the discharge to the treatment system), which could be harnessed by a small scale hydroelectric turbine to generate 795W of electrical power continuously, assuming a 50% efficiency for the turbine. Additionally, mine water temperatures have been shown to remain above 8°C throughout the year, suggesting that heat might be extracted with heat pump apparatus for space heating. A hydropower coupled heat-pump would offer a novel source of entirely renewable space heating to the old mine office, facilitating its transformation into a useable visitor space. It has been estimated that a 6kW heat pump might be suitable for heating of the existing mine office building. Operating at full capacity at a COP of 4, using 0.5L/s of the Force Crag mine water, the system would lower the temperature of the mine water flow by just 2.8°C. A heat pump system is likely to offer savings in the region of £8,103 over 25 years, compared to fuel oil heating. A hydropower turbine would also, at the time of writing, be eligible for the Generation Tariff subsidy of up to £1,071 as part of the Government Feed In Tarriff (FIT) scheme. Additionally, the coupled heat pump would be eligible for a £697 Renewable Heat Incentive (RHI) subsidy payment, per annum. These subsidies, however, are liable to change and have shown decreases over recent years.

5.8.4 Life-cycle cost scenarios

Life cycle cost scenarios with and without resource recovery were compared against each other and against alternative treatment with an active HDS type plant. HDS treatment using lime to achieve hydroxide precipitation of zinc would offer an effective means of treating the Force Crag mine water (Schade, 2015). Financial analysis, however, indicates that costs significantly outweigh those of passive treatment. Costs only become comparable when passive treatment substrate life is reduced to 5 years, and treatment has been taking place for 50 years (see Figure 5.8). Nevertheless, it is likely that a HDS plant would require major refurbishment or replacement within this period, entailing additional cost.

Decontamination of passive system substrates every 10 years offers a reduction in life-cycle costs of passive treatment to less than a third of comparable active treatment. The total cost of passive treatment with substrate washing after 50 years is £1.58m, compared to active treatment which is £4.86m. Even if substrate washing is required every 5 years, the life-cycle cost of passive treatment over the 50 year period would still be just £2.00m.

Chapter 6. Conclusions and Recommendations

6.1 Chapter contents and overview

This chapter summarises and concludes the thesis, explaining how the aims and objectives outlined in Chapter 1 have been addressed, and documents the key findings of the research conducted. Crucially, the original research contribution made by this thesis is stated and contextualised. The chapter then goes on to discuss the limitations of the study and recommendations for further research in the area.

6.2 Addressing thesis aims and objectives

The overarching aim of this thesis was to examine the potential for recovering resources at abandoned metal mine sites in order to minimise the life-cycle costs of passive mine water treatment systems. Two case studies in Cumbria, England, were explored: the Nenthead pilot scale system treating mine water flowing from the Rampgill Horse Level and the full-scale Force Crag system treating drainage from the Force Crag Level 1. Both these systems harness(ed) bacterial sulphate reduction for metals removal within vertical flow passive treatment units.

Sections 6.2.1 – 6.2.5 detail how each specific objective stated in Chapter 1 was addressed through a programme of laboratory, field and desk based investigations.

6.2.1 Objective 1. Review the resource potential of metal mine waters nationally and identify ways in which resources can be recovered

Through the process of reviewing both published and grey literature, two key areas of resource potential exist at discharges from abandoned metal mines. Resources found to be significant from the data reviewed consist of energy resources (thermal and potential) and metals contained within mine waters that accumulate within treatment systems. To date, reviews of the resource recovery options from passive metal mine water treatment systems have been conducted by Gray et al. (2012); Gusek et al. (2006); and Gusek and Clarke-Whistler (2005). The review in Chapter 2 builds upon these previous studies, providing figures from sites in England and Wales and assessing technologies for the recovery of energy and metals during the treatment process.

It has been identified that flows from abandoned mines contain thermal and potential energy, which might be readily captured at mine water treatment sites. Technology for recovery of heat energy for space heating applications and for generating electricity from gravity flows has been long established in the form of heat pumps and hydroelectric devices. Some of the earliest examples of these technologies were developed by pioneering engineers John Sumner, who developed the Norwich Heat Pump in 1945-6, and William Armstrong who, working with Sir Joseph Swan in the 1840s, was the first to install electric lighting powered by hydroelectricity at Craggside, Northumberland (Heald, 2010; Sumner, 1948). Since recovery of thermal and potential energy is achievable with mature technology, little research would be required before deployment at a mine water treatment site. Limited monitoring data indicate typical hydroelectric potential of 0.1 – 2.6kW of power from five cascading mine discharges, and 35 – 324kW³⁰ of thermal energy readily extractable from seven metal mine water flows. This demonstrates that significant energy potential exists at these sites from renewable sources, which may be utilised to enhance the treatment process or for applications off-site where nearby users exist. It is, however, acknowledged that this data is from a very small proportion of the flows that exist and, therefore, the energy available is likely to be far higher. Further field data collection is necessary in order to accurately characterise this resource more fully, although it might be advisable for this to be collected at sites where energy users or grid connections can be identified.

Review of literature highlights that metal loads contained within mine water flows are substantial, with 253t of zinc, 21t of lead, 39t of copper and 2t of nickel estimated to be discharged from monitored sites in England and Wales per annum (unpublished Environment Agency data, 2015³¹). Technology does exist to recover metals from flows as a solid sulphide product using active treatment technology (BioteQ, no date; Kratochvil et al., 2015) although the cost of this technology is high compared to alternatives (Younger et al., 2005). Additionally, the loads of individual metal mine waters in England and Wales are comparatively small (6.4 – 33.9t zinc at top 10 discharges – Environment Agency data, 2015) to even the most modest examples of commercial bio-sulphide plants (39t at Wellington Oro) (Bratty et al., 2006). Passive treatment systems are therefore preferred when tackling lower pollutant loads seen in Great Britain (Jarvis et al., 2012b), although over time metal loads accumulate within

³⁰ ΔT 4°C after Banks et al. (2003)

³¹ These figures are more recent than those published in Mayes et al. (2013)

substrates to form voluminous wastes (Gray et al., 2012). While, at the time of writing, there had been no major effort to investigate the recoverability of metals from these wastes, well established techniques from the mining, waste management and contaminated land industries have been identified which might be suitable. In particular, hydrometallurgical and bio-hydrometallurgical methods have shown to effectively recover metals from a range of materials with similar characteristics to compost-based mine water treatment substrates (refer to section 2.12). These techniques might be suitable for recovery of metals from spent treatment system substrates like those used at the case study sites, so that they would no longer be classified as wastes.

6.2.2 Objective 2. Characterise distribution of metals within passive metal mine water treatment system substrates

In order to characterise the metal content of a passive metal mine water treatment system, destructive sampling of the Nenthead pilot treatment system was undertaken at the time of its decommissioning in 2012 (further details of the Nenthead treatment system are provided in Chapter 1). The intention of this characterisation was to understand metal accumulation in passive treatment systems, and their amenability to recovery as a mechanism to offset or reduce operational costs. This is particularly significant for substrates like those from Nenthead, which were deemed by an independent laboratory to be hazardous due to their high zinc content (ESG, 2013). Geochemical analyses of 12 samples taken from three dimensions across the Nenthead system were conducted using the Tessier sequential extraction method (see section 4.2, for results and discussion).

Initially, sieving was undertaken to determine the relationship between the key contaminant zinc and substrate particle size. It was found by wet sieving that far more zinc was associated with the fine grained fraction (2,158mg/kg: <212 μ m) compared to coarser fractions (962mg/kg: 212 μ m–2mm; 541mg/kg: >2mm). This indicates that metals may be concentrated by sieving, although because these experiments were not repeated, further investigation is required to determine if these data are reproducible. Analysis of bulk substrates from different locations around the system identified substantially more zinc, cadmium, lead and manganese in upper layers of the treatment system, which operated in a down-flow configuration. For example, zinc concentration in upper substrate layers ranged between 2,987-14,050mg/kg (mean 7,716mg/kg, $n=6$)

compared to lower layers which were 808-5,851mg/kg (mean 2,421mg/kg $n=5$). This indicates that targeted removal of substrate layers may help separate highly contaminated material from that which is less contaminated. Sequential extractions showed that different metals varied in the sequence in which they were extracted, with copper most tightly and manganese least tightly bound. There was a degree of consistency between metal sulphide solubility products and the order in which metals were extracted, although there were exceptions. This suggests that other (non-sulphide) metal bearing phases were important for metal sequestration in the treatment substrate, which are known to be important during early phases of system operation (Neculita et al., 2007). Metal concentration in the influent mine water may also have a bearing on the phases present. Specifically, zinc appeared more easily solubilised than iron in these investigations, although its sulphide solubility product is lower than iron, implying that zinc sulphide should in fact be less soluble than iron sulphide. It is important to note that this system operated for just 2 years, and it is anticipated that systems of this type may last for 10 years or more, which could impact upon metal content and speciation in substrates.

6.2.3 Objective 3. Assess the options for metal recovery from passive treatment system substrates and undertake lab-scale proof-of-principle metal recovery tests

Chemical leaching using sulphuric acid was conducted on the Nenthead treatment system substrate over 100 hours, for a range of acid concentrations and pulp densities. By recovering metals from treatment system substrates, decontamination may be achieved, with simultaneous production of a metal rich concentrate that could be suitable for further processing to recover metal product(s). Results of these investigations are detailed in Chapter 4, section 4.3. Very high recovery efficiencies (>100%) were seen for zinc and manganese for 0.02M, 0.1M and 0.5M acids, with high recovery rates also seen for nickel and cadmium (>100% in the 0.1M and 0.5M acids), when compared to aqua regia digests of the same substrate. >100% recovery is attributed to longer exposure times to acids during leaching than during aqua regia digests. Leaching of lead and copper, however, was poor compared to other metals: 58% and 68% respectively in the most concentrated (0.5M) acid. Experiments were repeated using the 0.1M acid, but increasing pulp density from 1.875% (as in preceding experiments) to 3.75%, 7.5% and 15%. Little decrease in recovery efficiency was seen

as pulp density increases from 1.875% to 3.75% (zinc, cadmium and manganese still exhibit >100% recovery). Between 7.5% and 15% pulp density, however, metal recovery dropped dramatically, with <20% zinc recovered in the 15% test. This result demonstrates that there is a threshold beyond which increasing pulp density severely limits recovery efficiencies. It was observed that beyond this threshold pH rose sharply, suggesting that the acid was being buffered by the substrate. From these investigations, it has been determined that the optimum acid concentration is 0.1M, with optimum pulp density of between 1.875% and 3.75%. Under these conditions, $\geq 100\%$ of the key contaminants zinc and cadmium were recovered from the substrate, compared to aqua regia digests.

Sodium hydroxide was used to effectively raise the pH of the pregnant leach solutions, and recover a metal rich solid with zinc concentrations of $\leq 8\%$. When compared to the substrate zinc concentration of 0.69%, this represents a ten-fold increase in concentration.

Preliminary bioleaching tests were conducted to assess the potential for achieving metal recovery by biochemical means. This approach is widely discussed in the literature for recovery of metals from a range of wastes, primarily because it circumvents the need for large quantities of hazardous chemicals in leach procedures (e.g. Pathak et al., 2009b; Wu and Ting, 2006). Bioleaching was conducted using the same leach configuration as the chemical leach tests, but with sulphur addition, and acid mine water being used as the leach solution. It was hoped that use of an acid mine water would inoculate the experiments with sulphur oxidising organisms, often abundant in these environments (see section 3.5). After an initial rise in pH to 6.5-7, it was observed to rapidly decrease after two weeks in flasks containing the mine water ($\text{pH} \leq 4.2$), with concurrent increases in sulphate concentrations. This implies that sulphur was being oxidised to sulphuric acid: a reaction which occurs in the presence of sulphur oxidising bacteria (Rawlings et al., 2003). pH in the control flasks, which contained sterile filtered mine water (i.e. to remove inoculum) also decreased, although remaining above 4 for the duration of the 65 day experimental period. Yet, pH decreased to <3 in the inoculated flasks over the same 65 days, with inversely correlated increases in sulphate in the inoculated flasks ($r_s = -0.91$, $P < 0.001$). More rapid sulphur oxidation was observed in flasks which were heated (28-30°C) and stirred, compared to unstirred flasks at room temperature. Metal recovery efficiencies after 100 hours were negative for all metals excluding manganese

(indicating metals had been removed from the mine water leach solution, rather than leached from the substrate into it). Over time, however, solubilisation of metals started to occur, with recovery efficiencies of $\geq 100\%$ for zinc and manganese, and 71-92% for cadmium and nickel across all the inoculated flasks by the end of the leach test. Lower recovery efficiencies were seen for copper and lead, similarly to those in the chemical leaching tests. Additionally, iron recovery was very low ($<10\%$), although iron concentrations were not enriched in the Nenthead substrate due to mine water. Bioleaching experimentation demonstrated that recovery of the key contaminant metals zinc and cadmium is possible by this approach, achieved by sulphur oxidation which is thought to be biologically mediated. However, significantly longer time periods are required to achieve significant extraction using bioleaching when compared to chemical leaching. Investigations using stirred and heated replicates showed that these interventions improved recovery rates, implying that bioleaching processes can be optimised by careful control of these variables. Further investigation is required in order to confirm that the mechanisms of sulphur oxidation were indeed bacterially catalysed.

6.2.4 Objective 4. Monitor the performance of a passive treatment system to gain an understanding of rates of metal accumulation and thereby forecast future metal concentrations in the substrate

Chapter 5 is dedicated to the Force Crag mine water treatment system, and the performance of the system over the first year of operation (2014-15) is discussed in section 5.2.

Over this first 12 months, zinc removal rates and efficiencies for the VFPs were: $1.89\text{g}/\text{m}^3/\text{d}$; 95% and $1.90\text{g}/\text{m}^3/\text{d}$; 99% across VFPs 1 and 2, respectively. These metrics situate the treatment system within the upper-middle range of similar systems treating zinc rich discharges described in the literature. Given the zinc loading at Force Crag, 586kg of zinc per annum is accumulating in the VFP units, which would equate to 5.85t over 10 years assuming current rates of removal are sustained. An important observation was that in the final treatment system effluent, $<0.1\mu\text{m}$ zinc was below detection ($0.01\text{mg}/\text{L}$), indicating that the majority of zinc ($>0.07\text{mg}/\text{L}$) was associated with particulate matter (i.e. $>0.1\mu\text{m}$ particles). Whereas, zinc in the system influent was overwhelmingly dissolved: $3.07\text{mg}/\text{L}$ $<0.1\mu\text{m}$ vs. $3.11\text{mg}/\text{L}$ total. If it is possible to engineer a system to remove particulate zinc from VFP effluents, even higher zinc

removal would be achievable, albeit that because of the systems high performance, this would achieve only a small further reduction in load.

During the first year of operation, there was an overall export of some metals (iron and possibly copper and aluminium), which was associated with secondary contamination arising from leaching of the substrate. For instance, average influent iron concentrations during the experimental period were 0.51mg/L; with effluent concentrations decreasing from 1.96mg/L in the first 3 months to 0.33mg/L in the last 3 months. This pattern was seen across a range of other parameters, indicating that this issue is a short-lived phase following commissioning (Jarvis et al., 2015).

A 10 year life-time has been assigned to the system by its operator The Coal Authority, which appears to be conservative when considering analogous case studies from the literature (see section 2.9.2). There are several potential catalysts for eventual system failure, and given the nature of the Force Crag site, depletion of organic carbon and metal accumulation would appear most likely (see section 5.4)³². These factors may be overcome by dosing with labile liquid carbon and selective substrate removal/replenishment, respectively (section 5.4). By increasing system life-time, costly episodes of wholesale substrate disposal and renewal become less frequent. In addition, the longer the system has been effectively operating for, the higher the concentration of zinc within the substrate will be. At current rates of removal, it has been forecast that 21,500mg/kg (2%) zinc will have accumulated within the Force Crag substrate after 10 years.

6.2.5 Objective 5. Estimate life-cycle costs associated with an operational metal mine water treatment system and determine how resource recovery from the mine water might offer a mechanism of offsetting these costs

Section 5.3 in Chapter 5 gives baseline figures for the life-cycle costs forecast for the Force Crag treatment system by its operator (The Coal Authority). In subsequent sections, limits on system lifetime and means of extending it are investigated and options for recovering resources are detailed, which could be used to reduce life-cycle costs.

³² Observed reductions in substrate permeability at Force Crag in late 2015 suggest that this may also be a limit on system lifetime at this site.

Substrate disposal is considered to be the most costly part of operating the Force Crag passive treatment system, and has been forecast as £685,750 per life-cycle (Atkins, 2014b). By applying metal recovery principles investigated in earlier chapters, it may be possible to decontaminate substrates and produce a low volume metal rich material. Decontamination of the Force Crag substrate has been estimated at £55,475, generating a relatively small quantity of metal rich waste requiring disposal at a cost of ≤£70,000. This offers a saving of >£550,000 to the life-cycle of the treatment system. The decontaminated substrate might then be suitable for a beneficial re-use.

Over 10 years, extrapolation of data suggests that up to £6,165 zinc (as a native metal) might be recoverable from the treatment system substrate at Force Crag. While the value of this metal is low when compared to the cost of decontamination, logic dictates that a small quantity of metal rich concentrate would be more amenable to economically viable re-cycling than a large quantity of contaminated substrate, with a lower concentration but the same mass of metal (given a reduction in the mass of material that would need to be processed). Clearly, the longer the treatment system is removing metals for, the greater the quantity, and consequently value of metals recoverable will be. Long term monitoring and measurements of actual substrate metal concentrations is advisable to accurately determine the metal content in the future.

Passive treatment life-cycle costs have been evaluated against active treatment using lime dosing to remove metals as hydroxides at a high pH. Even without substrate decontamination (i.e. entailing high waste disposal costs), passive treatment represents the most cost-effective solution. By de-contaminating substrates to lessen waste disposal requirements, the cost difference between these two technologies increases further. Table 6.1 provides details of these three scenarios, assuming that substrate lifetime is 10 years. Substrate decontamination costs were provided by consultation with Acumen Waste Ltd (refer to section 5.7 for further details).

Table 6.1 Summary of costs associated with mine water treatment scenarios at Force Crag Mine: active, passive, and passive with substrate decontamination

Operational and ad-hoc costs	Active (Schade, 2015)	Passive (Atkins, 2012)	Passive with substrate decontamination
<i>Annual operational cost (averaged over life-cycle)</i>	£139,488.00	£91,245.00	£25,469.00
25 year operational cost, 3.5% DCF	£2,356,001.46	£1,537,147.60	£429,060.36
Capital cost	£1,550,000.00	£704,274.18	£704,274.18
25 year life cycle cost	£3,848,973.51	£2,241,421.78	£1,133,334.54

At the Force Crag site, other resources exist which might be used to offset the life-cycle costs of passive treatment. Specifically, 1.6kW of kinetic energy exists as mine water passes from the mine portal to the treatment system distribution chamber. This energy could be harnessed by a small hydroelectric turbine, which could then be used to provide electricity to a heat-pump to provide space heating to the adjacent mine buildings. The mine water at Force Crag remains $>8^{\circ}\text{C}$ throughout the year despite air temperature fluctuations, and therefore would offer an ideal source of heat for a heat-pump system. This energy, while not currently required, may act as a catalyst for the development of visitor facilities at the site. Under current regulations, these technologies qualify for Government subsidies which further increase their appeal, although these subsidies were in a state of flux at the time of writing. Regardless of subsidies, the potential for off-grid generation is of unique value at this site, given its tourist interest and remote off-grid location.

6.3 Research contribution

The findings presented in this thesis contribute to knowledge of resource recovery from passive metal mine water treatment systems in the following ways:

- First in-depth assessment of the resource potential of drainage from abandoned metal mine waters, using data from sites in England and Wales.

- Unique assessment of VFP substrates, characterising metal content in three dimensions by sequential extraction and a preliminary assessment of metal content in relation to particle size.
- Proof-of-principle chemical leaching of passive mine water treatment substrates for decontamination and recovery of a metal rich solid.
- Proof-of-principle bioleaching of passive mine water treatment substrates to recover metals.
- First of its kind assessment of the resource recovery potential of a passive metal mine water treatment system to offset life-cycle costs.

6.4 Study limitations

Whilst this study makes significant contributions to understanding of resource recovery at passive metal mine water treatment sites, the limitations of the study must be acknowledged. The research undertaken was based upon sites and data from Great Britain, with review of a selection of readily available international literature. It attempted to identify the potential for resource recovery and consider some technical aspects of doing so, although given the breadth of resource potential it is far from exhaustive. Substrate characterisation and metal recovery experimentation have been conducted at proof-of-principle stage, and are not representative of larger scale metal recovery operations. In addition, the mine waters investigated were from just two sites which were both poorly mineralised, and, while they had problematic zinc concentrations, many other metals were below analytical detection limits. This had implications upon the metal content of the Nenthead substrate, and the performance assessment of the Force Crag treatment system.

Some life-cycle cost projections were produced for the Force Crag mine water treatment system case study to contextualise the research conducted. These projections are based upon extrapolation of best available information, although future technological advances and financial conditions are likely to impact upon the actual life-cycle costs. No detailed life-cycle analyses were conducted, as this is out of the thesis scope and has been explored by others (e.g. Hengen et al., 2014).

6.5 Recommendations

Throughout this research, it became evident that there are many potential research avenues which were out of scope under the current investigation. Some of the most pressing of these areas are as follows:

- Geochemical investigations into metal mine water behaviour under conditions encountered within renewable energy systems (at the time of writing the author is not aware of any open-loop energy recovery systems at abandoned metal mine sites in Great Britain).
- More detailed investigations into particle size distribution of passive treatment system substrates. It was a limitation of this research that experiments into particle size distribution were only preliminary, and not repeated.
- Further investigations into biological leaching, in particular community assessment by 16s rRNA gene sequence analysis to understand the role of biological processes in these experiments.
- Long-term monitoring of passive VFP treatment units at Force Crag, in order to quantify limits on system life-time and more accurately forecast substrate composition at time of failure.
- Repeating the experimentation conducted in this thesis at geochemically different sites, to determine the impacts of geochemistry on treatment system performance and metal recoverability.

Further development of technology for the recovery of metals from treatment system wastes is required by industry, such as conducting pilot substrate leaching trials using soil washing techniques. Renewable energy potential has also been quantified, along with estimated costs and benefits, yet it is for other sectors to champion and exploit these resources for wider benefit.

6.6 Final remarks

Recovery of resources from passive mine water treatment systems has the potential for benefits which exceed the monetary savings afforded to operators. Metal concentrates recovered from passive treatment system wastes could be exported to mineral processing facilities, where metals could be recovered for re-cycling. This would divert potentially toxic metals from further dispersal into the environment through landfilling

of waste substrates. By recovering metals in this way, future mining operations along with their inherent environmental and social risk factors could be proportionately offset.

Renewable energy potential exists within mine waters which flow by gravity, and where stable temperatures exist. By recovering energy at passive treatment sites, the treatment process may be enhanced (for example, by powering of reagent dosing units), or power could be used for off-site applications. Where energy is exported from a fully-passive treatment system, either to the grid or for off-grid users near to the site, the system becomes a net exporter of renewable energy.

Mechanisms exist to recover metals from passive mine water treatment systems and recover energy from mine water flows; these have been shown by this research to offer a way of offsetting the financial costs of remediation. What is, perhaps, of greater significance is that resource recovery has knock on environmental benefits: recovery of metals from treatment substrates avoids landfill disposal of metalliferous wastes, yet generating a low-impact metal resource, while recovery and export of renewable energy offsets carbon emissions from fossil fuel generation elsewhere. These benefits are consistent with the current European agenda of resource efficiency within a circular economy (European Commission, 2016), a crucial strategy for protecting the world for future generations.

References

- Aaberg, R. J. (2003) 'Osmotic Power: A New and Powerful Renewable Energy Source?', *Refocus*, 4, (6), pp. 48-50.
- Abumaizar, R. and Khan, L. I. (1996) 'Laboratory Investigation of Heavy Metal Removal by Soil Washing', *Journal of the Air & Waste Management Association*, 46, (8), pp. 765-768.
- Abumaizar, R. J. and Smith, E. H. (1999) 'Heavy Metal Contaminants Removal by Soil Washing', *Journal of Hazardous Materials*, 70, (1-2), pp. 71-86.
- Alharthi, A., Blackley, R. A., Flowers, T. H., Hargreaves, J. S. J., Pulford, I. D., Wigzell, J. and Zhou, W. (2014) 'Iron Ochre - A Pre-Catalyst for the Cracking of Methane', *Journal of Chemical Technology & Biotechnology*, 89, (9), pp. 1317-1323.
- Allen, H. E. and Chen, P. (1993) 'Remediation of Metal Contaminated Soil by EDTA Incorporating Electrochemical Recovery of Metal and EDTA', *Environmental Progress*, 12, (4), pp. 284-293.
- Alloway, B. J. (2008) *Zinc in Soils and Crop Nutrition*. Brussels, Belgium and Paris, France: IZA and IFA
- Amec. (2011) 'Force Crag Part 2A Assessment', *Unpublished report*, pp. 85.
- Amer, S., Figueiredo, J. M. and Luis, A. (1995) 'The Recovery of Zinc from the Leach Liquors of the CENIM-LNETI Process by Solvent Extraction with Di(-2-ethylhexyl)phosphoric acid', *Hydrometallurgy*, 37, (3), pp. 323-337.
- Amos, P. W. and Younger, P. L. (2003) 'Substrate Characterisation for a Subsurface Reactive Barrier to Treat Colliery Spoil Leachate', *Water Research*, 37, (1), pp. 108-120.
- APHA. (2005) *Standard Methods for the Examination of Water & Wastewater*. 21 ed Washington, DC: American Public Health Association
- Aplin, A. C., Fabian, D., Morrison, M. I., Younger, P. L., Hallberg, K. and Johnson, D. B. (2008) 'Performance and Key Biogeochemical Reactions in Full-Scale Passive Mine Water Treatment Systems', *Geochimica Et Cosmochimica Acta*, 72, (12), pp. A30-A30.

- Appelo, C. A. J. and Postma, D. (2010) *Geochemistry, Groundwater and Pollution*. 2nd ed The Netherlands: CRC Press.
- Asad, M. W. A. (2007) 'Optimum Cut-Off Grade Policy for Open Pit Mining Operations Through Net Present Value Algorithm Considering Metal Price and Cost Escalation', *Engineering Computations*, 24, (7), pp. 723-736.
- Ashok, S. (2007) 'Optimised Model for Community-Based Hybrid Energy System', *Renewable Energy*, 32, (7), pp. 1155-1164.
- Ataei, M. and Osanloo, M. (2004) 'Using a Combination of Genetic Algorithm and the Grid Search Method to Determine Optimum Cutoff Grades of Multiple Metal Deposits', *International Journal of Surface Mining, Reclamation and Environment*, 18, (1), pp. 60-78.
- Atkins, W. S. (2010) 'North Pennines Metal Mines Monitoring Report. Catchment Monitoring - Nent', pp. 46.
- Atkins, W. S. (2012) 'Checkpoint 2 Presentation to the Coal Authority', pp. 28.
- Atkins, W. S. (2014a) *General Arrangement - 'As Built' Drawing, Force Crag Mine Water Treatment Scheme*
- Atkins, W. S. (2014b) 'Technical note: Compost Wetland Medium - Force Crag and Gate Gill. Unpublished report to The Coal Authority'.
- Bailey, M. T., Moorhouse, A. M. L., Byrom, J. A. and Kershaw, S. (2013a) 'Applications for Hydrous Ferric Oxide Mine Water Treatment Sludge: A Review', *International Mine Water Association Symposium*. Golden, Co, USA, 5 - 9 August 2013. Publication Printers, pp. 519 - 524.
- Bailey, M. T., Moorhouse, A. M. L. and Watson, I. A. (2013b) 'Heat Extraction from Hypersaline Mine Water at the Dawdon Mine Water Treatment Site', *Mine Closure*. Cornwall, UK, 18 - 20 September 2013. Australian Centre for Geomatics, pp. 1 - 12.
- Bailey, M. T., Watson, I., Wyatt, L. and Davies, T. (2011) 'Applications of Pumping Tests in the Development of Mine Water Management Strategies and Remediation Schemes', *11th International Mine Water Association Congress*. Aachen, Germany, 4 - 11 September 2011. Document Transformation Technologies, pp. 97 - 100.

- Baker, B. J. and Banfield, J. F. (2003) 'Microbial Communities in Acid Mine Drainage', *FEMS Microbiology Ecology*, 44, (2), pp. 139-152.
- Baltpurvins, K. A., Burns, R. C., Lawrance, G. A. and Stuart, A. D. (1997) 'Effect of Electrolyte Composition on Zinc Hydroxide Precipitation by Lime', *Water Research*, 31, (5), pp. 973-980.
- Bamforth, S. M., Manning, D. A. C., Singleton, I., Younger, P. L. and Johnson, K. L. (2006) 'Manganese removal from mine waters – investigating the occurrence and importance of manganese carbonates', *Applied Geochemistry*, 21, (8), pp. 1274-1287.
- Banks, D. (2008) *An Introduction to Thermogeology: Ground Sourced Heating and Cooling*. Oxford, UK: Blackwell.
- Banks, D., Fraga Pumar, A. and Watson, I. (2009) 'The Operational Performance of Scottish Minewater-Based Ground Source Heat Pump Systems', *Quarterly Journal of Engineering Geology and Hydrogeology*, 42, (3), pp. 347-357.
- Banks, D. and Robins, N. (2002) *An Introduction to Groundwater in Crystalline Bedrock*. Trondheim, Norway: Norges geologiske undersøkelse.
- Banks, D., Skarphagen, H., Wiltshire, R. and Jessop, C. (2003) 'Mine Water as a Resource: Space Heating and Cooling via use of Heat Pumps', *Land Contamination & Reclamation*, 11, (2), pp. 191 - 198.
- Banks, D., Younger, P. L., Arnesen, R.-T., Iversen, E. R. and Banks, S. B. (1997) 'Mine-Water Chemistry: the Good, the Bad and the Ugly', *Environmental Geology*, 32, (3), pp. 157 - 174.
- Banks, D., Younger, P. L. and Dumbleton, S. (1996) 'The Historical Use of Mine-Drainage and Pyrite-Oxidation Waters in Central and Eastern England, United Kingdom', *Hydrogeology Journal*, 4, (4), pp. 55-68.
- Batty, L. C. (2003) 'Wetland Plants, More Than a Pretty Face?', *Land Contamination & Reclamation*, 11, (2), pp. 173 - 180.
- Bayat, B. and Sari, B. (2010) 'Comparative Evaluation of Microbial and Chemical Leaching Processes for Heavy Metal Removal from Dewatered Metal Plating Sludge', *Journal of Hazardous Materials*, 174, (1-3), pp. 763-769.

- Bayat, O., Sever, E., Bayat, B., Arslan, V. and Poole, C. (2009) 'Bioleaching of Zinc and Iron from Steel Plant Waste using *Acidithiobacillus Ferrooxidans*', *Applied Biochemistry and Biotechnology*, 152, (1), pp. 117-126.
- Beauchamp, E. G. and Seech, A. G. (1990) 'Denitrification with Different Sizes of Soil Aggregates Obtained from Dry-Sieving and from Sieving with Water', *Biology and Fertility of Soils*, 10, (3), pp. 188-193.
- Bilek, F. (2006) 'Column Tests to Enhance Sulphide Precipitation with Liquid Organic Electron Donators to Remediate AMD-Influenced Groundwater', *Environmental Geology*, 49, (5), pp. 674-683.
- BioteQ. (no date) 'Case Study: Wellington Oro, Colorado (US EPA)', *Pamphlet*.
- Boonstra, J., van Lier, R., Janssen, G., Dijkman, H. and Buisman, C. J. N. (1999) 'Biological Treatment of Acid Mine Drainage', in Amils, R. and Ballester, A.(eds) *Process Metallurgy*. Vol. 9 Elsevier, pp. 559-567.
- Bosecker, K. (1997) 'Bioleaching: Metal Solubilization by Microorganisms', *FEMS Microbiology Reviews*, 20, (3-4), pp. 591-604.
- Boshoff, G., Duncan, J. and Rose, P. D. (2004) 'Tannery Effluent as a Carbon Source for Biological Sulphate Reduction', *Water Research*, 38, (11), pp. 2651-2658.
- Bratty, M., Lawrence, R., Kratochvil, D. and Marchant, B. (2006) 'Applications of Biological H₂S Production from Elemental Sulfur in the Treatment of Heavy Metal Pollution Including Acid Rock Drainage', *7th International Conference on Acid Rock Drainage*. St. Louis MO, USA, 26 - 30 March 2006. American Society of Mining and Reclamation, pp. 271 - 281.
- Brierley, J. A. and Brierley, C. L. (2001) 'Present and Future Commercial Applications of Biohydrometallurgy', *Hydrometallurgy*, 59, (2-3), pp. 233-239.
- Brombacher, C., Bachofen, R. and Brandl, H. (1998) 'Development of a Laboratory-Scale Leaching Plant for Metal Extraction from Fly Ash by *Thiobacillus* Strains', *Applied and Environmental Microbiology*, 64, (4), pp. 1237-1241.
- BSI. (1990) 'ISO 1377: Methods of Test for Soils for Civil Engineering Purposes', in *Part 2: Classification Tests* International Organization for Standardization.

- BSI. (1995a) 'ISO 10694: Determination of Organic Carbon and Total Carbon after Dry Combustion (Elementary Analysis)', in *Section 3.8, Soil Quality, Part 3, Chemical Methods* International Organization for Standardization.
- BSI. (1995b) 'ISO 11466: Soil Quality, Part 3, Chemical Methods', in *Section 3.9: Extraction of trace elements soluble in aqua regia* International Organization for Standardization.
- BSI. (2002) 'ISO 12457-2: Characterisation of Waste - Leaching. ', in *Compliance Test for Leaching of Granular Waste Materials and Sludges*. International Organization for Standardization.
- BSI. (2006) 'ISO 11464: Soil Quality ', in *Pretreatment of Samples for Physio-Chemical Analysis* International Organization for Standardization.
- BSI. (2009) 'ISO 11885: Water Quality', in *Determination of Selected Elements by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)* International Organization for Standardization.
- BSI. (2011) 'PAS 100:2011 Specification for composted materials', *Produced jointly by WRAP and BSI*.
- Burkin, A. R. (1976) 'Hydrometallurgy', *International Metals Reviews*, 21, (1), pp. 118 - 123.
- Burton, E. D., Phillips, I. R. and Hawker, D. W. (2006) 'Factors Controlling the Geochemical Partitioning of Trace Metals in Estuarine Sediments', *Soil and Sediment Contamination: An International Journal*, 15, (3), pp. 253-276.
- Cakmak. (2008) 'Enrichment of Cereal Grains with Zinc: Agronomic or Genetic Biofortification?', *Plant Soil*, 302, pp. 1-17.
- Chang, I. S., Shin, P. K. and Kim, B. H. (2000a) 'Biological Treatment of Acid Mine Drainage Under Sulphate-Reducing Conditions with Solid Waste Materials as Substrate', *Water Research*, 34, (4), pp. 1269-1277.
- Chang, M. B., Huang, C. K., Wu, H. T., Lin, J. J. and Chang, S. H. (2000b) 'Characteristics of Heavy Metals on Particles with Different Sizes from Municipal Solid Waste Incineration', *Journal of Hazardous Materials*, 79, (3), pp. 229-239.

- Chen, M. and Ma, L. Q. (2001) 'Comparison of Three Aqua Regia Digestion Methods for Twenty Florida Soils', *Soil Science Society of America Journal*, 65, (2), pp. 491-499.
- Chen, T.-C., Macauley, E. and Hong, A. (1995) 'Selection and Test of Effective Chelators for Removal of Heavy Metals from Contaminated Soils', *Canadian Journal of Civil Engineering*, 22, (6), pp. 1185-1197.
- Cheng, S., Dempsey, B. A. and Logan, B. E. (2007) 'Electricity Generation from Synthetic Acid-Mine Drainage (AMD) Water using Fuel Cell Technologies', *Environmental Science & Technology*, 41, (23), pp. 8149-8153.
- Cheong, Y.-W., Hur, W., Yim, G.-J., Ji, S.-W., Yang, J.-E., Baek, H.-J. and Shim, Y.-S. (2012) 'Longevity of Organic Layers of Vertical Flow Ponds for Sulfate Reduction in Treating Mine Drainages in South Korea', *Environmental Geochemistry and Health*, 34, (1), pp. 115-121.
- Cheong, Y.-W., Min, J.-S. and Kwon, K.-S. (1998) 'Metal Removal Efficiencies of Substrates for Treating Acid Mine Drainage of the Dalsung Mine, South Korea', *Journal of Geochemical Exploration*, 64, (1-3), pp. 147-152.
- Chiang, P.-N., Tong, O.-Y., Chiou, C.-S., Lin, Y.-A., Wang, M.-K. and Liu, C.-C. (2016) 'Reclamation of zinc-contaminated soil using a dissolved organic carbon solution prepared using liquid fertilizer from food-waste composting', *Journal of Hazardous Materials*, 301, pp. 100-105.
- CL:AIRE. (2007) 'Technical Bulletin 13: Understanding Soil Washing', in *Contaminated Land: Applications in Real Environments*(ed).
- Clark, M. W., Davies-McConchie, F., McConchie, D. and Birch, G. F. (2000) 'Selective Chemical Extraction and Grainsize Normalisation for Environmental Assessment of Anoxic Sediments: Validation of an Integrated Procedure', *Science of the Total Environment*, 258, (3), pp. 149-170.
- Clarke, A. M. (1995) *Coal Mining and Water Quality*. Unpublished report: International Energy Agency, London
- Cline, S. R., Reed, B. E. and Matsumoto, M. R. (1993) 'Efficiencies of Soil Washing Solutions for the Remediation of Lead Contaminated Soils', *25th Mid-Atlantic Industrial Waste Conference*. College Park, MD, USA, Technomic Publishing Company, pp. 169-177.
- Cortina, J.-L., Lagreca, I., De Pablo, J., Cama, J. and Ayora, C. (2003) 'Passive In Situ Remediation of Metal-Polluted Water with Caustic Magnesia: Evidence

from Column Experiments', *Environmental Science & Technology*, 37, (9), pp. 1971-1977.

Costa, M. C., Santos, E. S., Barros, R. J., Pires, C. and Martins, M. (2009) 'Wine Wastes as Carbon Source for Biological Treatment of Acid Mine Drainage', *Chemosphere*, 75, (6), pp. 831-836.

Coulton, R., Bullen, C., Dolan, J., Hallett, C., Wright, J. and Marsden, C. (2003) 'Wheal Jane Mine Water Active Treatment Plant - Design, Construction and Operation', *Land Contamination & Reclamation*, 11, (2), pp. 245-252.

Cui, M., Jang, M., Cho, S.-H., Khim, J. and Cannon, F. S. (2012) 'A Continuous Pilot-Scale System using Coal-Mine Drainage Sludge to Treat Acid Mine Drainage Contaminated with High Concentrations of Pb, Zn, and other Heavy Metals', *Journal of Hazardous Materials*, 215-216, pp. 122-128.

da Silva, G. (2004) 'Relative Importance of Diffusion and Reaction Control During the Bacterial and Ferric Sulphate Leaching of Zinc Sulphide', *Hydrometallurgy*, 73, (3-4), pp. 313-324.

Das, S. C., Singh, P. and Hefter, G. T. (1997) 'The Effects of 4-ethylpyridine and 2-cyanopyridine on Zinc Electrowinning from Acidic Sulfate Solutions', *Journal of Applied Electrochemistry*, 27, (6), pp. 738-744.

Davenport, W., King, M., Schlesinger, M. and Biswas, A. K. (2002) *Extractive Metallurgy of Copper*. 4 ed Oxford, UK: Pergamon.

Davis, A. P. and Singh, I. (1993) 'Washing of Zinc (II) from Contaminated Soil Columns', *Journal of Environmental Engineering*, 122, (2), pp. 174 - 185.

Davis, S. (2003) *Microhydro: Clean Power from Water*. British Columbia, Canada: New Society Publishers.

DEFRA and Environment Agency. (2007) *CLR11 Model Procedures for the Management of Land Contamination*. Bristol: Environment Agency.

Deorkar, N. V. and Tavlarides, L. L. (1998) 'An Adsorption Process for Metal Recovery from Acid Mine Waste: The Berkeley Pit Problem', *Environmental Progress*, 17, (2), pp. 120-125.

Díez, R. and Díaz-Aguado, M. (2014) 'Estimating Limits for the Geothermal Energy Potential of Abandoned Underground Coal Mines: A Simple Methodology', *Energies*, 7, (7), pp. 4241.

- Dinardo, O., Kondos, P. D., MacKinnon, D. J., McCready, R. G. L., Riveros, P. A. and Skaff, M. (1991) 'Study on Metals Recovery/Recycling from Acid Mine Drainage. Phase 1A: Literature Survey', *MEND*.
- Dudeney, B., Demin, O. and Tarasova, I. (2003) 'Control of Ochreous Deposits in Mine Water Treatment', *Land Contamination & Reclamation*, 11, (2), pp. 259-266.
- Dufresne, K., Neculita, C., Brisson, J. and Genty, T. (2015) 'Metal Retention Mechanisms in Pilot-Scale Constructed Wetlands Receiving Acid Mine Drainage', *10th International Conference on Acid Rock Drainage*. Santiago, Chile, 21 - 24 April 2015. Gecamin, pp. 1 - 6.
- Dufresne, S., Bousquet, J., Boissinot, M. and Guay, R. (1996) 'Sulfobacillus disulfidooxidans sp. nov., a New Acidophilic, Disulfide-Oxidizing, Gram-Positive, Spore-Forming Bacterium', *International Journal of Systematic and Evolutionary Microbiology*, 46, (4), pp. 1056-1064.
- Dumpleton, S., Donnelly, L. J. and Young, B. (1996) *A Survey of Force Crag Mine, near Keswick, Cumbria*. Keyworth: British Geological Survey
- Dvorak, D. H., Hedin, R. S., Edenborn, H. M. and McIntire, P. E. (1992) 'Treatment of Metal-Contaminated Water using Bacterial Sulfate Reduction: Results from Pilot-Scale Reactors', *Biotechnology and Bioengineering*, 40, (5), pp. 609-616.
- ECC. (2000) 'Directive of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy: Joint Text Approved by the Conciliation Committee', *European Journal*, 1997/0067(COD), (C5-0347/00).
- Energy Act. (2011) 'Chapter 16', *HM Government*, pp. 101.
- Environment Agency. (2009a) *Soil Guideline Values for Cadmium in Soil*. Bristol: Environment Agency.
- Environment Agency. (2009b) *Soil Guideline Values for Nickel in Soil*. Bristol: Environment Agency.
- Environment Agency. (2013a) *Guidance for Run-of-River Hydropower Development*. Bristol: Environment Agency.

- Environment Agency. (2013b) *Managing Water Abstraction* Bristol: Environment Agency.
- ESG. (2013) 'Covering Letter and Laboratory Certificate ESF130318 ', *Waste Classification Hazard Assessment - Newcastle University*.
- EST (2015) *Our Calculations (Ground Source Heat Pumps: Costs, Savings and Financial Support)*. Available at: <http://www.energysavingtrust.org.uk/domestic/content/our-calculations> (Accessed: 11-5-2015).
- European Commission (2016) *Circular Economy Strategy*. Available at: http://ec.europa.eu/environment/circular-economy/index_en.htm (Accessed: 29-01-2016).
- Fernández-Caliani, J. C., Barba-Brioso, C., González, I. and Galán, E. (2009) 'Heavy Metal Pollution in Soils Around the Abandoned Mine Sites of the Iberian Pyrite Belt (Southwest Spain)', *Water, Air, and Soil Pollution*, 200, (1-4), pp. 211-226.
- Flores, R. M. (1998) 'Coalbed Methane: From Hazard to Resource', *International Journal of Coal Geology*, 35, (1-4), pp. 3-26.
- Forrest, C. and Hughes, M. A. (1978) 'The Separation of Zinc from Copper by Di-2-ethylhexyl Phosphoric Acid - an Equilibrium Study', *Hydrometallurgy*, 3, (4), pp. 327-342.
- Fortin, D., Goulet, R. and Roy, M. (2000) 'Seasonal Cycling of Fe and S in a Constructed Wetland: The Role of Sulfate-Reducing Bacteria', *Geomicrobiology Journal*, 17, (3), pp. 221-235.
- Gallagher, J., Styles, D., McNabola, A. and Williams, A. P. (2015a) 'Current and Future Environmental Balance of Small-Scale Run-of-River Hydropower', *Environmental Science & Technology*, 49, (10), pp. 6344-6351.
- Gallagher, J., Styles, D., McNabola, A. and Williams, A. P. (2015b) 'Life Cycle Environmental Balance and Greenhouse Gas Mitigation Potential of Micro-Hydropower Energy Recovery in the Water Industry', *Journal of Cleaner Production*, 99, pp. 152-159.
- Gandy, C. and Jarvis, A. (2012) 'The Influence of Engineering Scale and Environmental Conditions on the Performance of Compost Bioreactors for the Remediation of Zinc in Mine Water Discharges', *Mine Water and the Environment*, 31, (2), pp. 82-91.

- German, J. and Svensson, G. (2002) 'Metal Content and Particle Size Distribution of Street Sediments and Street Sweeping Waste', *Water Science and Technology*, 46, (6-7), pp. 191 - 198.
- Geroni, J. N. and Sapsford, D. J. (2011) 'Kinetics of Iron (II) Oxidation Determined in the Field', *Applied Geochemistry*, 26, (8), pp. 1452-1457.
- Gibert, O., de Pablo, J., Luis Cortina, J. and Ayora, C. (2003) 'Evaluation of Municipal Compost/Limestone/Iron Mixtures as Filling Material for Permeable Reactive Barriers for In-Situ Acid Mine Drainage Treatment', *Journal of Chemical Technology & Biotechnology*, 78, (5), pp. 489-496.
- Gleyzes, C., Tellier, S. and Astruc, M. (2002) 'Fractionation Studies of Trace Elements in Contaminated Soils and Sediments: a Review of Sequential Extraction Procedures', *Trends in Analytical Chemistry*, 21, (6-7), pp. 451-467.
- Gouvea, L. R. and Morais, C. A. (2010) 'Development of a Process for the Separation of Zinc and Copper from Sulfuric Liquor Obtained from the Leaching of an Industrial Residue by Solvent Extraction', *Minerals Engineering*, 23, (6), pp. 492-497.
- Gozzard, E., Mayes, W. M., Potter, H. A. B. and Jarvis, A. P. (2011) 'Seasonal and Spatial Variation of Diffuse (non-point) Source Zinc Pollution in a Historically Metal Mined River Catchment, UK', *Environmental Pollution*, 159, (10), pp. 3113-3122.
- Gray, N. D., Gandy, C. J. and Jarvis, A. P. (2012) 'Mitigation of Pollution from Abandoned Metal Mines. Part 2, Review of Resource Recovery Options from the Passive Remediation of Metal Rich Mine Waters', *Environment Agency Publication, Project SC090024/1*.
- Greenway, G. M. and Song, Q. J. (2002) 'Heavy Metal Speciation in the Composting Process', *Journal of Environmental Monitoring : JEM*, 4, (2), pp. 300-305.
- Gribble, C. D. and Hall, A. J. (1992) *Optical Mineralogy: Principles and Practice*. London, UK: UCL Press.
- Gunawardana, C., Egodawatta, P. and Goonetilleke, A. (2014) 'Role of Particle Size and Composition in Metal Adsorption by Solids Deposited on Urban Road Surfaces', *Environmental Pollution*, 184, pp. 44-53.

- Gusek, J. and Clarke-Whistler, K. (2005) 'Where Does the Recovery of Metal Resources from Passive Treatment Systems Fit in with Sustainable Development Initiatives Associated with Large Mining Projects?', *National Meeting of the American Society for Mining and Reclamation*. Breckenridge, CO, USA, 19 - 23 June 2005. American Society for Mining and Reclamation, pp. 454 - 469.
- Gusek, J., Wildeman, T. R. and Conroy, K. W. (2006) 'Conceptual Methods for Recovering Metal Resources from Passive Treatment Systems', *7th International Conference on Acid Rock Drainage*. St. Louis MO, 26 - 30 March 2006. American Society of Mining and Reclamation, pp. 690 - 702.
- Gusek, J. J. (2002) 'Sulfate-Reducing Bioreactor Design and Operating Issues: Is this the Passive Treatment Technology for Your Mine Drainage?', *National Association of Abandoned Mine Land Programs Annual Conference*. Park City, Utah, pp. 1 - 13.
- Gusek, J. J., Wildeman, T., Miller, A. and Fricke, J. (1998) 'The Challenges of Designing, Permitting and Building a 1200 GPM Passive Bioreactor for Metal Mine Drainage, West Fork Mine Missouri', *15th National meeting of the American Association of Surface Mining and Reclamation*. St Louis, Montana, pp. 203 - 212.
- Gusiatin, Z. M. and Klimiuk, E. (2012) 'Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin', *Chemosphere*, 86, (4), pp. 383-391.
- Habibiandehkordi, R., Quinton, J. N. and Surridge, B. W. J. (2014) 'Enhancing Soluble Phosphorus Removal within Buffer Strips Using Industrial By-Products', *Environmental Science and Pollution Research*, 21, (21), pp. 12257-12269.
- Hacisalihoglu, G. and Kochian, L. V. (2003) 'How do some Plants Tolerate Low Levels of Soil Zinc? Mechanisms of Zinc Efficiency in Crop Plants', *New Phytologist*, 159, (2), pp. 341-350.
- Hall, A., Scott, J. A. and Shang, H. (2011) 'Geothermal Energy Recovery from Underground Mines', *Renewable and Sustainable Energy Reviews*, 15, (2), pp. 916-924.
- Hallberg, K. B. and Johnson, D. B. (2005) 'Microbiology of a Wetland Ecosystem Constructed to Remediate Mine Drainage from a Heavy Metal Mine', *Science of the Total Environment*, 338, (1-2), pp. 53-66.

- Hamilton, Q. U. I., Lamb, H. M., Hallett, C. and Proctor, J. A. (1999) 'Passive Treatment Systems for the Remediation of Acid Mine Drainage at Wheal Jane, Cornwall', *Water and Environment Journal*, 13, (2), pp. 93-103.
- Hancock, S. (2005) 'Quantifying Ochre Arisings: Output from the UK Coal Authority's Mine Water Treatment Sites', *9th International Mine Water Association Congress*. Oviedo, Spain, 5 —7 September 2005. University of Oviedo, pp. 395 - 402.
- Harries, R. C. (1985) 'A Field Trial of Seeded Reverse Osmosis for the Desalination of a Scaling-Type Mine Water', *Desalination*, 56, (0), pp. 227-236.
- Harris, R. A., Moorhouse, A. M. L., Hill, S., Davies, T. and Wyatt, L. M. (2014) 'Stakeholder Management: the Key to Successful Metal Mine Discharge Remediation', *12th International Mine Water Association Congress*. Xuzhou, China, 18 - 22 August 2014. China University of Mining and Technology Press, pp. 781 - 785.
- Hartley, S. (2009) *Remediation of Abandoned Metal Mine Drainage using Dealginated Seaweed*. thesis. Aberystwyth.
- Hartley, S., Pearce, N. J. G., Perkins, W. T., Dinelli, E., Edyvean, R. G. J., Priestman, G., Sandlands, L. and Bachmann, R. (2007) 'Dealginated Seaweed as a Bioadsorption Medium for Treating Metal Mine Drainage: Issues Surrounding its Pre-Treatment and Use in Small Scale Treatment Plants in the EU Life 'BIOMAN' Project', *International Mine Water Association Symposium*. Cagliari, Italy, 27th - 31st May 2007. Document Transformation Technologies, pp. 1-4.
- Harvey, A., Brown, A., Hettiarachi, P. and Inversin, A. (1993) *Micro-Hydro Design Manual: A Guide to Small-Scale Water Power Schemes*. Exeter: IT Publications.
- Haynes, R. J. and Swift, R. S. (1986) 'Effects of Soil Acidification and Subsequent Leaching on Levels of Extractable Nutrients in a Soil', *Plant and Soil*, 95, (3), pp. 327-336.
- Heald, H. (2010) *William Armstrong, Magician of the North*. Newcastle upon Tyne: Northumbria Press.
- Heat Pump Test Centre WPZ Switzerland (2012) Available at: <http://www.ntb.ch/ies/competences/heat-pump-test-center-wpz.html?L=1> (Accessed: 28-02-2012).

- Hedin, R. S., Narin, W. N. and Kleinmann, R. L. P. (1994a) 'Passive Treatment of Coal Mine Drainage', *Bureau of Mines, Information Circular*, (9389).
- Hedin, R. S., Watzlaf, G. R. and Nairn, W. (1994b) 'Passive Treatment of Acid Mine Drainage with Limestone', *Journal of Environmental Quality*, 23, (1338 - 1345).
- Hengen, T. J., Squillace, M. K., O'Sullivan, A. D. and Stone, J. J. (2014) 'Life Cycle Assessment Analysis of Active and Passive Acid Mine Drainage Treatment Technologies', *Resources, Conservation and Recycling*, 86, pp. 160-167.
- Henry, J. G. and Prasad, D. (2006) 'Biosolids from Two-Stage Bioleaching could Produce Compost for Unrestricted Use', *Environmental Technology*, 27, (6), pp. 665-672.
- Hiibel, S. R., Pereyra, L. P., Inman, L. Y., Tischer, A., Reisman, D. J., Reardon, K. F. and Pruden, A. (2008) 'Microbial Community Analysis of Two Field-Scale Sulfate-Reducing Bioreactors Treating Mine Drainage', *Environmental Microbiology*, 10, (8), pp. 2087-2097.
- HM Treasury. (2011) *The Green Book*. London: TSO.
- Holman, J. (2009) 'Water Reclamation Plant Reaches 99% Recovery', *Mining Weekly*.
- Holmes, D. (2008) 'The Investigation of Statutory Nuisance Mineshafts: A Project to Establish Awareness and Actions Amongst Local Authority Environmental Health Departments', *Journal of Environmental Health Research*, 7, (1), pp. 1.
- Hudson-Edwards, K. A., Macklin, M. G., Brewer, P. A. and Dennis, I. A. (2008) *Assessment of Metal Mining-Contaminated River Sediments in England and Wales*.
- Huisman, J. L., Schouten, G. and Schultz, C. (2006) 'Biologically Produced Sulphide for Purification of Process Streams, Effluent Treatment and Recovery of Metals in the Metal and Mining Industry', *Hydrometallurgy*, 83, (1-4), pp. 106-113.
- Infomine (2015) *United Keno Hill Mines*. Available at: http://technology.infomine.com/enviromine/wetlands/cw_cases.htm (Accessed: 23-06-2015).

- Inoue, S. N. K. (2000) 'Recovery of Lead and Zinc from Fly Ash Generated from Municipal Incineration Plants by Means of Acid and/or Alkaline Leaching', *Hydrometallurgy*, 56, (3), pp. 269-292.
- Irving, H. and Williams, R. J. P. (1953) 'The Stability of Transition-Metal Complexes', *Journal of the Chemical Society (Resumed)*, 637, (0), pp. 3192-3210.
- Ishigaki, T., Nakanishi, A., Tateda, M., Ike, M. and Fujita, M. (2005) 'Bioleaching of Metal from Municipal Waste Incineration Fly Ash Using a Mixed Culture of Sulfur-Oxidizing and Iron-Oxidizing Bacteria', *Chemosphere*, 60, (8), pp. 1087-1094.
- ITRC. (2013) *Biochemical Reactors for Mining-Influenced Water*. Interstate Technology and Regulatory Council.
- Jackson, P. and Kershaw, S. (1996) 'Reducing Long Term Methane Emissions Resulting From Coal Mining', *Energy Conservation Management*, 37, (6-8), pp. 801 - 806.
- Jameson, E., Rowe, O. F., Hallberg, K. B. and Johnson, D. B. (2010) 'Sulfidogenesis and Selective Precipitation of Metals at Low pH Mediated by Acidithiobacillus spp. and Acidophilic Sulfate-Reducing Bacteria', *Hydrometallurgy*, 104, (3-4), pp. 488-493.
- Jarvis, A., Aumonier, J. and Morrison, M. (2007) 'Renovation of the Compost Based Wetland Treatment System at Quaking Houses, Co. Durham', *Report to the BOC Foundation*.
- Jarvis, A., Gandy, C., Davis, J. and Orme, P. (2012a) *Comparative Importance of Point and Diffuse Sources of Pollution at the Force Crag Mine Site under Varying Hydrological Conditions*. Report to the Coal Authority: Newcastle University, UK.
- Jarvis, A. P. (2006) 'The Role of Dissolved Carbon Dioxide in Governing Deep Coal Mine Water Quality and Determining Treatment Process Selection', *7th International Conference on Acid Rock Drainage*. St. Louis, MO., 26 - 30 March 2006. American Society of Mining and Reclamation, pp. 833 - 843.
- Jarvis, A. P., Davis, J., Gray, N. D., Orme, P. H. A. and Gandy, C. J. (2014) *Mitigation of Pollution from Abandoned Metal Mines: Investigation of Passive Compost Bioreactor Systems for Treatment of Abandoned Metal Mine Discharges*. Bristol: Environment Agency.

- Jarvis, A. P., Gandy, C. J., Bailey, M. T., Davis, J. E. and Orme, P. H. A. (2015) 'Metal Removal and Secondary Contamination in a Passive Metal Mine Drainage Treatment System', *10th International Conference on Acid Rock Drainage* Santiago, Chile, 21 - 24 April 2015. Gecamin, pp. 1 - 9.
- Jarvis, A. P., Gandy, C. J. and Gray, N. D. (2012b) *Mitigation of Pollution from Abandoned Metal Mines: Part 1. Review of Passive Treatment Technologies for Metal Mine Drainage Remediation*. Bristol: Environment Agency.
- Jarvis, A. P., Mayes, W. M., Coulon, P., fox, A., Hill, S., Johnston, D., Potter, H. A. B., Thorn, P. and Watson, I. A. (2010a) *Prioritisation of Abandoned Non-Coal Mine Impacts on the Environment XIII. Hazards and Risk Management at Abandoned Non-Coal Mine Sites*.
- Jarvis, A. P., Mayes, W. M., Coulon, P., fox, A., Hill, S., Johnston, D., Potter, H. A. B., Thorn, P. and Watson, I. A. (2010b) *Prioritisation on Abandoned Non-Coal Mine Impacts on the Environment II. The National Picture*. Bristol: Environment Agency.
- Jarvis, A. P., Mayes, W. M., Coulon, P., Fox, A., Hill, S., Johnston, D., Potter, H. A. B., Thorn, P. and Watson, I. A. (2012c) *Prioritisation on Abandoned Non-Coal Mine Impacts on the Environment: Future management of abandoned non-coal mine water discharges*. Bristol: Environment Agency.
- Jarvis, A. P., Moustafa, M., Orme, P. H. A. and Younger, P. L. (2006) 'Effective Remediation of Grossly Polluted Acidic, and Metal-Rich, Spoil Heap Drainage Using a Novel, Low-Cost, Permeable Reactive Barrier in Northumberland, UK', *Environmental Pollution*, 143, (2), pp. 261-268.
- Jarvis, A. P. and Younger, P. L. (1999) 'Design, Construction and Performance of a Full-Scale Compost Wetland for Mine-Spoil Drainage Treatment at Quaking Houses', *Water and Environment Journal*, 13, (5), pp. 313-318.
- Jessop, A. (1995) 'Geothermal Energy from Old Mines at Sringhill, Nova Scotia, Canada', *World Geothermal Conference*. Firenze, Italy, 18 - 31 May 1995. International Geothermal Association, pp. 463 - 468.
- Jha, M. K., Kumar, V. and Singh, R. J. (2001) 'Review of Hydrometallurgical Recovery of Zinc from Industrial Wastes', *Resources, Conservation and Recycling*, 33, (1), pp. 1-22.
- Johnson, D. B. (2003) 'Chemical and Microbiological Characteristics of Mineral Spoils and Drainage Waters at Abandoned Coal and Metal Mines', *Water, Air and Soil Pollution: Focus*, 3, (1), pp. 47-66.

- Johnson, D. B. (2013) 'Development and Application of Biotechnologies in the Metal Mining Industry', *Environmental Science and Pollution Research*, 20, (11), pp. 7768-7776.
- Johnson, D. B. and Hallberg, K. B. (2002) 'Pitfalls of Passive Mine Water Treatment', *Reviews in Environmental Science and Biotechnology*, 1, (4), pp. 335-343.
- Johnson, D. B. and Hallberg, K. B. (2003) 'The microbiology of acidic mine waters', *Research in Microbiology*, 154, (7), pp. 466-473.
- Johnson, D. B. and Hallberg, K. B. (2005a) 'Acid Mine Drainage Remediation Options: a Review', *Science of the Total Environment*, 338, (1-2), pp. 3-14.
- Johnson, D. B. and Hallberg, K. B. (2005b) 'Biogeochemistry of the Compost Bioreactor Components of a Composite Acid Mine Drainage Passive Remediation System', *Science of the Total Environment*, 338, (1-2), pp. 81-93.
- Johnson, D. B., Jamerson, E., Rowe, O. F., Wakeman, K. and Hallberg, K. B. (2009) 'Sulfidogenesis at Low pH by Acidophilic Bacteria and its Potential for the Selective Recovery of Transition Metals from Mine Waters', *Advanced Materials Research*, 77-73, pp. 693 - 696.
- Johnson, D. B., Rowe, O., Kimura, S. and Hallberg, K. B. (2004) 'Development of an Integrated Microbiological Approach for Remediation of Acid Mine Drainage and Recovery of Heavy Metals', *International Mine Water Association Symposium*. Newcastle upon Tyne, UK, 20 - 24 September 2004. University of Newcastle, pp. 151 - 157.
- Johnson, D. B., Sen, A. M., Kimura, S., Rowe, O. F. and Hallberg, K. B. (2006) 'Novel Biosulfidogenic System for Selective Recovery of Metals from Acidic Leach Liquors and Waste Streams', *Mineral Processing and Extractive Metallurgy*, 115, (1), pp. 19-24.
- Johnston, D., Potter, H., Jones, C., Rolley, S., Watson, I. and Pritchard, J. (2008) *Abandoned Mines and the Water Environment*. Bristol: Environment Agency.
- Jong, T. and Parry, D. L. (2003) 'Removal of Sulfate and Heavy Metals by Sulfate Reducing Bacteria in Short-Term Bench Scale Upflow Anaerobic Packed Bed Reactor Runs', *Water Research*, 37, (14), pp. 3379-3389.
- Jong, T. and Parry, D. L. (2004) 'Heavy Metal Speciation in Solid-Phase Materials from a Bacterial Sulfate Reducing Bioreactor Using Sequential Extraction

Procedure Combined with Acid Volatile Sulfide Analysis', *Journal of Environmental Monitoring*, 6, (4), pp. 278-285.

Karwowska, E., Wojtkowska, M. and Andrzejewska, D. (2015) 'The Influence of Metal Speciation in Combustion Waste on the Efficiency of Cu, Pb, Zn, Cd, Ni and Cr Bioleaching in a Mixed Culture of Sulfur-Oxidizing and Biosurfactant-Producing Bacteria', *Journal of Hazardous Materials*, 299, pp. 35-41.

Keith, C. N. and Vaughan, D. J. (2000) 'Mechanisms and Rates of Sulphide Oxidation in Relation to the Problems of Acid Rock (mine) Drainage', in Cotter-Howells, J. D., Campbell, L. S., Valsami-Jones, E. and Batchelder, M.(eds) *Environmental mineralogy: microbial interactions, anthropogenic influences, contaminated land and waste management*. pp. 117-139.

Kensa Heat Pumps (2016) *6kw Shoebox Twin*. Available at: <http://www.kensaheatpumps.com/product/shoebox-twin-2/> (Accessed: 25-01-2016).

Klein, R., Tischler, J. S., Mühling, M. and Schlömann, M. (2013) 'Bioremediation of Mine Water', in *Advances in Biochemical Engineering/Biotechnology*. Springer Berlin Heidelberg, pp. 1-64.

Kleinmann, R. (1990) 'Acid Mine Water Treatment Using Engineered Wetlands', *Mine Water and the Environment*, 9, (1), pp. 269-276.

Knox, A. S., Paller, M. H., Nelson, E. A., Specht, W. L., Halverson, N. V. and Gladden, J. B. (2006) 'Metal Distribution and Stability in Constructed Wetland Sediment', *Environmental Quality*, 35, (5), pp. 1948-59.

Kongolo, K., Mwema, M. D., Banza, A. N. and Gock, E. (2003) 'Cobalt and Zinc Recovery from Copper Sulphate Solution by Solvent Extraction', *Minerals Engineering*, 16, (12), pp. 1371-1374.

Kratochvil, D., Songlin, Y. and Lopez, O. (2015) 'Commercial Case Studies of Life Cycle Cost Reduction of ARD Treatment with Sulfide Precipitation', *10th International Conference on Acid Rock Drainage*. Santiago, Chile, 21 - 24 April 2015. Gecamin, pp. 1 - 11.

Kuyucak, N. (2006) 'Selecting Suitable Methods for Treating Mining Effluents', *PerCan Mine Closure Course*.

Laurence, D. (2006) 'Optimisation of the Mine Closure Process', *Journal of Cleaner Production*, 14, (3-4), pp. 285-298.

- Lawrence, R., Ramey, D. and Kratochvil, D. (2005) 'A New Commercial Metal Recovery Technology Utilizing On-Site Biological H₂S Production', *International Copper Hydrometallurgy Workshop*, Santiago, Chile, pp. 1 - 5.
- Lefticariu, L., Walters, E. R., Pugh, C. W. and Bender, K. S. (2015) 'Sulfate Reducing Bioreactor Dependence on Organic Substrates for Remediation of Coal-Generated Acid Mine Drainage: Field Experiments', *Applied Geochemistry*, 63, pp. 70-82.
- Liu, Y.-G., Zhou, M., Zeng, G.-M., Wang, X., Li, X., Fan, T. and Xu, W.-H. (2008) 'Bioleaching of Heavy Metals from Mine Tailings by Indigenous Sulfur-Oxidizing Bacteria: Effects of Substrate Concentration', *Bioresource Technology*, 99, (10), pp. 4124-4129.
- Lizama, H. M. (2001) 'Copper Bioleaching Behaviour in an Aerated Heap', *International Journal of Mineral Processing*, 62, (1-4), pp. 257-269.
- LME (2015) *London Metal Exchange*. Available at: <http://www.lme.com/> (Accessed: 29-9-2015).
- Logan, M. V., Reardon, K. F., Figueroa, L. A., McLain, J. E. T. and Ahmann, D. M. (2005) 'Microbial Community Activities During Establishment, Performance, and Decline of Bench-Scale Passive Treatment Systems for Mine Drainage', *Water Research*, 39, (18), pp. 4537-4551.
- Loredo, J., Ordonez, A., Jardon, S. and Alvarez, R. (2011) 'Mine Water as Geothermal Resource in Asturian Coal Mining Basins (NW Spain)', *11th International Mine Water Association Congress*, Aachen, Germany, Document Transformation Technologies, pp. 177 - 182.
- Lund, J., Sanner, B., Rybach, L., Curtis, G. and Hellstrom, G. (2004) 'Geothermal (Ground Sourced) Heat Pumps: A World Overview', *GHC Bulletin*, September 2004, pp. 1 - 10.
- Macy, T. R., Kruse, N. A. and Stuart, B. J. (2015) 'Carbon Footprint Analysis of Source Water for Hydraulic Fracturing: A Case Study of Mine Water Versus Freshwater', *Mine Water and the Environment*, 34, (1), pp. 20-30.
- Matthies, R., Aplin, A. C., Boyce, A. J. and Jarvis, A. P. (2009) 'Is Bacterial Sulfate Reduction a Dominant Process for the Removal of Iron in Reducing and Alkalinity Producing Systems?', *8th International Conference on Acid Rock Drainage*, Skelleftea, Sweden, 22 - 26 June 2009. Swedish Association Of Mines, Minerals and Metal Producers, pp. 93.

- Matthies, R., Aplin, A. C. and Jarvis, A. P. (2010) 'Performance of a Passive Treatment System for Net-Acidic Coal Mine Drainage over Five Years of Operation', *Science of the Total Environment*, 408, (20), pp. 4877-4885.
- May, H. M., Helmke, P. A. and Jackson, M. L. (1979) 'Gibbsite Solubility and Thermodynamic Properties of Hydroxy-Aluminum Ions in Aqueous Solution at 25°C', *Geochimica et Cosmochimica Acta*, 43, (6), pp. 861-868.
- Mayes, W. M., Davis, J., Silva, V. and Jarvis, A. P. (2011) 'Treatment of Zinc-Rich Acid Mine Water in Low Residence Time Bioreactors Incorporating Waste Shells and Methanol Dosing', *Journal of Hazardous Materials*, 193, (0), pp. 279-287.
- Mayes, W. M. and Jarvis, A. P. (2011) 'Remediation of Aquatic Post-Industrial Inorganic Pollutants', in Jerome, O. N.(ed), *Encyclopedia of Environmental Health*. Burlington: Elsevier, pp. 789-800.
- Mayes, W. M., Jarvis, A. P., Coulon, P., Potter, H. A. B., Thorn, P., Fox, A., Watson, I. A., Hill, S. and Johnston, D. (2012) *Prioritisation on Abandoned Non-Coal Mine Impacts on the Environment: The Northumbria River Basin District*. Bristol: Environment Agency.
- Mayes, W. M., Johnston, D., Potter, H. A. B. and Jarvis, A. P. (2009a) 'A National Strategy for Identification, Prioritisation and Management of Pollution from Abandoned Non-Coal Mine Sites in England and Wales. I.: Methodology Development and Initial Results', *Science of the Total Environment*, 407, (21), pp. 5435-5447.
- Mayes, W. M., Potter, H. A. B. and Jarvis, A. P. (2009b) 'Novel Approach to Zinc Removal from Circum-Neutral Mine Waters Using Pelletised Recovered Hydrous Ferric Oxide', *Journal of Hazardous Materials*, 162, (1), pp. 512-520.
- Mayes, W. M., Potter, H. A. B. and Jarvis, A. P. (2010) 'Inventory of Aquatic Contaminant Flux Arising from Historical Metal Mining in England and Wales', *Science of the Total Environment*, 408, (17), pp. 3576-3583.
- Mayes, W. M., Potter, H. A. B. and Jarvis, A. P. (2013) 'Riverine Flux of Metals from Historically Mined Orefields in England and Wales', *Water, Air, & Soil Pollution*, 224, (2), pp. 1-14.
- McCauley, C. A., O'Sullivan, A. D., Milke, M. W., Weber, P. A. and Trumm, D. A. (2009) 'Sulfate and Metal Removal in Bioreactors Treating Acid Mine Drainage Dominated with Iron and Aluminum', *Water Research*, 43, (4), pp. 961-970.

- McGuinness, S. (1999) 'Research Paper: Treatment of Acid Mine Drainage.', *Science and Environment Section, House of Commons Library*, 99, (10).
- McGuinness, S. and Johnson, D. B. (1993) 'Seasonal Variations in the Microbiology and Chemistry of an Acid Mine Drainage Stream', *Science of the Total Environment*, 132, (1), pp. 27-41.
- McNabola, A., Coughlan, P. and Williams, A. P. (2014) 'Energy Recovery in the Water Industry: an Assessment of the Potential of Micro-Hydropower', *Water and Environment Journal*, 28, pp. 294-304.
- Meier, U. and Baumer, J. M. (1985) *Local Experience with Micro-Hydro Technology*. 3 ed St. Gallen: SKAT; ATOL.
- Mendez-Garcia, C., Pelaez, A. I., Mesa, V., Sánchez, J., Golyshina, O. V. and Ferrer, M. (2015) 'Microbial Diversity and Metabolic Networks in Acid Mine Drainage Habitats', *Frontiers in Microbiology*, 6, pp. 1-17.
- Mercier, G., Chartier, M. and Couillard, D. (1996) 'Strategies to Maximize the Microbial Leaching of Lead from Metal-Contaminated Aquatic Sediments', *Water Research*, 30, (10), pp. 2452-2464.
- Metcalf, P. J., Baker, W., Andrews, K., Atkinson, G., Bateman, I. J., Butler, S., Carson, R. T., East, J., Gueron, Y., Sheldon, R. and Train, K. (2012) 'An Assessment of the Nonmarket Benefits of the Water Framework Directive for Households in England and Wales', *Water Resources Research*, 48, (3), pp. n/a.
- Miles, L. D. (1962) 'Value Analysis and Engineering', *Presented at University of Michigan on 20 June 1962*.
- Moorhouse, A. M. L., Harris, R., Wyatt, L. M., Hill, S. and Potter, H. A. B. (2015) 'Up-Scaling from Trial to Operation: Practicalities of Construction and Permitting, Force Crag Mine', *10th International Conference on Acid Rock Drainage*. Santiago, Chile, 21 - 24 April 2015. Gecamin, pp. 1 - 11.
- Morin, D., Lips, A., Pinches, T., Huisman, J., Frias, C., Norberg, A. and Forssberg, E. (2006) 'BioMinE – Integrated Project for the Development of Biotechnology for Metal-Bearing Materials in Europe', *Hydrometallurgy*, 83, (1-4), pp. 69-76.
- Morin, D., Pinches, T., Huisman, J., Frias, C., Norberg, A. and Forssberg, E. (2008) 'Progress After Three Years of BioMinE—Research and Technological Development Project for a Global Assessment of Biohydrometallurgical

Processes Applied to European Non-Ferrous Metal Resources', *Hydrometallurgy*, 94, (1-4), pp. 58-68.

Morper, M. (1986) 'Anaerobic Sludge-A Powerful and Low-Cost Sorbent for Heavy Metals', in H. Eccles and S. Hunt(ed), *Immobilisation of Ions by Bio-sorption*. Horwood, pp. 91-99.

Mosher, J. (1994) 'Heavy Metal Sludges as Smelter Feedstock', *Engineering and Mining Journal*, 195, (9).

Motsi, T., Rowson, N. A. and Simmons, M. J. H. (2009) 'Adsorption of Heavy Metals from Acid Mine Drainage by Natural Zeolite', *International Journal of Mineral Processing*, 92, (1-2), pp. 42-48.

Moutsatsou, A., Gregou, M., Matsas, D. and Protonotarios, V. (2006) 'Washing as a Remediation Technology Applicable in Soils Heavily Polluted by Mining-Metallurgical Activities', *Chemosphere*, 63, (10), pp. 1632-1640.

Mukherjee, S. M. and Woods, H. J. (1953) 'X-ray and Electron Microscope Studies of the Degradation of Cellulose by Sulphuric Acid', *Biochimica et Biophysica Acta*, 10, (0), pp. 499-511.

Mulligan, C. N., Yong, R. N. and Gibbs, B. F. (2001) 'Remediation Technologies for Metal-Contaminated Soils and Groundwater: An Evaluation', *Engineering Geology*, 60, (1-4), pp. 193-207.

Nan, J., Han, D., Yang, M., Cui, M. and Hou, X. (2006) 'Recovery of Metal Values from a Mixture of Spent Lithium-Ion Batteries and Nickel-Metal Hydride Batteries', *Hydrometallurgy*, 84, (1-2), pp. 75-80.

Neculita, C.-M., Zagury, G. J. and Bussière, B. (2008a) 'Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: I. Effect of hydraulic retention time', *Applied Geochemistry*, 23, (12), pp. 3442-3451.

Neculita, C. M., Yim, G.-J., Lee, G., Ji, S.-W., Jung, J. W., Park, H.-S. and Song, H. (2011) 'Comparative Effectiveness of Mixed Organic Substrates to Mushroom Compost for Treatment of Mine Drainage in Passive Bioreactors', *Chemosphere*, 83, (1), pp. 76-82.

Neculita, C. M., Zagury, G. J. and Bussière, B. (2007) 'Passive Treatment of Acid Mine Drainage in Bioreactors using Sulfate-Reducing Bacteria', *Journal of Environmental Quality*, 36, (1), pp. 1-16.

- Neculita, C. M., Zagury, G. J. and Bussière, B. (2008b) 'Effectiveness of Sulfate-Reducing Passive Bioreactors for Treating Highly Contaminated Acid Mine Drainage: II. Metal Removal Mechanisms and Potential Mobility', *Applied Geochemistry*, 23, (12), pp. 3545-3560.
- Neville, K. (2007) *The Use of Mine Water Ochre in Artificial Soils*. thesis. Imperial College London.
- Nordwick, S., Zaluski, M., Park, B. and Bless, D. (2006) 'Advances in Development of Bioreactors Applicable to the Treatment of ARD', *7th International Conference on Acid Rock Drainage*. St Louis, MO, 26 - 30 March 2006. American Society of Mining and Reclamation, pp. 1410 - 1420.
- NRW, SEPA, NIEA and Environment Agency. (2015) 'Guidance on the classification and assessment of waste', *Technical Guidance WM3*, 1st edition.
- Nuttall, C. A. (1999) *Aquatic Zinc Pollution from Abandoned Mines: Assessment and Passive Treatment in the Nent Valley, Cumbria, UK*. thesis. University of Newcastle upon Tyne.
- Nuttall, C. A. and Younger, P. L. (1999) 'Reconnaissance Hydrogeochemical Evaluation of an Abandoned Pb – Zn Orefield, Nent Valley, Cumbria, UK', *Proceedings of the Yorkshire Geological and Polytechnic Society*, 52, (4), pp. 395-405.
- Nuttall, C. A. and Younger, P. L. (2000) 'Zinc Removal from Hard, Circum-Neutral Mine Waters Using a Novel Closed-Bed Limestone Reactor', *Water Research*, 34, (4), pp. 1262-1268.
- Ofgem (2015) *Tariffs that apply for Non-Domestic RHI for Great Britain*. Available at: <https://www.ofgem.gov.uk/environmental-programmes/non-domestic-renewable-heat-incentive-rhi/tariffs-apply-non-domestic-rhi-great-britain> (Accessed: 11-05-2015).
- Ofgem (2016) *Feed-in Tariff (FIT) Scheme*. Available at: <https://www.ofgem.gov.uk/environmental-programmes/feed-tariff-fit-scheme> (Accessed: 25-01-2016).
- Oliver, B. G. and Carey, J. H. (1976) 'Acid solubilization of sewage sludge and ash constituents for possible recovery', *Water Research*, 10, (12), pp. 1077-1081.

- Ortiz, I., San Román, F. and Galán, B. (2001) 'Kinetics of the Recovery of Cd from Highly Concentrated Aqueous Solutions by Non-Dispersive Solvent Extraction', *Chemical Engineering Journal*, 81, (1–3), pp. 129-136.
- Osanloo, M. and Ataei, M. (2003) 'Using Equivalent Grade Factors to Find the Optimum Cut-Off Grades of Multiple Metal Deposits', *Minerals Engineering*, 16, (8), pp. 771-776.
- Paish, O. (2002) 'Small Hydro Power: Technology and Current Status', *Renewable and Sustainable Energy Reviews*, 6, (6), pp. 537-556.
- Palágyi, Š., Salzer, P. and Mitro, A. (2006) 'Sorption, Desorption and Extraction of Cadmium from some Arable and Forest Soils', *Journal of Radioanalytical and Nuclear Chemistry*, 269, (1), pp. 103-113.
- Paques (2015) *THIOTEQ™ Metal*. Available at: www.paques.nl/products/other/thioteqmetal (Accessed: 10-02-2015).
- Paradelo, R., Villada, A., Devesa-Rey, R., Moldes, A. B., Domínguez, M., Patiño, J. and Barral, M. T. (2011) 'Distribution and Availability of Trace Elements in Municipal Solid Waste Composts', *Journal of Environmental Monitoring*, 13, (1), pp. 201-211.
- Parker, K. (2003) 'Mine Water Management on a National Scale - Experiences from the Coal Authority', *Land Contamination & Reclamation*, 11, (2), pp. 181-190.
- Pathak, A., Dastidar, M. G. and Sreekrishnan, T. R. (2009a) 'Bioleaching of Heavy Metals from Sewage Sludge by Indigenous Iron-Oxidizing Microorganisms Using Ammonium Ferrous Sulfate and Ferrous Sulfate as Energy Sources: A Comparative Study', *Journal of Hazardous Materials*, 171, (1–3), pp. 273-278.
- Pathak, A., Dastidar, M. G. and Sreekrishnan, T. R. (2009b) 'Bioleaching of Heavy Metals from Sewage Sludge: A Review', *Journal Environmental Management*, 90, (8), pp. 2343-2353.
- Pearce, N. J. G., Hartley, S., Perkins, W. T., Dinelli, E., Edyvean, R. G. J., Priestman, G., Bachmann, R. and Sandlands, L. (2007) 'Dealginated Seaweed for the Bioremediation of Mine Waters in Mid-Wales: Results of Field Trials from the 'BIOMAN' EU Life Environment Project', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Mako Edizioni, pp. 1-5.

- Peltier, E., Dahl, A. L. and Gaillard, J. (2004) 'Metal Speciation in Anoxic Sediments: When Sulfides can be Construed as Oxides', *Environmental Science & Technology*, 39, (1), pp. 311-316.
- Pennanen, T., Fritze, H., Vanhala, P., Kiikkilä, O., Neuvonen, S. and Bååth, E. (1998) 'Structure of a Microbial Community in Soil after Prolonged Addition of Low Levels of Simulated Acid Rain', *Applied and Environmental Microbiology*, 64, (6), pp. 2173-2180.
- Perez-Cid, B., Lavilla, I. and Bendicho, C. (1996) 'Analytical Assessment of Two Sequential Extraction Schemes for Metal Partitioning in Sewage Sludges', *Analyst*, 121, (10), pp. 1479-1484.
- Perkins, W. T., Hartley, S., Pearce, N. J. G., Dinelli, E., Edyvean, R. G. J., Priestman, G., Sandlands, L. and Bachmann, R. (2007) 'Laboratory Testing of the Adsorption Characteristics of Dealginated Seaweed: Results from the BIOMAN Project', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Mako Edizioni, pp. 249 - 253.
- Peters, R. W., Ku, Y. and Bahattacharyya, D. (1985) 'Evaluation of Recent Treatment Techniques for Removal of Heavy Metals from Industrial Wastewaters', *AIChE Symposium Series Separation of Heavy Metals*, 81, pp. 1605-1703.
- Peters, R. W., Li, W., Miller, G. and Brewster, M. D. (1989) 'Batch Chelant Extraction of Heavy Metals from Contaminated Soils', *4th Great Lakes Geoenvironmental Conference on In-situ Remediation of Contaminated Sites*. IL, USA, Document Transformation Technologies, pp. 241 - 253.
- Petersen, J. and Dixon, D. G. (2007) 'Modelling Zinc Heap Bioleaching', *Hydrometallurgy*, 85, (2-4), pp. 127-143.
- PIRAMID Consortium. (2003) *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters*. Newcastle Upon Tyne UK: University of Newcastle Upon Tyne
- Pomfret, J., Jarvis, A. and Liss, D. (2009) *Force Crag Minewater Scoping and Feasibility Study*. Unpublished report: Environment Agency
- Postgate, J. R. (1979) *The sulphate reducing bacteria*. Cambridge University Press.
- Preene, M. and Younger, P. L. (2014) 'Can You Take the Heat? – Geothermal Energy in Mining', *Mining Technology*, 123, (2), pp. 107-118.

- Qin, W., Li, W., Lan, Z. and Qiu, G. (2007) 'Simulated Small-Scale Pilot Plant Heap Leaching of Low-Grade Oxide Zinc Ore With Integrated Selective Extraction of Zinc', *Minerals Engineering*, 20, (7), pp. 694-700.
- Rabah, M. A. and El-Sayed, A. S. (1995) 'Recovery of Zinc and Some of its Valuable Salts from Secondary Resources and Wastes', *Hydrometallurgy*, 37, (1), pp. 23-32.
- Rafferty, K. (1999) 'Scaling in Geothermal Heat Pump Systems', *Unpublished report to the US Department of Energy, Idaho Operations Office*.
- Rafferty, K. (2003) 'Ground Water Issues in Geothermal Heat Pump Systems', *Ground Water*, 41, (4), pp. 408-410.
- Raikova, S., Smith-Baedorf, H., Bransgrove, R., Barlow, O., Santomauro, F., Wagner, J. L., Allen, M. J., Bryan, C. G., Sapsford, D. J. and Chuck, C. J. (2016) 'Assessing Hydrothermal Liquefaction for the Production of Bio-Oil and Enhanced Metal Recovery from Microalgae Cultivated on Acid Mine Drainage', *Fuel Processing Technology*, 142, pp. 219-227.
- Rapin, F., Tessier, A., Campbell, P. G. C. and Carignan, R. (1986) 'Potential Artifacts in the Determination of Metal Partitioning in Sediments by a Sequential Extraction Procedure', *Environmental Science & Technology*, 20, (8), pp. 836-840.
- Rauret, G., F. Lopez-Sanchez, J., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, P. (1999) 'Improvement of the BCR Three Step Sequential Extraction Procedure Prior to the Certification of New Sediment and Soil Reference Materials', *Journal of Environmental Monitoring*, 1, (1), pp. 57-61.
- Rawlings, D. E. (2002) 'Heavy Metal Mining Using Microbes', *Annual Review of Microbiology*, 56, (1), pp. 65-91.
- Rawlings, D. E., Dew, D. and du Plessis, C. (2003) 'Biomineralization of Metal-Containing Ores and Concentrates', *Trends in Biotechnology*, 21, (1), pp. 38-44.
- Rawlings, D. E. and Johnson, D. B. (2007) 'The Microbiology of Biomining: Development and Optimization of Mineral-Oxidizing Microbial Consortia', *Microbiology*, 153, (2), pp. 315-324.
- REALL. (2007) *Community Renewable Energy at Local Level: Whitfield Parish Hall*. Pamphlet.

- Reed, B., Carriere, P. and Moore, R. (1996) 'Flushing of a Pb(II) Contaminated Soil Using HCl, EDTA, and CaCl₂', *Journal of Environmental Engineering*, 122, (1), pp. 48-50.
- Reisman, D., Rutkowski, T., Smart, P. and Guskek, J. (2008) 'The Construction and Instrumentation of a Pilot Treatment System at the Standard Mine Superfund Site, Crested Butte, CO ', *National Meeting of the American Society of Mining and Reclamation*. Richmond, VA, USA, 14 - 19 June 2008. American Society of Mining and Reclamation, pp. 892 - 909.
- Renman, R., Jiankang, W. and Jinghe, C. (2006) 'Bacterial Heap-Leaching: Practice in Zijinshan Copper Mine', *Hydrometallurgy*, 83, (1-4), pp. 77-82.
- Ritcey, G. M. and Ashbrook, A. W. (1984.) *Solvent Extraction. Principles and Applications to Process Metallurgy. Part I* Amsterdam, The Netherlands: Elsevier Science Publishers.
- Roberts, M. (2011) *Technical Evaluation of the Potential for Harnessing Micro-hydroelectric Power from Abandoned Mine Water Discharges*. thesis. Newcastle University.
- Roijen, E. I. E. (2011) 'The Use of an Open-Loop Heat-Pump System to Heat Social Housing and an Office Building throughout the Town of Heerlen, the Netherlands', in Faull, M. L.(ed), *Heat Pump Technology Using Minewater*.
- Rose, A. W. (2006) 'Long-Term Performance of Vertical Flow Ponds - An Update', *7th International Conference on Acid Rock Drainage*. St Louis, MO, 26 - 30 March 2006. American Society of Mining and Reclamation, pp. 1704 - 1716.
- Rose, M. (2015) *An Investigation into the Options Available for Providing Small-Scale Hydropower at the Force Crag Abandoned Mine Site*. thesis. Newcastle.
- Rosenqvist, T. (2004) *Principles of Extractive Metallurgy*. Tapir Academic Press.
- Rotting, T. S., Ayora, C. and Carrera, J. (2007) 'Chemical and Hydraulic Performance of 'Dispersed Alkaline Substrate' (DAS) for Passive Treatment of Acid Mine Drainage with High Metal Concentrations', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2004. Mako Edizioni, pp. 255 - 259.
- Rötting, T. S., Cama, J., Ayora, C., Cortina, J.-L. and De Pablo, J. (2006) 'Use of Caustic Magnesia to Remove Cadmium, Nickel, and Cobalt from Water in Passive

Treatment Systems: Column Experiments', *Environmental Science & Technology*, 40, (20), pp. 6438-6443.

Rötting, T. S., Caraballo, M. A., Serrano, J. A., Ayora, C. and Carrera, J. (2008) 'Field Application of Calcite Dispersed Alkaline Substrate (Calcite-DAS) for Passive Treatment of Acid Mine Drainage with High Al and Metal Concentrations', *Applied Geochemistry*, 23, (6), pp. 1660-1674.

Rowan, J. S., Barnes, S. J. A., Hetherington, S. L., Lambers, B. and Parsons, F. (1995) 'Geomorphology and pollution: the environmental impacts of lead mining, Leadhills, Scotland', *Journal of Geochemical Exploration*, 52, (1-2), pp. 57-65.

RPA. (2013) 'River Derwent Catchment: Benefits Assessment Update', *Unpublished report*.

Rutkowski, T. (2013) 'Passive Treatment of Mining Influenced Wastewater at the Standard Mine Superfund Site, Crested Butte, Colorado, USA', *Mine Water Solutions*. Lima, Peru, April 15 - 17 2013. InfoMine, pp. n/a.

Sadegh Safarzadeh, M., Bafghi, M. S., Moradkhani, D. and Ojaghi Ilkhchi, M. (2007) 'A Review on Hydrometallurgical Extraction and Recovery of Cadmium from Various Resources', *Minerals Engineering*, 20, (3), pp. 211-220.

Sainju, U. M. (2006) 'Carbon and Nitrogen Pools in Soil Aggregates Separated by Dry and Wet Sieving Methods', *Soil Science*, 171, (12), pp. 937-949.

Salgueiro, M. J., Zubillaga, M., Lysionek, A., Sarabia, M. I., Caro, R., De Paoli, T., Hager, A., Weill, R. and Boccio, J. (2000) 'Zinc as an Essential Micronutrient: A Review', *Nutrition Research*, 20, (5), pp. 737-755.

Sand, W., Gehrke, T., Jozsa, P.-G. and Schippers, A. (2001) '(Bio)chemistry of bacterial leaching—direct vs. indirect bioleaching', *Hydrometallurgy*, 59, (2-3), pp. 159-175.

Sanner, B., Karytsas, C., Mendrinou, D. and Rybach, L. (2003) 'Current Status of Ground Source Heat Pumps and Underground Thermal Energy Storage in Europe', *Geothermics*, 32, (4-6), pp. 579-588.

Sapsford, D. J., Santonastaso, M., Thorn, P. and Kershaw, S. (2015) 'Conversion of Coal Mine Drainage Ochre to Water Treatment Reagent: Production, Characterisation and Application for P and Zn Removal', *Journal of Environmental Management*, 160, (0), pp. 7-15.

- Schade, H. (2015) 'Desk Study - Active Treatment Review (Force Cragg - Mine Water Treatment Plant)', *unpublished report*.
- Schippers, A., Breuker, A., Blazejak, A., Bosecker, K., Kock, D. and Wright, T. L. (2010) 'The biogeochemistry and microbiology of sulfidic mine waste and bioleaching dumps and heaps, and novel Fe(II)-oxidizing bacteria', *Hydrometallurgy*, 104, (3–4), pp. 342-350.
- Schlumberger Water Services. (2014) 'Diver Manual', November 2014 Edition, pp. 31.
- Seidel, H., Löser, C., Zehnsdorf, A., Hoffmann, P. and Schmerold, R. (2004) 'Bioremediation Process for Sediments Contaminated by Heavy Metals: Feasibility Study on a Pilot Scale', *Environmental Science & Technology*, 38, (5), pp. 1582-1588.
- SEPA. (2011) *Review of Metal Concentrations Data Held for Glengonnar Water and Wanlock Water, South Central Scotland*. Scottish Environment Protection Agency, pp: 19.
- Sharma, P., Vyas, S., Sharma, S. N., Mahure, N. V., Rustagi, A., Sivakumar, N. and Ratnam, M. (2010) 'Acid Mine Discharge–Challenges Met in a Hydro Power Project', *International Journal of Environmental Sciences*, 1, (6), pp. 1274 - 1282.
- Shin, S. M., Kim, N. H., Sohn, J. S., Yang, D. H. and Kim, Y. H. (2005) 'Development of a Metal Recovery Process from Li-ion Battery Wastes', *Hydrometallurgy*, 79, (3–4), pp. 172-181.
- Siegel, S. M., Siegel, B. Z. and Clark, K. E. (1983) 'Bio-Corrosion: Solubilization and Accumulation of Metals by Fungi', *Water, Air, & Soil Pollution*, 19, (3), pp. 229-236.
- Silva, J. E., Paiva, A. P., Soares, D., Labrincha, A. and Castro, F. (2005) 'Solvent Extraction Applied to the Recovery of Heavy Metals from Galvanic Sludge', *Journal of Hazardous Materials*, 120, (1–3), pp. 113-118.
- Singh, A. K., Hasnain, S. I. and Banerjee, D. K. (1999) 'Grain Size and Geochemical Partitioning of Heavy Metals in Sediments of the Damodar River – a Tributary of the Lower Ganga, India', *Environmental Geology*, 39, (1), pp. 90-98.

- Skilhagen, S. E., Dugstad, J. E. and Aaberg, R. J. (2008) 'Osmotic Power — Power Production Based on the Osmotic Pressure Difference Between Waters with Varying Salt Gradients', *Desalination*, 220, (1–3), pp. 476-482.
- Soares, H. M. V. M., Boaventura, R. A. R., Machado, A. A. S. C. and Esteves da Silva, J. C. G. (1999) 'Sediments as Monitors of Heavy Metal Contamination in the Ave River Basin (Portugal): Multivariate Analysis of Data', *Environmental Pollution*, 105, (3), pp. 311-323.
- Solisio, C., Lodi, A. and Veglio', F. (2002) 'Bioleaching of Zinc and Aluminium from Industrial Waste Sludges by Means of Thiobacillus Ferrooxidans', *Waste Management*, 22, (6), pp. 667-675.
- Song, H., Yim, G.-J., Ji, S.-W., Neculita, C. M. and Hwang, T. (2012) 'Pilot-Scale Passive Bioreactors for the Treatment of Acid Mine Drainage: Efficiency of Mushroom Compost vs. Mixed Substrates for Metal Removal', *Journal of Environmental Management*, 111, (0), pp. 150-158.
- Song, Y., Fitch, M., Burken, J., Nass, L., Chilukiri, S., Gale, N. and Ross, C. (2001) 'Lead and Zinc Removal by Laboratory-Scale Constructed Wetlands', *Water Environment Research*, 73, (1), pp. 37-44.
- Souza, A. D., Pina, P. S., Lima, E. V. O., da Silva, C. A. and Leão, V. A. (2007) 'Kinetics of Sulphuric Acid Leaching of a Zinc Silicate Calcine', *Hydrometallurgy*, 89, (3–4), pp. 337-345.
- Stumm, W. and Morgan, J. J. (1996) *Aquatic Chemistry*. 3 ed New York: Wiley and Sons.
- Su, W., Zhang, L., Tao, Y., Zhan, G., Li, D. and Li, D. (2012) 'Sulfate Reduction with Electrons Directly Derived from Electrodes in Bioelectrochemical Systems', *Electrochemistry Communications*, 22, (0), pp. 37-40.
- Sumner, J. A. (1948) 'The Norwich Heat Pump', *Proceedings of the Institution of Mechanical Engineers*, 158, (1), pp. 22-29.
- Teeri, T. T. (1997) 'Crystalline Cellulose Degradation: New Insight into the Function of Cellobiohydrolases', *Trends in Biotechnology*, 15, (5), pp. 160-167.
- Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) 'Sequential Extraction Procedure for the Speciation of Particulate Trace Metals', *Analytical Chemistry*, 51, (7), pp. 844-851.

The Coal Authority. (2014) 'Business Case: Force Crag Mine Water Treatment Scheme (Non-Coal)', *Unpublished report*.

The Coal Authority (2015a) *About The Coal Authority*. Available at: <https://www.gov.uk/government/organisations/the-coal-authority/about> (Accessed: 17-09-2015).

The Coal Authority. (2015b) *Annual Report and Accounts 2014-15*. London: Her Majesty's Stationery Office

The Coal Authority (2015c) *Treating Mine Water*. Available at: <https://www.gov.uk/government/policies/providing-regulation-and-licensing-of-energy-industries-and-infrastructure/supporting-pages/treating-mine-water> (Accessed: 17-09-2015).

Tichy, R., Grotenhuis, J. T. C., Rulkens, W. H. and Nydl, V. (1996) 'Strategy for Leaching of Zinc from Artificially Contaminated Soil', *Environmental Technology*, 17, (11), pp. 1181-1192.

Tomlinson, G. H. (2003) 'Acidic Deposition, Nutrient Leaching and Forest Growth', *Biogeochemistry*, 65, (1), pp. 51-81.

Trumm, D. and Ball, J. (2014) 'Use of Sulfate-Reducing Mussel Shell Reactors in New Zealand for Treatment of Acid Mine Drainage', *West Virginia Mine Drainage Task Force*. Morgantown, WV, USA, 25 - 26 March 2014. pp. 9.

Tsukamoto, T. K., Killion, H. A. and Miller, G. C. (2004) 'Column Experiments for Microbiological Treatment of Acid Mine Drainage: Low-Temperature, Low-pH and Matrix Investigations', *Water Research*, 38, (6), pp. 1405-1418.

Turan, M. D., Altundoğan, H. S. and Tümen, F. (2004) 'Recovery of Zinc and Lead from Zinc Plant Residue', *Hydrometallurgy*, 75, (1-4), pp. 169-176.

Turek, M. (2004) 'Electrodialytic desalination and concentration of coal-mine brine', *Desalination*, 162, (0), pp. 355-359.

Tuttle, J. H., Dugan, P. R. and Randles, C. I. (1969) 'Microbial Sulfate Reduction and Its Potential Utility as an Acid Mine Water Pollution Abatement Procedure', *Applied Environmental Microbiology*, 17, (2), pp. 297-302.

UK Parliament. (1991) *Water Resources Act*.

- Ure, A. M., Davidson, C. M. and Thomas, R. P. (1995) '20. Single and Sequential Extraction Schemes for Trace Metal Speciation in Soil and Sediment', in Ph. Quevauviller, E. A. M. and Griepink, B.(eds) *Techniques and Instrumentation in Analytical Chemistry*. Vol. 17 Elsevier, pp. 505-523.
- US Department of Energy. (2001) 'Small Hydropower Systems', *Pamphlet*.
- USEPA. (2002) 'Anaerobic Compost Constructed Wetlands System (CWS) Technology: Innovation Technology Report', *U.S. Environmental Protection Agency*.
- USEPA. (2011) 'Shining a Light on a Bright Opportunity ', *Developing Solar Energy on Abandoned Mine Lands*, Unpublished report.
- Uster, B., O'Sullivan, A., Ko, S., Evans, A., Pope, J., Trumm, D. and Caruso, B. (2015) 'The Use of Mussel Shells in Upward-Flow Sulfate-Reducing Bioreactors Treating Acid Mine Drainage', *Mine Water and the Environment*, 34, (4), pp. 442-454.
- Utgikar, V. P., Harmon, S. M., Chaudhary, N., Tabak, H. H., Govind, R. and Haines, J. R. (2002) 'Inhibition of Sulfate-Reducing Bacteria by Metal Sulfide Formation in Bioremediation of Acid Mine Drainage', *Environmental Toxicology*, 17, (1), pp. 40-48.
- Vaclav, P. and Gulikova, E. (2007) 'Humic Based Sorbent: Potential of Toxic Metal Removal from Mine Waters or Increase of Efficiency in Passive Mine Water Purification ', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Mako Edizioni, pp. 273 - 275.
- Valenzuela, F., Basualto, C., Tapia, C. and Sapag, J. (1999) 'Application of Hollow-Fiber Supported Liquid Membranes Technique to the Selective Recovery of a Low Content of Copper from a Chilean Mine Water', *Journal of Membrane Science*, 155, (1), pp. 163-168.
- Vegliò, F., Quaresima, R., Fornari, P. and Ubaldini, S. (2003) 'Recovery of Valuable Metals from Electronic and Galvanic Industrial Wastes by Leaching and Electrowinning', *Waste Management*, 23, (3), pp. 245-252.
- Verhoeven, R., Willems, E., Harcouët-Menou, V., De Boever, E., Hiddes, L., Veld, P. O. and Demollin, E. (2014) 'Minewater 2.0 Project in Heerlen the Netherlands: Transformation of a Geothermal Mine Water Pilot Project into a Full Scale Hybrid Sustainable Energy Infrastructure for Heating and Cooling', *Energy Procedia*, 46, (0), pp. 58-67.

- Villar, L. D. and Garcia, O. (2002) 'Solubilization Profiles of Metal Ions from Bioleaching of Sewage Sludge as a Function of pH', *Biotechnology Letters*, 24, (8), pp. 611-614.
- Vračar, R. Ž., Vučković, N. and Kamberović, Ž. (2003) 'Leaching of Copper(I) Sulphide by Sulphuric Acid Solution with Addition of Sodium Nitrate', *Hydrometallurgy*, 70, (1-3), pp. 143-151.
- Waksman, S. A. and Joffe, J. S. (1922) 'Microorganisms Concerned in the Oxidation of Sulfur in the Soil: II. Thiobacillus Thiooxidans, a New Sulfur-oxidizing Organism Isolated from the Soil', *Journal of Bacteriology*, 7, (2), pp. 239-256.
- Walton, K. C. and Johnson, D. B. (1992) 'Microbiological and Chemical Characteristics of an Acidic Stream Draining a Disused Copper Mine', *Environmental Pollution*, 76, (2), pp. 169-175.
- Warrender, R., Pearce, N., Perkins, W. T., Florence, K. M., Brown, A. R., Sapsford, D. J., Bowell, R. J. and Dey, M. (2011) 'Field Trials of Low-cost Reactive Media for the Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK', *Mine Water and the Environment*, 30, pp. 82 - 89.
- Warrender, R. and Pearce, N. J. G. (2007) 'Remediation of Circum-Neutral, Low Iron Waters by Permeable Reactive Media', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Mako Edizioni, pp. 289 - 293.
- Watson, I. (2007) 'Managing Mine Water in Abandoned Coalfields using Engineered Gravity Discharges', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Document Transformation Technologies, pp. 355 - 359.
- Watson, I. A., Taylor, K., Sapsford, D. J. and Banks, D. (2009) 'Tracer Testing to Investigate Hydraulic Performance of a RAPS Treating Mine Water in South Wales', *8th International Conference on Acid Rock Drainage*. Skelleftea, Sweden, 22 - 26 June 2009. Swedish Association Of Mines, Minerals and Metal Producers, pp. 1 - 10.
- Watzlaf, G. R. and Ackman, T. E. (2006) 'Underground Mine Water for Heating and Cooling using Geothermal Heat Pump Systems', *Mine Water and the Environment*, 25, pp. 1 - 14.
- Watzlaf, G. R., Kairies, C. L., Schroeder, K. T., Danehy, T. and Beam, R. (2002) 'Quantitative Results from the Flushing of Four Reducing and Alkalinity-

Producing Systems', *The West Virginia Surface Mine Drainage Task Force Symposium*. Morgantown, WV, USA, 16-17 April 2002. pp. 1-11.

Whysner, K., Figueroa, L. A., Petri, E. and Holmes, M. (2012) 'Economic Recovery of Zinc from Mining Influenced Water', *Colorado School of Mines*, unpublished presentation.

Wieber, G. and Pohl, S. (2008) 'Mine Water: A Source of Geothermal Energy – Examples from the Rhenish Massif', *10th International Mine Water Association Congress*. Karlsbad, Czech Republic, 2 - 5 June 2008. VSB – Technical University of Ostrava, pp. 113 - 116.

Wills, B. A. (2006) *Wills' Mineral Processing Technology*. Oxford: Butterworth-Heinemann.

Winfield, I. J. (2014) *Adult Vendace, Britain's Rarest Freshwater Fish, Found in Bassenthwaite Lake*. Available at: http://www.ceh.ac.uk/news/news_archive/adult-vendace-found-in-bassenthwaite-lake-2014-49.html (Accessed: 4-06-2015).

Winfield, I. J., Adams, C. E., Bean, C. W., Durie, N. C., Fletcher, J. M., Gowans, A. R. D., Harrod, C., James, J. B., Lyle, A. A., Maitland, P. S., Thompson, C. and Verspoor, E. (2013) 'Positive Steps for Conservation of the Vendace (*Coregonus Albula*), the U.K.'s Rarest Freshwater Fish', *Newsletter of the Freshwater Fish Specialist Group*, 1. , p.14-15.

Wingenfelder, U., Hansen, C., Furrer, G. and Schulin, R. (2005) 'Removal of Heavy Metals from Mine Waters by Natural Zeolites', *Environmental Science & Technology*, 39, (12), pp. 4606-4613.

Wu, H.-Y. and Ting, Y.-P. (2006) 'Metal Extraction from Municipal Solid Waste (MSW) Incinerator Fly Ash—Chemical Leaching and Fungal Bioleaching', *Enzyme and Microbial Technology*, 38, (6), pp. 839-847.

Yang, W., Zhou, J., Xu, W. and Zhang, G. (2010) 'Current Status of Ground-Source Heat Pumps in China', *Energy Policy*, 38, (1), pp. 323-332.

Yim, G., Ji, S., Cheong, Y., Neculita, C. M. and Song, H. (2015) 'The Influences of the Amount of Organic Substrate on the Performance of Pilot-Scale Passive Bioreactors for Acid Mine Drainage Treatment', *Environmental Earth Sciences*, 73, (8), pp. 4717-4727.

- Yoo, K., Sasaki, K., Hiroyoshi, N. and Tsunekawa, M. (2004) 'Fundamental Study on the Removal of Mn²⁺ in Acid Mine Drainage using Sulfate Reducing Bacteria', *Materials Transactions*, 45, (7), pp. 2422-2428.
- Younger, P. L. (1993) 'Possible Environmental Impact of the Closure of Two Collieries in County Durham', *Water and Environment Journal*, 7, (5), pp. 521-531.
- Younger, P. L. (2000) 'The Adoption and Adaptation of Passive Treatment Technologies for Mine Waters in the United Kingdom', *Mine Water and the Environment*, 19, pp. 85-97.
- Younger, P. L. (2002) 'The Importance of Pyritic Roof Strata in Aquatic Pollutant Release from Abandoned Mines in a Major, Oolitic, Berthierine-Chamosite-Siderite Iron Ore Field, Cleveland, UK', *Geological Society, London, Special Publications*, 198, (1), pp. 251-266.
- Younger, P. L. (2009) *Groundwater in the Environment: an Introduction*. Oxford: Blackwell.
- Younger, P. L., Banwart, S. A. and Hedin, R. S. (2002) 'Mine Water: Hydrology, Pollution, Remediation', *Kulwer Academic Publisher, Environmental Pollution*, Vol. 5, pp. 464 p.
- Younger, P. L., Coulton, R. H. and Froggatt, E. C. (2005) 'The Contribution of Science to Risk-Based Decision-Making: Lessons from the Development of Full-Scale Treatment Measures for Acidic Mine Waters at Wheal Jane, UK', *Science of the Total Environment*, 338, (1-2), pp. 137-154.
- Younger, P. L., Jayaweera, A., Elliot, A., Wood, R., Amos, P., Daugherty, A. J., Martin, A., Bowden, L., Aplin, A. C. and Johnson, D. B. (2003) 'Passive Treatment of Acidic Mine Waters in Subsurface-Flow Systems: Exploring RAPS and Permeable Reactive Barriers', *Land Contamination & Reclamation*, 11, (2), pp. 127-135.
- Younger, P. L. and Mayes, W. M. (2015) 'The Potential Use of Exhausted Open Pit Mine Voids as Sinks for Atmospheric CO₂: Insights from Natural Reedbeds and Mine Water Treatment Wetlands', *Mine Water and the Environment*, 34, (1), pp. 112-120.
- Yu, J. and Klarup, D. (1994) 'Extraction Kinetics of Copper, Zinc, Iron, and Manganese from Contaminated Sediment using Disodium Ethylenediaminetetraacetate', *Water, Air, & Soil Pollution*, 75, (3), pp. 205-225.

- Yu, M.-H., Jefferson, I. and Culshaw, M. G. (2009) 'Geohazards Caused by Rising Groundwater in the Durham Coalfield, UK.', *In: Culshaw, M. G., Reeves, H. J., Jefferson, I. & Spink, T. W. (eds). Engineering geology for tomorrow's cities.*, 367.
- Zagury, G. J., Kulnieks, V. I. and Neculita, C. M. (2006) 'Characterization and Reactivity Assessment of Organic Substrates for Sulphate-Reducing Bacteria in Acid Mine Drainage Treatment', *Chemosphere*, 64, (6), pp. 944-954.
- Zaluski, M. H., Trudnowski, J. M., Harrington-Baker, M. A. and Bless, D. R. (2003) 'Post-mortem findings on the performance of engineered SRB field-bioreactors for acid mine drainage control', *6th International Conference on Acid Rock Drainage*. Cairns, QLD, 12 - 18 July 2003. AusIMM, Carlton South, Victoria, Australia, pp. 12-18.
- Zamzow, K., Tsukamoto, T. K. and Miller, G. C. (2007) 'Biodiesel Waste Fluid as an Inexpensive Carbon Source for Bioreactors Treating Acid Mine Drainage (California-Nevada, United States)', *International Mine Water Association Symposium*. Cagliari, Italy, 27 - 31 May 2007. Mako Edizioni, pp. 295 - 298.
- Zhang, W. and Cheng, C. Y. (2007) 'Manganese Metallurgy Review. Part II: Manganese Separation and Recovery from Solution', *Hydrometallurgy*, 89, (3-4), pp. 160-177.
- Ziemkiewicz, P. F., Skousen, J. G. and Simmons, J. (2003) 'Long-term Performance of Passive Acid Mine Drainage Treatment Systems', *Mine Water and the Environment*, 22, (3), pp. 118-129.
- Zinck, J. (2005) 'Review of Disposal, Reprocessing and Reuse Options for Acidic Drainage Treatment Sludge', *MEND Report 3.42.3*.
- Zinck, J. and Griffith, W. (2013) 'Review of Mine Drainage Treatment and Sludge Management Operations', *MEND, CANMET-MMSL 10-058 (CR)*.

Publications Arising from Research

- Bailey, M. T. Gandy, C. J. and Jarvis, A. P (2016) 'Reducing Life-Cycle Costs of Passive Mine Water Treatment by Recovery of Metals from Treatment Wastes' *Annual Conference of the International Mine Water Association*, Leipzig, Germany, 11-15 June 2016. Curran Associates Inc.
- Bailey, M. T., Gandy C. J., Watson, I. A., Wyatt, L. W. and Jarvis, A. P. (2016) 'Heat Recovery Potential of Mine Water Treatment Systems in Great Britain', *International Journal of Coal Geology*, article in press.
- Bailey, M. T., Jarvis, A. P. and Gandy C. J., (2015) 'Characterization of Passive Treatment System Substrates and Potential for Zinc Recovery', *10th International Conference on Acid Rock Drainage* Santiago, Chile, 21-24 April 2015. Gecamin.
- Bailey, M. T., Moorhouse, A. M. L., Byrom, J. A. and Kershaw, S. (2013) 'Applications for Hydrous Ferric Oxide Mine Water Treatment Sludge: A Review', *International Mine Water Association Symposium*. Golden, Co, USA, 5-9 August 2013. Publication Printers, pp 519-524.
- Jarvis, A. P., Gandy, C. J., Bailey, M. T., Davis, J. E. and Orme, P. H. A. (2015) 'Metal Removal and Secondary Contamination in a Passive Metal Mine Drainage Treatment System', *10th International Conference on Acid Rock Drainage* Santiago, Chile, 21-24 April 2015. Gecamin.

Appendices

Appendices accompany this thesis in electronic format

- A. 'Bioreactor database' for treatment systems tackling zinciferous discharges
- B. Trial sieving of Nenthead substrate
- C. Total cell counts, using SYBR gold nucleic acid stain
- D. Nenthead substrate characterization data
 - Nenthead substrate sequential extraction data – sieved samples
 - Nenthead substrate sequential extraction data – spatial samples
- E. Nenthead substrate acid leaching data
 - Nenthead substrate chemical leach test data – variable acid concentration
 - Nenthead substrate chemical leach test data – variable pulp density
 - Recovery of metals from Nenthead substrate leach solutions
- F. Nenthead substrate bioleaching data
 - Nenthead substrate biological leach test data
- G. Force Crag treatment system performance data
 - Force Crag treatment system performance and metal accumulation data
- H. Force Crag treatment system life cycle cost scenarios