

REMEDIATION OF ABANDONED METAL MINE DRAINAGE USING DEALGINATED SEAWEED

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DECLARATION

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ABSTRACT

This thesis develops and demonstrates an innovative method for adsorbing metals from metal mine drainage in mid-Wales and northern Italy using dealginated seaweed (DS) as a biosorbent. The chemical composition of 15 mine drainages and two receiving waters in Wales was determined over a two year period in relation to precipitation and season. The waters were circum-neutral, iron-poor (<1 mg/L) but metal-rich, dominated by Zn (≤ 42 mg/L), Cu (≤ 188 $\mu\text{g/L}$), Cd (≤ 99 $\mu\text{g/L}$) and Pb (≤ 2.7 mg/L). The chemical composition varied throughout the year, but did not necessarily show clear seasonal variation, with Zn, Cd and Pb tending to show a winter maximum.

The physico-chemical adsorption characteristics of the DS were determined. Over 80 % of Zn, Cd and Pb were removed from solution within 15 minutes of contact; adsorption was not affected by pH (between 3.3 and 6.6) nor by additional elements in solution. The adsorption capacity of the DS was Pb > Cd > Zn. The main removal mechanisms were determined to be adsorption and ion exchange with Ca, Na, Mg released from the DS surface.

Treatment plants containing DS were deployed at three sites in mid-Wales and one site in Italy. In mid-Wales, Zn, Pb and Cd adsorption peaked within an hour (at ~98 %) associated with a significant release of Ca, Mg and Na. The DS adsorbed Pb > Cd > Zn, with the DS adsorbing ~1 % of its dry weight of Pb, ~0.01 % Cd and ~2 % Zn. The saturation of the DS was dependent on the mine drainage composition, with adsorption continuing for several months when low metal concentration (<1 mg/L) mine drainages were remediated. In Italy, acidic (~pH 2.5), metal-rich (≤ 120 mg/L Al, ≤ 420 mg/L Fe and ≤ 99 mg/L Cu) mine drainage required neutralisation and Fe-removal before entering the DS treatment plant to remove the remaining metals.

The treatment plants improved the quality of mine drainage and reduced their impact on receiving water courses; the plant was designed to be a practical, low-cost, solution which uses a waste product (from the alginate industry). This thesis demonstrated a novel method for remediation of neutral, low Fe waters, and is applicable as a final 'polish' when acidic, Fe-rich water has been neutralised and the Fe removed.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
Algavi _(c)	Algavi DS containing some carbonate particles
Algavi _(f)	Algavi DS containing minimal carbonate particles
ALD	Anoxic Limestone Drain
AMD	Acid Mine Drainage
BET	Brunauer, Emmett and Teller (surface area analysis)
BIOMAN	BIOsorption of Metals from Abandoned miNes
CADW	The historic environment service of the Welsh Assembly Government
DS	Dealginated seaweed
EC	European Commission
EQS	Environmental quality standards
EU	European Union
FT-IR	Fourier Transform – Infra Red spectrometer
G	L-guluronic acid residues
Girvan _(a)	Acid washed Girvan DS
Girvan _(r)	Untreated Girvan DS
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IR	Infra red
ISP	International Speciality Products
LLB	Limestone Leach Bed
M	D-Mannuronic acid residues
MilliQ	Millipore water with a specific resistance of 18 megaohms
NMR	Nuclear Magnetic Resonance

OLC	Open Limestone Channel
PCA	Principal Component Analysis
PRB	Permeable Reactive Barrier
r	Pearson product-moment correlations
RAPS	Rapid Alkalinity Producing Systems or Reducing and Alkalinity Producing System
RSD	Relative standard deviation
SAC	Special Area of Conservation
SCOOFI	Surface Catalysed Oxidation Of Ferrous Iron
SSSI	Site of Special Scientific Interest
SRB	Sulphate reducing bacteria
UV-VIS	UltraViolet-Visual Spectrophotometer
VFW	Vertical flow wetlands
WFD	Water Framework Directive

CHAPTER 1:

Introduction

The chemical composition of natural waters is derived from weathering products, atmospheric fallout and from anthropogenic sources, which include agriculture, forestry, urban development, industrial and domestic wastes (Leckie and James, 1974). Anthropogenic activities often release metallic pollutants into waters; the metals tend to persist indefinitely either being transported directly to the oceans, deposited and stored in floodplains or circulating until eventually accumulating through the food chain (Volesky and Holan, 1995), thus posing a severe threat to the environment, flora and fauna. Of particular concern are the metals released from mining (past and present) and smelting sites (Cortina *et al.*, 2003; Petty and Barker, 2004).

Worldwide, numerous adits, shafts, spoil tips and tailing dams remain long after mining activities have been abandoned (Runkel *et al.*, 2007). The mining and subsequent mineral processing often occupy only comparatively small areas; but their activities can modify and have a significant impact (visually and chemically) on the wider environment (National Rivers Authority, 1994; Antunes *et al.*, 2002).

The chemical composition of mine drainage waters is controlled by weathering and dissolution reactions between the host rock, ore minerals, groundwater and infiltration waters (Desbarats and Dirom, 2007). Mining introduces oxygen into the geological environment (which it would not normally have access to), for example through the adits that were driven into the mine to assist ore handling and mine drainage (Desbarats and Dirom, 2005) and within mine's spoil tips at the surface. Once within an oxygenated environment the ore minerals become unstable and the surface area available for erosion, weathering and dissolution is increased (Walder and Chavez, 1995; Clark *et al.*, 2001; Antunes *et al.*, 2002; Desbarats and Dirom, 2007). Infiltrating, oxygen-rich, waters flow through the mine and spoil tips on the surface, reacting with the sulphide ore minerals producing soluble metal salts (Clark *et al.*, 2001; Desbarats and Dirom, 2005). Evaporation within the mine can also concentrate the metals in standing water (Desbarats and Dirom, 2007). The resulting metal-rich waters drain through adits or spoil tips to the

surface (Desbarats and Dirom, 2005). This process is completely passive and can persist indefinitely unless mitigation or remediation occurs; therefore some of the worst effects of mining are related to mine drainage (Desbarats and Dirom, 2005; 2007), with the associated pollution persisting long after mining and/or smelting has ceased (Vivian and Massie, 1977).

The pollution caused by metal mining is not limited to mine and spoil drainage; fine-grained waste and metals within the spoil tips can be easily transported by fluvial and aeolian processes, leading to contamination of surrounding land and floodplains (Davies, 1987; Evans, 1991; Nimick and Moore, 1991; Antunes *et al.*, 2002; Dennis *et al.*, 2003). Once within the fluvial system the metals may not be permanently incorporated into the sediments, but may be released through biological and chemical means, both within the sediments and water column (Förstner and Kersten, 1988).

Within water courses the presence of metals is a major concern. Discharges from abandoned mines frequently cause river and local groundwater pollution (Bowell and Bruce, 1995; Younger, 1997; 2000a) and this has led to the implementation of rigorous environmental quality standards (EQS) being set by the European Union (EU) and local regulatory agencies (Kelly, 1988; Younger, 2000a). Worldwide, many mine sites require some degree of remediation of the resultant mine drainage (Clark *et al.*, 2001).

1.1 Legislation

The British Government has attempted to control water pollution through legislation since the 1860s. The first relevant Parliamentary Act was the Rivers Pollution Prevention Act of 1876 and since then various legislation has been introduced and new criminal offences created (Wolf *et al.*, 2002). The modern system of water quality control began with the Rivers (Prevention of Pollution) Act, 1951 which required all new industrial or sewage discharges to inland waters to have a licence. Existing discharges did not require a licence unless altered; although the Rivers (Prevention of Pollution) Act, 1961 required some discharges (operational prior to 1951) to gain a licence (Bell and McGillivray, 2000). Both these River Acts became obsolete with the introduction of the Control of Pollution Act,

1974. One of the first EU directives regarding water pollution; arguably the most important, was the Dangerous Substances Directive of 1976 (Bell and McGillivray, 2000).

Dangerous Substances Directive (74/464/EEC)

The purpose of the Dangerous Substances Directive was to reduce and/or eliminate the presence of various substances (with toxic, persistent, carcinogenic or bioaccumulative properties) from surface waters. The substances were separated into two lists: List 1- Black list and List 2 - Grey list. Black list substances were to be eliminated and regulated using the discharge consent system. In 1982 the EU identified 129 substances (mainly pesticides, organic solvents and a small number of metals) and adopted subsidiary 'daughter directives' which set standards for individual substances, for example, cadmium (Cd) (83/513) and mercury (Hg) (82/176 and 84/156). Substances on the Grey list were regulated by the Member States (rather than the EU) setting their own EQS. The Grey list contains a broad list of substances, including metals, to be reduced, for example zinc (Zn), iron (Fe), lead (Pb), copper (Cu), tin (Sn), nickel (Ni) and chromium (Cr). The EQS (for both the Black and Grey list) are separated into two parameters: standards which Member States must try to achieve (Guideline) and those standards which must be adhered to (Imperative).

The Water Act, 1989

The Water Act of 1989 fundamentally restructured the water industry. The National Rivers Authority was created as a wide ranging regulatory agency whose responsibilities included tackling water pollution (Bell and McGillivray, 2000). The Water Act introduced the procedure of setting water quality standards and objectives (the applicable sections are now found in section 82-84 of the Water Resources Act, 1991) which are dependent on the classification and use of the controlled waters. Numerous classification regulations were introduced under section 82, including Bathing Waters, Surface Water (River Ecosystem), Surface Waters (Fishlife), and most relevant to this thesis, Surface Water (Dangerous Substances) Regulations which brought into effect the Dangerous Substances Directive (76/464/EEC) and its daughter directives.

Water Resources Act, 1991

Water pollution law was consolidated under the Water Resources Act, 1991 and provides the main regulatory control framework relating to the prevention and control of water

pollution in England and Wales (Wolf *et al.*, 2002). Any industrial (including metal mines) or sewage discharge to controlled waters is managed through a series of consents gained from the National Rivers Authority (merged with Her Majesty's Inspectorate of Pollution to form the Environment Agency under the Environment Act, 1995); if a consent has not been granted or where the consent is exceeded then it is a punishable offence under the Water Resources Act, 1991 (section 85) if an owner or operator "*knowingly permits any poisonous, noxious or polluting matter or solid waste to enter any controlled waters.*" Abandoned mines, however, are not included (section 89) and an amendment of the Water Resources Act (by the 1995 Environment Act) meant that from 2000 an operator could no longer walk away from a mine, as they have to give the Environment Agency six months notice before they intended to abandon a mine or part of a mine; unfortunately this still does not cover historically abandoned mines.

One of the main weaknesses of the discharge consent scheme under the Water Resources Act, 1991 is that it only applies to specific identifiable discharges from a known location (point source); diffuse pollution can not be as easily controlled (Wolf *et al.*, 2002).

Water Framework Directive (2000/60/EC)

The Water Framework Directive (WFD) provides a major overhaul of the EU's water policy by introducing a single system of co-ordinated objectives to be met through integrated river basin management plans (Wilby *et al.*, 2006). Article 4 of the WFD states that the default environmental objectives are:

- Prevent deterioration in status for water bodies;
- Aim to achieve good ecological and chemical status by 2015;
- For water bodies that are designated as artificial or heavily modified, aim to achieve good ecological potential by 2015;
- To promote sustainable water consumption based on the long-term protection of available water resources;
- Comply with objectives and standards for protected areas where relevant; and
- Reduce pollution from priority substances and cease discharges, emissions and loss of priority hazardous substances.

The overriding objective is that Member States ensure that 'good' chemical and ecological status is achieved in all waters by the end of 2015.

The WFD will rationalize and replace seven of the original directives: the Surface Water and its two related Directives, the Freshwater Fish Directive, the Shellfish Water Directive the Groundwater Directive and the Dangerous Substances Directive. By 1990, only 18 of the identified 129 substances within the Black list had been regulated (through five daughter directives) and the EU ceased regulation of other substances because the regulation process was slow and ineffective. At present, the Dangerous Substance Discharges Directive (86/280/EEC) and its daughter directives, for example, Cd Discharges Directive (83/513/EEC) are still relevant, but the WFD requires a review of all daughter directives within two years of the WFD coming into force (ENV/191000/01) and after the 22nd December 2012 the daughter directives will no longer be applicable (COM(2006)397 final).

Article 16 of the WFD replaces the Dangerous Substances Directive and identifies priority substances (“*the progressive reduction of discharges, emission and losses of substances concerned*”) and a number of these are designated as priority hazardous substances (“*the cessation or phasing out of discharges, emissions and losses of substances*”) (ENV/191000/01). Article 16 also states the EU’s strategy for co-ordinated quality standards and emission controls of certain substances posing a risk to or via the aquatic environment (ENV/191000/01). The EU proposed a list of 33 priority substances in February 2000 (COM(2000)397 final) and aims for a high level of protection against risk to, or via the, aquatic environment by setting EQS (COM(2006)397 final). The EQS define the environmental objective of ‘good surface water chemical status’ and may be modified in view of ongoing risk assessment under other EU legislation (COM(2006)398 final). The EQS relevant to this thesis are shown in Table 1.1; and many of the standards vary according to the hardness of the water.

The Environment Agency’s Western Wales River Basin Management Plan details the current status of water bodies and the action plan which needs to be followed to implement the EU’s WFD. The management plan details actions to both improve and/or remediate metal mine waters:

- a) The implementation of best practice controls and remediation of abandoned mine sites by 2015. The driver for this action is the Dangerous Substances Directive (74/464/EEC);

- b) To produce and deliver a strategy for the implementation of best practice controls and remediation via the production of a methodology followed by the pilot and full scale remediation of selected priority sites by 2015, with an extended programme to 2027. The driver for this action is the Dangerous Substances Directive (74/464/EEC);
- c) An Environment Agency led project to investigate and remediate metal mine sites in Wales. The driver for this action is the Dangerous Substances Directive (74/464/EEC);
- d) The investigation of discharges from abandoned metal mines and prioritise sites for inclusion in agreement with metal mine partner organisations by 2015. The driver for this action is the Dangerous Substances Directive (74/464/EEC);
- e) The prevention of pollution where waters are contributing to potential EQS failures by 2015. The driver for this action is the WFD (2000/60/EC);
- f) To co-ordinate research and develop sustainable and integrated remediation options for: i) using heat from mine water, ii) alternatives for ochre, and iii) co-treatment of mine water and sewage; and
- g) Continue to investigate mine water impacts, ongoing remediation at priority sites and develop a long-term strategy for remediation in accordance with the metal mine strategy for Wales.

The restrictive legislation and knowledge of the problems caused by mine discharges has led to the remediation of the mine drainage waters before entry into their receiving water courses. The high cost and associated problems of conventional remediation techniques (for example, methods which are non-selective for the removal of dilute, though toxic, metals from waters) has led to the search and subsequent development of unconventional low-cost, efficient and simple methods for remediating mine drainage (Kuyucak and Volesky, 1988a; Marques *et al.*, 2000).

Table 1.1. Environmental Quality Standards for certain Black and Grey list elements.

Element	Fraction	Statistic	Unit	Matrix	Class	Value	Hardness (mg/L CaCO ₃)	Notes
Cd	Total	AA	µg/L	Fresh	I	1 5		a b
Cu	Dissolved	AA	µg/L	Fresh	I	1 6 10 28	0-50 >50-100 >100-250 >250	c, d
Fe	Dissolved	AA	µg/L	Fresh	I	1000		
Zn	Total	AA	µg/L	Salmonid	I	8 50 75	0-50 >50-100 >100-250	d
Ni	Dissolved	AA	µg/L	Fresh	I	50 100 150 200	0-50 >50-100 >10-200 >200	d
Pb	Dissolved	AA	µg/L	Salmonid	I	4 10 20	0-50 >50-150 >150	d, e, f
pH		95%		Fresh	I	6-9		

AA = Annual Average

95 % = 95 % of samples

I = Imperative

Notes: -

a = National network monitoring. Sediment standstill

b = Sediment standstill

c = Higher concentrations may be acceptable where the presence of organic matter may lead to complexation

d = Stricter values may be required to protect particularly sensitive flora and fauna

e = Where populations of breeding trout are present, the standard should be halved

f = If organic Pb is present, stricter values may be required

1.2 Research aims

The aim of the research described in this thesis is to develop a novel remediation technique for the removal of metals from the drainage waters of abandoned metal mine sites. During the past two decades, there has been a considerable amount of research investigating the use of biomass, especially waste products, as a tool for remediation i.e. as a biosorbent (Davis *et al.*, 2003). Using a waste product as a biosorbent is advantageous because it is usually produced in large quantities (Stirk and van Staden, 2000), can usually be acquired at a low cost, can offer a competitive alternative to conventional remediation techniques

(Bakkaloglu *et al.*, 1998) and the use of waste materials helps solve the disposal issue faced by the manufacturer.

The waste product used in this research for the remediation of mine drainage waters is dealginated seaweed (DS), which is a by-product from the alginate production industry. To date, only a small number of researchers have investigated the biosorptive properties of this material and it has previously only been used to remediate synthetic mine drainage within a laboratory environment (Wilson and Edyvean, 1993a; 1993b; Aderhold *et al.*, 1996; Williams *et al.*, 1997; 1998; Williams and Edyvean, 1997a; 1997b; Romero-Gonzalez *et al.*, 2000; 2001). This is explored in more detail in Chapter 5.

This research has four principal aims:

- Determine the chemical composition and temporal variation of drainage waters from abandoned mines in mid-Wales on a seasonal timescale. The mine drainage waters were collected over a two-year period (fortnightly during the first year and monthly during the second year) to determine the range and average concentration of elements and whether the concentration varies over a seasonal timescale. The mine drainage was collected from two sites approximately every 30 minutes to determine the element variation over a diurnal timescale.
- Characterise and optimise the physical and chemical conditions for the biosorption of metals by DS; the data will then be used to design a treatment plant.
- Deploy and monitor the performance of treatment plants containing DS (treating varying volumes of mine drainage) at various sites (circum-neutral mine drainage with differing chemical compositions) within mid-Wales.
- Investigate, whether, with modifications, the treatment plant can be used to treat acidic mine drainage at a site in Italy.

By concentrating on the aforementioned aims the anticipation is that this research will provide a novel remediation method for the drainage waters of abandoned metal mines using a low-cost biosorbent in a low-technology, low visual impact, low-maintenance

treatment plant. The treatment plant will be designed to enable the water courses, into which the remediated mine water flows, to comply with EQS set by the EU, see Table 1.1.

1.3 Study Sites

Two contrasting areas of Europe were selected for detailed study within this thesis: mid-Wales and Libiola in Italy. These sites were chosen for a number of reasons:

1) Both areas contain abandoned mine sites from which highly metalliferous mine drainage emanates, discharging into local water courses and causing pollution of those waters. The mine discharges are within steep sided valleys and not easily accessible, therefore conventional remediation techniques which normally require a large flat land area can not be used.

The mines within mid-Wales selected for study within this thesis were chosen partially in view of those mines which are listed in the Environment Agency's Metal Mine Strategy for Wales (Environment Agency, 2002). The Metal Mine Strategy describes 50 mines which have the greatest environmental impact on surface waters and have been prioritised for remedial work to reduce the contaminant loading of streams and rivers. The strategy includes the views of various stakeholders, including those interested in the historical, archaeological, mineralogical and biological aspects of the mines. This study concentrates on mines within Ceredigion as it contains 38 of the 50 mines contained within the strategy.

One of the big disadvantages of the Metal Mine Strategy is that where remedial works have already been carried out at mine sites, for example by levelling and covering the mine-spoil and re-vegetating the area, they are no longer considered within the Strategy. This seems somewhat of an oversight bearing in mind that at those mines, although the problem of wind blown dust from the spoil heaps may have been resolved, they may still contribute large concentrations of metals to the local waters. At Bwlch mine (grid reference: 70131 82581), for example, the spoil heaps have been levelled and re-vegetated, but the mine drainage still contributes ~30 mg/L of Zn at a flow rate of ~10 L/minute (average concentration between 2004 and 2006) to the Nant Silo (a tributary of the Afon Clarach) (see Chapter 4).

2) The two studied mining areas have different geologies. The geology of mid-Wales is dominated by Lower Palaeozoic turbiditic sandstones and mudstones with a mainly galena-sphalerite mineralisation, whereas the Italian mine site is associated with ophiolite outcrops with a mainly Cu-Fe sulphide mineralisation.

3) The abandoned mines discharge contrasting mine waters. The mine drainage waters from mid-Wales are slightly acidic to circum-neutral, Fe-poor and metalliferous, with elevated concentrations of Zn, Pb and Cu. The Libiola mine drainage waters are acidic, Fe- and metal-rich with elevated concentrations of Fe, Al and Cu.

4) The two different sites have varying climates. The selected sites in mid-Wales are located in upland areas (mostly above 300 m) and have an annual rainfall above 1000 mm per year (www.metoffice.gov.uk/climate/uk/averages/images/RainAnnual6190.gif). Western mid-Wales has a mild wet climate dominated by Atlantic weather systems and a predominant south-westerly air stream. The Libiola area has a Mediterranean climate with warm (25-30 °C) dry summers and cold (5-6 °C) wet winters (www.eurometeo.com/english/climate/city_LIMJ/id_Tmax/meteo_genoa-sestri%20italy). The local area has an average precipitation of 1200 mm per annum (Dinelli and Lombini, 1996).

1.4 Thesis structure

This thesis is divided into nine chapters. Following this introduction, the geology and mining history of mid-Wales are described plus a more detailed description of the mid-Wales study sites are discussed in Chapter 2. The field sampling and analytical techniques employed in this thesis are outlined in Chapter 3. The impact of mining on the environment and the variability of the chemical composition of the mine drainage water are detailed in Chapter 4. Chapter 5 introduces the concept of bioremediation and describes the DS which is used as a biosorbent. Chapter 6 investigates the metal adsorption capacity of the DS through a series of laboratory experiments. Chapter 7 investigates metal adsorption from abandoned metal mine drainage in mid-Wales using field trials. Chapter 8 explores the remediation of acid mine drainage and examines the adsorption of metals at a site in Italy.

The principal conclusions are summarised in Chapter 9, along with further associated research that could be conducted.

1.5 BIOMAN

The work reported in this thesis expands on research conducted as part of a three-year (between 2003 and 2006) EU-LIFE Environment project (LIFE03 ENV/UK/000605) called “BIOsorption of Metals from Abandoned miNes” (or BIOMAN).

The project built upon existing research and expertise across the EU to demonstrate an innovative method for the biosorption of hazardous and toxic metals from waters draining from abandoned metal mines (both circum-neutral, Fe-poor, metal-rich waters and acidic, Fe- and metal-rich mine waters). The overall aim of the project was to improve the quality of the mine drainage water and reduce its impact on the receiving water course i.e. the waters comply with the EU’s EQS. The chemical composition of the mine drainage water, from a number of sites, in relation to the seasons was determined during the first year; these data were then used to select sites for treatment. The physico-chemical and adsorption characteristics of DS were determined. Using the mine drainage and DS data, a treatment plant was designed and then deployed and monitored at several mine sites. The treatment plant was designed to be a practical low-cost, low-technology and low-maintenance, which would offer potential as a best available technique not entailing excessive cost.

The BIOMAN project involved three partners:

Partner 1: Aberystwyth University (Manager of the project). Researchers from the Institute of Geography and Earth Sciences provided the chemical expertise and knowledge of the mine drainage problems in mid-Wales.

Partner 2: University of Bologna. Researchers from the School of Earth and Geoenvironmental Sciences provided the mineralogical expertise and a detailed knowledge of the mine drainage problems in Italy, especially the Libiola mine complex.

Partner 3: University of Sheffield. Researchers from the School of Chemical and Process Engineering provided the engineering and manufacturing expertise i.e. the design and build of the treatment plant and the investigation of DS using analytical equipment not available

at Aberystwyth University (i.e. Fourier Transform-Infra Red spectrometer (FT-IR), Brunauer, Emmett and Teller (BET) surface area analysis and grain size analysis).

The project was separated into eight tasks:

- 1) Project management
 - Develop a management model and detailed work plan for the partners
- 2) Preliminary site investigations and initial on-site trials
 - Desk study to identify target sites, and select sites for mine drainage sampling
 - Evaluation of the physico-chemical parameters of mine drainage water for one year
 - Installation and evaluation of the DS only treatment plant (to treat 1 L/minute) (designed by the University of Sheffield)
- 3) Small scale testing
 - Define the optimum physico-chemical conditions for metal adsorption from mine waters
 - Determine the adsorption characteristics of DS in mixed element solutions
 - Define the optimum physico-chemical conditions for removing high dissolved Fe from mine waters (by the University of Bologna)
- 4) Pilot treatment plant design and build
 - Compare the results from the DS only treatment plant with the small scale testing
 - Compile and evaluate the data to produce design constraints for the pilot treatment plant
 - Design and build the pilot treatment plant to treat 10 L/minute (by the University of Sheffield)
- 5) Pilot treatment plant field trials and evaluation
 - Install and monitor the pilot treatment plant
 - Relocate the pilot treatment plants to two mines in a more extreme climate and monitor the performance
 - Modify the treatment plant if necessary (by the University of Sheffield)
- 6) Design and build of a large scale demonstration plant
 - Design and build a large scale demonstration plant, using the results from the previous plants to treat 100 L/minute (by the University of Sheffield)
- 7) Field operation of the large scale demonstration plant
 - Install and monitor the treatment plant
 - Demonstrate the operation of the treatment plant through field workshops

8) Reporting and dissemination

- To compile the data, produce reports, present the findings at national and international conferences, produce DVDs of the treatment plants and to disseminate the findings to a non-technical audience.

Throughout the BIOMAN project, the author of this thesis was employed as a junior research scientist. The role within the project was to:

- Compile the desk study detailing the mid-Wales mine sites
- Sample and analyse the drainage waters from the selected mines (3 primary and 2 reserve mines) every fortnight for one year
- The preparation of the DS before use
- Conduct laboratory batch and column experiments to determine the physico-chemical characteristics of the DS and analyse the results
- Assist in the installation of the DS treatment plant
- Monitor the DS treatment plant at the selected sites and analyse samples
- Compile the collected data from the laboratory experiments and field trials
- Assist in the preparation of reports
- Prepared papers for presentation at national and international conferences
- Prepared a report for a non-technical audience
- Design and produce a related website (www.aber.ac.uk/bioman/)

The EU-LIFE Environment project was a demonstration project and therefore the main aim was to prove that the idea of using dealginated seaweed to remediate metal mine drainage worked; but not to examine the scientific reasoning, which this thesis examines.

CHAPTER 2:

Study Site: The mid-Wales orefield and its mining history

Metalliferous ores have been mined in every county in Wales, to varying extents (Rees, 1969); the county with the longest mining history and which was one of the most productive was Ceredigion, which included the heart of the mid-Wales orefield (Foster-Smith 1979; Carr and Schöne, 1993). The mid-Wales orefield produced over 457,221 tonnes of Pb ore, 142,247 tonnes of Zn ore and 80 tonnes of silver (Ag) since records began in 1845 (www.wales-underground.org.uk/llywernog.shtml). These figures are however certain to be a gross underestimation of the total produced, as much of the mining had already occurred before official returns were kept (Bick, 1978; Mason, 1997).

2.1 Geology of mid-Wales

All the ores worked in the mid-Wales orefield (Figure 2.1), near Aberystwyth, were obtained from deposits which occur in Lower Palaeozoic rocks (Foster-Smith, 1979). These Lower Palaeozoic rocks are dominated by turbiditic sandstone and mudstones comprised of the youngest series of the Ordovician (Ashgill) and the oldest series of the Silurian (Llandovery), see Figure 2.2 and 2.3. A detailed geological and mining history of the mid-Wales orefield can be found in Appendix 1.

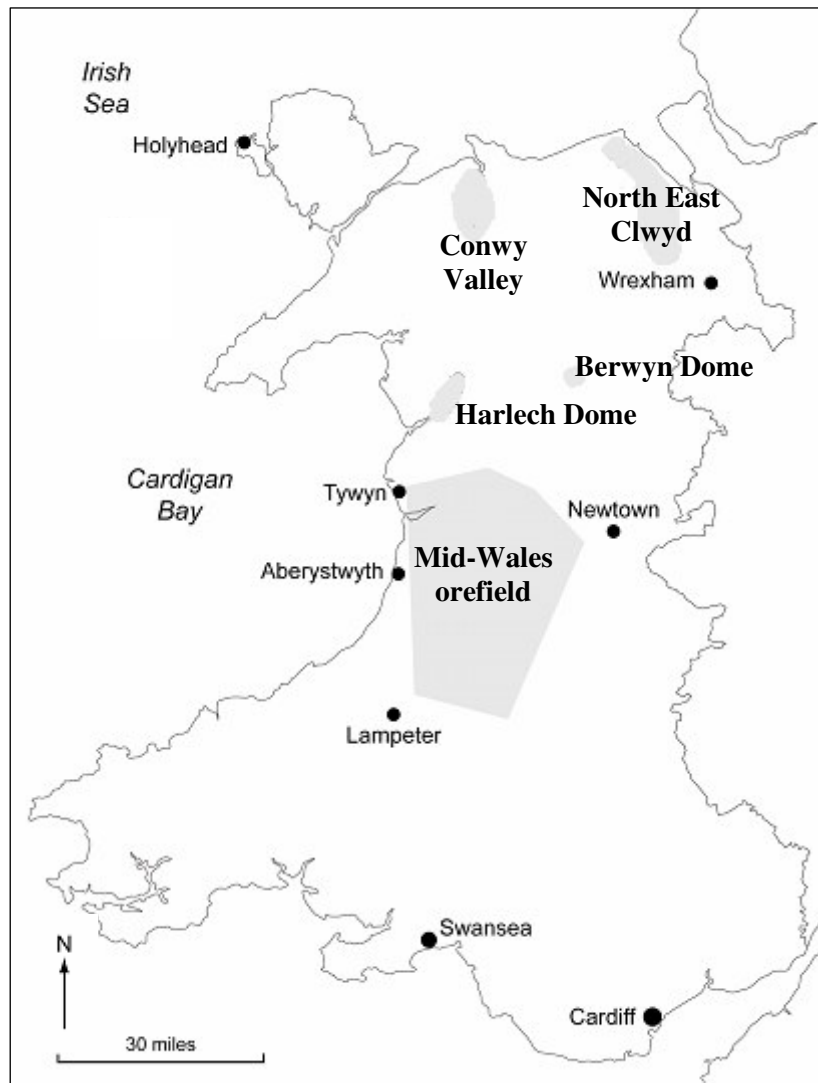
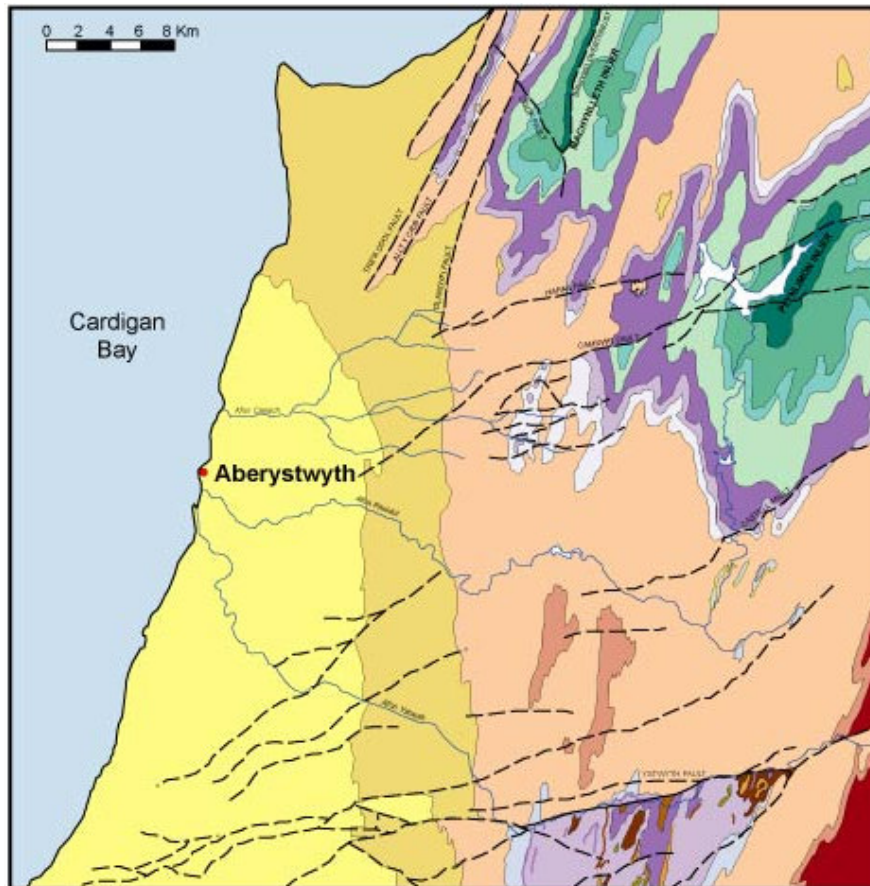


Figure 2.1. Generalised location of the main orefields in Wales.
After: Fuge *et al.* (1993) and www.geologywales.co.uk/centralwales.htm



Key

North and East of Aberystwyth

Ordovician (Ashgill series)

Nant-y- Môch Fm. To Bryn glâs Fm.

Silurian (Llandovery series) –

Cwmere Fm. to Aberystwyth Grits Fm.

South and East of Aberystwyth

Silurian (Llandovery series)



----- Fault - - - - - River

Figure 2.2. Geological map of mid-Wales.

Source: British Geological Survey: Sheet E163 (1984) (Country between Aberystwyth and Machynlleth) and Sheet E178 (1994) (Country between Llanilar and Rhayader).

Compiled by A. Moorhouse

Series and Stages		Old Formation Name*	New Formation Name	Formation Thickness
SILURIAN Llandovery	Upper (Telychian Stage)	Frongoch Formation	Aberystwyth Grits Formation	240 m seen
			Borth Mudstones Formation	Up to at least 350 m
			Devil's Bridge Formation	10 – 600 m
	Middle (Aeronian Stage)		Cwmsymlog Formation	0 – 140 m
	Derwenlas Formation		20 – 80 m	
	Lower (Rhuddian Stage)		Gwestyn Formation	Cwmere Formation
ORDOVICIAN Ashgill		Van Formation	Bryn-glâs Formation	30 – 195 m
			Drosgol Formation	290 – 405 m
			Nant-y-Môch Formation	≥ 280 m

Figure 2.3. Summary of late Ordovician and early Silurian Stratigraphy in the Aberystwyth area. The shaded cells represent the Formations containing the majority of the mineralisation in the mid-Wales orefield.

Modified from Cave and Hains, 1986; after Jones, 1922

* Formation names used within Jones, 1922; Raybould, 1974 and Foster-Smith, 1979

2.1.1 Geological formations within the mid-Wales orefield

Ordovician

The rocks assigned to the Ordovician series are sedimentary, consisting of siltstones, mudstones and sandstones. Within the Nant-y-Môch and Drosgol Formations layered siltstones, mudstones and sandstones occur, though in the Bryn-glâs Formation massive mudstones, with only rarely occurring massive arenites, pebbly or feldspathic mudstones, are present. The Ordovician rocks occur mainly in two inliers, one around Plynlimon (an estimated 700 m are exposed) and the other south of Machynlleth, see Figure 2.2 (Cave and Hains, 1986).

Silurian

Silurian rocks crop out over by far the largest part of the mid-Wales orefield and appear to be perfectly conformable with the underlying rocks. The multilayered sequences and parallel cleavage of the Silurian rocks provide a sharp contrast to the massive mudstones of the Bryn-glâs Formation. At the beginning of the Silurian, there is a 5 – 25 m occurrence of a homogeneous mudstone, but this is soon replaced by the very dark shales of the Cwmere Formation; these dark shales contain an abundance of pyrite and occasional thin beds of sandstone (Cave and Hains, 1986). In contrast to the Cwmere Formation, the subsequent Formations are predominately multilayered turbiditic siltstones, mudstones and sandstones. The Silurian Formations are comprised of sequences which generally coarsen upwards (Cave and Hains, 1986).

2.1.2 Development of the Welsh Basin

In England and Wales, the Lower Palaeozoic was characterised by the movement of the Eastern Avalonia micro-continent (James, 2005). During the Ordovician, Avalonia detached from the southern continent of Gondwana and headed north towards Laurentia; causing the area which is now Wales to experience periods of extension leading to the formation of the Welsh Basin (Brenchley and Rawson, 2006) which is approximately 200 by 100 km in size (Mason, 1997).

At the Ordovician-Silurian boundary there was a large and rapid glacio-eustatic sea level fall and rise associated with the southern Gondwana ice cap (Brenchley and Rawson, 2006). The expansion of the ice cap in the late Ordovician was marked by a

fall in sea level (Brenchley *et al.*, 2006) possibly giving rise to a marine regression and a complete retreat of the sea from the eastern basinal shelf (Cave and Hains, 1986). The melting of the Gondwana ice cap occurred in the Silurian with a rapid rise in sea level (Doyle *et al.*, 1994; Loydell, 1998) giving rise to the anoxic slope-apron mudstone of the Cwmere Formation (Brenchley *et al.*, 2006; Cherns *et al.*, 2006). The slope-apron system (westward thinning deposits of turbiditic and hemipelagic mudstones) was active between the Nant-y-Môch and Devil's Bridge Formations (Cherns *et al.*, 2006). The slope-apron system was replaced by a southerly sourced sandstone lobe system of the Telychian. The oblique collision of Avalonia with Laurentia caused the basin to experience a significant period of extensional faulting and subsidence (Cherns *et al.*, 2006) instigating a major alteration of the sediment dispersal patterns, first recorded within the Aberystwyth Grits Formation (Wilson *et al.*, 1992).

2.1.3 Structure

The major folding and cleavage formation is commonly thought to have occurred by the end of the Silurian (Cave and Hains, 1986; Robinson and Bevins, 1986). The Lower Palaeozoic rocks developed a close succession of north north east trending anticlines and synclines (Raybould, 1974; Cave and Hains, 1986). Small folds commonly occur on the thinly multi-layered sequences in the Silurian, but similar Ordovician lithologies are unaffected (Cave and Hains, 1986).

A large number of faults occur in the Lower Palaeozoic rocks of the Welsh Basin. The faults are grouped into two main classes: east north east faults and east west faults. The majority of large faults in the area trend approximately east north east to west south west in the south and in the north their course alters to mainly trend east to west (Cave and Hains, 1986); within Jones (1922) and Foster-Smith (1979) they are noted as east west trending veins. Less frequent are the minor north north west faults that occur in the north west of the area (Cave and Hains, 1986). Both of these faults contain mineralised veins which, economically, are the most important faults (Jones, 1922).

2.2 Mineralisation

The mid-Wales orefield has a complex history of mineralisation; mineralised lodes occur in the east north east trending normal faults and breccia zones of the area (Raybould, 1974; Cave and Hains, 1986). Mason (1994; 1997) separated the mineralisation into two groups – A1 ‘early complex’ and A2 ‘late simple’ and these are reviewed below. The two mineralisation types vary considerably in both texture and mineralogy and have both been further divided into six assemblages (a-f). The principal metals mined from the ‘early complex’ group were Pb, Cu and Ag; Zn was a minor metal in most deposits. Important A1 deposits occur at Esgair Hir, Esgair Ffraith, Daren and Eaglebrook. The A1-c assemblage (polymetallic) was the most widespread and of great economic importance, as the mineralization was highly argentiferous, with Daren and other mines in the area containing 800–1000 mg of Ag per kg of Pb concentrate. Mines working other assemblages typically contained ≤ 150 mg Ag per kg of Pb concentrate. The most important sulphides of this assemblage are galena and chalcopyrite which occur within quartz-cemented breccias. Ferroan dolomite (A1-e assemblage) is also very widespread and fills the quartz cavities in the A1-c assemblage. At Daren, ferroan dolomite overgrows previous assemblages; whereas it occurs in large amounts and is coarsely crystalline, cementing brecciated A1-c assemblages at Esgair Ffraith and Eaglebrook.

The ‘late simple’ mineralization occurs both in previously unmineralized and reactivated ‘early complex’ mineralized lodes. This mineralisation type occurs extensively and the A2-a assemblage (sphalerite-galena-quartz) was the major source of Pb and later Zn in mid-Wales. Important ‘late simple’ deposits occur at Ystumteun and Frongoch. At Ystumteun, the A2-b chalcopyrite-galena-quartz assemblage occurs (minus ullmanite) and at the end of the primary mineralisation iron-sulphide mineralisation (A2-f assemblage) deposited coarsely crystalline marcasite and pyrite (Mason, 1997). Not all mines within this thesis have been designated as having ‘early complex’ or ‘late simple’ mineralogy; but generally ‘early complex’ mineralisation occurs in the mines between Talybont and Goginan and ‘late simple’ mineralisation between Goginan and the Ystwyth Valley; although many of the mineralised veins contain both groups because of recurring tectonic and mineralisation events.

The mid-Wales orefield mineralisation was related to periodic tectonic activity with fluid flow, which generated repeat fracturing and brecciation. Mason (1994; 1997) established, using tectonic and isotopic evidence, that the ‘early complex’ and ‘late simple’ mineralisation occurred in two separate events. The ‘early complex’ mineralisation occurred in faults caused by relaxation, as maximum Caledonian compression started to extend (Foster-Smith, 1979; Mason, 1994; 1997). Water trapped as sediment deposition occurred was released when the Welsh Basin was inverted. This water leached into solution metals (as bisulphide complexes) from the surrounding sediments and precipitated the minerals as an area of low pressure was encountered, for example, as hydraulic extension of the faults occurred (Raybould, 1974). The rising hydrothermal fluids assisted in the development of the fractures (Raybould, 1974; Cave and Hains, 1986). The mineralisation occurred at the same time as the tectonic activity, although, as seen at Frongoch mine, not all of the tectonic activity resulted in mineralised lodes (Mason, 1997).

The ‘late simple’ mineralisation was also caused by an extensional stress regime, but occurred in the late Devonian, early Carboniferous Variscan (Hercynian) Orogeny. The Variscan Orogeny led to the final assemblage of Pangaea, with the collision of Gondwana and Laurussia (Doyle *et al.*, 1994). The ‘late simple’ mineralisation contains far greater concentrations of Zn, calcite and iron sulphides and Barium (Ba) minerals are locally abundant. As the metals leached by the basinal waters were used to form the ‘early complex’ mineralisation, another source of metals is required for the ‘late simple’ mineralisation. The most likely source is the downward percolation of precipitation. Connate brines migrating from the Cardigan Bay basin are the potential source of the third, Pennine Style phase of mineralisation (Mason, 1994).

The majority of the mines occur between the Derwenlas Formation and the Devil’s Bridge Formation (Cave and Hains, 1986), the “Frongoch Formation” of various authors (Jones, 1922; Raybould, 1974; Foster-Smith, 1979), see Figure 2.3. Raybould (1974) suggested that a powerful pressure drop may have occurred when the fractures moved from the pyritous mudstones of the Cwmere Formation to the more brittle siltstones of the Derwenlas Formation, therefore there are very few mines found working the dark pyritous shales of the Cwmere Formation. The mineralised lodes are frequently related to anticlinal axes and tend to be richer where the faults alter their

course (Raybould, 1974; Cave and Hains, 1986). The ore bodies tend to be enriched or more concentrated both horizontally and vertically, in the immediate area surrounding the junction of two or more lodes at an acute angle. There are a number of variations whereby two lodes intersect including the splitting of a single lode, which occurs at Esgair Hir; and the intersection of two independent lodes, for example at Bwlch and the Comet and Kingside Lodes at Cwmystwyth (Jones, 1922).

The most common association in the mineralised lodes is between sphalerite and galena (Raybould, 1974) or their alteration products, with minor or trace amount of gold (Ag), arsenic (As), manganese (Mn), bismuth (Bi), selenium (Se), antimony (Sb), Co, Au Hg, Cu, Fe, Cd, and Ni (Foster-Smith, 1979; Mason, 1997). Within the lodes quartz is ubiquitous and is the major gangue mineral in the deposit (with minor amounts of calcite). Raybould (1974) assumed that the quartz precipitated throughout the mineralisation process. The mineralised fault zones may contain several parallel ribs of mineralisation with country rock between them, and this country rock may also contain small mineralised lodes (Foster-Smith, 1979). Each rib of mineralisation was determined by the miner to be a single lode, and was named accordingly, even though it occurred within the limits of a single fault. At Esgair Hir, for example, the fault is of considerable width and successive mining companies found new mineralised lodes alongside previous workings (Jones, 1922). More specific details of the geology of the individual mine sites are given in Chapter 2.4.

2.3 Mining history of Ceredigion

Metalliferous ores in Ceredigion have been worked almost continuously from the Bronze Age to the beginning of the nineteenth century. The industry was most active during the eighteenth and nineteenth centuries during which, it was sporadically the largest producer of Pb, Cu and Zn ores in the world (Richardson, 1974; Foster-Smith, 1979; Fuge *et al.*, 1994).

Bronze Age peat and charcoal samples (radiocarbon dates of 1900-1200 B.C.) have been found in opencast workings at Cwmystwyth (references within Ixer and Budd, 1998) and evidence of Roman mining has been found at Cwmystwyth and Roman coins

were found in the spoil tips at Goginan (Lewis, 1967). When the Romans departed, mining rapidly declined as did the demand for the metals and mining occurred on a relatively small scale. Mining increased again until the fifteenth century when it declined (Lewis, 1967; Environment Agency, 2002).

Mining increased again during the sixteenth and seventeenth centuries as Cu and Pb were required for the production of bronze and Ag was required to make coins (Pearce and Armfield, 1998). From 1690 to the 1720s there were few operational mines, though the industry started to recover in the 1730s with the discovery of a new lode at Old Daren and it was linked with the increase in independent mining companies (Lewis, 1967; Burt, 1984); and by the end of the 1750s there was a strong demand for Pb (Burt, 1984; Bick, 2004). The mining industry, however, did not fully recover until the 1770s with an increase in both foreign and domestic markets (Burt, 1984). The increase in mining in the latter part of the eighteenth century in Wales and parts of England and Scotland made Great Britain the largest producer of Pb ore in the world (Pearce and Pearce, 1993). Mining decreased again in the 1790s as shallow deposits were exhausted and more investment was needed before deeper ores could be raised (Lewis, 1967).

The British Pb mining industry was slow to recover after the Napoleonic Wars; though in Europe, especially Spain and Germany, the mining industry quickly expanded (Pearce and Pearce, 1993). Until the increase of Pb prices in 1834, many of the mines in the mid-Wales orefield were inactive and many miners left the area (Lewis, 1967). The increase and stability in Pb prices caused a rapid expansion of mining from the 1830s to the 1880s (Lewis, 1967; Burt *et al.*, 1985). The expansion was partially caused by the interest of English (mainly Cornish) workers with an influx of skills, capital and improved technology, for example, compressed air drills and ore-dressing techniques (Burt *et al.*, 1985; Pearce and Armfield, 1998).

The decline of Pb mining began in the 1870s, partially because of falling Pb prices, but also because the known ore deposits had been worked (North, 1962; Pearce and Pearce, 1993). Another major contributor to the downfall of the mining industry was the discovery of easily worked Pb and Cu ores in the 1880s at Broken Hill in Australia, Leadville in the USA and in Spain. It was more economical to import these ores, rather

than mine them in Wales, as a result the Welsh mining industry collapsed (Foster-Smith, 1979; Pearce and Armfield, 1998; Environment Agency, 2002).

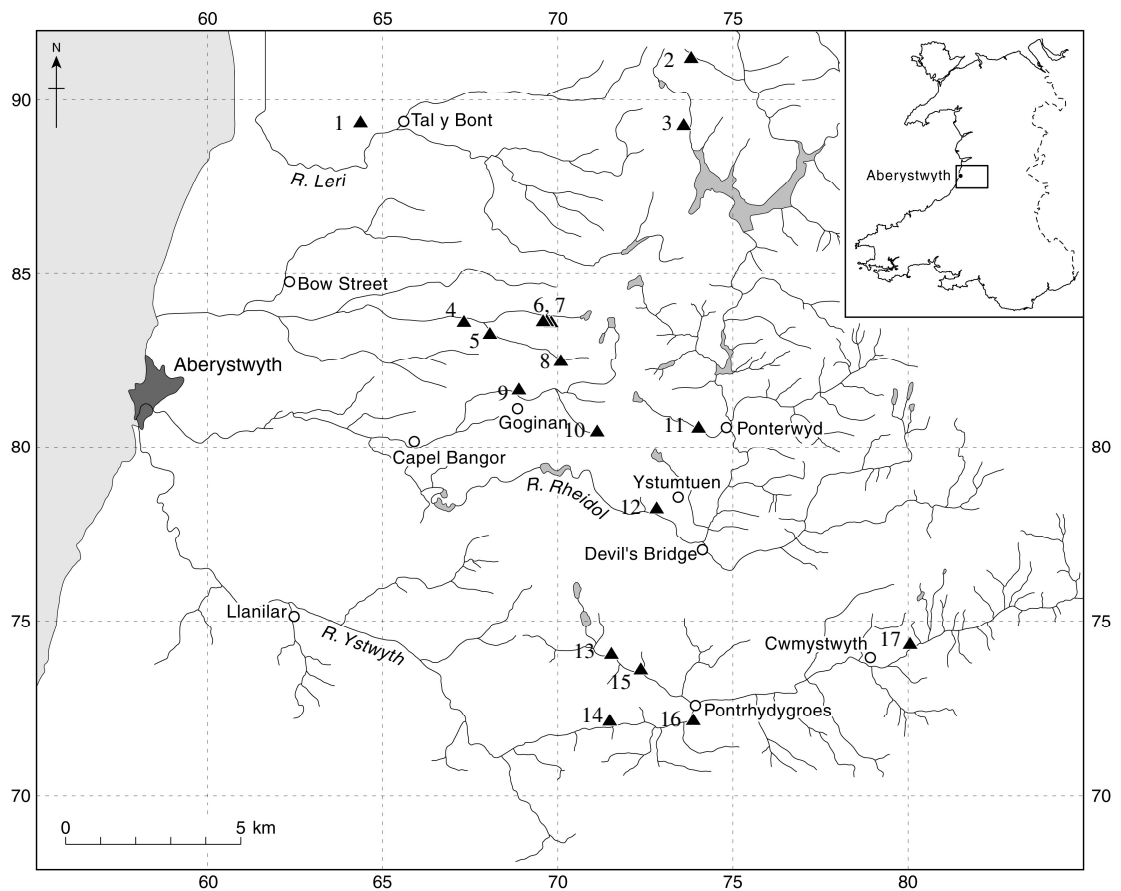
Metalliferous mining had, until the mid nineteenth century, concentrated on extracting Pb and Ag, with a small number of mines extracting Zn to increase their profits (Lewis, 1967). With the price of Pb and Ag high and stable there was no impetus to mine the Zn; previously, sphalerite had been a waste product either left on the mine walls or within the waste dumps (Richardson, 1974; Evans, 1991; Pearce and Pearce, 1993). With the rapid decrease in the price of Pb in the 1880s, Zn mining suddenly became economical and mines focussed on removing all available Zn (Burt *et al.*, 1985), especially after 1837 when galvanisation was patented and Zn replaced Cu in roof sheeting (Lewis, 1967; Pearce and Pearce, 1993). There is no doubt that the removal of Zn slowed the decline of the mining industry, without it the mines would have closed much earlier (Lewis, 1967; Burt *et al.*, 1985; Pearce and Pearce, 1993). Cheaper and higher quality foreign imports and low Zn prices in Britain meant that it was not worthwhile for most mines to raise the ore and the remaining Zn producing mines reduced their output and mining ceased (Lewis, 1967; Burt *et al.*, 1985). Even the high metal prices caused by the World War I could not restore the industry (Environment Agency, 2002).

2.4 Study sites

Fifteen mine sites with adit drainage and two local water courses were selected for study (Figure 2.4); the sites were chosen because they were within 25 km of Aberystwyth, which allowed frequent sampling to occur; the mines were known to have extracted Pb and Zn; the mine drainages could be collected from a point source and eleven of the mines are listed within the Metal Mine Strategy for Wales (Environment Agency, 2002) as requiring remediation. The samples were anticipated to provide a wide range of chemical and physical water characteristics. Where possible the sampling was undertaken directly from the mine adit, but where this was not possible, the samples were taken from a convenient and accessible point. The concentrations of metals within the mine drainage waters are likely to be much higher than those in the water courses because of the additional non-polluting water. The two water courses, the Afon

Llywernog and the Nant Silo, were chosen for sampling to indicate whether they comply with EU EQS.

Several authors have published comprehensive accounts of the various mines geology and history including Jones (1922); Lewis (1967); Bick (1978); Foster-Smith (1979) and Burt *et al.* (1985); and the reader is directed towards these for more information. Where production figures are quoted, a gross underestimation is often produced as official returns were not kept until 1845 (Bick, 1978; Mason, 1997).



Key

The grid reference is given in brackets.

- | | |
|-----------------------------|---------------------------------|
| 1 Alltycrib (64442 89490) | 10 Cwmbryno (71158 80452) |
| 2 Esgair Hir (73889 91205) | 11 Afon Llywernog (74043 80559) |
| 3 Eaglebrook (73611 89284) | 12 Cwm Rheidol (72800 78200) |
| 4 Nant Silo (67278 83758) | 13 Wemyss (71531 74084) |
| 5 Daren (68075 83325) | 14 Grogwynion (71494 72145) |
| 6 Cwmsymlog 1 (69812 83686) | 15 Frongoch (72427 73587) |
| 7 Cwmsymlog 2 (69738 83799) | 16 Level Fawr (73849 72245) |
| 8 Bwlch (70131 82581) | 17 Cwmystwyth (80113 74432) |
| 9 Goginan (68965 81763) | |

Figure 2.4. Location of the sample sites.

1. Alltycrib (Grid reference: 64442 89490)

Alltycrib is one of the oldest mines in the mid-Wales orefield, with complex workings and history (Lewis, 1967; Richardson, 1974). There are various lodes within the mine and these were worked both individually and as a group by various mining companies (Foster-Smith, 1979). There are two main lodes striking approximately east-west and occur in the “Frongoch Formation” (see Figure 2.2). The north north east lode of the Tanyralt mine severs the two Alltycrib lodes to the west. The ore deposits occurred in stockwork-like lodes with associated quartz. The ore seems to have been richer in the upper parts of the mine, diminishing at depth (Foster-Smith, 1979) with neither of the lodes continuing for great distances (Jones, 1922). Alltycrib was first worked by Thomas Bushell from ~1630 to 1660. The mine was worked sporadically from 1660 by various companies with the Company of Mine Adventurers working the mine between 1720 and 1750 (Bick, 1978). During the nineteenth century the mine was reworked on a number of occasions, finally closing in 1914. The total output from the mine was ~1830 tonnes of Pb ore with minor amounts of Ag also produced (www.mindat.org/loc-5188.html).

The sampled waters issue from a disused mine level and flow over ~10 m of grass and earth before flowing into a road drain underneath the road and being discharged into a local watercourse (see Figure 2.5). The samples were collected before the water entered the road drain.

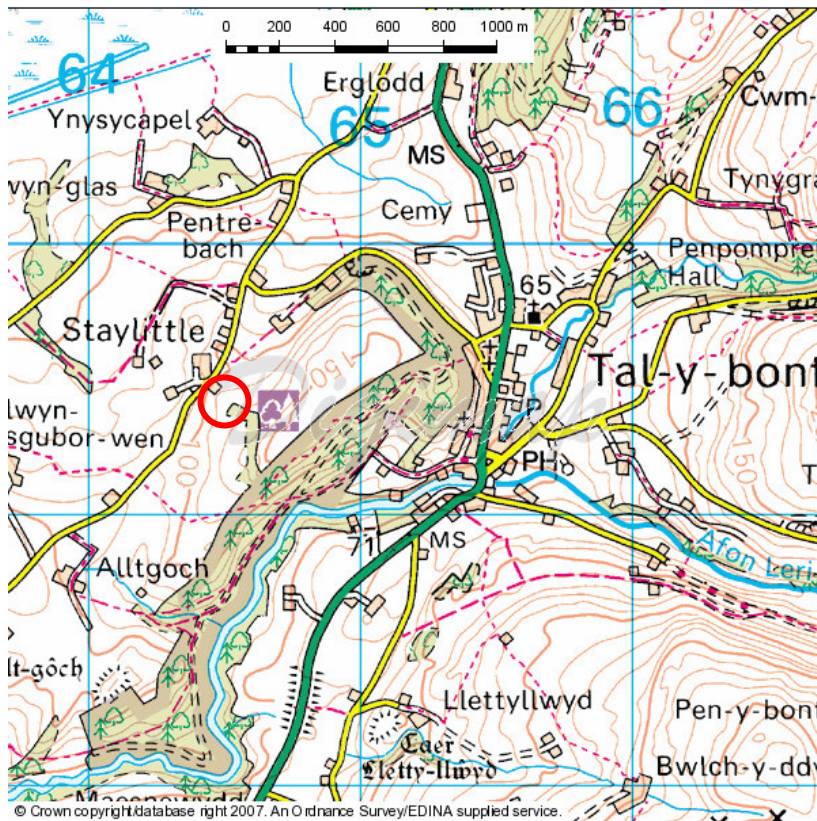


Figure 2.5. The Alltcrib sampling site.

The sample was taken from the centre of the red circle.

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2. *Esgair Hir* (Grid reference: 73889 91205)

Lead ore at Esgair Hir was discovered in the late 1680s and was not worked until 1691, relatively late in the history of the mid-Wales orefield (Palmer, 1983). As an Ag mine Esgair Hir had a notable reputation in the early days of its working, and the mine was coined the ‘Welsh Potosi’ by William Waller as an indication that the mine was analogous with the Ag mines of Bolivia (Bick, 1978). This great claim was not supported, with the ore only containing an average of 200-260 g of Ag per tonne of Pb ore (Jones, 1922; Foster-Smith, 1979; www.mindat.org/loc_4262.html). Both Esgair Hir and Esgair Ffraith (further to the east) had a reputation for being far richer and successful than they actually were. The name proved an alluring attraction to many companies and was subject to much speculative development, with large sums of money being spent on buildings and machinery without large quantities of ore being produced in return (Foster-Smith, 1979).

Esgair Hir and Esgair Ffraith were commonly worked together and they lie on a 2 km long lode which can be partially traced for 4 km (www.mindat.org/loc_4262.html). The lode is of variable strike direction, but generally follows an east-west direction (Foster-Smith, 1979). At Esgair Hir the lode lies within the Devil's Bridge Formation and is cemented with quartz and some calcite (Palmer, 1983); whereas at Esgair Ffraith the lode descends into the Cwmere Formation and is dominated by ferroan dolomite, where an increase in Cu content coincided with a decrease in Pb content (Foster-Smith, 1979). At Esgair Hir, the spoil tips indicate that the ore was more than likely spread throughout the vein system (www.mindat.org/loc_4262.html). Ribs and spots of ore minerals occur up to 1.8 m wide, largely consisting of galena, although sphalerite is also common (Jones, 1922). At the eastern end of the Esgair Hir workings the richest ore occurred as oreshoots (also known as 'pipes') 25 m long, 2 m wide and 120 m deep, within a brecciated zone of up to 18 m wide. The 'pipes' produced >100 tonnes of ore each, with ore content decreasing with depth (Foster-Smith, 1979; www.mindat.org/loc_4262.html). A plan of Esgair Hir was drawn in 1698 showing six Pb ore lodes (total width of 9 m) and two Cu veins running parallel to each other at very close distances. Over 18 mine shafts were sunk, mostly to reach the ore, although some were used as ventilation shafts (Jones, 1922). The working of the ore proved problematic because of the amount of water within the mine. The country rock was very hard and it proved difficult to drive a drainage adit into the mine workings (Lewis, 1967). An east level adit was driven from near Esgair Ffraith to exploit other ore bodies (Bick, 1978).

Output for the mine was 2840 tonnes of Pb ore and 2700 tonnes of Cu ore, with >2000 tonnes Pb ore being raised between 1702 and 1708 (www.mindat.org/loc_4262.html). There are no production figures for the amount of Ag produced, although the average concentration was ~200 g per tonne of Pb ore (www.mindat.org/loc_4262.html). Mining ceased in 1849 (Palmer, 1983) although after this period the mine was periodically re-opened and worked, but very little ore was produced (Lewis, 1967). For more detailed information the reader is directed towards Palmer (1983).

Samples were collected as the water discharges from the East Level adit at an average of ~100 L/min, see Figure 2.6. The mine drainage enters the Afon Lluestgota, which flows into the Nant-y-moch Reservoir (source of the Afon Rheidol).

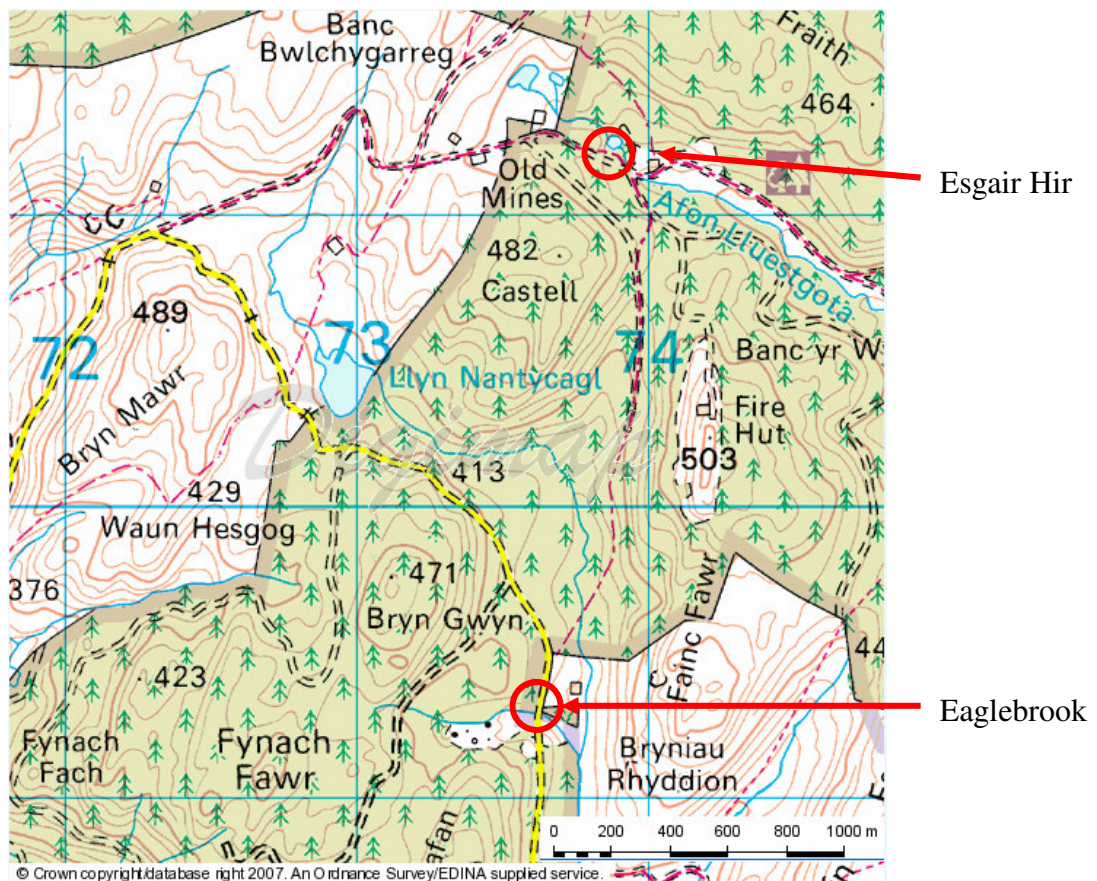


Figure 2.6. The Esgair Hir and Eaglebrook sampling sites.

The sample was taken from the centre of the red circle.

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3. Eaglebrook (Grid reference: 73611 89284)

Eaglebrook has a long history and was first worked by the Company of Mine Adventurers for Pb and Cu in the 1700s (www.mindat.org/loc.php?loc=4293). The mine was originally known as Dolrhyddlan or Nantycagl; it was given its English name by Robert Mushet, who declared that it was Eaglebrook, not Esgair Hir that was the real Welsh Potosi, as two recently opened adits contained solid ore some 0.3 m wide. This disclosure increased share prices, but they soon fell after the release of a letter stating that the mine could not be anything like a Potosi (Bick, 1978).

The primary ore minerals found at Eaglebrook are galena, sphalerite and chalcopyrite. The lode strikes a little north of west and has only been found where it crosses a small anticline in the “Van Formation” with the “Gwestyn Formation” on either side (Foster-Smith, 1979); it cannot be traced either east or west into the base of the “Frongoch

Formation” (Jones, 1922). The gangue mineral is coarsely crystalline ferroan dolomite, which cements brecciated sulphides and quartz (Mason, 1997). Before 1853 there were only small scale workings on this site (Foster-Smith, 1979). Eaglebrook reached a depth of 91 m before it closed in 1874. From 1853 the mine produced 610 tonnes of Pb ore (333 tonnes produced between 1856 and 1859) and 72 tonnes of Cu ore (Jones, 1922; Bick, 1978; Foster-Smith, 1979). The site was designated a mineralogical Site of Special Scientific Interest (SSSI) in 1992 (www.sea.unep-wcmc.org/wdpa/sitedetails.cfm?Siteid=139590&level=nat).

The sampled water originates in Forestry Commission land and flows through the mine’s spoil heaps before flowing under the road (unclassified), eventually entering into the Nant Rhuddlan, which flows into the Nant-y-moch Reservoir (source of the Afon Rheidol). The water was collected before the water flowed under the road. For sample site location see Figure 2.6.

4. Nant Silo (Grid reference: 67278 83758)

The Nant Silo drains several mines including Cwmsymlog, Daren, Cwmerfyn and Bwlch which are individually detailed below, with the exception of Cwmerfyn. The Nant Silo also contains surface water run-off from the surrounding hillsides and precipitation. Cwmerfyn is an ancient mine, with lodes occurring in short bunches within the “Frongoch Formation” containing between 0.7 and 1.77 tonnes of Pb ore per 1.8 m. The ore bunches varied dramatically in the amount of Pb ore that they contained and became unproductive at the base of the ore body around 85 m. Between 1849 and 1877 Cwmerfyn produced >10,000 tonnes of Pb ore and >5.7 tonnes of Ag (Jones, 1922; Bick, 1978). The spoil heaps at Cwmerfyn, as at Bwlch (number 8, see below), were remediated in the 1990s and the slopes have been re-graded to 1 in 4 along the river bank and 1 in 7 throughout the rest of the area. The 1 in 4 slopes have been covered with a polythene membrane, then 40 cm clay stabilising layer and 50 cm subsoil. The 1 in 7 slopes are covered with the polythene membrane and 50 cm subsoil. The polythene membrane is to prevent precipitation percolating down through the spoil. Surrounding the encapsulated area, drains have been installed to channel water straight into the Nant Silo (Fielding pers. comm., 2007).

The Nant Silo was sampled as it passes under the road bridge (unclassified road) in Pen-bont Rhydybeddau. Sampling at this location allows the contributing mine waters to have become fully mixed and therefore provides a more representative sample of the water course; see Figure 2.7 for the sample location.

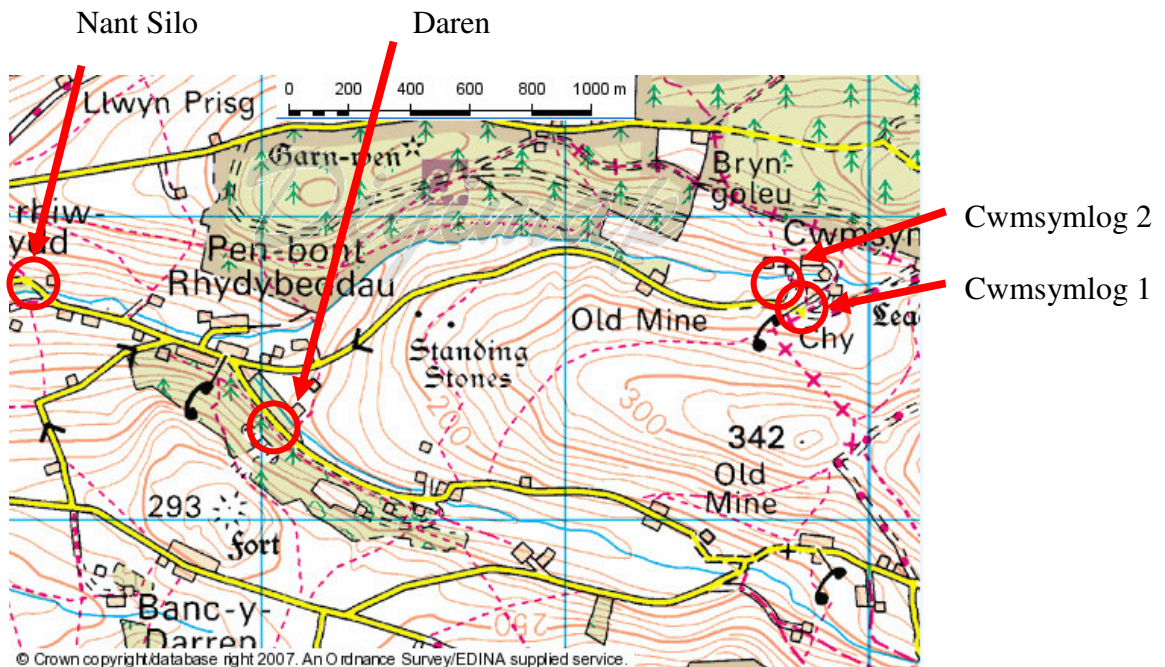


Figure 2.7. The Nant Silo, Daren, Cwmsymlog 1 and Cwmsymlog 2 sampling sites. The sample was taken from the centre of the red circle.

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5. Daren (Grid reference: 68075 83325)

At times during Daren’s long history it was one of the most celebrated mines in Ceredigion. Daren was already of considerable age when the Society of Mines Royal took over the mine, with a patent granted in 1568 (Jones, 1922). The mine may have been worked in the middle Bronze Age (1300 B.C.) and a large pre-Roman fort exists very close to the mine (Lewis, 1967; www.mindat.org/loc-4261). During the reigns of Queen Elizabeth I, King James I and King Charles I; small mining trials occurred here; it was surprising that the Company of Mine Adventurers never worked or leased this mine, as they were involved with most of the other successful mines in the county (Bick and Davies, 1994). The Daren lode trends north east – south west and dips to the north west. The mineralised vein is situated in the pale-green mudstones of the lower “Frongoch Formation” (Jones, 1922). The vein varies in width from 1.5 to 3 m. Over the mine’s long history it was most successfully worked from 1720 to 1740. The output

between 1850 and 1879 was 1685 tonnes of Pb ore and 53 tonnes of Cu ore (Jones, 1922; Foster-Smith, 1979). The ore also contained ~2 kg Ag per tonne of Pb ore (Mason, 1997). The total production would have been much higher, but the mine was largely exhausted before official returns were kept. Daren finally closed between 1850 and 1879 (www.mindat.org/loc-4261). The Daren mine workings and adit have been designated as a Scheduled Ancient Monument site (7/3590/CD144[CER]//) by CADW (Welsh Historical Monuments).

The Daren mine was sampled as the mine drainage issued from Oliver's adit. Oliver's adit can be found on the south side of the road from Pen-bont Rhydybeddau when travelling south-east, opposite a small domestic garage (see Figure 2.7).

6. and 7. Cwmsymlog (Cwmsymlog 1 grid reference: 69812 83686; Cwmsymlog 2 grid reference: 69738 83799)

Cwmsymlog was worked purely for Pb ore and is a very old mine with a long and successful history (Foster-Smith, 1979). The mine was actively mined by German miners during the reign of Queen Elizabeth I; but it was not until Sir Humphrey Middleton acquired the lease in the 1620s that the mine became extremely successful. The eastern end of the workings are known as Blaen Cwmsymlog and this area was alleged to contain ~3 kg Ag per tonne with an income of £24,000 per year from the Ag alone (Bick, 1978); the workings are now buried beneath Forestry Commission land (Bick and Davies, 1994). Between 1852 and when the mine finally closed in 1901 (Jones, 1922; Lewis, 1967; Foster-Smith, 1979) >25,000 tonnes of Pb ore and ~1 tonne of Ag was produced (Bick, 1978). The mines of Cwmsymlog, Cwmerfyn and Goginan all lie on the eastern flank of the same anticline. The mineralised lodes lie within the pale green compact mudstones of the lower "Frongoch Formation". The workings descended to 240 m, but were unproductive at depth (comparatively little ore below 210 m); possibly because of a band of calcareous grits located ~40 m above the base of the Formation. The Cwmsymlog lode commonly strikes north east, but alters its course across the mine workings (Jones, 1922), turning east west towards the productive area of Cwmsymlog and then at the end of the workings back to a north east direction (Foster-Smith, 1979). The lode comprises two branches, each ~1.8 m wide and at varying distances apart from 1 to ~12 m. The North branch (the main lode) was far richer than the southern branch (Jones, 1922; Foster-Smith, 1979).

In 1983 remediation work was undertaken to decrease the problem of wind blown dust, but this had no impact in reducing the concentration of potentially harmful elements being released into the river (Environment Agency, 1999). Scheduled Ancient Monument designations were awarded to Cwmsymlog in 1996 and Blaen Cwmsymlog in 2001.

Two samples were collected at Cwmsymlog. The first was taken as the water issued from an underground pipe; this is supposedly precipitation which has had no contact with the mine spoil. The second Cwmsymlog sample was taken after the water had percolated through the mine spoil. See Figure 2.7 for the sample locations.

8. Bwlch (Grid reference: 70131 82581)

Mining activity started at Bwlch in the seventeenth century, and the mine has had a variety of names including Cwmerfyn, Bwlch Cwmerfyn, Bwlch Consols (or Bwlchrhennaid) and Bwlch United (Jones, 1922). There are three distinct lodes, the North or Main lode (Goginan lode), the middle or Bwlch lode and the South lode (Level Newydd or Bwlchrhennaid lode). The Goginan and Level Newydd lodes are continuous and are thought of as the principal or master-lode. The majority of the ore was worked from the area surrounding the junction of the Goginan and Bwlch lode, with the ore becoming unproductive with distance from the junction (Jones, 1922). During the 1990s the area around Bwlch and Cwmerfyn was remediated (see number 4, above).

The drains were piped to flow out of a walled area that was built alongside the Nant Silo (a tributary of the Afon Clarach), see Figure 2.8. There are two pipes, one on the left hand wall and the second is on the facing wall (when stood in the Nant Silo), see Figure 2.9. The sample was taken from the left hand drainage pipe, which has a relatively steady flow of 10-15 L/min, though this does increase after a period of heavy rainfall. Water issues only after a period of very heavy rainfall from the pipe facing the stream.

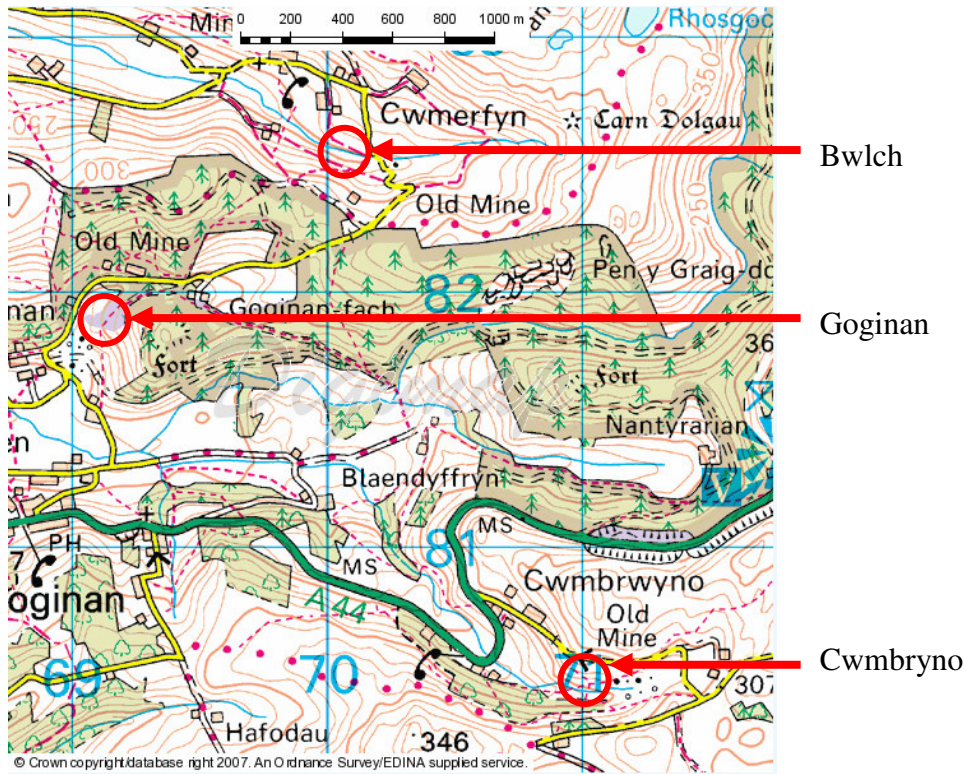


Figure 2.8. The Bwlch, Goginan and Cwmbryno sampling sites.
The sample was taken from the centre of the red circle.
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Figure 2.9. Outlet pipes at Bwlch.

9. Goginan (Grid reference: 68965 81763)

Goginan has a long and largely uninterrupted mining history. Roman coins have been found within the spoil tips (Lewis, 1967; Bick, 1978), but recorded workings began around 1620 when the Society of Mines Royal worked the mine for Ag

(www.mindat.org/loc.php?Loc=5227). The mine was considered to be only barely less well known for its Ag content than Cwmsymlog. The topography of the mine site made it ideal for development by adits. The workings contain a very long inclined shaft or plane that was used as a walkway for the miners and for removing the ore via trams rather than kipples (Bick, 1978; 2004).

At Goginan three separate ore bodies were worked, with the Goginan body being the largest (Jones, 1922); the lode strikes north east and branches off to the east of the main workings towards Bwlch (Foster-Smith, 1979). The lode was worked in the lower beds of the “Frongoch Formation”, though the lowest parts of the mine reached into the “Gwestyn Formation”. The most valuable deposits were found at 110 m and above, with the ore rapidly decreasing after 220 m (Richardson, 1974). The lode consists of mudstones, cemented with quartz with the Pb ore occurring as strings, ribs and bunches and was commonly ~5.5 m in width. Between Goginan and Brynpica to the east, the ground was unproductive, although it did contain small bunches of mixed Pb and Cu ore (Jones, 1922). Between 1837 and 1886 (when mining ceased) ~25,511 tonnes of Pb ore, 61 tonnes of Zn ore and over 14.2 tonnes of Ag were raised (Bick, 1978; Foster-Smith, 1979). The site has now been levelled and re-vegetated and very little of the old mine workings remain, with the exception of the inclined shaft. A concrete channel has been constructed around the site channelling the majority of the water away from the buried spoil.

The Goginan sample was taken from where the concrete water channel begins, after the water had passed through the mine spoil further upstream, see Figure 2.8.

10. Cwmbryno (Grid reference: 71158 80452)

Cwmbryno was discovered c.1840, but it was not until 12 years later that it produced significant quantities of ore (Jones, 1922). There is one major ore lode, which continues to the east to form part of the Llywernog mine. The lode trends west south west and follows a curving strike line from east-west at the western end of the workings, altering its course to east north east at the eastern end of the workings and turning back east-west towards Llywernog (Foster-Smith, 1979). The ore body lies approximately midway between two well marked anticlinal axes and was between 220 and 290 m in length, descending to a depth of 125 m (Jones, 1922). Cwmbryno produced ~6200

tonnes of Pb ore and ~810 tonnes of Zn ore from 1840 to 1892, when the mine finally closed (Foster-Smith, 1979). Remediation works, including the capping of spoil tips and the diversion of the Nant Bryno to reduce metal loadings was completed in 1999 at a cost of £300,000 (Environment Agency, 1999; 2002).

The water sample was taken at the bottom of the valley in the diverted Nant Bryno after the spoil tips, see Figure 2.8.

11. Afon Llywernog (Grid reference: 74043 80559)

The Afon Llywernog eventually flows into the Afon Rheidol and drains the Llywernog, Clara, Bog and Powell's mines, which are all detailed below. The Afon Llywernog also contains surface water run off from the surrounding area and precipitation. This group of mines occur within the lower beds of the "Frongoch Formation" and worked several mineralised lodes. The southerly lode is the same one that occurs at Cwmbryno. The output from this group of mines was 5588 tonnes of Pb ore and 1313 tonnes of Zn ore (Foster-Smith, 1979).

Llywernog (locally known as Poole's mines or Gwaith Poole)

The Llywernog mineral vein was discovered around 1742. Most of the ore came from the intersection of the worked Llywernog lode with the Powell's mine lode. The lode became unproductive as pumping costs grew with depth (Bick, 1978; www.silvermines.co.uk/llywernog_history.php). The mine had one main shaft, 122 m deep through which ore, waste rock and water were removed (www.wales-underground.org.uk/llywernog/). Mining began to decline in 1878, although attempts to revive the mine continued until 1907 (Bick, 1978). The chief mineral worked was galena, with lower amounts of Ag, sphalerite, marcasite; chalcopryrite was also occasionally found. After 1845 this mine produced 3874 tonnes of Pb ore, 569 tonnes of Zn ore and 121 kg of Ag (www.wales-underground.org.uk/llywernog/). The Llywernog mine closed in 1883 (Carpenter, 1924) and has been designated as a Scheduled Ancient Monument. The mine was reopened in 1973 as a museum.

Powell's mine

Powell's mine was worked independently during periods and worked together with the Llywernog mine under the name of Powell Consolidated, Powell's United or Ponterwyd

Mines. The mine finally closed in the 1890s having reached a depth of 150 m and worked several lodes. Two lodes converged eastwards and met in the mine, one lode trends to the west and appears to correspond with the north lode of Poole's mine and the other trends south towards the Bog mine (Jones, 1922). Together the Llywernog and Powell's mine produced 3874 tonnes of Pb ore and 567 tonnes of Zn ore (Bick, 1978).

Clara (or Clara United)

Clara mine was worked on a relatively small scale before 1845. After this, the Llywernog, Powell's, Clara and Bog mine were worked separately or as a whole until 1890 and occasionally on a fairly large scale (Foster-Smith, 1979). The waste dumps from the mine contained large strings of sphalerite and 10 cm wide veins with some galena and a little marcasite (Jones, 1922). Between 1859 and 1875, 563 tonnes of Pb ore were produced. The mine finally closed in 1882 (Bick, 1978).

Bog (or Craignant Bach)

The Bog mine was first worked in 1830 and was sporadically worked by varying companies until 1882, when low Pb prices and failing equipment culminated in the closure of the mine (Bick, 1978). The main lode strikes east south east and crosses a north east trending lode from the Llywernog mine, lying 0.8 km to the west (Jones, 1922; Foster-Smith, 1979). Bog produced around 1600 tonnes of Pb ore and over 700 tonnes of Zn ore (Bick, 1978).

The Afon Llywernog was sampled as it passed under the road bridge (unclassified road) leading to Ystumteun, just off the A44, see Figure 2.10. The sample was taken far enough down stream to allow a thorough mixing of the waters issuing from the above mines.

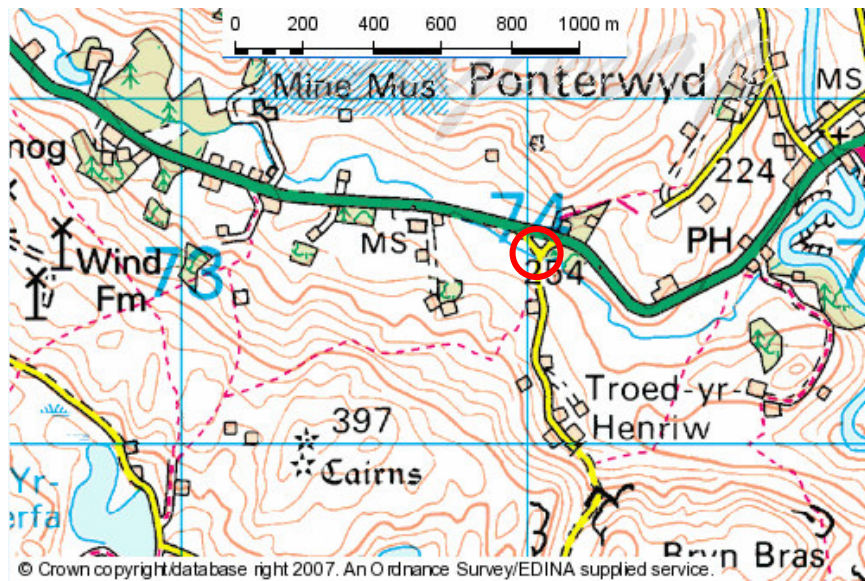


Figure 2.10. The Afon Llywernog sampling site.
The sample was taken from the centre of the red circle.
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12. Cwm Rheidol (Grid reference: 72800 78200)

Cwm Rheidol formed part of the Ystumteun mine complex, which included Ystumteun, Ty'n-y-fron, Penrhiw, Bwlchgwyn, Llwyn Teifi and Temple mines to the north (Foster-Smith, 1979; Hughes, 1993). These mines all lie along the Castell Lode which is of considerable length (10 km) and depth (Fuge *et al.*, 1991), striking north of east and dipping steeply to the west. The lode is constrained to the north by the Cwmere Formation and to the south by the sharply folded basal beds of the "Frongoch Formation". Within this mine complex the main mineral extracted was sphalerite, with minor quantities of galena (Jones, 1922). Uniquely within the mid-Wales orefield these mines contained large amounts of pyrite and marcasite (Bick, 1978), the A2-f assemblage of Mason (1997) (see Chapter 2.2). The pyrite and marcasite were so abundant in some areas of the sphalerite-galena-quartz assemblage (A2-a) of the Castell lode that it made the ore body unworkable (Raybould, 1974) because of the difficulties of separation. Ribs of solid marcasite >2 m wide are still found within the Ystumteun mine (Mason, 1997).

Deep levels were constructed from the northern side of the Rheidol valley towards the Ystumteun and Ty'n-y-fron lodes. Alderson's Level was at a depth of 430 m (Number 9 adit – the lower adit) from the surface at Ystumteun which is connected only to the lower Ystumteun mine and because of its lack of connection with surface water sources

has a relatively stable flow and composition; another later level was cut at a depth of 220 m (Number 6 adit – the upper adit), which is connected to, and drains, Penrhiw, Bwlchgwyn and the upper Ystumteun mine and has a variable flow and composition. These adits were driven into the hillside to access the ores, but also acted as a drainage adit for the Ystumteun, Bwlchgwyn and Penrhiw mines. Dressing floors were built by the lower level and this became known as Cwm Rheidol (Jones, 1922; Bick, 1978; Foster-Smith, 1979). During 1875-1882, 1901 and 1903-1912 Ystumteun and Ty'n-y-fron produced 829 tonnes of Pb ore, 9952 tonnes of Zn ore and 3922 tonnes of pyrites. Between 1885 and 1895 Ystumteun and Penrhiw were worked together and produced 237 tonnes of Pb ore, 590 tonnes of Zn ore and ~4 tonnes of pyrite (Jones, 1922). These pyrites were mined for the production of sulphuric acid (Mason, 1997).

In the 1960s a hydro-electric power station was built downstream from the mines. As part of the planning consent, the company (the Central Electricity Generating Board) were obliged to reduce the metal content from the area's adits and tips; they constructed a limestone filter where the channelled water flowed through three limestone chip beds before discharging into the river. During the 1960s the filter beds raised the pH from ~pH 3.2 to ~pH 6 and reduced the Zn concentration by >80%. The beds, however, soon became ineffective because of the large concentration of ochre being deposited, especially after October 1969, when the plug blocking the lower Number 9 adit was breached during exploratory prospecting, releasing 3106 mg/L of suspended solids, 1500 mg/L Fe, 230 mg/L of soluble Zn and 148 mg/L of soluble Pb, which caused a major fish kill in the River Rheidol (Jones and Howells, 1975; Davies, 1987). In 1984, the Welsh Water Authority introduced a number of measures to try and lower the metal concentrations being released from the adits. The flow was reduced from the upper adit by reducing surface drainage and seepage from the Ystumteun, Penrhiw and Bwlchgwyn mines; the adit discharges were diverted to a natural channel to the north to prevent the passage of the water over the spoil tips and to reduce the concentration of metals being mobilised by the water. The filter beds were also renovated and improved (Jones, 1986). In the 1990s, even though the pH was no longer being raised, Zn and Pb were still being removed (Fuge *et al.*, 1991). After flowing through the treatment plant, the discharge enters the River Rheidol. This discharge contributes over half of the metal loading in the river and causes it to fail EQS for Zn 16 km down river; this also means that it fails to achieve 'good' chemical and ecological quality that is

required by the Water Framework Directive (Environment Agency, 2002). From March 2008, the Environment Agency has been working towards reducing the impacts of the mine drainage; they have drained the lower adit and are aiming to transfer the mine drainage directly, via a pipeline, from the adit to a treatment plant at the site (Environment Agency, 2008b).

The samples were taken after the two adit discharges have met, been well mixed and flowed down ~30 m of mine spoil, see Figure 2.11. This water then passes under the road and is channelled into the 1960s treatment plant. Iron oxides are visible coating the bed of the water channel and the River Rheidol.

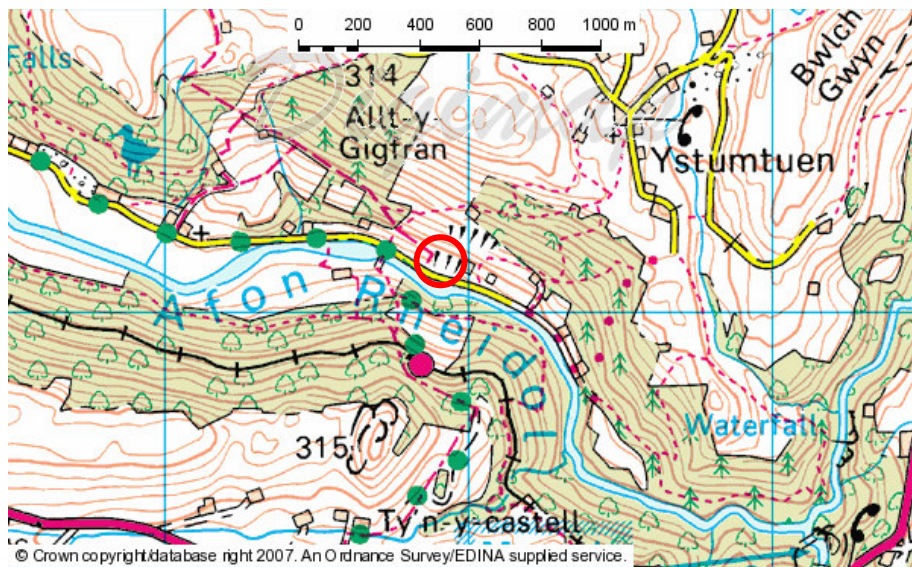


Figure 2.11. The Cwm Rheidol sampling site.
The sample was taken from the centre of the red circle.

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13. Wemyss (Grid reference: 71531 74084)

Wemyss mine was commonly worked together with Frongoch. The lodes worked at Wemyss are a westerly continuation of those found at Frongoch and the two mines share a common adit level (Jones, 1922). The mine was worked sporadically between 1861 and 1899 producing ~1300 tonnes of Pb ore and >2000 tonnes of Zn ore (Bick, 1978). More detailed information is given in the literature regarding Frongoch (see number 15 below) as this was the principal mine.

The Wemyss water sample was taken after the water had passed alongside the large fine grained spoil heaps, just before the drainage enters the Nant Cwmnewyddion, a tributary of the Afon Ystwyth. The road (unclassified) curves around the large spoil tips to the south east, see Figure 2.12.

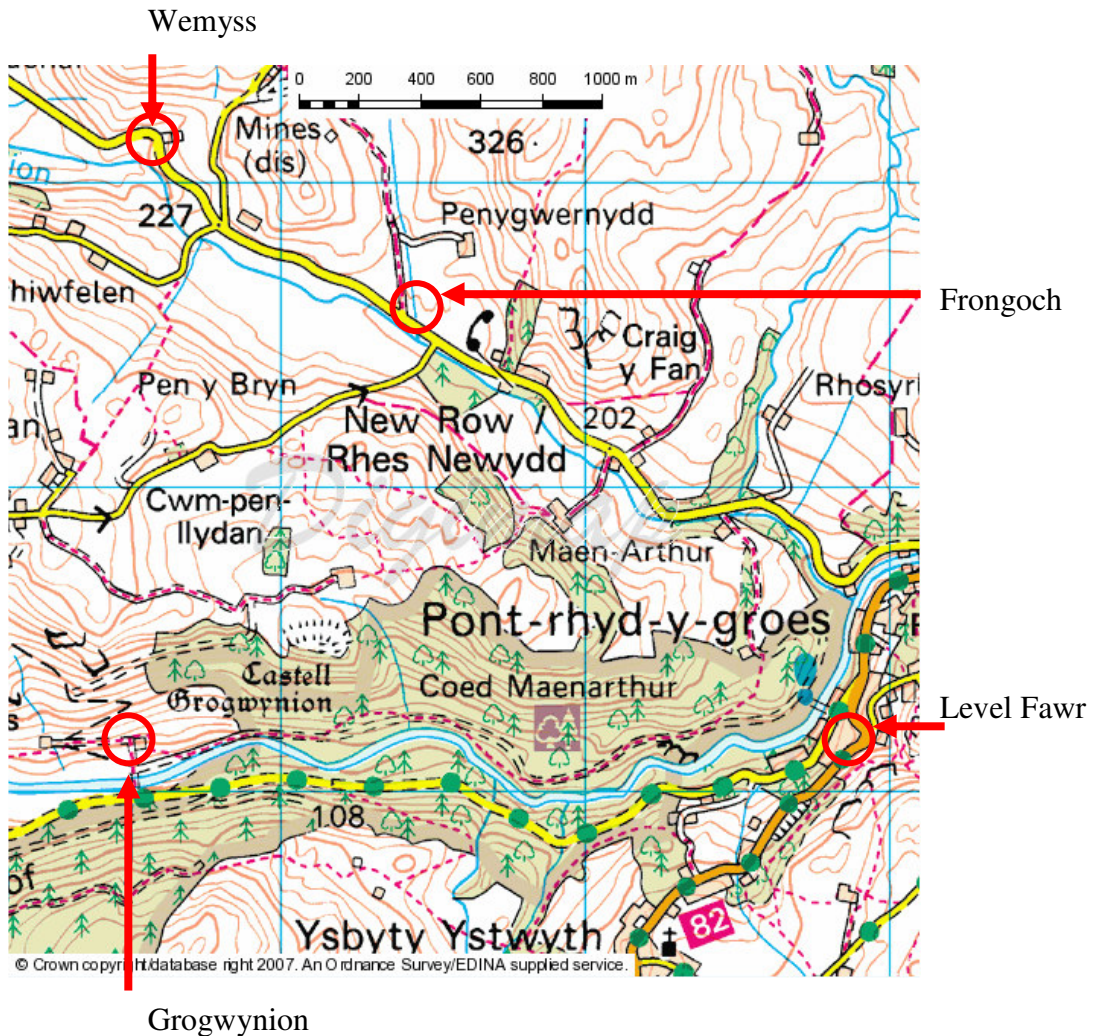


Figure 2.12. The Wemyss, Grogwynion, Frongoch and Level Fawr sampling sites. The sample was taken from the centre of the red circle.

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14. Grogwynion (Grid reference: 71494 72145)

There are four parallel lodes and these have been exploited via shallow, intermediate and deep adits and the spoil tips can be seen covering the 215 m high valley sides down to the river. The lodes are restricted and consist of quartz, galena and sphalerite within cemented brecciated country rock within the “Frongoch Formation”. The four lodes strike to the north east and most of the ore occurred above the deep adit. The ore body

was around 350 m long and ended abruptly both vertically and horizontally. The mine was worked from around 1588 to 1889 producing >9000 tonnes of Pb ore (Jones, 1922; Lewis, 1967; Bick, 1978 and Foster-Smith, 1979). The Grogwynion site has been designated as a Site of Special Scientific Interest (SSSI) and also as a Special Area of Conservation (SAC) in 2004 by the Joint Nature Conservancy Council. The area was designated as a SAC as it is the largest known area of shingle heath in England and Wales and it exhibits one of the best examples of Calaminarian grasslands of the *Violetalia calaminariae* (www.jncc.gov.uk).

The sample was taken as the water emerged from a disused level, which can be found across the footbridge over the Afon Ystwyth and along the track to the north, see Figure 2.12. The level emerges next to the house and water passes underneath the track, the sample was taken as the stream passes under the fence, before reaching the shingle of the Afon Ystwyth.

15. *Frongoch* (Grid reference: 72427 73587)

Mining at Frongoch began in 1759; although its greatest period was not until 1834 when mining occurred continuously until it closed in the early twentieth century (Jones, 1922; Richardson, 1974; Bick, 1978). Sphalerite was abundant in numerous mines in the mid-Wales orefield, especially south of the Rheidol; and Frongoch was one of the most successful Zn mines (Lewis, 1967; Foster-Smith, 1979). The mine was worked by various companies and they all encountered the problem of excess water within the mine. Water wheels were first used to drain the mine; but in 1841 a steam engine was assembled for winding and crushing, however, the cost of transporting the coal to the mine from Aberystwyth was too expensive and the engine was decommissioned. In 1899 a Belgian mining company took over the lease and built an electrically driven ore processing plant and a new tramway that transported the ore from the mine to the plant, which was situated near to Wemyss (Bick, 1978). Between 1834 and 1903 the mine produced >60000 tonnes of Pb ore, ~51000 tonnes of Zn ore (Foster-Smith, 1979) and from incomplete records ~680 kg of Ag (www.mindat.org/loc.php?loc=4724).

In 1922 a dressing plant was built at Gwaith Goch nearly 3 km away with financing from the government to reprocess the spoil tips of Frongoch for Pb and Zn. The spoil tip material was transferred to Gwaith Goch via an aerial ropeway (Jones, 1922; Bick,

1978; Foster-Smith, 1979). Today there is a wood mill on the north east of the site where the spoil tips once stood. The woodchips from the mill previously covered the spoil and in 2003 these spoil tips were moved 200 m to the south as they contain geologically valuable secondary minerals and have been designated as a SSSI (www.mindat.org/loc.php?loc=4724).

There are two distinct mineralised lodes within the Devil's Bridge Formation at Frongoch in which the ore occurs, one to the north and one to the south (Jones, 1922; www.mindat.org/loc.php?loc=4724). The lode varied between 6 and 9 m wide, though the mineralised sections were only ~1.7 m wide (Foster-Smith, 1978) commonly splitting into numerous strings and then coming together, the richer ore was located where the strings met (www.mindat.org/loc.php?loc=4724). The mineralisation is the A2-a (sphalerite-galena-quartz) assemblage of Mason (1997). The quantity of galena decreased with depth; but sphalerite, and minor quantities of galena, still occurred at the lowest depths of the mine and these mineralised lodes seem to continue below the deepest workings. The workings were not continued to greater depths to take advantage of the remaining ore possibly because of the hardness of the country rock and the expense of keeping the mine floor dry from the large quantities of water. Droughts in summer and hard frosts in winter made water wheels inadequate for pumping the water out of the mine (Jones, 1922). The galena occurred in the centre of the mineralised sections, with sphalerite on the outer edge (Foster-Smith, 1979). When the mine was originally worked, galena was the principal ore; because of the low price of sphalerite little effort was given to removing the ore and therefore large quantities of sphalerite remained, either within the mine or in the spoil tips. From the 1840s the sphalerite proved to be a valuable source of income (www.mindat.org/loc.php?loc=4724). Frongoch became primarily a Zn mine after 1880 and was the largest Zn mine in the area raising over 50,800 tonnes of Zn ore, 44 % of the total produced in Ceredigion (Burt *et al.*, 1985). Jones (1922) believed there were still large quantities of ore to be worked. The site was designated as a Scheduled Ancient Monument in 1995. Detailed historical and geological information can be found within Bick (1996).

The sample was taken from the man-made drainage channel to the south of the mine site (Figure 2.12), which has an average flow of ~200 L/min. The drainage channel collects water that emerges from a low archway, which appears to be an outflow from the

disused workings (Jones, 1940); the drainage channel water also collects metals from water draining through the spoil tips. The sample was taken before this water flowed under the road (unclassified road); this water course eventually drains into the Afon Ystwyth.

16. Level Fawr (Grid reference: 73849 72245)

The Level Fawr drainage tunnel was begun in 1785 and drained the Glogfach, Glogfawr, Logaulas and Penygrist mines to the south. It is the longest drainage tunnel in central Wales and has a complicated history (Bick, 1978).

Logaulas

The Logaulas mine is probably the oldest of the four mines (Bick, 1978) and was very large and successful. The workings were active in the eighteenth century (Foster-Smith, 1979). Level Fawr was designed to cut the lode 660 m from the tunnel entrance. The work advanced very slowly and it took over 30 years to reach the lode, which was so poor that the project was abandoned. The mine, however, was not closed and when the lease passed to another company, the tunnel was continued and after a metre or so the lode was found. The lode was within a large ore deposit and the company mistook a small lode to the south as the true lode; this as well as falling Pb prices led the company to give up the lease. When the next company took over in 1834 Pb prices were increasing and they located a rich parallel lode containing 15 cm wide veins of galena (Jones, 1922; Bick, 1978). Between 1768 and 1775 Logaulas produced 861 tonnes of Pb ore (Lewis, 1967; Bick, 1978) and between 1834 and 1891 nearly 34,000 tonnes of Pb ore were produced, second only to Frongoch (Bick, 1978).

The Logaulas lode within the lower beds of the “Frongoch Formation” strikes east west and lies to the south of the Ystwyth Fault. The orebody extends for 6600 m and to a depth of 220 m (Foster-Smith, 1979). The majority of the ore occurred in two main strings 30 m apart. The ore was mainly galena, but some sphalerite and chalcopyrite occurred, especially towards the western end of the workings, although the mine was never worked for its Zn content (Jones, 1922).

Glogfach and Glogfawr

Glogfach and Glogfawr were operational on a small scale during the eighteenth and early nineteenth century (Foster-Smith, 1979). The mines produced ore soon after opening, but both closed in the early 1840s. Glogfach was reopened in 1856 and produced regular returns from 1859 to 1889; Glogfawr re-opened in 1860 and was worked from 1864 to 1893 (Bick, 1978). The mines shared a cross course (where the lode was displaced about 9 m to the south by the north south trending faults); in Glogfach no ore occurred within the cross course, but at Glogfawr the ore occurred both in the cross course and the lode. The lode was richer and more continuous near to the cross course (Jones, 1922). Level Fawr drained Glogfach from 1872 to a depth of 220 m. Above this the ore was found in well defined veins and was easily mined in the soft ground, however, below this the mine was less productive; the ground was much harder and the ore was scattered throughout the lode (Jones, 1922). At Glogfach the output from 1834 to 1889 was just over 10,000 tonnes of Pb ore. The lode at Glogfawr was large and of an even grade, though not very rich. The total recorded output was 18,820 tonnes of Pb ore (Foster-Smith, 1979).

Penygrist

Penygrist was the smallest of the four workings. In the mid-1840s two lodes were being worked and Level Fawr had probably made a connection (Bick, 1978).

The mine drainage from Level Fawr flows underneath the B4574 road; the majority flows through a rusty pipe into a channel, but some cascades over rocks into the same channel. The water within the channel mixes before entering a drain under an unclassified road eventually flowing into the Afon Ystwyth. The sample was taken just before the water flows beneath the road, see Figure 2.12.

17. Cwmystwyth (Grid reference: 80113 74443)

The area of the Cwmystwyth mine is scattered along the valley sides with over 30 lodes, which were exploited for Pb and Cu and numerous mine workings, many of which are ancient. There are around 84 surface workings which are marked by huge spoil tips, tram roads, leats, old mine buildings and many adit levels (Bick, 1978; 2004). The mine had been worked from the early and middle Bronze Age, where Cu was extracted from a single open cast working. Radiocarbon dates by Timberlake (references within

Ixer and Budd, 1998) from charcoal derived from fire settings suggests that the mines were first operational between 1200 B.C. and 1900 B.C. The mines have been periodically operational from the seventeenth century until they finally closed in the early twentieth century (Ixer and Budd, 1998).

The Cwmystwyth mines are within the “Cwmystwyth Grit Formation” detailed by Jones (1922) occurring around 1500 m above the base of the “Frongoch Formation”. The Formation is slightly younger than the Aberystwyth Grits and consists of grits and dark mudstones. The Cwmystwyth mines have a confusing and complex number of lodes, see Hughes (1981) for details of the various lodes. In some mines six or eight lodes are important (Jones, 1922), although there are three main lodes which occur, generally trending north east, but they form a complex system of fractures, which are further complicated by the Ystwyth Fault. In the mid-Wales orefield the lodes are worked at a higher horizon than any other major mine (Foster-Smith, 1979).

a) Comet Lode

The Comet Lode is a continuous body and is a major part of the Ystwyth Fault (Jones, 1922). The lode is a Pb-Zn-Cu vein with a quartz and occasionally calcite gangue. The Comet Lode was the first to be worked and varied between 3.7 to 12.2 m wide; it was extremely wealthy because of its large proportions (Hughes, 1981). To the western end of the ore body large quantities of pyrite occur (Jones, 1922; Ixer and Budd, 1998).

b) Kingside Lode

The Kingside Lode is dominated by quartz and galena, with a little sphalerite, but no pyrite and is denser than the Comet Lode. The lode has an average width of 1 m, contains 183 m of high grade ore (Hughes, 1981) and typically occurs a few tens of metres away, parallel to the Comet Lode, though they do sometimes meet (Jones, 1922).

c) Mitchell's Lode

Mitchell's Lode is of a later age than the two previous lodes. The middle of Mitchell's Lode is parallel with the Comet and Kingside Lodes, but it does intersect them at a variety of levels. The Lode is mineralised and very productive in some places, but it is variable (Jones, 1922).

The workings are divided into three areas, which until 1844 were worked as separate mines (Bick, 1978): -

i) Pugh's workings (western)

These workings contain two important lodes, the Comet and the Main which dip to the south. The Comet Lode is an open structure containing galena, sphalerite, quartz and occasionally calcite. Large amounts of pyrite often occur mixed in with the other ores, but branches leaving the Lode normally contain galena. The Main Lode is 1 m wide and consists of galena and quartz (Jones, 1922).

ii) Kingside workings (central)

There are numerous lodes encountered in these workings. The orebody was extremely rich, but tapered downwards. The main lode is the Kingside Lode and the Belshazzar or Copper Lode. Other lodes encountered include the Pumpsink Lode and the Pegeulan (or Penglin) Group. The Kingside Lode is very similar to the Main Lode in the western workings. The Belshazzar Lode is between 3.7 and 12 m and contains large amounts of galena and sphalerite, but no pyrite and corresponds to the Comet Lode to the west (Jones, 1922).

iii) Copper Hill (eastern)

The Kingside Lode at the eastern end of the mine complex has a number of branches which are in the same direction as the Main Lode. The Kingside Lode here contains a large quantity of sphalerite. The Comet Lode contains sphalerite, galena and chalcopyrite in a gangue of dolomite, calcite, quartz and country rock (Jones, 1922).

The galena that was worked was very soft and there were large quantities of sphalerite at depth (Bick, 1978; Hughes, 1981). The sphalerite was envisaged as the saviour of the mine and it was mined predominately for Zn from 1886 (Burt *et al.*, 1985); in 1896 the newly formed Kingside Zinc Blende Company concentrated on working the Zn ore. Large amounts of money were spent on machinery and equipment, including a large turbine driven Zn concentration plant, tramways and inclined planes. A large amount of Zn ore was raised; but the small amount of money made from selling the poor quality ore was not enough to pay back the investment and the mine struggled on until it closed in 1921 (Lewis, 1967; Bick, 1978). Between 1834 and 1903 over 33,530 tonnes of Pb ore and 19,216 tonnes of Zn ore were produced with 13,447 tonnes of Pb ore being produced from November 1826 to March 1827 (Bick, 1978; Foster-Smith, 1979). CADW declared the site a Scheduled Ancient Monument (7/3591/CD145[CER]/R) in 1997. The site is also a mineralogical SSSI as it is the classic site for studying mid-Wales orefield mineralisation (Environment Agency, 2002).

The sampled water discharges from Pugh's adit to the south of the site, which drains the western workings (Fuge *et al.*, 1991), see Figure 2.13. The adit is easily distinguished because of its ochreous nature in comparison to the other mine discharges in the area.

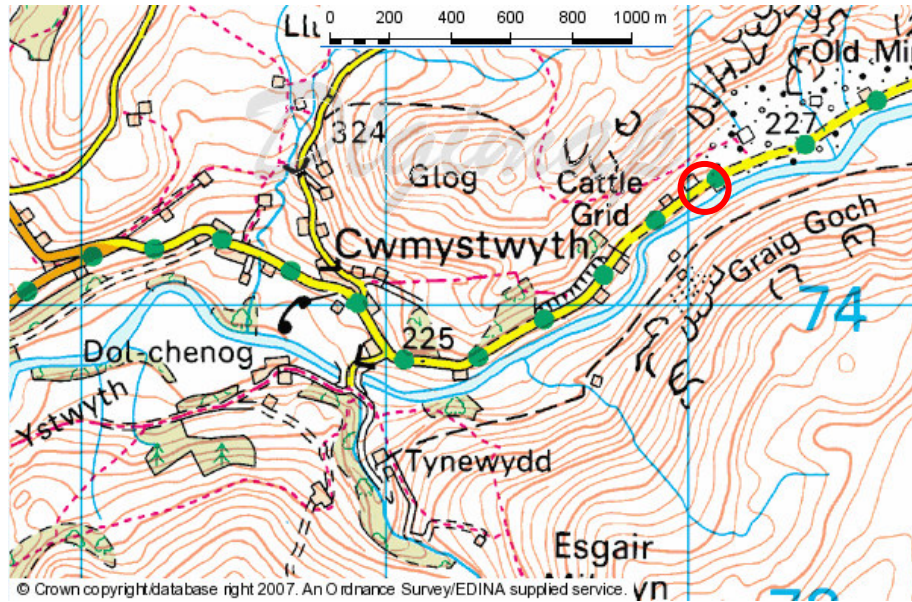


Figure 2.13. The Cwmystwyth sampling site.

The sample was taken from the centre of the red circle.

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CHAPTER 3:

Field methodology and analytical techniques

There were two primary aims of this research. The first was to identify the chemical composition of fifteen mine drainage waters and two receiving water courses in the mid-Wales orefield and to determine whether variations occurred over a seasonal or diurnal timescale (Chapter 4). The second aim was the removal of metal ions from the mine drainage waters using DS as a biosorbent. This was evaluated through a series of laboratory experiments (Chapter 6) and field trials (Chapter 7).

A common set of field methods were employed to sample the mine drainage waters and the water courses for the seasonal variation study and during the field trials. All laboratory procedures and methods used within this research were common to the determination of the chemical composition of the waters during the seasonal variation study, laboratory experiments and field trials. These common field and experimental methods are described below. There are, however, a number of field and experimental methods that were used infrequently during this study and these will be described in the relevant chapters.

3.1 Field methods

The reliability of analytical data depends upon sample collection, storage and analysis (Cook and Miles, 1980; Massee *et al.*, 1981).

Sample collection

Before sample collection the bottles were washed in Decon 90, rinsed three times in tap water, rinsed with MilliQ water (Millipore water with a specific resistance of 18 megaohms) and then soaked in 10 % HNO₃ (v/v) for ~24 hours and finally rinsed three times in MilliQ water and air dried at 60 °C. Water samples were collected and filtered immediately in a pre-contaminated, reusable Nalgene[®] holder using a Nalgene[®] hand operated vacuum pump or a Zn Mityvac[®] hand operated vacuum pump. Pre-contamination involved the upper section of the filter holder being rinsed three times with the raw water

before filtration commenced, with the lower, receiving, section being rinsed three times with the filtrate prior to the collection of the sample. The waters were filtered through a 0.45 µm pore size Whatman[®] cellulose nitrate (WCN) membrane filter. The fraction remaining on the filter is particulate matter and the fraction that passes through the filter is generally accepted to be the dissolved filtrate (Cook and Miles, 1980; Golterman and Clymo, 1969; Ramsey, 1995). Within this thesis, the term 'dissolved' refers to any substance which passes through 0.45 µm filter; although this dissolved filtrate could contain colloids or suspended solids therefore overstating the metal concentration (Faure, 1998; Nimick *et al.*, 2003; Desbarats and Dirom, 2007). A new filter was only used when the filter became blocked or after use at Cwmystwyth and the Fe-rich Cwm Rheidol. Samples were collected in low density polyethylene bottles (leaving no head space) which had previously been rinsed three times with filtered sample, a few drops of 50 % (v/v) HNO₃ (AnalaR) were then added to acidify the sample. The filter equipment and storage bottles were rinsed with sample prior to collection to minimise the loss of elements through sorption onto the surfaces. One set of triplicate samples was collected during the sample run of 17 sample sites; the site where the triplicate samples were collected was chosen at random to allow the determination of the precision of the procedure.

Duplicate samples were taken of all the waters, one for anion determination (non-acidified) and the other for cation determination (acidified). The water samples for cation determination were acidified to <pH 2 with a few drops of 50 % (v/v) HNO₃ (AnalaR) (see Levinson, 1974); although Jones *et al.* (2004) concluded that the acid used should not affect the concentration of elements. The samples were acidified to stabilise them, suppressing precipitation and further biological activity and to discourage adsorption onto the surface of the sample bottle. Levinson (1974), however, states that acidifying the water sample could cause the release of elements that were previously adsorbed onto clays and/or dissolve metal containing colloids or soluble minerals. Acidifying the sample (to pH 1-3) could also cause the precipitation of humic substances with the co-precipitation of elements such as Fe, Mn and aluminium (Al), if the water contains significant quantities of organic material (Cook and Miles, 1980; Faure, 1998).

Filtering effects

A large proportion of the suspended matter within the water is removed when waters are filtered to <0.45 µm. The suspended matter may have metals associated with it (Rolfe and

Jennet, 1973) and therefore once removed significant anomalies may be missed if the suspended material is removed before the water sample is analysed (Levinson, 1974). To determine the affect of filtering on the chemical composition of the water, samples collected from Bwlch were filtered through progressively smaller pore size filters (unfiltered, 1.2, 0.45, 0.22 and 0.1 μm) and then analysed. Table 3.1 shows that filtering does not significantly affect the chemical composition of the water (within analytical error, with the exception of the 0.1 μm Mg fraction), though these mine drainage waters/water courses contain trace concentrations of Fe and suspended matter and are therefore unlikely to have high concentrations of associated metals. Fuge *et al.* (1991) and Bearcock (pers. comm., 2007), also determined that element concentrations in unfiltered and filtered (0.45 μm) waters were the same, or within analytical error, at Cwm Rheidol (the mine drainage waters contains high Fe concentration) and Cwmystwyth (the bed of the adit is highly ochreous).

Table 3.1. Changes in element concentration with filtering at Bwlch and Cwm Rheidol.

	Bwlch							Cwm Rheidol*
	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Mn $\mu\text{g/L}$	Co $\mu\text{g/L}$	Ni $\mu\text{g/L}$	Fe (mg/L)
Unfiltered	8.33	2.90	7.41	25.2	14.0	7.25	12.5	52.6
1.2 μm	8.30	2.99	6.88	25.2	16.7	8.82	14.2	44.6
0.45 μm	8.37	2.89	7.41	25.1	14.8	7.51	13.3	46.4
0.20 μm	8.38	2.89	7.00	25.1	16.6	7.59	13.9	45.0
0.10 μm	8.34	2.86	14.1	25.2	15.2	8.21	14.8	

	Cu $\mu\text{g/L}$	Zn mg/L	Rb $\mu\text{g/L}$	Sr $\mu\text{g/L}$	Cd $\mu\text{g/L}$	Ba $\mu\text{g/L}$	Pb $\mu\text{g/L}$
Unfiltered	18.4	16.0	1.90	36.6	39.0	15.9	791
1.2 μm	20.3	19.6	1.89	30.5	46.7	16.9	790
0.45 μm	21.5	16.5	2.24	39.2	53.4	16.9	777
0.20 μm	19.9	19.7	2.08	39.9	45.8	16.8	692
0.10 μm	20.8	19.3	1.91	37.1	55.8	17.2	711

* Data from Bearcock (pers.comm., 2007)

Analysis

All the collected samples were stored in the dark before analysis. Analysis of the major ions typically occurred within 48 hours of sample collection, trace elements normally within a week; but the anions (chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-})) were not analysed until all of the samples had been collected in January 2006 because of instrument problems. Although the NO_3^- concentration was determined, it has not been included within this thesis, as ideally water samples should be analysed for NO_3^- within three to four

days of collection, as after this period the sample deteriorates and meaningful determinations cannot be made (Levinson, 1974).

Measurement of field parameters

At the time of sampling, unfiltered water was used to determine the pH, Eh, water temperature and conductivity (specific conductivity). pH was measured using a Hannah HI98103 Checker[®] pH stick meter and calibrated using Fisher[®] pH buffer pH 4 and pH 7 solutions. Water temperature and Eh were determined using Hanna HI 9025 microcomputer meter and conductivity was determined using a Hannah DiST WP 3 stick meter calibrated with a 1417 μS conductivity standard (0.01 M KCl). From May 2005 a Myron L Ultrameter 6P was used and pH was calibrated using BDH Limited Buffer tablets to create pH 4, 7 and 9.22 (± 0.02) solutions and the same conductivity standard as above was used. The field parameter instruments were recalibrated at the beginning of each sample day.

Sample location

Careful consideration has to be taken in the location of the sample taken from the mine drainage/water course so that a representative sample was taken. Where possible the samples were collected in the centre of the channel and at mid-depth, although this was not always possible; for example, at Bwlch the whole of the mine drainage flow was collected and sampled. This collection procedure was followed to minimise the potential that the water being sampled has a heterogeneous chemical composition; as some channels have chemically distinct plumes of water (Faure, 1998). Only waters with a high turbulence and therefore mixing will have a homogeneous composition (Adam, 2001).

Rainfall measurements

Rainfall was measured daily by the Institute of Grassland and Environmental Research, Aberystwyth at the Plas Gogerddan weather station (SN(22) 627 835). This site is the nearest local weather station and is situated on the coastal lowland; the rainfall totals given will be an underestimation of the precipitation within upland areas, where most of the mines are situated, but will provide an indication of the rainfall and the regional rainfall variability through the year.

3.2 Analytical methods

Analyses were performed to determine major and trace element chemistry of 52 elements/ions within the mine drainage waters (see Chapter 4), laboratory experiments (see Chapter 6), field trials (see Chapter 7 and 8) and seaweed digestions (see Chapter 7). The elements that were determined include metals in the “Priority Hazardous Substances” (ENV/191000/01) list 1 (Cd) and list 2 (Cu, Fe, Ni, Zn and Pb). These analyses involved the following techniques:

- * *Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)* for the analysis of a suite of trace elements, including Co, Ni, Mn, Cu, Cd, Ba and Pb
- * *Atomic Absorption Spectrometry (AAS)* for the analysis of Zn, Fe, calcium (Ca) and magnesium (Mg)
- * *Flame Emission Spectrometry* for the analysis of sodium (Na) and potassium (K)
- * *Ion Chromatography* for the analysis of Cl^- , NO_3^- and SO_4^{2-} .

Details of each technique are given below.

3.2.1 Inductively Coupled Plasma – Mass Spectrometry

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) enables rapid multi-element analysis of very low concentrations of elements (Pearce, 1991; Perry *et al.*, 1995; Barefoot and Van Loon, 1999). The sample is introduced into the ICP-MS as a solution and is nebulised to form a fine aerosol, droplets $>10\ \mu\text{m}$ are removed (Jarvis, 1997). The aerosol is transported into a plasma where it vaporises to molecular level and dissociates into atoms, which may become ionised (Perkins and Pearce, 1995). The ions are extracted from the plasma and transferred to a mass spectrometer (Savory and Herman, 1999). To transfer the ions from the high temperature and pressure plasma to the high vacuum mass spectrometer the sampled ions flow through an interface (sampling cone and skimmer) which consists of several pressure reduction stages (Thompson, 1986). The resulting ion beam is focussed into a quadrupole mass spectrometer where the ions are differentiated according to their mass and charge. The number of ions of each mass is recorded by an electron multiplier and the proportion of each element present within the sample is calculated (Jarvis and Jarvis, 1992). The advantages of using an ICP-MS are that it has simple spectra, wide linear dynamic range, the ability to measure isotopic ratios (Rao and Reddi, 2001) and excellent detection limits (Thompson, 1986; Perry *et al.*, 1995). The

main disadvantage of ICP-MS analysis is that some masses are not element specific (Helmers, 1996), and the instrument only measures the mass/charge ratio. For singly charged ions formed in the ICP the mass/charge ratio is equivalent to the isotopic mass. The element concentrations quoted within this thesis are the total concentration of a particular element, determined from one or more isotopes of that element. Thus, for example, where a concentration is tabulated as ^{112}Cd , this gives the total concentration of Cd in the sample measured using the ^{112}Cd isotope: it is not a measurement of isotopic abundance/ isotopic concentration.

Interferences

Jarvis and Jarvis (1992) determined that there were three main categories of interferences: 1) polyatomic ions – where the most abundant ions, argon (Ar), oxygen (O), hydrogen (H) and nitrogen (N) react in the plasma, for example, ArO^+ and ArH^+ . The acids used in stabilising the samples upon collection or used in sample preparation may also contain trace concentrations of elements that can lead to the formation of polyatomic species; 2) doubly charged ions; and 3) refractory oxides from the incomplete disassociation of the molecules within the plasma, or the recombination of ions in the tail of the plasma. The possible interferences can be predicted with knowledge of the sample and method of preparation; and alternative isotopes may be chosen to avoid any interferences.

Analysis

The elements/ions were analysed using a Fisons PlasmaQuad II+ STE ICP-MS with a PTFE V-groove nebuliser. The concentrations of elements were analysed using the single internal standard method. All analyses were prepared using 9.8 mL sample and 0.2 mL of a ruthenium (Ru) internal standard solution to give 100 ng/mL Ru per sample. Ruthenium was used as an internal standard as it is near the centre of the mass range and is an uncommon element and may therefore be assumed to be absent from the samples. The addition of Ru also helps determine any sensitivity changes between the samples and can therefore be used to compensate for instrument drift (Pearce, 1991).

The samples were introduced to the ICP-MS in a random order and instrument calibration was undertaken by the analysis of a blank (9.6 mL MilliQ water, 0.2 mL Ru internal standard and 0.2 mL concentrated HNO_3) and a standard solution (100 ng/mL lithium (Li), beryllium (Be), Na, Al, scandium (Sc), Co, gallium (Ga), As, yttrium (Y), rhodium (Rh),

Iodine (I), cesium (Cs), praseodymium (Pr), terbium (Tb), holmium (Ho), thulium (Tm), rhenium (Re), Bi, thorium (Th), uranium (U)). The results were manipulated using Excel to determine the final concentration in ng/mL. Samples from June 2006 were determined using the instrument's software, by subtracting the blank and calibrating using a regression line created by using 3 multi-element solutions (50 ng/mL, 100 ng/mL and 200 ng/mL).

Precision

During each sample collection period one mine drainage was selected to calculate the precision of the ICP-MS analysis. The precision for mines with a high (>10 mg/L), medium (1-2 µg/L) and low (<1 µg/L) concentration of Cd is shown in Table 3.2. The eight mines chosen to show precision were: Frongoch (four duplicate and two triplicate samples), Cwmystwyth (two duplicate and one triplicate samples), Wemyss (four duplicate and two triplicate samples), Alltycrib (two triplicate samples), Cwmbryno (two triplicate samples), Esgair Hir (two duplicate and two triplicate samples), Daren (three duplicate samples) and Goginan (two triplicate samples). The concentrations for the duplicate and triplicate samples are shown in Appendix 2. Only Co, Ni, Cu, Cd, Ba and Pb are mentioned as they are the main metals of interest. The relative standard deviation (RSD) of the samples was calculated by:

$$\text{Relative Standard Deviation (\%)} = \text{standard deviation} / \text{mean} * 100 \quad (3.1)$$

Where the standard deviation was calculated (by Microsoft Excel) by:

$$\text{Standard Deviation} = \left(\frac{\sum(X - X^*)^2}{(n-1)} \right) \quad (3.2)$$

Where X = sample value, X* = mean value of the samples and n = sample size

Table 3.2. Relative standard deviations (%) of duplicate and triplicate samples.

	Co	Ni	Cu	Cd	Ba	Pb
High Cd concentration (>10 µg/L)						
Frongoch	5.6	7.2	9.8	2.7	9.8	8.5
Cwmystwyth	5.1	1.9	12.9	4.7	12.3	4.9
Wemyss	12.4	10.0	11.3	5.2	7.0	6.0
Medium Cd concentration (1 - 2 µg/L)						
Alltycrib	10.7	20.1	13.1	12.9	n.a.	7.7
Cwmbryno	18.9	30.0	10.4	10.2	5.6	4.4
Low Cd concentration (< 1 µg/L)						
Esgair Hir	6.3	4.2	6.1	13.1	4.6	5.8
Daren	13.5	11.2	3.1	n.d.	2.1	9.3
Goginan	8.5	n.d.	8.7	n.d.	3.0	5.5

n.a. not analysed

n.d. not detected

The typical analytical variation using ICP-MS is $\pm 10-15\%$ as determined by Pearce (pers. comm., 2007), although Jarvis (1997) concluded that precision is between 2-5 % RSD. Any variation below $\pm 10\%$ is not significant, but variation $\pm 15\%$ represents a real variation that cannot be attributed to analytical or sampling errors. Most analyses are below 15 % variation with the exception of Co at Cwmbryno and Ni at Alltycrib and Cwmbryno. These high RSDs are caused because of a low concentration ($< 2\ \mu\text{g/L}$) of the metal in the mine waters. Nickel from the sample and skimmer cones (Perkins and Pearce, 1995) may also contribute a significant concentration to the water blank (Jarvis, 1997), which could have caused the high RSD value. Elements with concentrations $< 1\ \mu\text{g/L}$ are disregarded within this thesis as they give high RSD values and therefore can not be treated with a high degree of confidence.

3.2.2 Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is a well established analytical method and allows the rapid analysis of large numbers of aqueous samples for a restricted range of elements (Croft, 1986). More abundant elements within the mine drainage waters/water courses (Zn, Fe, Ca and Mg) were measured using AAS. The AAS has a better precision than the ICP-MS and is more suited to the measurement of elements with a higher concentration. Another advantage of using AAS to measure Zn concentrations is that when Zn is analysed by ICP-MS it occurs in an area of the mass spectrum that has a wide range of potential

poly-atomic interferences (see above); this does not occur when Zn concentrations are measured by AAS. Measurement of Zn present in solutions, in the mg/L range, by ICP-MS would also require dilution to bring it into the working range of the instrument.

The solution is atomised in an air-acetylene flame which breaks down the compounds of the elements in the atomised solution to their atomic ground state (neutral unbound atoms). A beam of light (with a characteristic radiation) from a hollow cathode lamp is passed through the flame. The cathode in the lamp is made from the same element to be determined. The element in its atomic ground state within the flame absorbs the radiation from the hollow cathode lamp at the element's characteristic wavelength. The radiation from the lamp, now reduced because of the element absorbing some of the radiation, is isolated in a monochromator and measured by a detector. The reduction in radiation is proportional to the concentration of the required element and follows the Beer-Lambert law (Levinson, 1974; Croft, 1986; Rowland, 1997; Ahmad *et al.*, 2001).

Savory and Herman (1999) determined that AAS is relatively sensitive in the ~100 µg/L range, and for solutions containing mg/L concentrations, precision can be ~1 % RSD. Analysis by AAS is relatively free from interferences because of the characteristic wavelength emitted by the hollow cathode lamp and absorbed by the element in solution. Some interferences do occur, however, including (a) matrix effect - variations in the bulk composition of the sample; (b) chemical interferences - when another element forms a compound with the required element; and (c) spectral interferences - when another element is absorbed at the same wavelength (Levinson, 1974; Ahmad *et al.*, 2001). One of the major disadvantages to this method, however, is that it only measures the concentrations of one element at a time, as each individual element requires its own hollow cathode lamp (Croft, 1986).

Two instruments were used within this study, a Perkin-Elmer 5000 and a Perkin-Elmer 2380, both using an air/acetylene flame. Both instruments were calibrated using three synthetic standards and a blank (MilliQ water). Samples were diluted as necessary and concentrations were taken as an average of three sub-samples which were averaged by the instrument's software. Standards were re-analysed approximately every 15 samples. The elements were determined using the principal wavelengths provided by Whiteside and Milner (1981): Zn – 213.9 nm, Fe – 248.3 nm, Ca – 422.7 nm and Mg – 202.6 nm. The

detection limit of the AAS (Perkin-Elmer 5000) was calculated by three times the standard deviation of the procedural blank. The detection limits are: Zn – 0.03 mg/L, Fe – 0.018 mg/L, Ca – 0.003 mg/L and Mg – 0.003 mg/L (Warrender pers. comm., 2008)

3.2.3 Flame Emission Spectrometry

The two instruments detailed above were employed as a flame emission spectrometry to determine the concentrations of Na (589.0 nm principal wavelength) and K (766.5 nm principal wavelength). The solution is atomised within the air-acetylene flame and a proportion of the atoms are excited, as they return to their ground state they emit radiation characteristic of that metal, which is measured by a photomultiplier tube (Vogel, 1979; Lewis, 1997; Ahmad *et al.*, 2001).

As above, the instruments were calibrated using three synthetic standards and a blank (MilliQ water). Samples were diluted as necessary and the concentrations were taken as an average of three sub-samples which were averaged by the instrument's software. Standards were re-analysed approximately every 15 samples.

3.2.4 Ion Chromatography

Ion chromatography is the separation of ionic species in solution into different components as it flows through an ion exchange column. The solution (5 mL) is injected into an eluant fluid which carries the solution through the ion exchange column. The eluant and sample ions react with functional groups within the column, and ions separate according to size and ionic charge, with the smaller and monovalent ions flowing faster through the column. The concentration is registered by ion conductivity, ultra-violet or by an electrochemical detector and the individual components are identified by the difference in time from the injection of the solution to the detection of the component (Rowland, 1997; Gjerde and Fritz, 1987).

A Dionex DX 100 ion chromatograph with a TS-2 thermal stabiliser module and an IonPac[®] AS4A-SC analytical column was used. Samples were introduced using an AS-40 auto sampler. A 1.8 mM carbonate/1.7 mM bicarbonate anion eluant was used and was prepared fresh each morning, as it easily deteriorates. The eluant stock solution was prepared using 19.0805 g NaCO₃ and 14.2805 g NaHCO₃ made up to 1 L with MilliQ

water. The eluant for use within the instrument was prepared by pipetting 20 mL of the stock solution, made up to 2 L with MilliQ water. The instrument was calibrated using a blank and three standards; two blanks were analysed before and after the standards. Standards were re-analysed every ~24 samples and blanks were analysed sporadically throughout the sample run.

The detection limit of the instrument was calculated using the blank samples as Cl – 0.01 mg/L, NO₃ – 0.06 mg/L and SO₄ – 0.06 mg/L (Perkins pers. comm., 2008). Precision and accuracy was determined by Fuge *et al.* (1991) to be generally better than 10 %.

CHAPTER 4:

Impact of metal mining and mine water variability

Historic mining activities have left a legacy of adits, shafts, spoil tips and tailings dams (Runkel *et al.*, 2007) across the mid-Wales orefield. Mining and mineral-processing activities may only affect a relatively small area; but they can have a significant impact on the local environment, both visually and chemically (National Rivers Authority, 1994; Antunes *et al.*, 2002).

The mined material brought to the surface included host rock, the sought after ore and gangue minerals. To separate the ore minerals from the detritus, the mined material was crushed, sieved and separated using water-assisted gravity separation techniques (Environment Agency, 2002). The ore was then sold to a smelter and the waste would be deposited onto large spoil tips. The separation and concentration of the ores was totally reliant on water and was an inefficient process (Davies, 1987; Evans, 1991; Fuge *et al.*, 1991; 1994). The water used within the separation process was subsequently released into local water courses, with no pre-treatment (Davies, 1987), causing long-term damage. In Wales the 1873 Rivers Pollution Commissioner's Report stated that during ore processing 35 % of the ore raised to the surface was lost to the environment (Davies, 1987).

Abandoned mine drainage and run-off/leachate from old spoil tips may contain very high concentrations of metals (Environment Agency, 2002). Metcalfe (1983; cited in Thornton *et al.*, 1986) identified four metal sources to rivers: 1) discharge from mine water drainage adits; 2) action of subsurface drainage and ground water on metalliferous mine spoil; 3) action of surface drainage on mine spoil; and 4) outwash of metalliferous material from river banks and mine spoil. The discharges from abandoned mines are a frequent cause of river and local groundwater pollution (Bowell and Bruce, 1995; Younger, 1997; 2000a).

4.1 Chemical Weathering

The chemical composition of mine drainage results from the dissolution and chemical interactions with solids, liquids and gases during the hydrological cycle (Stumm and Morgan, 1996). Chemical weathering involves the breakdown by chemical means of rocks and minerals (Levinson, 1974) by dissolution, alteration, and sometimes by replacement of such minerals and the precipitation of new minerals, such as clays, Fe^{3+} and Al-oxyhydroxides (Langmuir, 1997). Chemical weathering is one of the major processes controlling the global hydrogeochemical cycle of elements (Stumm and Morgan, 1996). The order of resistance of rock-forming minerals is generally oxides > silicates > carbonates and sulphides (Levinson, 1974).

Meybeck (1987 cited in Bluth and Kump, 1994) assigned a weathering scale to rocks with increasing susceptibility: evaporites > carbonates > shales > volcanics > sandstones > granites. The elements released via weathering of sandstones and shales, include Na and Cl from halite inclusions within shales, which formed through interstitial seawater being trapped as the shales were being deposited (Meybeck, 1987; Berner and Berner, 1996; Drever, 1997). Potassium is also released from silicate weathering (Sullivan and Drever, 2001; Jacobson *et al.*, 2002; Mortattia and Probst, 2003) though little is present in most waters because minerals that contain K weather more slowly than those which contain Na, Ca and Mg (Berner and Berner, 1996). Cation exchange can occur on detrital clay minerals during marine shale weathering between Ca and Na (Berner and Berner, 1996). Shales are a variable rock type, containing varying amounts of pyrite, marine clays, detrital carbonate minerals, organic matter etc. therefore the water draining these rocks is also highly variable, but usually contain SO_4^{2-} or Cl^- as major anions (Meybeck, 1987; Drever, 1997). Both quartz and illite are abundant minerals in shales but are relatively unreactive to weathering and therefore do not contribute a great deal to runoff chemistry (Drever, 1997).

Sulphide minerals are present in a large number of natural environments (Acero *et al.*, 2007) and their weathering is an important source of pollution (Elberling and Langdahl, 1998; Acero *et al.*, 2007). Jambor (1994) produced a general sequence of the reactivity of sulphides within a spoil tip environment (from most to least susceptible): pyrrhotite > galena > sphalerite > pyrite > arsenopyrite > chalcopyrite > magnetite (cited in Boulet and

Larocque, 1998; Holmström *et al.*, 2001). Sulphide minerals are chemically unstable and react readily with exposure to air and water (Berner and Berner, 1996; Drever, 1997). Krauskopf (1967 cited in Levinson, 1974) observed that all chemical weathering reactions involved four relatively simple processes: -

1) Ionization

Ionization occurs where an atom or molecule is converted to an ion by changing the difference between the number of protons and electrons (Levinson, 1974).

2) Addition of water

Water is a very important agent of weathering and mainly acts to catalyse weathering reactions; the reactions occur very slowly or not at all without water. Water contains (and holds into contact with the rocks and ore minerals) other agents that enhance chemical weathering, including free oxygen, carbon dioxide, organic acids and nitrogen acids. Nitrogen acids are produced through the decay of organic matter, bacterial action within the soils or by rainwater dissolving nitrous oxides (Krauskopf and Bird, 1995). Carbon dioxide dissolves in rainwater to form carbonic acid; therefore all water in the atmosphere is a dilute form of this acid. Carbonic acid oxidises the S:

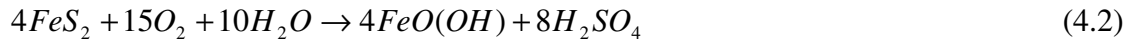


3) Hydrolysis

Where the ionic species H^+ and OH^- become incorporated into the structure of the minerals, more specifically, there is a reaction between water and the ion of a weak acid or a weak base (Levinson, 1974).

4) Oxidation

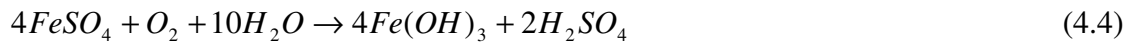
Oxidation is usually accompanied by hydrolysis and often by hydration and carbonation. The sulphide anion usually oxidises to form sulphate (Faure, 1998) and associated metals are also released. Water increases the rate of oxidation, most likely dissolving minute quantities of minerals and other materials; reactions with oxygen are faster with dissolved substances than with solids (Krauskopf and Bird, 1995), for example, iron sulphides where both the Fe and S are oxidised:



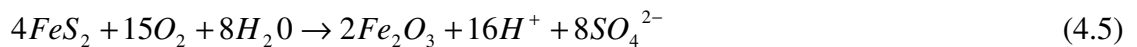
Once the H₂SO₄ has formed it may react with more iron sulphides:



The FeSO₄ is then available for oxidation and more H₂SO₄ is produced:

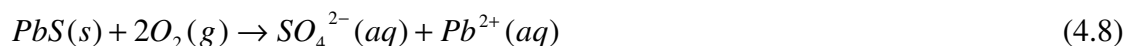
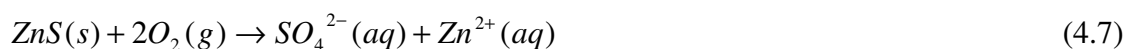


Ferrous sulphate and H₂SO₄ are powerful agents in the decomposition of other sulphide, silicate and carbonate minerals (Levinson, 1974; Berner and Berner, 1996). Sulphide oxidation is catalysed by bacteria (Stumm and Morgan, 1996; Drever, 1997; Langmuir, 1997). The produced acidity depends on the composition of the sulphides and the presence of other minerals, especially carbonates, which can neutralise the acid (Berner and Berner, 1996):



Acid neutralisation occurs at Cwmystwyth (pyrite, marcasite and calcite), Eaglebrook (chalcopyrite and ferroan dolomite) and Esgair Hir (chalcopyrite, calcite and ferroan dolomite) producing ochre coated streams, but slightly acidic (pH 6.1 – 6.4) mine drainage. Silicate minerals (Berner and Berner, 1996) and bacterial sulphate reduction (Herlihy *et al.*, 1988 cited in Moses and Herman, 1991) can also, to a certain extent, act to neutralise the acidity. Cwm Rheidol mine drainage is an exception in mid-Wales with an average pH of 3.4 and very little carbonate present within the mine to neutralise the acid. The other mines studied, not mentioned above, are also slightly acidic (pH between 5 and 6.6) and metal-rich; the slightly acidic mine drainage is not caused by the acid neutralisation of pyrite, marcasite or chalcopyrite. Instead, the slightly acidic mine drainage is caused by the direct oxidation of simple sulphides (Levinson, 1974), for example, sphalerite and galena, which does not produce any acidity. Galena is one of the most insoluble Pb

minerals, but when exposed to air and water, it becomes highly unstable (Hsieh and Huang, 1989):



The release of metals is non-linear with decreasing reaction rates over time; and may be ascribed to the formation of leached layers or secondary precipitates on the mineral surface (Salmon and Malmström, 2006). Galena oxidation is primarily a surface reaction determined by surface availability (Hsieh and Huang, 1989). Surface coatings may form on the minerals, for example, insoluble PbSO_4 (anglesite) or $\text{Pb}(\text{CO}_3)$ (cerrusite) may form and inhibit further oxidation (Levinson, 1974; Younger, 2000a). Boulet and Larocque (1998) and Acero *et al.* (2007) observed that the dissolution of sphalerite creates an S-rich layer, either Zn polysulphide and/or elemental S on the surface, but it fails to reduce the reactivity once steady-state is achieved, allowing continued dissolution to occur (see references within Acero *et al.*, 2007). Sphalerite is preferentially weathered to a soluble sulphate, while greenockite (CdS) is weathered to a lesser extent and may form a coating on the sphalerite (Fuge *et al.*, 1993). During dissolution of sulphide minerals secondary mineralisation can occur, creating a more stable form under surface conditions, such as hydroxides, carbonates, sulphates and silicates, which can act as temporary storage for these elements (Clark *et al.*, 2001). Secondary mineralisation is widespread throughout the mid-Wales orefield, both formed within the spoil tips and *in situ* within the mine (Mason, 1997).

The mine drainage waters contain high concentrations of metals that were not specifically mined for and/or occur in concentrations not economical to extract (Clark *et al.*, 2001), for example, the ore minerals invariably contain minor and trace amounts of other elements (Davies, 1987), typically As, Mn, Bi, Hg, Se, Cu, Fe, Sb, Cd, Ni, Co, Ag and Au (Foster-Smith, 1979; Mason, 1997), the dissolution of the sulphide minerals also releases these elements into solution.

Levinson (1974) stated that there are three end products produced during chemical weathering: (1) Soluble constituents resulting from the breakdown of sulphates, silicates

and carbonates; (2) insoluble constituents including clay minerals, Fe and Mn oxides, sulphates, chlorides, silicates and native metals; and (3) residual primary minerals that are resistant to chemical weathering, which are generally hard, lack cleavage, or have properties that allow them to be transported and deposited as placers. It is important to remember that although the minerals' solution rates may be slow, they will all eventually dissolve and leach away (Langmuir, 1997).

4.2 Causes of element variations in the environment

There are numerous complex biological, geochemical and physical processes that control the variability of mine drainage composition (Holmström *et al.*, 2001) on daily, seasonal and yearly time scales. Water courses and mine drainage waters rarely have a constant flow rate and/or composition throughout the year, therefore a single 'grab' sample cannot be wholly representative, as it would lead to variable, misleading or contradictory results (Levinson, 1974). The geochemistry of the mine drainage/water course is affected by factors which are relatively stable throughout the year, for example, the underlying geology; and those which vary over time, for example, precipitation, though the dominant factor is still cause for debate (Dalai *et al.*, 2002). The causes of these variations in element concentration include:

- 1) Anthropogenic sources – including road salting, mining, sewage discharges, industrial wastewaters, urban runoff and agriculture (Bluth and Kump, 1994; Stumm and Morgan, 1996).
- 2) Atmospheric deposition – including deposition from industry, combustion of fossil fuels, emissions from cars and marine sources (Stumm and Morgan, 1996).
- 3) Lithology and the physical properties of the host rock – the specific minerals and secondary minerals included in the host rocks can have a strong influence on the solutes present within the mine drainage. The purity and crystal size of minerals, the rock texture and porosity, the regional structure, the degree of fracturing and many other factors can influence the water's composition (Hem, 1985).

- 4) Mineralisation – the amount and availability of ore minerals and cements, for example, galena, sphalerite, calcite and the trace elements contained within the ore minerals.
- 5) The degree and rate of chemical weathering – chemical weathering can be controlled by numerous factors: -
- (a) Hydrology – contact time between the water and the host rock/ore minerals; and the water–rock ratio (Fairchild *et al.*, 2000). An increase in contact time should increase the element concentration in solution because of the slow weathering kinetics of the sulphide and silicate minerals (Mitchell *et al.*, 2005).
 - (b) Physical properties of the host rock/ore minerals – finely crushed spoil material will have a greater solubility than larger spoil material because of its increased surface area (Stumm and Morgan, 1996).
 - (c) Climatic factors – weathering rates of minerals are assumed to be influenced by differences in climate (White and Blum, 1995). The amount and rate of precipitation, runoff, and evaporation are all important factors in the control of natural-water composition, with some elements being more affected than others (Hem, 1985). Precipitation or runoff is thought to be one of the primary controls on chemical weathering at a global scale (Bluth and Kump, 1994; White and Blum, 1995; Gaillardet *et al.*, 1999) and becomes more important at higher temperatures. Increasing the water flow through the mine or spoil tip can accelerate chemical weathering by increasing the wetted surface area of the minerals (Levinson, 1974; White and Blum, 1995). The height of the water table within the mine and/or spoil tip influences the proportion of rock and ore minerals available for dissolution (Desbarats and Dirom, 2005). Mineral dissolution rates increase with increasing temperature (Hem, 1985; Drever and Zorbrist, 1992; Langmuir, 1997; Dalai *et al.*, 2002); Levinson (1974) stated that for every 10 °C rise in temperature the rate of chemical weathering increases by a factor of two or three; although Peters (1984 cited in Bluth and Kump, 1994) found no conclusive evidence that temperature controlled weathering rates. Higher temperatures can concentrate weathering products and any related bacterially-mediated reactions via evaporation (Desbarats and Dirom, 2005). Peters (1984 cited in Bluth and Kump, 1994) examined the relationship between river chemistry, stream temperature, human population, rock type and concluded that the dominant factor was the amount of precipitation, causing 58-71 % of the water chemistry variation; with rock type being of secondary importance.

- (d) Physical weathering – physical weathering increases the surface area available for chemical weathering (Berner and Berner, 1996; Langmuir, 1997) and constant abrasion of ore minerals in river bed sediments continually produces fresh surfaces for dissolution (Environment Agency, 2002).
- (e) Relief – the relationship between the rate of chemical weathering and relief is controversial. Drever and Zobrist (1992) determined that the rate of chemical weathering decreases more or less exponentially with elevation; White and Blum (1995) observed no relationship between relief and chemical weathering rate; and Stallard (1985) and Edmond *et al.* (1995) observed an increase in the rate of chemical weathering with relief in the Andes (cited in Drever, 1997).
- (f) Biota – biological processes can generate acidity (generation of organic acids and releasing CO₂ into the surrounding environment), transfer nutrients through the soil and physically work the soil through root growth (Bluth and Kump, 1994; Drever, 1994; Stumm and Morgan, 1996). Plants can also influence the formation of secondary minerals, especially those containing Fe, Al, and Si. Plants cause a higher rate of weathering than if they were not present, though the direct effect on silicate weathering rates is relatively small (factor of ~2) (Drever, 1994). The seasonal and diurnal effect of living organisms (photosynthesis, respiration, cycles of growth and decay) can influence the concentrations of certain elements within the water (Holloway and Dahlgren, 2001), for example, K, Ba (Gaillardet *et al.*, 1999), Co, Cu, Zn, and Mg (Hem, 1985). Biological activity depends upon the water temperature, weather conditions and sunlight, which influences photochemical reactions, which can lead to alterations in chemical solubility and therefore concentrations of elements within the waters.
- 6) Hydrology – including changes in the amount and source of the water, for example, ground water and infiltration water and the route the water takes from within the mine to the water course and through the spoil tip.
- 7) Reactions – the reactions between the elements in the stream water and particulate matter, for example, clays, Mn and Fe oxides, organic matter and humic acids, on the stream bed and within the water column. These reactions play a vital role in controlling the concentration of most dissolved trace elements, with a larger concentration in the solid or surface phase than within the water phase (Stumm and Morgan, 1996).

8) Soil forming processes or reactions – including the dissolution and alteration of minerals; removal and circulation of various nutrients; the production of CO₂ and the conversion of gaseous N; sorption and desorption of elements by mineral and organic surfaces; concentration by evapotranspiration; with the production of CO₂ being the most important (Hem, 1985).

9) Location of the sample - As discussed in Chapter 3.1, the composition of mine drainage waters are not homogeneous throughout the water course, other than in waters with high turbulence and mixing (Adam, 2001); in some channels chemically distinct plumes of water may occur (Faure, 1998).

4.3 Impact of metal mining on mid-Wales

Throughout Wales, mining has left a legacy of abandoned mine shafts, adits, spoil tips, contaminated land and metalliferous contamination of water courses, many of which are in environmentally sensitive areas (Davies, 1987; Environment Agency, 1999).

The metals released by chemical weathering can result in an environmental or human health risk (Clark *et al.*, 2001); for example, the mine drainage from Cwm Rheidol causes a 16 km stretch down river to fail EQS set by the EU (Environment Agency, 2002). Ceredigion rivers, especially the Ystwyth, were extremely polluted prior to the 1876 Rivers Pollution Prevention Act and their reputation as first class salmon and trout rivers destroyed (Davies, 1987).

The 1876 Act, together with the cessation of mining, has slowly improved river quality, with some river stretches totally recovered (Grimshaw *et al.*, 1976; Davies, 1987; Fuge *et al.*, 1991), though the rivers have suffered intermittent setbacks with the opening of new mines (Newton, 1944). Abdullah and Royle (1972) determined that background concentration of metals in uncontaminated Welsh waters was 0.7 µg/L Cu, 11 µg/L Zn, and 0.7 µg/L Pb. River waters ultimately transport the metals to the sea; within Cardigan Bay, the mean concentrations are ~1.7 µg/L Cu, ~7.5 µg/L Zn, ~1.1 µg/L Cd, and ~2.2 µg/L Pb (Abdullah *et al.*, 1972). By the 1970s the Water Pollution Survey of England and Wales found that stretches of the Rheidol and Ystwyth were still contaminated, with Pb, Zn and

Cu concentrations over an order of magnitude higher than those in uncontaminated waters (Jones, 1986).

To determine the 'good' ecological status of streams and rivers required by the EU's WFD the biological indicators are aquatic flora (macrophytes, benthic algae and phytoplankton), benthic invertebrates and fish (Hering *et al.*, 2003). The ecological status comprises (Environment Agency, 2008a):

- The condition of biological elements, for example, fish;
- the concentration of supporting physico-chemical elements, for example, oxygen and ammonia;
- the concentration of specific pollutants, for example, Cu; and
- for high status, largely undisturbed hydromorphology

The fauna within the lower Ystwyth and Rheidol rivers has slowly improved since 1922 (Newton, 1944). The lower Ystwyth was found to contain nine species between 1919 and 1921, subsequent studies found 26 species after 1922 (Carpenter, 1924), 63 species in 1939 (Jones, 1940) increasing to 111 species between 1975 and 1977 (Brooker and Morris, 1980). This increase of species over time is also seen within the Rheidol; Carpenter (1924) determined that lower reaches contained 14 species between 1919 and 1921, subsequent studies found 29 studies after 1922; 103 species between 1931 and 1932, 130 species between 1947 and 1948 (Jones and Howells, 1975) and 134 species between 1975 and 1977 (Brooker and Morris, 1980). These faunal species were dominated by Insecta (Brooker and Morris, 1980). A recent study conducted by Atkins (2008) within the Ystwyth found that at nearly all polluted sites macroinvertebrate communities demonstrated clear signs of impact in relation to the location of metal input i.e. a decrease in species diversity, abundance and loss or reduction in sensitive species taxa and an increase in more tolerant groups. Jones (1940) also determined that certain species appeared to be more tolerant of the high Zn concentrations and a number of species were found in the most heavily polluted of effluent streams.

Jones (1940) determined that there was no apparent evidence that the Insecta species found were limited by the concentration of Zn within the river, with certain species appearing to be very tolerant to the high metal concentrations with some of species living in the most

polluted watercourses. Zn is a physiologically essential element and poses a hazard to a host of flora and fauna; Pb, however, has no known positive biological function and creates serious environmental and health hazards (Hofmann and Schuwirth, 2008). Zinc concentrations >1 mg/L can reduce the growth and survival of aquatic organisms (Besser and Rabeni, 1978 cited in Gao and Bradshaw, 1995) and many aquatic organisms are particularly sensitive to Zn. At low concentrations Cd and Cu are also toxic and have been shown to act synergistically with Zn (Hoiland *et al.*, 1994).

Fish have a metabolic requirement for Zn, Cu and Fe, but high concentrations of Pb, Cd, Hg, Cr and Ni can cause high mortality rates (Abdullah and Royle, 1972; Environment Agency, 2002). Fish acquire metal ions or salts via their respiratory system; they excrete the metals either via their kidneys (accumulating to toxic levels) or by their gills (the metals produce a mucus which collects on the gills and suffocates the organisms) (Carpenter, 1924; Environment Agency, 2002). Salmon began spawning again during the 1950s in the Ceredigion rivers. The Clarach, Rheidol and Ystwyth rivers were surveyed in 1994 and the Environment Agency (in the 1999 Local Environmental Agency Plan for North Ceredigion) determined that “over 70 % of sites sampled on the Clarach were classed as either containing ‘Excellent’ or ‘Good’ juvenile trout stocks, but no salmon were found during the survey. One site, on the Silo, remained fishless, affected by abandoned lead mines. Over 66 % of sites within the Rheidol catchment were classed as either ‘Excellent’ or ‘Good’ for trout. No sites sampled on the Ystwyth were found to be fishless, and 60 % of sites contained ‘Excellent’ or ‘Good’ trout populations, though this survey did not include historically polluted sites; salmon were less abundant.” A recent survey of the River Rheidol by Shannon (2006) found there to be no detrimental impact on salmonid fry populations downstream of the Cwm Rheidol mine, even though Zn concentrations are 20 times those specified in the EQS (cited in Edwards and Potter, 2007). A recent study by the Cwm Rheidol fisheries (2007) indicated that high concentrations of dissolved metals, Pb and Zn in particular and possibly Cd, were limiting to the trout populations present in the area (cited in Atkins, 2008).

McLean and Jones (1975) surveyed metal concentrations in fauna along the Ystwyth and Clarach and found that the rivers were still polluted, though certain organisms seemed to be unaffected by the metals. Studies of ground cover vegetation conducted by Johnson *et*

al. (1978) found Pb concentrations increased up to five-fold during the growth period between April and September.

The spoil tips which are littered over the mining landscape are mostly devoid of vegetation (Davies, 1987), caused by the toxic nature and nutrient deficiency of the mine spoil (Jones and Howells, 1975). The fine-grained material contained within the spoil tips can be dispersed via wind and water erosion of the unstable slopes; the material may be moved 0.5–1 km from the spoil tips by aeolian processes (Johnson *et al.*, 1978). In the mid 1970s studies at Cwmsymlog showed increased blood Pb concentrations in the local population (including children); nearby tips contained very fine particles, which contained up to 1.4 % Pb (Environment Agency, 2002). Lead is a neurotoxin and associates with the alkaline earths within the body and is therefore stored, along with Ca, Sr and Ba within the bones (Faure, 1998). Lead can also interfere with haemoglobin production, act as an inhibitor for the immune system, cause kidney dysfunction, and may cause mental retardation, with children being particularly susceptible (World Health Organisation, 2000). The Pb contained in the spoil can also be deposited on the land in periods of flood. An 1874 Rivers Pollution Commissioner's Report stated that the mining wastes were causing the death of livestock and the failure of crops in the Ystwyth, Rheidol, Clarach and Dyfi catchments (Griffith, 1919 cited in Pearce, 1992; Newton, 1944).

Discharge of metal-rich waters from abandoned mines and spoil tips is a continuing source of pollution in mining districts (Davies, 1987; Fuge *et al.*, 1991, 1993; Desbarats and Dirom, 2005) and its treatment is an ongoing concern at many mine sites around the world (Clark *et al.*, 2001). The Environment Agency has not yet assessed the overall current status of the rivers Ystwyth and Rheidol in terms of its ecological or chemical status as required by the WFD (Environment Agency, 2008a). To fully understand the nature of mine discharge waters, enabling effective remediation, site-specific details regarding the water's composition are required and whether changes occur in chemical composition on a seasonal or shorter timescale (National Rivers Authority, 1994; Runkel *et al.*, 2007).

4.4 Mine drainage variability

Numerous spatial variation studies have been conducted on changes in major ion chemistry in river basins; where the composition changes as the water passes from one geological environment to another (Smolders *et al.*, 2004). Variations in chemical composition on a temporal basis at a location can be just as dramatic as spatial variations. Abdullah and Royle's (1972) study on heavy metal concentrations in Welsh rivers and lakes, found considerable seasonal variations in concentrations of up to 60 % of the mean value. The chemical composition of stream water is a function of numerous complex processes acting within the watershed, as described in Chapter 4.2. These processes are active on a seasonal and storm-event scale and are spatially complex at the watershed scale; therefore determining the major process is very difficult (Holloway and Dahlgren, 2001). Understanding the dynamics of metals and other solutes from mine drainage is essential to successfully plan a remediation strategy (Petty and Barker, 2004).

Methodology

Waters were collected and analysed according to the methods given in Chapter 3. The characterisation of temporal variations in mine drainage water quality and receiving water courses was based on long-term monitoring of selected field parameters, along with frequent sampling of the waters for chemical analysis. The seventeen sample sites are described in Chapter 2.4 and the mine drainage and water courses were sampled regardless of flow conditions between January 2004 and January 2006. Water samples were collected every fortnight from the 15th January 2004 until the 18th January 2005, further sampling was undertaken on a monthly basis, until the 10th January 2006.

Inter-element Correlations

Pearson product-moment correlations (r) were undertaken on the raw data and values above 0.43 are deemed to be statistically significant at the 99 % confidence level (Shaw and Wheeler, 1994). Figure 4.1a shows an example of an r value of 0.48 (correlation between Cd and Rb at Frongoch) and it can be seen that this produces a large spread of data points. A large number of positive ratios are also produced, which may not assist in the determination of dominant relationships or the interpretation of the data. Only r values above 0.6 have therefore been considered and Figure 4.1b shows that the spread of data

points (correlation between Pb and Mn at Frongoch; $r = 0.64$) are much more constrained and are likely to provide a more relevant relationship between elements as when the r value increases the data can be considered at a higher confidence level. A summary table of the correlations may be found in Table 4.1 and the complete correlation data tables may be found in Appendix 3.

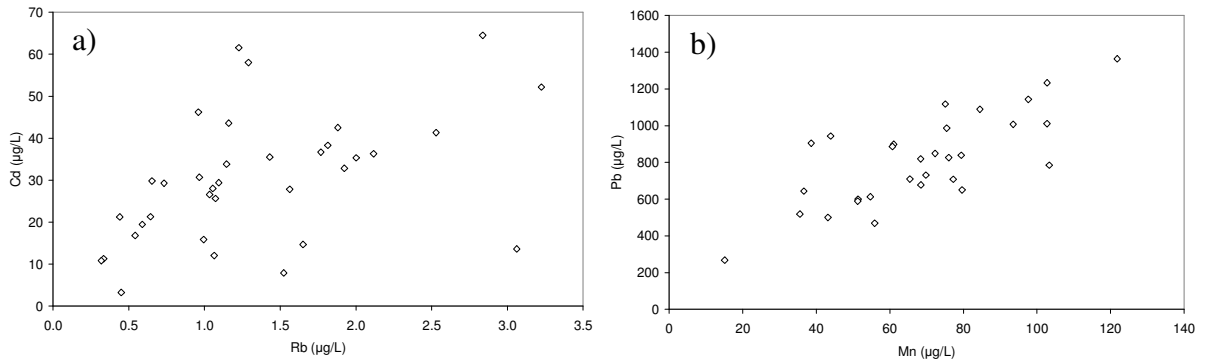


Figure 4.1. Correlation between: a) Cd and Rb at Frongoch ($r = 0.48$) and b) Pb and Mn at Frongoch ($r = 0.64$)

Quadratic polynomial smoothing

Smoothing was undertaken on all mine drainage data (excluding field parameters) to separate the ‘signal’ generated by the elements from the ‘noise’ produced by random interferences (Figure 4.2), according the method of Swan and Sandilands (1995). The mine drainage data was smoothed by arithmetically averaging the observed value at that point and two adjacent points, with the observed value having a greater influence; this is done by approximate weighting of the values. Swan and Sandilands provided a 5, 7 and 9 term (i.e. points or values) smoothing, but care must be taken so that the signal is not smoothed out as well. A 5 term smoothing was used on the temporal variation data.

To calculate the smoothed concentration of the observed value, the following calculation is used:

$$y_s = (-3y_{i-2} + 12y_{i-1} + 17y_i + 12y_{i+1} - 3y_{i+2}) / 35 \quad (4.9)$$

Where y_s is the smoothed concentration, y_i is the observed concentration, y_{i-1} is the previous observed concentration, y_{i+1} is the subsequent observed concentration and so on. The equation is divided by the sum of the weights (see Table 4.2) to produce a total weight of 1 and therefore avoid systematic overestimation. At the beginning and end of the data

series, the full equation can not be used and the observed concentrations and weightings need to be removed from the equation and the sum of the weights changed accordingly (Swan and Sandilands, 1995).

Table 4.1. Summary of correlations

Only significant correlations (i.e. over 0.6) are included

Those elements whose concentrations are below detection limit (1 µg/L) have not been included.

Afon Llywernog	N/A				
Alltycrib	SO ₄ -Mg 0.86	SO ₄ -K -0.63	SO ₄ -Ca 0.89	SO ₄ -Pb -0.64	Na-K 0.64
	Na-Zn 0.66	Mg-K -0.75	Mg-Ca 0.86	Mg-Cd -0.61	Mg-Pb -0.68
	Ca-Pb -0.61	Co-Cu 0.86	Cd-Pb 0.74	Zn-Cd 0.83	Zn-Pb 0.70
Bwlch	SO ₄ -Mg 0.93	SO ₄ -K 0.91	SO ₄ -Ca 0.94	SO ₄ -Ni 0.78	SO ₄ -Cu 0.61
	SO ₄ -Zn 0.95	SO ₄ -Cd 0.74	SO ₄ -Ba 0.72	SO ₄ -Pb 0.63	Mg-K 0.86
	Mg-Ca 0.91	Mg-Ni 0.62	Mg-Cu 0.60	Mg-Zn 0.84	Mg-Cd 0.68
	Mg-Ba 0.72	K-Ca 0.83	K-Ni 0.71	K-Cu 0.74	K-Zn 0.82
	K-Cd 0.72	K-Ba 0.77	K-Pb 0.66	Ca-Ni 0.66	Ca-Zn 0.86
	Ca-Cd 0.78	Ca-Ba 0.80	Co-Ni 0.69	Ni-Cu 0.77	Ni-Zn 0.76
	Ni-Cd 0.62	Ni-Ba 0.64	Ni-Pb 0.63	Cu-Cd 0.60	Cu-Ba 0.79
	Zn-Cd 0.71	Zn-Ba 0.62	Zn-Pb 0.63	Cd-Ba 0.90	Cd-Pb 0.88
	Ba-Pb 0.79				
	Cwm Rheidol	SO ₄ -Ca 0.79	SO ₄ -Zn 0.74	Ca-Zn 0.68	Cd-Ba 0.66
Cwmbryno	Na-Mg 0.95	Na-K 0.97	Na-Ca 0.92	Mg-K 0.93	Mg-Ca 0.87
	K-Ca 0.90				
Cwmsymlog 1	Ca-Ba 0.66				
Cwmsymlog 2	SO ₄ -Na 0.71				
Cwmystwyth	Na-Mg 0.99	Na-K 0.98	Na-Ca 0.98	Mg-K 0.97	Mg-Ca 0.98
	K-Ca 0.96	Cd-Pb 0.62			
Daren	Na-Ca 0.70	Mg-Ca 0.73	Ba-Pb 0.87		
Eaglebrook	Ni-Zn 0.61	Zn-Cd 0.61	Zn-Pb 0.78		
Esgair Hir	SO ₄ -Ca 0.68	SO ₄ -Ni 0.62	SO ₄ -Zn 0.61	Co-Ni 0.73	Cu-Ba 0.61
	Ba-Pb 0.60				
Frongoch	SO ₄ -Co 0.85	SO ₄ -Cu 0.68	SO ₄ -Zn 0.94	SO ₄ -Cd 0.80	Na-Ca 0.66
	K-Ba 0.70	Co-Cu 0.62	Co-Zn 0.78	Co-Cd 0.70	Cu-Zn 0.65
	Cu-Cd 0.82	Zn-Cd 0.75	Cd-Ba 0.60	Cd-Pb 0.61	Ba-Pb 0.72
Goginan	Na-Mg 0.75	Na-Ca 0.81	Na-Ba 0.79	Mg-Ba 0.68	Ca-Ba 0.60
Grogwynion	SO ₄ -Na	SO ₄ -Mg 0.69	SO ₄ -K 0.82	SO ₄ -Ca 0.61	Na-Mg 0.61
	Na-K 0.79	Na-Ca 0.63	Mg-Ca 0.72	K-Ca 0.65	
Level Fawr	SO ₄ -Na 0.83	SO ₄ -Mg 0.95	SO ₄ -Ca 0.88	SO ₄ -Zn 0.70	Na-Mg 0.83
	Na-Ca 0.88	Mg-Ca 0.93	Mg-Zn 0.64	Co-Cu 0.63	Cd-Pb 0.67
Nant Silo	SO ₄ -Ca 0.63	K-Ca 0.65	K-Ba 0.63	Ba-Pb 0.65	
Wemyss	SO ₄ -Zn 0.63	K-Ni 0.64	Cd-Ba 0.78	Cd-Pb 0.85	Ba-Pb 0.73

Table 4.2. 5 term quadratic polynomial smoothing weightings.

t_{i-2}	t_{i-1}	t_i	t_{i+1}	t_{i+2}
-3	12	17	12	-3

Where t_i is time

Care needs to be taken, however, where an extremely high or low concentration is present within the data set as it can create artificial peaks and troughs, whereas in the raw data there was only one extreme value, which is a result of the negative weighting applied to a single high concentration.

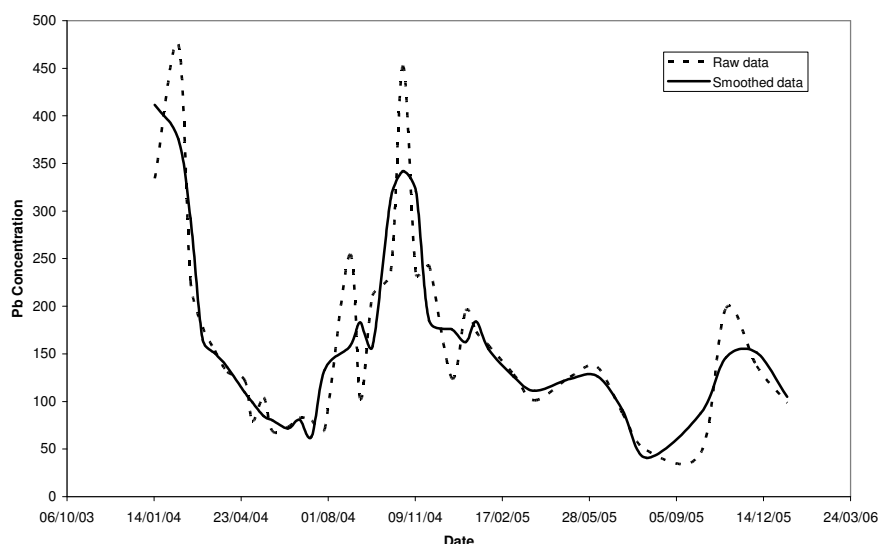


Figure 4.2. Comparison between raw and 5 term smoothed Pb concentrations at Alltycrib. Concentrations displayed in µg/L.

4.4.1 Mine water variability

A summary of the mine drainage and water course data collected between January 2004 and January 2006 is shown in Table 4.3. Although the concentration of numerous trace elements were analysed they are not all considered; only those elements which occur as major or trace elements within the ore minerals (galena and sphalerite) are discussed. Many of the trace elements occur near or below the detection limit. For a full table of data, see Appendix 4. It is immediately obvious that the most abundant elements within these mine drainages and water courses are Zn (≤ 42 mg/L) and Pb (≤ 2.7 mg/L). In all the mine drainages and water courses Zn was present in a higher concentration than Pb, this was also identified by Newton (1944). The differences in concentration reflects the solubilities of sphalerite ($K_{sp} = 2 \cdot 10^{-4}$) and galena ($K_{sp} = 3 \cdot 10^{-7}$) (Gao and Bradshaw, 1995; Lide, 2003) and Zn oxidises more readily than Pb (Newton, 1944). Zinc is also more abundant in the slightly acidic and acidic waters, because pH values less than 4 are required to mobilise Pb in higher amounts (Hofmann and Schuwirth, 2008).

Table 4.3. Minimum, maximum and average values of element concentrations.

	pH	Eh mV	Cond µS	Temp ° C	Cl mg/L	SO4 mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Mn µg/L	Fe mg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn mg/L	Rb µg/L	Sr µg/L	Cd µg/L	Ba µg/L	Pb µg/L
Afon Llywernog																					
Minimum	6.2	79	0.1	4.7	6.6	1.4	5.2	1.4	0.4	2.3	11.5	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	8.1	n.d.	n.d.	18.1
Maximum	8.6	296	0.1	19.0	28.0	7.6	14.9	4.5	0.7	8.3	37.9	n.d.	1.8	1.5	5.1	0.5	1.6	38.3	1.3	4.8	65.0
Mean	6.9	154	0.1	12.1	12.2	5.6	7.7	2.8	0.5	4.8	20.6	n.d.	n.d.	n.d.	2.4	0.3	n.d.	15.5	n.d.	2.9	33.9
Alltycrib																					
Minimum	6.1	31	0.0	9.4	18.3	17.3	11.0	8.8	2.5	15.7	6.1	n.d.	n.d.	n.d.	n.d.	0.4	1.7	21.9	1.4	9.5	46.2
Maximum	8.0	285	0.4	14.0	30.5	32.6	15.2	13.7	5.2	31.0	48.0	0.2	6.8	3.1	10.3	2.0	6.1	73.9	6.7	23.1	475
Mean	6.9	150	0.3	11.5	24.3	23.4	13.6	11.1	4.2	20.7	20.5	n.d.	1.9	1.4	4.5	0.9	3.6	42.1	3.0	15.8	162
Bwlch																					
Minimum	6.1	93	0.0	7.9	0.7	60.4	6.4	4.7	2.2	17.6	n.d.	n.d.	5.8	4.8	20.4	11.9	n.d.	19.2	30.2	9.2	413
Maximum	6.9	279	0.6	15.1	10.2	247	9.1	13.2	5.0	48.5	40.8	0.3	17.4	74.4	84.6	42.4	4.8	83.8	99.2	33.5	1311
Mean	6.4	195	0.4	11.3	5.7	134	8.1	8.7	3.4	30.4	21.3	0.1	10.2	30.7	36.1	28.9	2.6	48.3	56.7	17.5	759
Cwmbryno																					
Minimum	5.1	75	0.1	4.6	6.4	9.1	4.9	1.9	0.5	3.5	1.5	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	12.2	2.5	1.4	101
Maximum	7.3	275	0.1	21.7	13.6	15.3	6.2	4.3	0.9	7.0	6.7	0.5	7.1	3.7	9.1	2.2	1.6	29.2	7.2	6.2	237
Mean	6.6	186	0.1	13.2	8.5	12.0	5.6	2.9	0.7	5.7	3.8	n.d.	1.3	n.d.	3.6	1.4	1.1	18.6	4.4	4.1	149
Cwmystwyth																					
Minimum	5.8	78	0.2	7.0	n.d.	76.9	5.2	7.1	0.5	11.5	135	n.d.	10.1	1.0	2.0	12.5	n.d.	40.4	18.4	10.1	50.3
Maximum	7.0	180	0.3	12.1	n.d.	98.7	7.0	11.2	0.7	20.9	545	0.6	24.0	15.4	24.9	33.2	1.5	123	45.0	23.5	806
Mean	6.4	134	0.3	10.0	n.d.	87.3	6.0	9.0	0.6	15.1	291	0.2	15.1	11.0	12.9	23.0	n.d.	71.7	28.5	14.4	297
Cwm Rheidol																					
Minimum	2.4	307	0.4	7.0	n.d.	34.2	6.3	8.4	0.7	9.9	138	2.5	21.7	27.3	21.8	10.3	n.d.	36.8	24.7	3.3	266
Maximum	4.1	510	0.9	18.4	3.5	329	8.0	21.7	1.1	22.7	947	21.1	93.5	196	189	31.9	2.0	128	72.1	11.1	1410
Mean	3.4	434	0.6	12.1	0.3	206	7.1	15.6	0.8	14.3	506	7.6	41.6	86.0	64.4	20.6	1.2	62.9	39.5	7.2	641

Cond - conductivity

Temp - water temperature

n.d. - below detection limit

Table 4.3 continued. Minimum, maximum and average values of element concentrations.

	pH	Eh mV	Cond µS	Temp ° C	Cl mg/L	SO4 mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Mn µg/L	Fe mg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn mg/L	Rb µg/L	Sr µg/L	Cd µg/L	Ba µg/L	Pb µg/L	
Cwmsymlog 1																						
Minimum	5.5	69	0.0	4.6	5.2	2.6	4.3	0.9	0.0	0.4	5.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.5	n.d.	n.d.	6.3	
Maximum	7.7	270	0.1	19.8	8.8	10.3	5.7	4.7	0.3	3.8	58.1	0.4	5.3	1.5	7.1	0.2	n.d.	15.7	1.0	4.2	39.5	
Mean	6.7	147	0.1	11.6	7.3	5.1	5.0	2.3	0.1	2.1	17.4	0.1	1.0	n.d.	2.2	n.d.	n.d.	9.4	n.d.	1.9	20.9	
Cwmsymlog 2																						
Minimum	5.2	27	0.0	4.2	10.3	6.0	6.6	1.2	0.4	0.2	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.6	n.d.	1.6	30.5	
Maximum	7.9	292	0.1	17.4	13.5	9.3	8.7	4.0	0.9	6.2	78.4	0.5	5.7	2.7	7.2	0.2	3.9	23.7	1.1	6.5	519	
Mean	6.4	163	0.1	11.1	11.9	7.3	7.4	2.4	0.5	2.5	23.0	0.1	1.0	0.7	2.3	0.1	n.d.	11.8	n.d.	3.7	166	
Daren																						
Minimum	6.2	87	0.2	8.1	18.3	10.5	10.7	5.0	2.7	8.3	2.2	n.d.	n.d.	n.d.	1.1	0.0	n.d.	33.8	n.d.	5.7	175	
Maximum	7.6	283	0.2	12.3	47.0	14.4	13.1	9.8	3.2	15.8	11.7	0.5	6.3	3.1	8.9	0.2	3.9	98.6	n.d.	16.4	340	
Mean	7.1	173	0.2	10.2	22.7	11.9	11.9	6.3	2.9	11.3	5.6	0.0	2.0	1.7	4.3	0.0	2.4	58.7	n.d.	10.2	237	
Eaglebrook																						
Minimum	4.8	73	0.0	4.2	6.6	3.4	5.3	0.1	0.1	0.4	46.9	n.d.	1.4	n.d.	19.8	0.0	n.d.	2.5	n.d.	1.9	122	
Maximum	6.9	284	0.1	14.9	10.8	6.4	7.1	4.5	0.3	4.0	112	0.3	7.5	5.0	51.8	0.6	1.9	12.2	2.6	7.9	308	
Mean	6.1	169	0.1	10.0	9.3	5.2	5.9	1.7	0.2	1.5	78.5	0.0	2.9	2.3	30.2	0.3	n.d.	6.7	1.0	3.8	193	
Esgair Hir																						
Minimum	5.0	65	0.0	5.7	7.7	5.2	5.0	0.8	0.2	0.2	11.2	n.d.	1.6	n.d.	4.6	0.2	n.d.	6.4	n.d.	1.7	69.2	
Maximum	7.8	243	0.1	12.0	11.0	9.1	6.7	3.6	0.5	5.1	379	0.4	7.2	5.5	22.4	0.7	1.3	20.3	2.8	7.8	429	
Mean	6.1	154	0.1	8.8	9.1	7.1	5.7	2.3	0.4	2.8	225	0.1	3.5	2.5	10.4	0.4	n.d.	13.3	1.5	3.9	191	
Frongoch																						
Minimum	5.4	8	0.1	6.7	7.5	12.5	4.9	1.3	0.5	4.2	15.1	n.d.	n.d.	n.d.	1.2	2.1	n.d.	11.8	3.3	n.d.	268	
Maximum	9.0	224	0.3	24.3	10.6	48.7	6.1	4.5	3.7	10.0	122	0.5	9.0	8.3	45.8	25.7	3.2	34.1	64.5	8.5	1364	
Mean	6.8	149	0.2	13.7	9.2	31.5	5.4	2.9	1.5	6.5	68.7	0.1	4.3	2.8	18.4	15.0	1.3	19.4	30.0	5.1	820	
Cond - conductivity				Temp - water temperature																		
																		n.d. - below detection limit				

Table 4.3 continued. Minimum, maximum and average values of element concentrations.

	pH	Eh mV	Cond µS	Temp ° C	Cl mg/L	SO4 mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Mn µg/L	Fe mg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn mg/L	Rb µg/L	Sr µg/L	Cd µg/L	Ba µg/L	Pb µg/L
Goginan																					
Minimum	6.0	80	0.1	5.8	17.3	9.7	11.3	3.3	0.6	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	n.d.	15.0	n.d.	1.8	3.2
Maximum	7.3	274	0.2	22.9	35.5	14.5	15.3	6.4	1.1	7.6	4.7	0.2	6.4	1.3	7.9	0.3	3.2	61.8	5.4	8.5	45.5
Mean	6.8	171	0.1	12.3	21.5	11.2	13.2	4.5	0.8	4.4	2.0	n.d.	1.4	n.d.	3.3	0.1	1.0	27.7	n.d.	5.0	15.1
Grogwynion																					
Minimum	6.6	69	0.1	8.9	7.4	13.4	7.2	3.8	1.0	7.6	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	15.7	n.d.	4.1	32.8
Maximum	8.3	239	0.2	13.7	12.6	25.4	13.9	7.7	2.0	15.8	5.5	0.3	6.8	2.1	10.0	0.7	6.0	131	1.9	11.6	271
Mean	7.3	156	0.2	10.8	10.4	18.8	9.6	5.9	1.4	10.7	1.5	n.d.	1.1	n.d.	3.3	0.4	2.3	67.8	1.0	6.9	159
Level Fawr																					
Minimum	6.5	60	0.0	7.7	7.3	17.1	5.6	3.5	0.5	6.6	n.d.	n.d.	n.d.	n.d.	1.7	0.5	n.d.	28.3	n.d.	n.d.	144
Maximum	8.1	243	0.3	12.6	8.9	45.8	8.6	10.5	1.0	20.5	4.8	0.3	5.9	3.8	8.8	2.0	3.2	141	5.0	15.4	400
Mean	7.2	149	0.2	9.6	8.1	30.9	6.8	7.3	0.7	12.6	1.8	n.d.	1.7	1.5	4.4	1.3	n.d.	75.8	2.2	8.7	215
Nant Silo																					
Minimum	5.6	62	0.1	6.3	11.4	8.4	7.9	3.1	0.7	3.8	2.7	n.d.	n.d.	n.d.	2.1	0.1	n.d.	13.6	n.d.	1.4	54.2
Maximum	7.8	253	0.1	18.7	22.2	11.6	9.8	6.3	1.2	7.4	17.8	0.3	6.2	1.7	14.4	0.4	1.5	39.8	1.0	5.4	214
Mean	6.7	163	0.1	11.8	14.8	9.7	8.9	4.0	0.8	5.4	8.4	n.d.	1.6	n.d.	6.4	0.2	n.d.	22.4	n.d.	3.4	95.9
Wemyss																					
Minimum	4.4	90	0.0	6.5	4.6	11.5	5.1	1.2	0.4	0.4	5.8	n.d.	1.0	n.d.	6.5	3.7	n.d.	7.5	9.0	4.6	650
Maximum	7.8	285	0.1	23.7	23.4	30.3	10.0	4.6	0.7	3.1	19.1	0.2	8.2	4.1	35.2	21.5	1.3	22.2	32.6	17.8	2764
Mean	6.1	182	0.1	13.6	10.3	20.7	6.3	2.3	0.5	1.9	12.1	n.d.	2.8	2.1	16.2	9.7	n.d.	11.3	19.7	9.7	1306

Cond - conductivity

Temp - water temperature

n.d. - below detection limit

The majority of element concentrations measured in the mine drainage waters exceed those set by EU regulations (though not all elements have EQS), see Table 4.4. The relevant EQS concentration depends upon the hardness of the water and whether the river has been designated as Salmonid or Cyprinid. Fuge *et al.* (1991) determined the hardness to be ~12 mg/L for the Ystwyth and Rheidol, though a total hardness as calcium carbonate (CaCO₃) for the Rheidol was given as 24.8 mg/L by Jones and Howells (1975), therefore the EQS concentration which relates to a hardness between 0-50 mg/L CaCO₃ is used. Significant lengths of the Clarach, Ystwyth and Rheidol were designated as Salmonid under the EU Freshwater Fish Directive (78/659/EEC) (Environment Agency, 1999; 2008a). The waters draining from the mine sites, i.e. adit drainage and water from the spoil tips drain into local rivers and water courses. Even though the mine drainages are diluted by their receiving water courses, these may still fail EQS, especially for Zn and Pb. For example, the concentrations of Pb within the Afon Llywernog and Nant Silo (both modest watercourses, see Figure 4.3) exceed the 4 µg/L imperative value set by the Dangerous Substances Directive (76/464/EEC). At the 17 sample sites, the concentrations of Cu, Zn and Pb cause the sites to fail the EQS; Cd fails at five of the mine sites and only at Cwm Rheidol do the concentrations of Fe and Ni cause the mine drainage to fail. During the subsequent chapters Zn, Cd and Pb are to be studied in more detail.

The composition of mine drainage waters/water courses is derived from a combination of weathering reactions, dilutions and precipitation processes (Smolders *et al.*, 2004). The waters commonly contain higher concentrations of Na followed by Ca, Mg and then K, which demonstrate the major role of silicate rock weathering. The contaminants that are associated with mining typically show high concentrations with SO₄ > Zn > Pb, with much lower concentrations of Mn, Co, Ni, Cu, Cd and Ba.

Sodium and Chloride

Atmospheric deposition of Na and Cl⁻ is important (Foster and Walling, 1978), with the dissolution of sea salt being the main source (Gaillardet *et al.*, 1999; Mortattia and Probst, 2003). Once the sea salt component has been subtracted the remainder of the Na⁺ derives from silicate weathering (Meybeck, 1987; Mortattia and Probst, 2003). The Cl⁻ anion is highly reactive and is present within fluid inclusions in the ore and gangue minerals and may play an important part in the transport of metals in ore-forming solutions. The

Table 4.4. Compliance of mine waters and water courses with environmental quality standards.

	Cd	Cu	Fe	Pb	Ni	Zn	pH
Environmental Quality Standard	5	1	1000	4	50	8	6-9
Unit	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	
Statistic	AA	AA	AA	AA	AA	AA	95 %
Afon Llywernog	✓	X	✓	X	✓	X	✓
Alltycrib	✓	X	✓	X	✓	X	✓
Bwlch	X	X	✓	X	✓	X	✓
Cwmbryno	✓	X	✓	X	✓	X	X
Cwm Rheidol	X	X	X	X	X	X	X
Cwmystwyth	X	X	✓	X	✓	X	X
Cwmsymlog 1	✓	X	✓	X	✓	X	✓
Cwmsymlog 2	✓	X	✓	X	✓	X	X
Daren	✓	X	✓	X	✓	X	✓
Eaglebrook	✓	X	✓	X	✓	X	X
Esgair Hir	✓	X	✓	X	✓	X	X
Frongoch	X	X	✓	X	✓	X	✓
Goginan	✓	X	✓	X	✓	X	✓
Grogwynion	✓	X	✓	X	✓	X	✓
Level Fawr	✓	X	✓	X	✓	X	✓
Nant Silo	✓	X	✓	X	✓	X	X
Wemyss	X	X	✓	X	✓	X	X

AA = Annual Average

95 % = 95 % of samples

✓ = complies with the Environmental Quality Standard

X = exceeds the Environmental Quality Standard

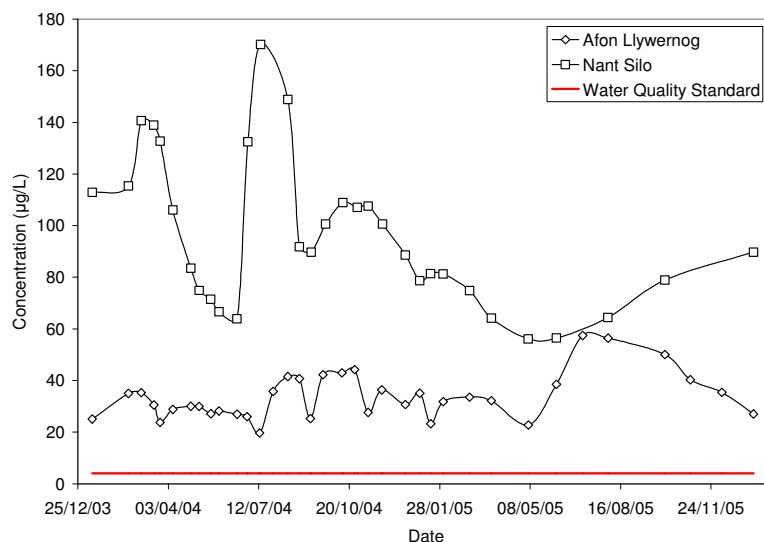


Figure 4.3. Pb concentrations in the Nant Silo and Afon Llywernog compared with the Imperative Water Quality Standard of 4 µg/L.

concentrations within the local ore and bedrock are too low to be the major source of Cl, so the proximity of the mines to the sea would be the most obvious source (Andrews *et al.*, 1984). The mine drainage waters containing the highest concentration of Na and Cl is the Alltycrib mine, which is situated closest to the sea. High correlations exist between Na and Cl within the Afon Llywernog ($r = 0.97$), at Esgair Hir ($r = 0.7$) and Goginan ($r = 0.83$).

Calcium and Strontium

Calcium and Sr are chemically similar and are enriched in sea water compared to stream waters (Faure, 1998). They are also released from silicate weathering and globally 25 % originates from sedimentary rocks (Meybeck, 1987); but the major source is the dissolution of carbonates (Gaillardet *et al.*, 1999; Jacobson *et al.*, 2002). Correlations occur between the elements released from carbonate minerals, for example at Level Fawr: Mg and Ca ($r = 0.93$), Mg and Sr ($r = 0.81$) and Ca and Sr ($r = 0.9$). Calcium is the most abundant alkaline earth metal and even a small amount of calcite present in the host rock (<1 %) can exert a significant control on the chemistry of the waters (Meybeck, 1987; Hren *et al.*, 2007). Mast *et al.* (1990 cited in Langmuir, 1997) found that just 0.005–0.4 % calcite in a silicate rock watershed in Colorado contributed nearly 40 % of the total cations in the runoff. Variable Ca concentrations are likely to be caused by the variable amounts of calcite present in the gangue (Fuge *et al.*, 1994), for example at Cwmystwyth; or by the dissolution of the limestone chips surrounding the reclaimed spoil area at Bwlch. All of the mines/water courses studied are thoroughly undersaturated with respect to CaSO₄, therefore no Ca is precipitated and any correlations between Ca (and associated elements) and SO₄ are positive, for example, Bwlch ($r = 0.94$). Strontium can also be released through the selective leaching of silicate minerals (Fairchild *et al.*, 2000).

Magnesium

Magnesium is supplied via sea salt dissolution; but other sources include silicate weathering and the dissolution of carbonates, and ferromagnesian minerals (Gaillardet *et al.*, 1999; Holloway and Dahlgren, 2001; Mortattia and Probst, 2003). The highest concentration occurs at Cwm Rheidol, which may be caused by the acidic waters increasing the dissolution of the minerals (Fuge *et al.*, 1991; 1994).

Potassium and Rubidium

Potassium has the lowest concentration of all the major cations, with all the sampled waters containing <1 mg/L, with the exception of Alltycrib and Bwlch. Potassium is derived from the bedrock, for example within illite (Neal *et al.*, 1990) and is also strongly regulated by biological cycling (Hem, 1985; Holloway and Dahlgren, 2001). The low concentration of K within the waters may reflect the low concentration of K within the bedrock and that the K is not easily weathered from silicate minerals. Once removed K has a strong tendency to be reincorporated into solid weathering products, for example clays. The chemical behaviour of K and Rb are very similar and the most likely source is from clays, from which they are easily weathered; though they are also enriched in seawater compared to stream water (Faure, 1998). The low concentration of Rb within the waters (<4 µg/L) may be caused because Rb is strongly held at cation exchange sites (Hem, 1985).

Iron, Cobalt and Nickel

The only mine in Mid-Wales within this thesis where Fe is present in concentrations above 1 mg/L within the mine drainage waters, i.e. above the EU EQS, is Cwm Rheidol which is caused by the pyrite and marcasite present within the mine. Although Cwmystwyth, Eaglebrook and Esgair Hir have ochreous streambeds, the majority of Fe has already precipitated out and is no longer detectable within the mine drainage. Cobalt and Ni are both commonly associated with Fe because the Co^{2+} and Ni^{2+} ions are similar in size to the Fe^{2+} ion (6-fold co-ordination Co^{2+} 0.73 Å, Ni^{2+} 0.77 Å and Fe^{2+} 0.69 Å) so they can occur as common trace elements within iron sulphides (Fuge *et al.*, 1991; Holmström *et al.*, 2001). No significant correlation occurs between Fe, Co and Ni within the mine drainage at Cwm Rheidol, this may be because sphalerite and galena were the predominant ore minerals mined and the Co and Ni will be most likely to be associated with these rather than the pyrite. The acidity produced through the dissolution of iron sulphides acts to increase the dissolution of associated ore minerals, for example sphalerite and galena.

Zinc and Cadmium

The minor and trace elements within the sphalerite and galena include Mn, Fe, Co, Ni, Cu and Cd (Foster-Smith, 1979; Mason, 1997; Moorhouse pers. comm., 2009); concentrations of these elements within the waters are dictated by the concentration of metals within the ore minerals. Cadmium is mainly associated with Zn mineralisation (Fuge and Perkins,

1991; Walder and Chavez, 1995), with Mason (1997) determining that sphalerite in mid-Wales contained up to 0.5 % Cd; positive correlations exist between Cd and Zn at Alltycrib ($r = 0.83$), Bwlch ($r = 0.71$) and Frongoch ($r = 0.75$). The concentration of Cd found within sphalerite is controlled by the temperature at the time of deposition, with low temperature zones containing more Cd (Fuge *et al.*, 1993). Both Cd and Zn are easily weathered from the sphalerite, though Cd is more chalcophile than Zn and therefore endures in the sulphide as Zn is removed (Goldschmidt, 1954 cited in Fuge *et al.*, 1993). Cadmium can also substitute for Pb within galena and positive correlations are found at Alltycrib ($r = 0.74$), Bwlch ($r = 0.88$), Cwmystwyth ($r = 0.68$), Frongoch ($r = 0.61$), Level Fawr ($r = 0.67$), and Wemyss ($r = 0.85$); Cu may also substitute for Pb within galena (Clark *et al.*, 2001).

Sulphate

The main source of SO_4 in the waters is from sulphide weathering (Jacobson *et al.*, 2002; Smolders *et al.*, 2004). Within the mines and spoil tips sphalerite still occurs, because during the height of Pb and Ag mining, minimal Zn was extracted as it was not profitable. Sphalerite oxidation is the most likely source of SO_4 because sphalerite has a lower solubility product ($K_{\text{sp}} = 2 \cdot 10^{-4}$) than galena ($K_{\text{sp}} = 3 \cdot 10^{-7}$) (Lide, 2003) therefore the oxidation of sphalerite leads to the alteration of Zn from an immobile species to an easily mobilised species (Hofmann and Schuwirth, 2008); the dissolution of galena and iron sulphides will also contribute. The relatively low concentrations of Pb, and to a lesser extent, Ba are caused by the solubility control exerted by the SO_4 caused by the common ion effect, which causes the elements to correlate with each other, for example at Daren ($r = 0.87$) and Bwlch ($r = 0.79$). Lead sulphate and BaSO_4 have relatively low solubilities, with K_{sp} values of 10^{-10} and $10^{-7.8}$ respectively (Faure, 1998). Mine waters and water courses are undersaturated with respect to PbSO_4 and therefore any correlations between Pb (and associated elements) and SO_4 are positive. At Alltycrib, however, a negative correlation occurs between Pb and SO_4 suggesting that oversaturation has occurred and PbSO_4 is precipitating out of solution; Bevins (1994) states that Anglesite (PbSO_4) occurs widely throughout the mid-Wales orefield. The negative correlation between Pb and SO_4 may be influenced by the seasonal variation of the two elements (see Figure 4.4) with Pb increasing during the winter and SO_4 increasing during the summer.

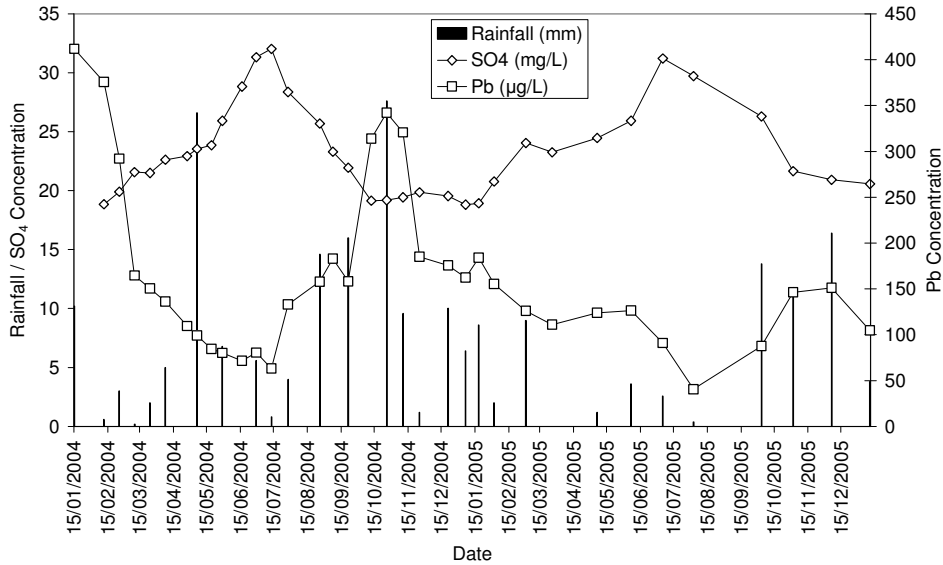


Figure 4.4. Pb and SO₄ concentrations at Alltcrib (smoothed data).

Correlations between SO₄ and other elements may exist because the H₂SO₄ containing mine drainage waters and water courses (only produced when pyrite or marcasite is weathered) may cause further dissolution of ore minerals, calcite (within the gangue) or silicate minerals, for example Na and K are released when silicate minerals are weathered (Dalai *et al.*, 2002).

The most contaminated mines are Bwlch, Cwm Rheidol, Cwmystwyth, Frongoch and Wemyss, i.e. these mines contain the highest concentrations of SO₄, Mn, Fe, Co, Ni, Zn, Cd, Ba and Pb of all the mine drainage waters and water courses sampled. Bwlch mine waters contain the highest concentration of Ca, Zn and Cd; the mine or buried spoil must therefore still contain significant quantities of sphalerite which is available for dissolution. The acidic nature of the mine drainage at Cwm Rheidol encourages the dissolution of the host rock and associated ore minerals resulting in high element concentrations. High element concentrations are also found at Cwmystwyth, though the acidic nature of the water is neutralised by the large quantities of calcite and ankerite present within the gangue (White, 2000), therefore promoting ochre precipitation which co-precipitates other metals. As the Frongoch and Wemyss mines are located along the same lode and were worked together, so it may be expected that the composition of their drainage water would be similar. The higher levels of element concentrations at Frongoch mine may be explained by more water-rock interaction within the mine, in addition to greater interaction of the water with the fine-grained spoil. The water at Wemyss, however, has little contact with

the spoil and therefore a shorter time for the dissolution of the minerals to occur, therefore producing lower element concentrations within the waters. After periods of heavy rainfall, water emerges from the base of the tips and this drainage contains far greater concentrations of elements than the Wemyss sample which is normally collected. The concentration of Na, Mg, K, Ca and Pb is double normal concentrations within the sampled water, and Co, Ni, Cu, Zn and Cd are over 10 times higher. In warmer, drier periods the sulphides oxidise near the surface of the tip and the released metals may then be transported downwards and/or precipitate or be adsorbed onto grains of spoil material (Holmström *et al.*, 2001); therefore when there is more precipitation, the water can flow further into the tip and mobilise the metals. Low concentrations occur at Goginan and Cwmsymlog 1; the Goginan mine has been remediated and the sampled water does not interact with the ore minerals, and at Cwmsymlog 1 the sampled water does not interact with any ore minerals and is simply precipitation and runoff from the surrounding land.

There are many inter-element correlations which are more difficult to explain than those detailed above, for example Cd and Ba at Bwlch ($r = 0.90$), Cwm Rheidol ($r = 0.66$), Frongoch ($r = 0.60$) and Wemyss ($r = 0.78$). High correlations do not always show a direct relationship between the different elements; they show that a high concentration of one element occurs at the same time as another element. The correlation may have been caused by another control; for example, when Cd is released from sphalerite SO_4 is also released, which in turn may control the Ba concentration. At Bwlch, Cwm Rheidol and Frongoch there is a positive correlation between Cd and SO_4 (Bwlch $r = 0.74$; Cwm Rheidol $r = 0.63$; and Frongoch $r = 0.80$). The correlation of Cd and Ba may also imply that barite occurs within the mineral veins. Sulphate may also exert a control on other elements.

Previous Studies

Previous authors have determined the metal concentrations from Cwm Rheidol (Table 4.5), Frongoch and Wemyss mine drainage (Table 4.6) (Fuge *et al.*, 1991; Jones, 1940; Jones; 1986) and generally the samples taken during this study are within the same range as those samples taken by Fuge *et al.* (1991), though the range shown within this study is much larger; this is probably because the samples for this study were collected over a two year period, whereas Fuge *et al.* (1991) only collected samples for the first three months of 1990. Direct comparisons between the data from this study and previous studies can not be

made because: a) different instruments were used to determine the data, i.e. data from Fuge *et al.* (1991) were determined using AAS and automated photometry; b) the samples may not have been collected in precisely the same location; and c) the previous studies were single ‘grab’ samples rather than continuous sampling over a longer period.

Table 4.5. Cwm Rheidol mine water composition through time.

Values in brackets denote the concentration range, where given.

	pH	SO ₄ mg/L	Mg mg/L	Ca mg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn mg/L	Cd µg/L	Ba µg/L	Pb µg/L
1961 ^a	3.6							26.6			640
1981 – 1982 ^a	3.8							17			450
1969 ^b	3.5							22.5			
1971 ^b	3.1	261				600		23.7	100		
1973 ^b	3.2							50			
1982 ^b	3.8							19			
1988 ^b	3.4					550		46.8	65		
1990 ^b	3.3 (3.2- 3.5)	149 (125- 173)	8.1	17.6 (15.7- 19.4)	32 (30- 34)	152 (128- 176)	69.5 (65- 74)	14.1 (12- 16.1)	30.5 (27- 34)	8.3 (6- 10.5)	1012 (838- 1186)
This study ^c	3.4 (2.4- 4.1)	206 (122- 329)	14.3 (8.4- 21.7)	14.4 (9.9- 22.7)	41.6 (21.0- 93.5)	86.0 (27.3- 196)	64.4 (21.8- 189)	20.6 (10.3- 31.9)	39.5 (24.7- 72.1)	7.6 (3.2- 11.0)	641 (265- 1410)

^a from Jones, 1986

^b from Fuge *et al.*, 1991

^c mean value from sampling period between 2004 and 2006

Table 4.6. Frongoch and Wemyss mine water composition in 1940 and this study.

	pH	Zn mg/L	Pb mg/L
Frongoch			
1940 ^a	5.8	57	3
This study ^b	6.8	14.8	0.8
Wemyss			
1940 ^a	6.4	5.2	0.4
This study ^b	6.2	9.3	1.2

^a from Jones, 1940

^b median value from sampling period between 2004 and 2006

Ternary diagrams

To determine whether any of the mine waters show any similarities or patterns related to their element concentration and therefore enabling the detection of mines lying along the same lode, ternary diagrams have been plotted, displaying Zn, SO₄ and Pb (using unsmoothed data). When these elements are plotted they show a skew towards SO₄, see Figure 4.5, therefore the diagrams would be biased towards that element; as a result of this, the concentrations were scaled to make the numbers broadly similar (a crude approximation of means centring, Pearce pers. comm., 2007), see Figure 4.6. In general, the data from the mines do not overlay each other and therefore do not have similar characteristics; some mines, however, do possess some similarities: Frongoch and Wemyss, Eaglebrook and Esgair Hir; Cwmsymlog 2 and Daren; and Cwm Rheidol and Cwmbryno. Frongoch and Wemyss mines worked the same lode; the lode at Wemyss was a westerly continuation of that found at Frongoch (Jones, 1922) and therefore similarities between element concentrations may be expected; this is also true for Cwmsymlog 2 and Daren which occur along the same fault/vein system (www.mindat.org/loc-4261.html). Eaglebrook and Esgair Hir, although they occur in the same geographical location, do not lie along the same lode (see Chapter 2.4); Cwm Rheidol and Cwmbryno do not share a common lode, nor are they in the same geographical location; therefore it may just be coincidence that these mines show similar patterns. Principal components analysis was undertaken to provide an additional method to determine whether any similarities between the mines exist.

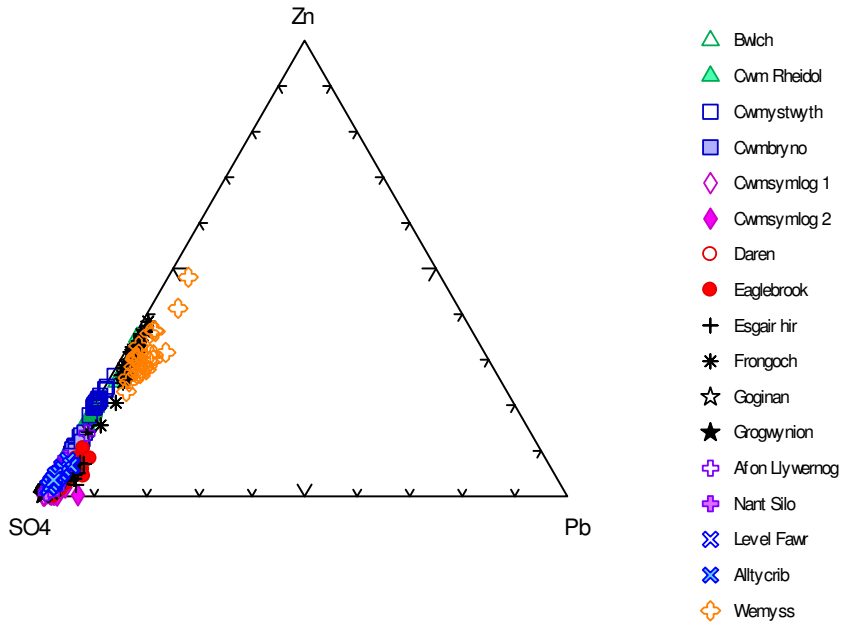


Figure 4.5. Major element composition (unsmoothed data) of the sampled mine waters and water courses.
Concentrations are mg/L.

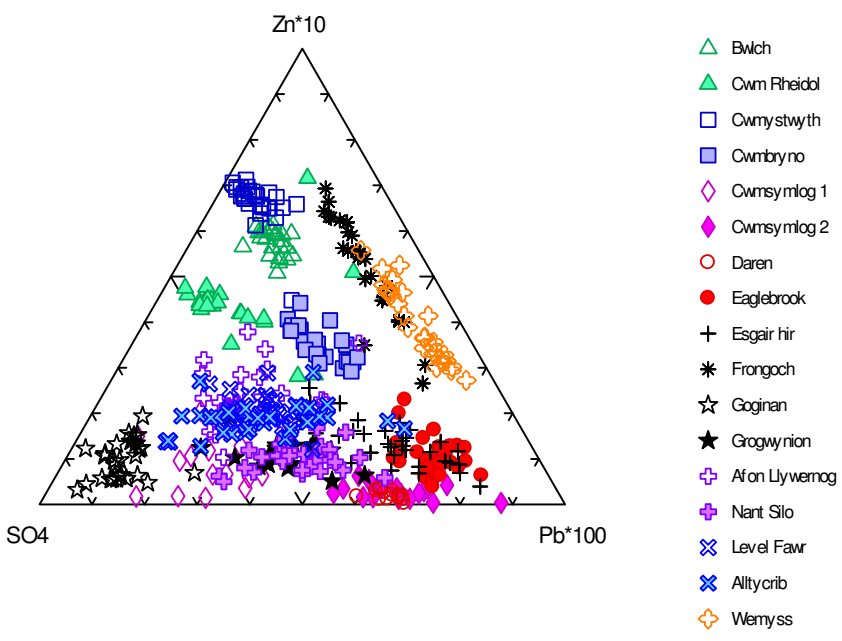


Figure 4.6. Major element composition (crude approximation of means centred data) of the sampled mine waters and water courses.
Concentrations are mg/L.

Principal Components Analysis

Principal components analysis (PCA) was conducted on the unsmoothed data for all mines sampled; PCA was conducted using Statistics Package for Social Sciences version 14.

Only pH, SO₄, Mn, Zn, Cd and Pb concentrations were used as they are the main elements within the mine waters and represent the most complete dataset (where values were missing for certain dates, these dates and the data associated with them were not included). Unsmoothed data was used to provide an accurate depiction of the relationships between element concentrations, whereas artificially smoothed data sets remove extreme values which may be of interest to this study. The data were scaled to make the concentrations broadly similar (a crude approximation of means centred data; Pearce pers. comm., 2007) so that no one variable will influence and/or dominate the results of the PCA.

PCA looks at a large number of variables (for example, the elements) and can combine these variables into principal components (a smaller set of variables) which retain as much of the variance of the original data set as possible. It is common in PCA to plot PC1 against PC2 to differentiate between data sets in the original matrix (Pearce *et al.*, 2008). PC1 and PC2 show over 70 % of the variance, see Appendix 5. In this study, analysis of the same variables at different mine sites will hopefully provide a means of separating or grouping the different drainage waters. Four different analyses were carried out: 1) all variables; all mines; 2) variables except pH; all mines; 3) all variables, mines without the severely contaminated mine sites; and 4) variables except pH; mines without the severely contaminated mine sites.

When PCA was performed on the mine data and PC1 plotted against PC2; the most severely contaminated mines were separated (Bwlch, Cwm Rheidol, Cwmystwyth, Frongoch and Wemyss) and the less severely contaminated waters are clustered together, see Figure 4.7. When the pH variable was removed (because most of the mine drainage waters are circum-neutral, with the exception of Cwm Rheidol) the most severely contaminated mines are still separated from the rest, but their locations on the graph change. The removal of the pH variable has also separated Esgair Hir from the cluster of less severely contaminated mines, see Figure 4.8.

When severely contaminated mines are removed from the PCA (Figure 4.9) the mine plots are scattered and the various lodes can not be distinguished. The analysis with and without pH show similar plots, therefore only the analyses without pH are shown. The mines along the same lode are not clustered together and the mines that show similarities in their principal components, for example, Alltycrib and Cwmbryno do not lie along the same

lode and therefore do not explain their similarities in principal components. Esgair Hir and Eaglebrook have also been separated from the remaining mines; although they do not lie along the same lode, they do contain the highest concentrations of Mn, Ni and Co of the remaining mines and are the only two mines where ochreous deposits occur on the water channel. The component matrix shows which variable creates the most variance. In all four analyses the most variance is caused by SO_4 , Zn and Cd, with almost identical component matrices. This shows that the dissolution of sphalerite is the major factor in controlling the variability of the mine water composition.

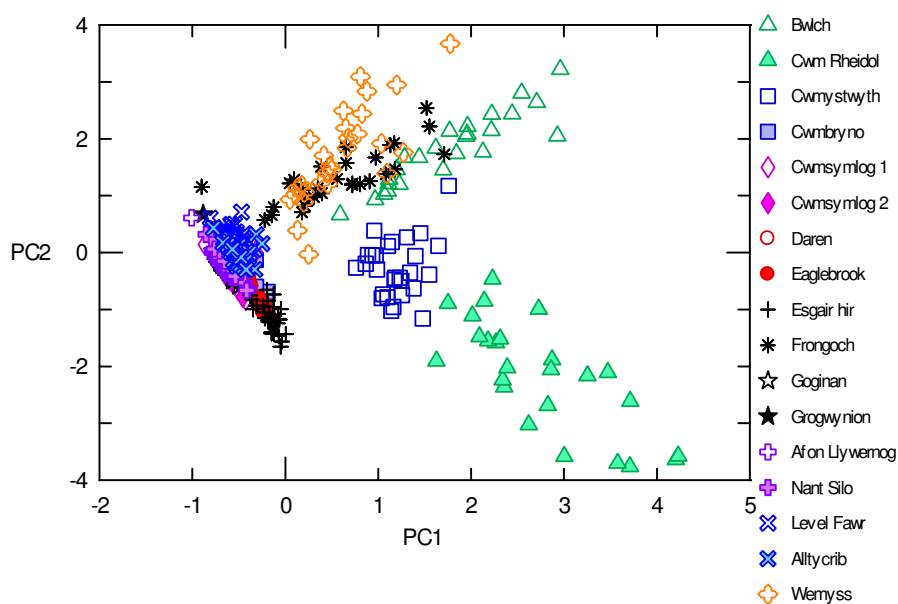


Figure 4.7. Principal components analysis of pH, SO_4 , Mn, Cd*10, Zn*20 and Pb/10 on all mines.

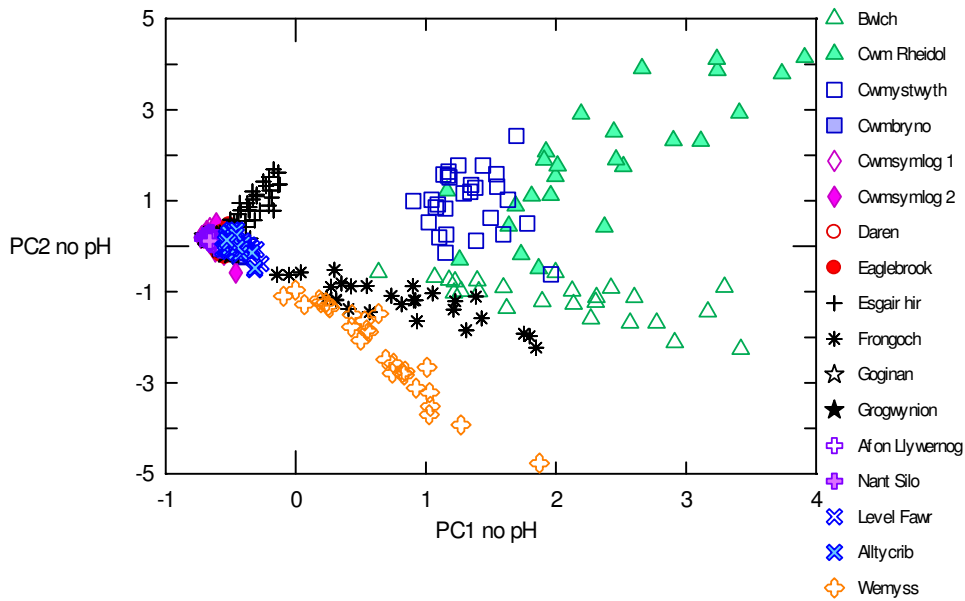


Figure 4.8. Principal components analysis of SO₄, Mn, Cd*10, Zn*20 and Pb/10 on all mines.

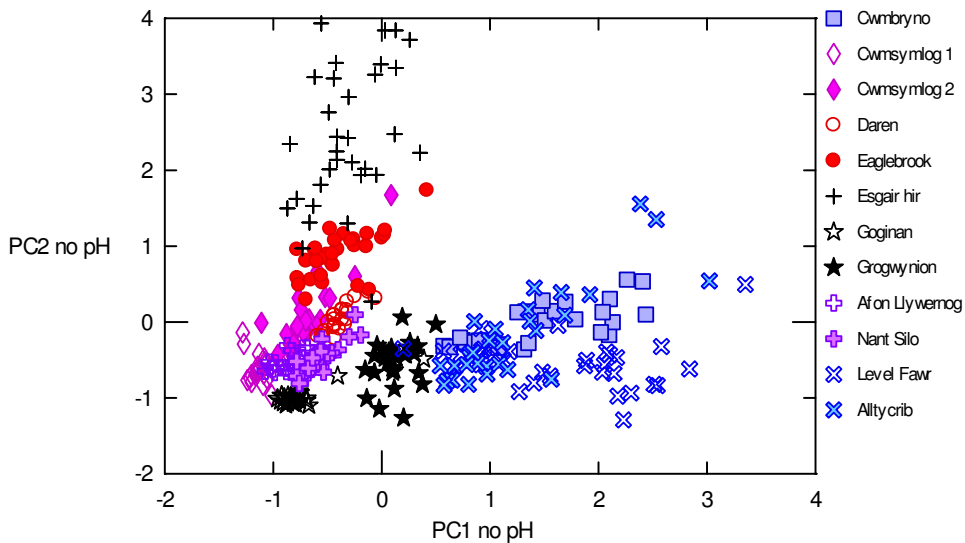


Figure 4.9. Principal components analysis of SO₄, Mn, Cd*10, Zn*20 and Pb/10. The most severely contaminated sites of Bwlch, Cwm Rheidol, Cwmystwyth, Frongoch and Wemyss are not included.

4.5 Seasonal Variations

Variations in the concentration of elements on a seasonal timescale are found across numerous drainage basins with contrasting climates and ecosystems (Holloway and Dahlgren, 2001) and are evident in many European rivers (Foster and Charlesworth, 1996). Determining the composition of mine drainage waters and the receiving water courses over

a seasonal timescale is an essential step in being able to remediate the water course (Pentreath, 1994).

Determining the variation in element concentration in water courses and mine drainage requires regular monitoring to detect important changes in the water chemistry. Where stream flow is controlled by large reservoirs or groundwater inflow, a sample taken weekly can be assumed to be representative of the water course's composition; but in most surface water courses this is not the case, as the composition can change daily or in some cases hourly (Hem, 1985 and see below). Rolfe and Jennet (1973), however, resolved that samples taken fortnightly or monthly are adequate for determining seasonal and longer-term patterns, providing a statistical base for determining changes in water quality. Limiting the sampling to every fortnight or month means that very few samples are taken during storm hydrographs (Blake *et al.*, 2003) and therefore disregards the effect that storm pollution has on the water course. As most of the samples in this study are taken directly from the mine adit and the discharge is relatively constant, storm events may not cause as dramatic changes in sample composition compared to samples taken from a water course. Storm events will, of course, affect the waters emanating from the spoil tips and therefore the overall quality of the water courses which the drainage flows into. Studies of storm hydrographs give a much more accurate, reliable and complete picture of maximum concentration occurrences when modelling water quality and metal fluxes in water courses (Blake *et al.*, 2003). Sandén *et al.* (1997) found that in the early stages of the storm hydrograph only small changes occurred in element concentration, followed by a rapid decrease of total organic C, Cu and Zn, whilst other elements increased. After this peak the concentration decreased, most likely resulting from the dilution by precipitation, after which concentrations rose to their pre-storm levels. Grimshaw *et al.* (1976), however, found that Zn concentrations increased during the initial phases of storm runoff caused by 'flushing' of soluble metal salts. Bambic *et al.* (2006) disregarded storm events in long-term monitoring for data consistency and argued that this most accurately represent seasonal variations on a weekly timescale.

4.5.1 Seasonal mine water quality variability

The fortnightly and monthly sampling strategy adopted provides detailed information regarding the composition of the sampled waters and how composition varies over the two year period (2004-2006). The fortnightly and monthly sampling regime is adequate to

produce water quality averages over long periods, covering a random selection of flow conditions, which allows the determination of seasonal variations and the comparison of water quality parameters between the different mine drainage waters and water courses.

Typical seasonal variations of the mine waters are discussed below. The mines have been divided into those severely, moderately and slightly contaminated with respect to Cd as it is one of the most toxic elements present within the mine drainages. Severely contaminated waters (Cd concentration $>10 \mu\text{g/L}$) are Bwlch, Cwm Rheidol, Cwmystwyth, Frongoch and Wemyss mine waters; moderately contaminated waters ($1-10 \mu\text{g/L}$ Cd) occur at Alltycrib, Cwmbryno, Esgair Hir, Grogwynion and Level Fawr; and slightly contaminated waters ($<1 \mu\text{g/L}$ Cd) occur at Afon Llywernog, Cwmsymlog 1, Cwmsymlog 2, Eaglebrook, Daren, Goginan and Nant Silo. This division of mines is also partially true when using Zn, Pb and SO_4 , although some discrepancies do occur in the average concentrations of different elements at certain mines.

The monthly averages of rainfall, air temperature and solar radiation are shown in Figure 4.10 and show distinct seasonal variations. Rainfall varies throughout the year with spring-summer being the driest and the maximum in the autumn with only a minor amount falling as snow. Air temperature and solar radiation both show dramatic seasonal variation with solar radiation peaking between late spring and early summer, a couple of months before the air temperature (rising to a maximum between late summer-early autumn 2004 and summer 2005). The discharge of the mine drainage waters and water courses were not measured; instead the rainfall shown in Figure 4.10 was used as a proxy for discharge i.e. that discharge should increase in the autumn (the total rainfall for three days prior to sampling is included within the subsequent figures to provide a more detailed indication of whether measured rainfall, as opposed to the general pattern, may be used as a proxy for discharge). Hren *et al.* (2007) determined that the use of rainfall provided an adequate measure of discharge, though this can not to be taken precisely as it does not take into account the loss of the rainfall through infiltration, evaporation or transpiration, or the gain from any snowmelt. Desbarats and Dirom (2005) found that seasonal variations in rainfall had a profound effect on the flow of mine drainage emanating from a mine. As stated in Chapter 3.1 the rainfall measurements were taken at Plas Gogerddan (SN(22) 627 835) which is ~ 35 m above mean sea level, however regionally the amount of rainfall will increase with elevation (English *et al.*, 2000); Havel *et al.* (1996 cited in Peters *et al.*,

1999) found that rainfall increased linearly with elevation increasing by 70 mm every 100 m, therefore the amount of rainfall can only be used as a rough guide to the discharge.

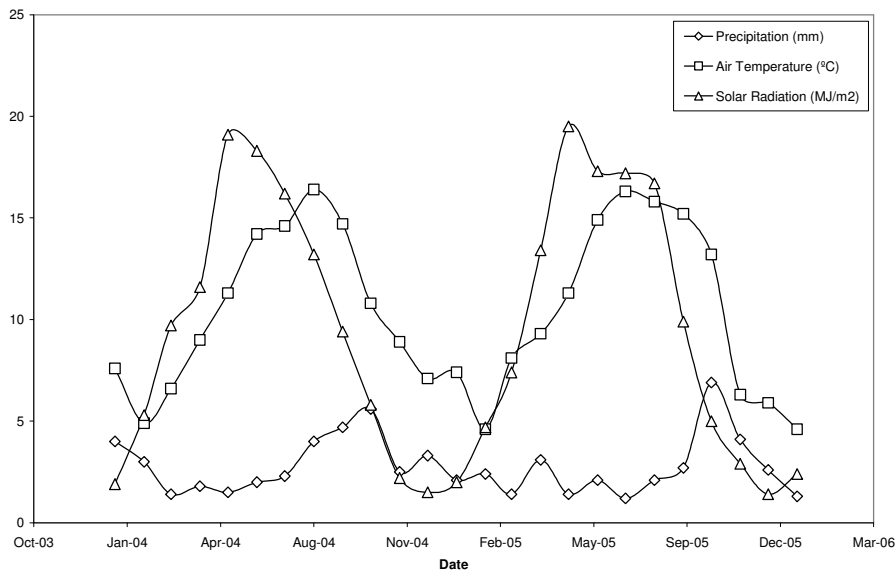


Figure 4.10. Measured monthly average rainfall, air temperature and solar radiation for the Aberystwyth area (non-smoothed).

Data provided by Institute of Grasslands and Environmental Research, Aberystwyth

The element concentrations in both mine drainage waters and water courses are all variable, although they do not all vary seasonally. Those which exhibit seasonal variation may not show the same patterns between different mines and between different elements at the same mine. They differ in the timing of the minimum and maximum concentrations, for example Cd at Cwm Rheidol rises to a maximum in June and July, and at Cwmystwyth Cd increases to a maximum in September-October, see Figure 4.11a and b. For this reason when describing the timing of the variations the individual months shall not be used, but winter (December, January and February), spring (March, April and May), summer (June, July and August) and autumn (September, October and November) will be used instead. Care must be taken when interpreting the seasonal trends. The overall pattern needs to be considered because, as described in Chapter 4.4, smoothing the data can over exaggerate any small decrease in concentration, for example, in Figure 4.11b the lower Cd concentration which occurred at the beginning of September 2004, is created by one low concentration (17.7 µg/L) being preceded and followed by higher concentrations (28.7 µg/L, 29.7 µg/L, 33.1 µg/L and 41.5 µg/L). The smoothing process creates an artificial trough, whereas in reality there is only one low data point. The seasonal variations may not be consistent between the two sample years; for example, Ca at Cwmystwyth was relatively constant in 2004, but showed a more pronounced seasonal variation in 2005

(Figure 4.12a) and Zn at Cwm Rheidol showed a more pronounced seasonal variation in 2004 and limited variation in 2005, see Figure 4.12b; which may be a result of the fortnightly sampling in 2004 and monthly sampling in 2005. The sampling frequency can either make it easier or more difficult to determine seasonal variations; for example, a lower sampling frequency may make the determination of seasonal variations more difficult as there are fewer data points.

Element concentrations were variable at all studied mines and those elements exhibiting a seasonal variation are listed in Table 4.7. The table shows the percentage change between the average concentration in June and July and the average concentration in December and January, with a positive number indicating higher concentrations in summer and a negative number indicating higher concentrations in winter. In general, the severely contaminated waters displayed greater seasonal variations than the moderately and slightly contaminated waters.

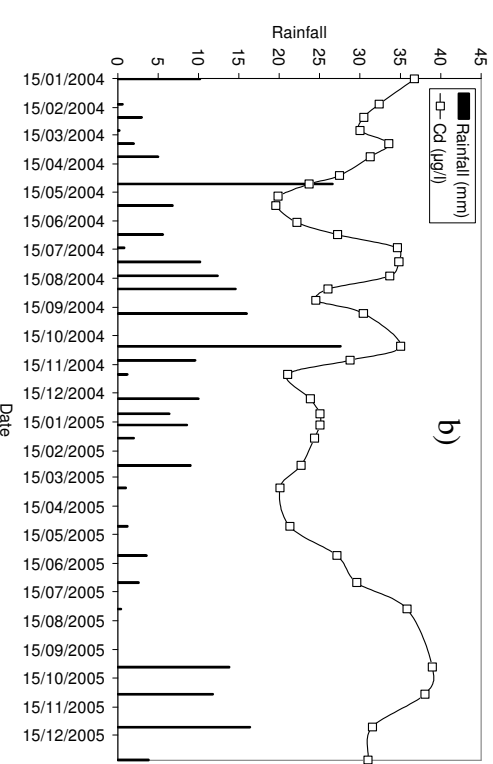
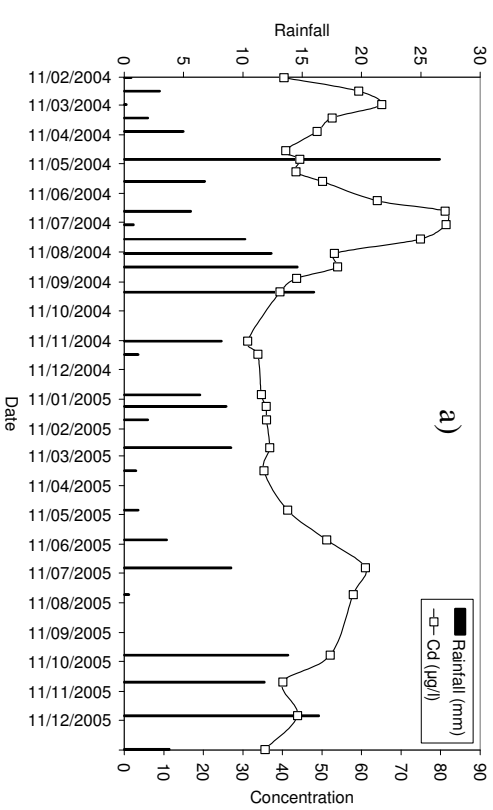


Figure 4.11. Cadmium concentrations at: a) Cwm Rheidol and b) Cwmystwyth.

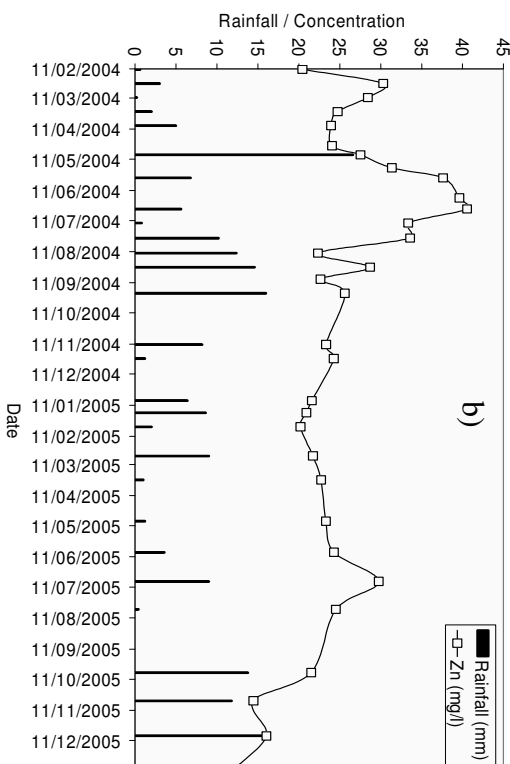
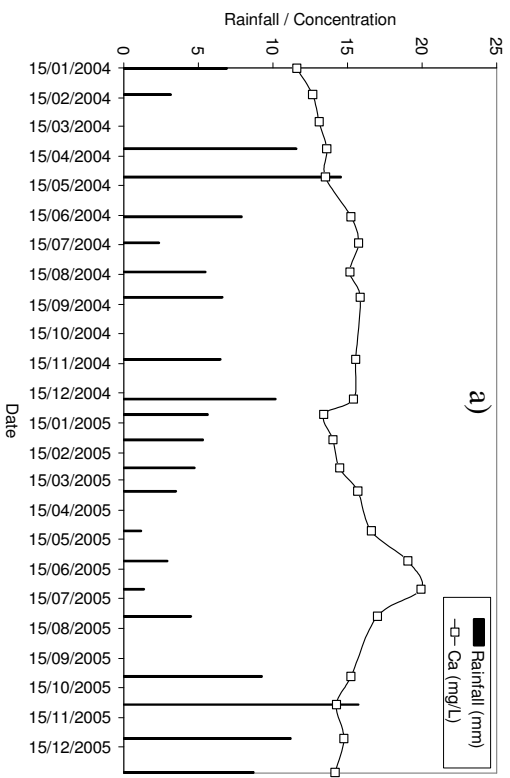


Figure 4.12. Differences in variations between 2004 and 2005: a) Ca at Cwmystwyth and b) Zn at Cwm Rheidol.

Table 4.7. Percentage change in concentration from summer to winter (smoothed data).

	SO ₄	Na	Mg	K	Ca	Fe	Co	Ni	Cu	Zn	Cd	Pb
Severely contaminated												
Bwlch	55		38.2	32.7	43.2		38.1	70.7	56.3	51.4	48	33.9
Cwm Rheidol	49.3		36.2		42.9	64.9	60.5			47.3	39.7	
Cwmystwyth	27.6				35.3						-11.1	-234
Frongoch	-70				20.9					-145	-112	-9.4
Wemyss	×										34.9	50.8
Moderately contaminated												
Alltycrib	34.4	-5.9	27.3	-41.2	36.3						-94.5 ¹	-223
Cwmbryno	24.3				21.1						34.4	-15.4
Esgair hir		4.1			64.2			84.0				
Grogwynion	37.3	14.6	26.0	19.3	15.9							
Level Fawr	50.5	22.7	42.9		45.4			85.8		36.3	27.8	
Slightly contaminated												
Afon Llywernog		14.4			37							
Cwmsymlog 1												
Cwmsymlog 2					43.4							54.8 ²
Daren	13.3	12.5			14				*			18.4
Eaglebrook			9.3		57.5			64.1	×			
Goginan	9.4											
Nant Silo	17.5	8.2			17.9					-46.4	-44.7	

* = increases in winter, × = increases in summer (no percentage change has been calculated because of variable data)

¹ Seasonal variation only occurs in the first year. Values used are April to July (instead of June-July) and the preceding January-February, and following October-November (instead of December-January).

² Seasonal variation only occurs in the second year. Only the January data was used.

Sodium and Potassium

The main source of both Na and K into the aqueous environment is silicate weathering with a contribution from sea salt in coastal environments. Those mines which show seasonal variation all have maximum concentrations in summer, with the exception of Alltycrib which shows maximum concentrations in winter. Daren, Grogwynion, Level Fawr have >10 % difference between the Na concentrations in summer and winter, which may be explained by all three mines have very long tunnel systems with increased time for water-rock interaction. Grogwynion also shows a summer increase in K concentration; similar patterns between elements may indicate that the elements derive from the same source i.e. the host rock or the mineralisation (Pearce, 1992), see Figure 4.13, though this may be a product of another controlling factor, for example SO₄. The Afon Llywernog shows a large increase between summer and winter concentrations which may result from the Afon Llywernog collecting runoff from local mines and land, or because there are exposed silicate rocks on the river bed or there may be an influence from sea salt. Potassium shows little variation within the sampled waters as K is not easily weathered and is strongly controlled by biological cycling. The K concentration increases in the summer at Bwlch and increases in winter at Alltycrib. At Alltycrib K may show an increase in winter because of the K within the vegetation leaching out into soils and soil water in the plant's dormant season or as the plants die or the leaves are shed (Hem, 1985; Neal *et al.*, 1990). The mine drainage at Alltycrib issues from a disused mine level and flows over ~10 m of grass and earth (which are regularly trampled by ruminants who drink the waters) prior to the location of sample collection. Potassium is also accumulated in the upper soil layer by biological uptake and the mineralisation process (Sandén *et al.*, 1997). Winter rainfall results in the downward leaching of K, increasing concentrations within the soil water (Holloway and Dahlgren, 2001). When the Bwlch mine was remediated, the spoil tips along the riverside were covered in a layer of clay which may be the source of the K.

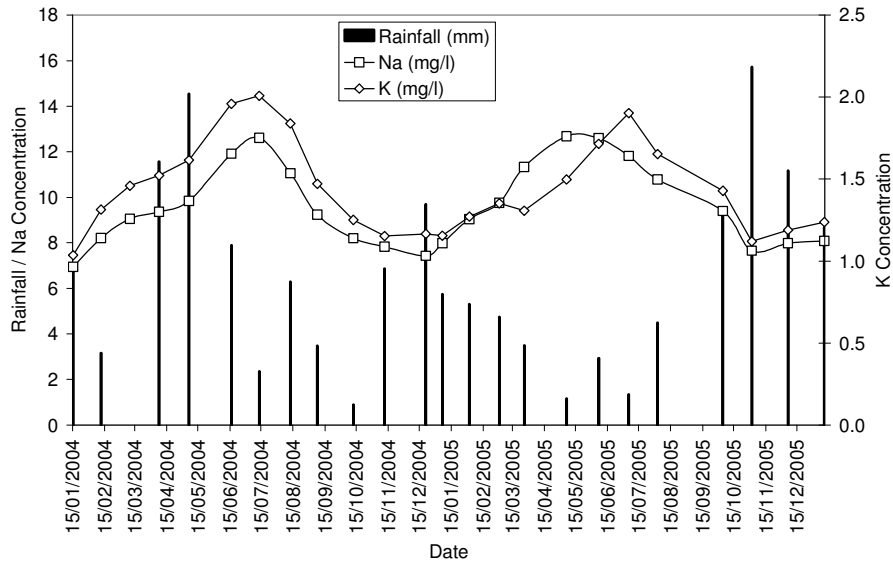


Figure 4.13. Na and K concentrations at Grogwynion.

Calcium and Magnesium

The dissolution of carbonate minerals is the main source of Ca and Mg. No seasonal Ca variations occur at Cwmsymlog 1, Goginan and Wemyss. The sample taken at Cwmsymlog 1 should have had no contact with mine spoil, and be solely rainfall and run off derived, therefore no seasonal variation is expected; Goginan has been remediated and therefore the sampled waters should have little contact with the spoil. The Wemyss sample only flows along the side of the spoil tip and does not have prolonged contact with the spoil. These mines have low Ca concentrations indicating either that there is low calcite within the gangue or that the calcite has already been dissolved and removed into solution. The maximum concentrations of Ca and Mg always occur in the summer. Only Bwlch (see Figure 4.14), Cwm Rheidol, Alltycrib, Grogwynion, Level Fawr and Eaglebrook show a seasonal Mg variation. The Mg may be present because of the dissolution of the calcite gangue, or via dissolution of ferromagnesian minerals and ferroan dolomite dissolution at Cwm Rheidol and Eaglebrook.

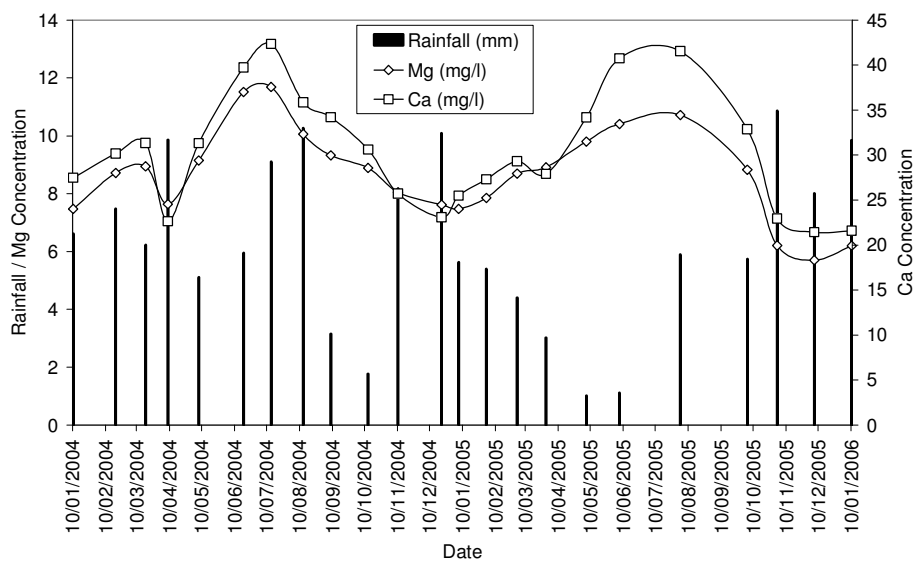


Figure 4.14. Mg and Ca concentrations at Bwlch.

Iron, Cobalt and Nickel

Cwm Rheidol is the only mine with appreciable Fe present in its waters and the concentration increases during the summer months. Cobalt also increases during the summer; as the Co^{2+} ion (6-fold co-ordination 0.73\AA) is similar in size to the Fe^{2+} ion (6-fold co-ordination 0.69\AA) the Co can substitute into iron sulphides. Nickel, Co and Cu also occur as trace elements in sphalerite and galena and where the concentrations of Zn and/or Pb show increases at the same time it may suggest that they derive from the same source. At Bwlch, Co and Ni increase at the same time as Zn and Pb; Co at Cwm Rheidol, Ni at Level Fawr and Eaglebrook increase at the same time as Zn, which all suggest a strong link to sulphides.

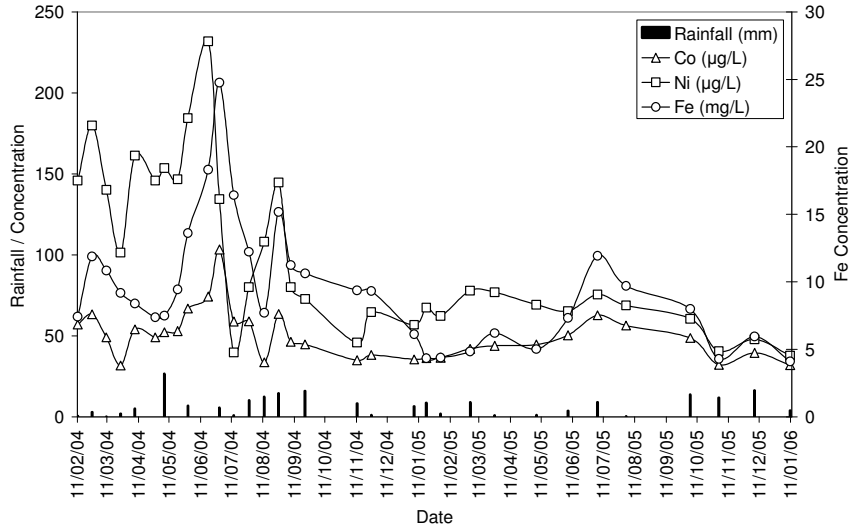


Figure 4.15. Fe, Co and Ni concentrations at Cwm Rheidol.

Zinc and Cadmium

Most of the mines do not show seasonal Zn variation, whilst other elements show seasonal patterns. Zinc concentrations increase during the summer at Bwlch, Cwm Rheidol and Level Fawr and during the winter at Frongoch and Nant Silo. Despite the dissolution of sphalerite being the main source of Cd (similar seasonal patterns are shown in Figure 4.15); Zn and Cd do not necessarily show the same seasonal variation, with more mines showing a seasonal variation for Cd than Zn and generally Zn concentrations are less variable than Cd (Bambic *et al.*, 2006). Cadmium can show a seasonal variation at the same time as Zn or Pb, but the latter does not necessarily mean that the Cd is derived from the galena.

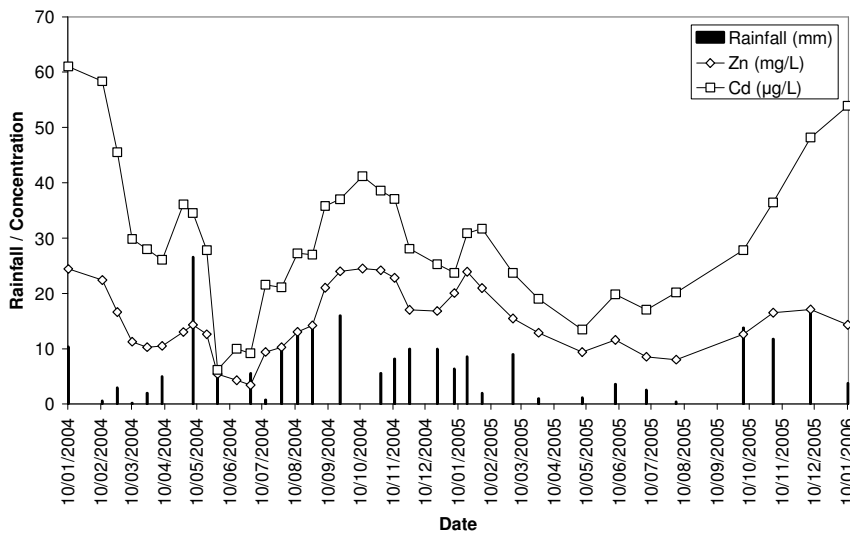


Figure 4.16. Zn and Cd concentrations at Frongoch.

Sulphate

The majority of the mine drainage waters/water courses sampled show a seasonal SO₄ variation, for example, at Bwlch, Zn and SO₄ show almost identical seasonal patterns (Figure 4.16); with the exception of Frongoch, all of the mine drainage waters/water courses have maximum concentrations in the summer. Esgair Hir, the Afon Llywernog, Cwmsymlog 1, Cwmsymlog 2 and Eaglebrook, however, do not show a SO₄ seasonal variation. The seasonal variation in SO₄ concentration is typically controlled by the dissolution of sulphides (sphalerite, galena and iron sulphides).

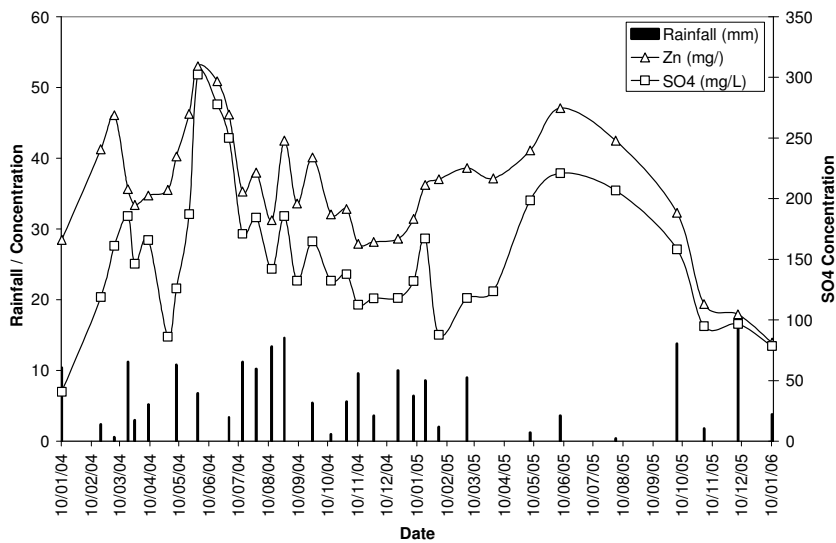


Figure 4.17. Zn and SO₄ concentrations at Bwlch.

Most maximum metal concentrations occur during the summer, which may be caused by a number of factors. An inverse relationship between concentration and discharge has been described for many rivers and occurs where the factors controlling the water chemistry are constant (Edwards, 1973); though no correlation occurs between rainfall and element concentration in this study. The concentration of soluble elements is generally higher in summer when low flows occur, because dilution by uncontaminated runoff is at a minimum (Grimshaw *et al.*, 1976; Antunes *et al.*, 2002; Olias *et al.*, 2004). It is unlikely that this is the only mechanism occurring as the percentage increase between summer and winter is greater than the 23 % decrease in rainfall in the summer. An increased temperature during the summer causes an increase in weathering and evaporation (Drever and Zorbrist, 1992; Olias *et al.*, 2004) and the relatively constant discharge from the mines directly removes the released metals. Lower rainfall in the summer results in a slower flow of water through the mine compared to winter and

therefore there is more time for water-rock interaction to occur, consequently higher concentrations of elements may be contained in the waters (Edwards, 1973; Holloway and Dahlgren, 2001). The temperatures within mid-Wales mines are unlikely to change more than a few degrees throughout the year; therefore the temperature will not be the main variable controlling mineral weathering. The temperature effect is likely to be much more prominent within the spoil tips.

The main elements that increase during the winter months are Zn, Cd and Pb; SO₄ at Frongoch and Na and K at Alltycrib. These winter increases may be caused by the flushing of oxidised soluble salts and/or increased rainfall, causing more dissolution of the host rock and ore minerals. Higher concentrations at the start of the rainy season in the autumn may be caused by flushing of accumulated weathering products from the mines or spoil tips. At Cwm Rheidol, Newton (1944) observed a white powdery substance on the surface of the spoil tips; this was not classified by Newton, but it is principally Goslarite (ZnSO₄·7H₂O) (Perkins pers. comm., 2008). More recently Palumbo-Roe *et al.* (2007) discovered bianchite (zinc sulphate hexahydrate) on the spoil tips at Grogwynion. The dissolution of these salts may cause temporary increases in concentration in spite of the dilution effect caused by the increased rainfall (Grimshaw *et al.*, 1976; Sullivan and Drever, 2001; Smolders *et al.*, 2004), for example SO₄ is a very mobile ion (Olías *et al.*, 2004) and may be removed in solution as soon as dissolution occurs, therefore the concentration increases during the summer, except at Frongoch and within the Afon Llywernog. Increased rainfall can also flush out the highly concentrated waters within the soil (Neal *et al.*, 1990; Peters *et al.*, 1999; Smolders *et al.*, 2004), for example, water soluble SO₄ that accumulated during drier periods can be flushed out of upland and/or wetland soils (Wieder and Lang, 1984). The increased weathering and dissolution in summer can also produce pools of concentrated water and as the water level within the mine or spoil tips increases the concentrated waters can be flushed out (Sandén *et al.*, 1997). Increased weathering and dissolution may occur because of the increased amount of slightly acidic rainwater and a higher proportion of infiltrating surface waters (Pearce, 1992). Not all elements are affected by these processes because of their different solubilities (Smolders *et al.*, 2004).

4.6 Diurnal variations

Determining field parameters and element concentrations in adit water over a fortnightly or monthly basis is not sufficient to reveal changes which occur on smaller timescales, for example, over 24 hours (Bourg and Bertin, 1996), which can be significant (Sullivan and Drever, 2001). Over the past 15 years considerable research has been undertaken to characterise the geochemical changes that occur within a 24 hour period. In neutral and alkaline waters the concentrations of many metals can markedly change regardless of changes in flow or whether waters are severely, moderately or slightly contaminated (Nimick *et al.*, 2003). The changes that can occur on a daily basis may be considerable, and may be comparable to changes which occur on a seasonal basis (Nimick *et al.*, 2005). If diurnal variations are significant and are not taken into account when sampling, large errors could be introduced into the data set (Sullivan *et al.*, 1998). This could lead to uncertain, misleading or potentially inaccurate long-term trends, especially if samples are collected at different times of the day (Nimick *et al.*, 2003). Therefore, consideration of potential diurnal variations is vital in the examination of any long-term data. The timing of sample collection can also influence whether waters comply with EQS i.e. the sample may fail as it was taken at the time of day when the maximum concentration occurs, when at all other times the waters comply with the EQS (Parker *et al.*, 2007). If the water course shows diurnal cycles of metals this may also affect aquatic life within the ecosystem, presenting a major risk to the aquatic life even if the metals only exceed EQS for short periods every day (Brick and Moore, 1996; Nimick *et al.*, 2003).

Chemical and physical parameters, including streamflow, pH, conductivity, water temperature, redox speciation, dissolved and particulate trace and major elements are all known to show diurnal variations (Brick and Moore, 1996; Nimick *et al.*, 2003; Parker *et al.*, 2007). A number of physical, geochemical and biological mechanisms can be used to explain the daily changes in these parameters, including daily cycles of temperature; metal loading; stream flow; biological uptake, including photosynthesis and respiration; rainfall and dissolution reactions; adsorption and desorption reactions (Sullivan *et al.*, 1998; Jones *et al.*, 2004; Parker *et al.*, 2007).

Two sample sites in this study were chosen to examine diurnal variations (Cwm Rheidol and Cwmystwyth). The samples were collected at the same location as the sites used for the determination of seasonal variations (see Chapter 2.4 for site locations and descriptions). The sampling was undertaken at Cwm Rheidol from 0500 h on the 16th July 2005 until 0500 h on the 17th July 2005 and at Cwmystwyth from 1400 h on the 17th July 2005 until 1400 h on the 18th July 2005. The flow of mine drainage from the adit would not have significantly altered during the sampling period because there was no recorded rainfall between the 6th and 16th July, 2.6 mm of rain fell on the 17th July 2005 and 0.6 mm fell on the 18th July 2005. Therefore, there was little rainfall to cause a significant increase in mine drainage flow. Although the rainfall was not measured at the exact location of sampling, it gives a good indication of the conditions experienced at the time. These localities were chosen for monitoring to determine the diurnal variations of various elements in both ochreous acidic and ochreous circum-neutral mine drainage.

4.6.1 Field collection

Samples were collected at 30 minute intervals, except during the hours of darkness when samples were taken at 2300 h, 2400 h, 0130 h and 0300 h at both Cwm Rheidol and Cwmystwyth; and also at 0600 h and 0700 h at Cwm Rheidol. Water temperature, pH, Eh, conductivity, light intensity and stream flow were determined at the time of sample collection, and the instruments were recalibrated sporadically throughout the sampling period. The samples were collected and immediately filtered through 0.45 µm pore size Whatman[®] cellulose nitrate (WCN) membrane filter for both major and trace element analysis and for Fe speciation. The samples were collected and analysed following the methods described in Chapter 3. Stream flow was measured at the time of sample collection using a Braystoke current meter. Light intensity was measured using a Ravenscourt Ltd. digital lux tester, model RY 139L.

4.6.2 Iron speciation

Total Fe and Fe²⁺ were analysed using the colorimetric method of Ander and Fuge (1997). The colorimetric method uses the colour forming agent 2,2 bipyridyl, in a pH buffered solution, which complexes with the Fe²⁺ and forms a red colour; 2,2 bipyridyl is one of the most often used complexing agents (Gonzalvez *et al.*, 2009). This

colorimetric method, using 2,2 bipyridyl, has been used by numerous authors to determine Fe speciation (Heaney and Davison, 1977; Davison *et al.*, 1999; Carlson *et al.*, 2002) and Bearcock (2007) found that the concentration of total Fe analysed using the colorimetric analysis was in good agreement with the concentration of total Fe analysed using AAS.

An aliquot (5 mL) of the filtrate was added to the sample bottles before being kept in the dark and analysed within seven days. Studies by Ander and Fuge (1997) show that the developed colour is generally stable over 12 days. The concentration of Fe^{2+} and Fe^{total} were analysed by determining the intensity of colour formed and calibrating these against a series of synthetic standards. The dissolved total Fe and Fe^{2+} were quantified using a Camspec M202 Ultraviolet-Visible Spectrophotometer (UV-VIS) using a wavelength of 518 nm. The concentration of Fe^{3+} was calculated as the difference between the Fe^{2+} and total Fe concentration, the Fe^{3+} having been reduced using hydroxylammonium chloride.

To produce the reagents for Fe^{2+} and Fe^{total} determination, the following solutions were prepared:

1) Bipyridyl reagent

140 g sodium acetate, CH_3COONa (BDH general purpose reagent) and 0.4 g 2,2 Bipyridyl ($\text{C}_{10}\text{H}_8\text{N}_2$), made up to 1 L with MilliQ water

2) Hydroxylammonium Chloride reagent

40 g of Hydroxylammonium Chloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$ (BDH Analar[®]) reagent made up to 500 mL with MQ water

These solutions were then used to prepare sample bottles for Fe^{2+} and Fe^{total} determination:

Fe^{2+} : 10 mL of Bipyridyl reagent and 8 mL of MQ water

Fe^{total} : 10 mL of Bipyridyl reagent and 8 mL of Hydroxylammonium Chloride reagent

Multiple analysis was performed on five samples, see Table 4.8, with a relative standard deviation of <3 %.

Table 4.8. Multiple analysis data for repeated colourimetric samples.

	CR 2 Fe ²⁺	CR 2 Fe ^{total}	CR 12 Fe ²⁺	CR 18 Fe ²⁺	CR 18 Fe ^{total}
Average concentration	8.91	11.36	8.18	7.94	10.30
Standard Deviation	0.00	0.10	0.00	0.21	0.13
Relative Standard Deviation (%)	0.00	0.87	0.00	2.60	1.22

4.6.3 Diurnal variations

Cwmystwyth has slightly acidic-neutral mine drainage with an average pH range of 5.8–7.0 and Cwm Rheidol has acidic mine drainage with an average pH range of 2.4–4.1 (between January 2004 and January 2006). The diurnal pH change at Cwmystwyth was 0.4 pH units with an average of 6.9, and there was no diurnal pH change at Cwm Rheidol which had a constant measured pH of 3.7. Minimal pH changes may show that there is limited photosynthesis or respiration occurring within the sampled water courses or that any photosynthesis or respiration that occurs has a localised effect (cf. Brick and Moore, 1996; Goulet and Pick, 2001). See Appendix 6 for a full table of results.

No diurnal variations occurred in any other field parameter at either mine with the exception of water temperature. The increase in water temperature at Cwmystwyth is much smaller and less pronounced than that at Cwm Rheidol; Cwmystwyth water increased in temperature from 10 °C to 19.5 °C, whereas the temperature of the water at Cwm Rheidol rose from 9.1 °C to 25.3 °C, see Figure 4.17. This difference may be because: a) Cwmystwyth has a greater flow (average flow of 70 L/second, as opposed to an average flow of 4 L/second at Cwm Rheidol) and therefore it takes longer for the sunlight to warm the water, b) the sample location at Cwmystwyth is much closer to the adit entrance, only ~ 2 m, compared to ~30 m at Cwm Rheidol or c) there was more cloud cover and light drizzle when the Cwmystwyth samples were taken.

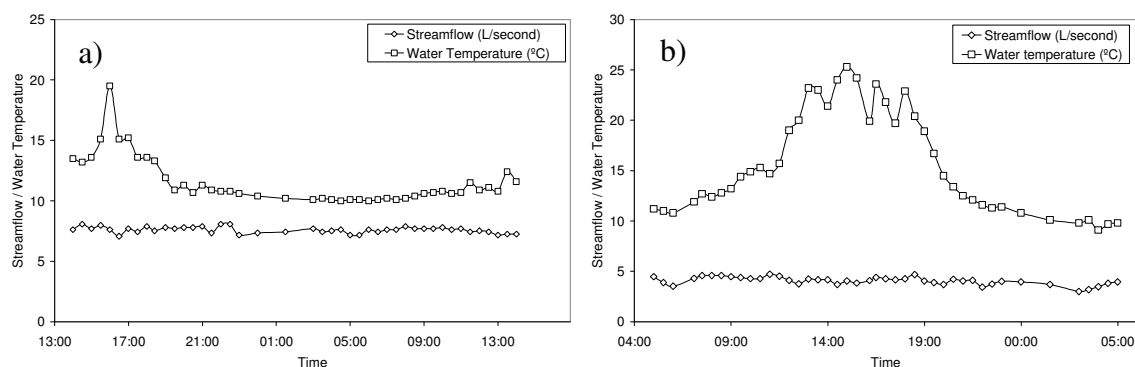


Figure 4.18. Streamflow and water temperature diurnal variations for: a) Cwmystwyth and b) Cwm Rheidol. Note the different time periods for Cwmystwyth and Cwm Rheidol.

In acidic mine waters, i.e. Cwm Rheidol, it is common to find that Fe is the only metal to show a diurnal variation (Nimick *et al.*, 2003; Gammons *et al.*, 2005). When Fe^{2+} oxidises to Fe^{3+} at a pH of 8 or 9, other metals (including Cu, Zn and Cd) co-precipitate regardless of the typical pH at which the element precipitates (Coulton *et al.*, 2003), and at a lower pH only Fe will precipitate. The diurnal variations of Fe^{2+} , Fe^{3+} , Fe^{total} and water temperature at Cwm Rheidol are shown in Figure 4.18. Both Fe^{2+} and Fe^{total} increase slightly at night and decrease during the day, the opposite of what would be expected in acidic mine drainage if photochemical reduction took place (cf. Kimball *et al.*, 1992; Nimick *et al.*, 2003; Gammons *et al.*, 2005).

Brick and Moore (1996) found an increase of acid-soluble particulate Fe at night in pH 8-8.7 river waters caused by an increase in suspended matter attributable to an increase in benthic macroinvertebrate activity. Bäckström *et al.* (2002) and Gammons *et al.* (2005) observed an increase in Fe^{2+} at night in ~pH 7 waters which was explained by decreasing reaction rates for Fe^{2+} oxidation and Fe^{3+} hydrolysis kinetics caused by the lower water temperature at night. Goulet and Pick (2001) also observed a night time increase in Fe concentration at two surface-flow wetlands and attributed this increase to low oxygen and pH caused by the microbial reduction of Fe^{3+} oxides at the water-sediment interface (see Lovely *et al.*, 1987). All of these repeated nocturnal increases of Fe^{2+} concentration are accompanied by changes in pH, which does not occur in this study. Wieder (1994), however, observed nocturnal increases in constructed acid mine drainage treatment wetlands and has attributed the increase to bacterially-mediated anaerobic Fe^{3+} reduction, which generates alkalinity (consuming 2 moles of H^+ per mole of Fe oxyhydroxide reduced) and the anoxic oxidation of reduced organic

sulphides which generates acidity (14 moles of H^+ per mole of FeS_2 oxidised). Any pH changes observed in the wetlands may reflect the relative importance of the Fe^{2+} producing mechanism. Bäckström *et al.* (2002) concluded that further investigation for the nocturnal increase in concentration is required. If photochemical reduction was occurring, solar radiation would encourage the dissolution of hydrous ferrous oxides providing an increase in Fe^{2+} and Fe^{total} during the day (Nimick *et al.*, 2003). The concentration of Fe^{2+} however, is controlled by the exposure of the water body to near ultra-violet radiation, therefore the short time it takes for the water to leave the adit at Cwm Rheidol and reach the sampling location, may be a factor in the concentration of the Fe. The increase in Fe^{2+} and Fe^{total} concentrations during the night may be a result of warmer surface waters entering the Ystumteun, Penrhiw and Bwlchgwyn mines (which are drained by the Cwm Rheidol adits) causing the dissolution of pyrite and/or marcasite; the higher concentrations at night may be a product of the length of time that the Fe-rich water takes to exit the Cwm Rheidol adits.

A decrease in the concentration of Fe^{3+} and a simultaneous increase in the concentration of Fe^{2+} started around 05.30 am and 21.00 pm, though the Fe^{total} concentration did not change. On the 16th July 2005, the sun rose at 05.15 am and set at 21.22 pm (www.timeanddate.com/worldclock/astronomy.html?n=298&month=7&year=2005&obj=sun&afl=-11&day=1); although these times are correct for Cardiff, it may be presumed that the variations in Fe concentration are related to the sun rise and sun set times. The increase in Fe^{2+} may be caused by photochemical reduction encouraging the dissolution of hydrous ferrous oxides or it may be caused by bacterially mediated reduction of Fe^{3+} (hence the decrease in Fe^{3+} and the increase in Fe^{2+} concentration). The bacteria may be stimulated by low light levels at dawn and dusk and by the temperature of the mine water. It is likely that a combination of factors control any biological processes that affect the water chemistry.

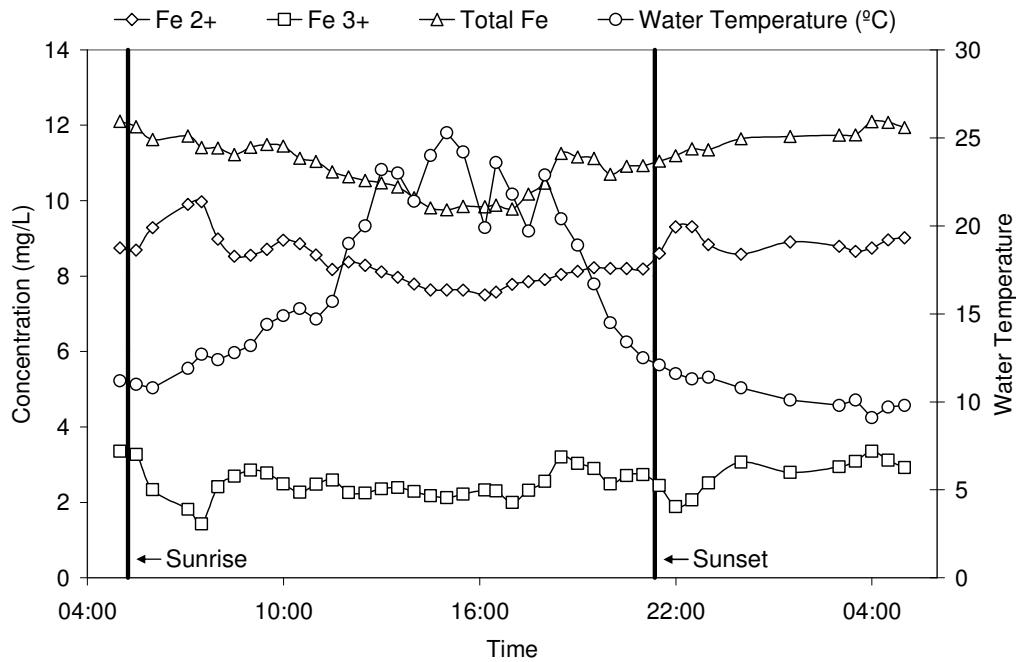


Figure 4.19. Fe²⁺, Fe³⁺ and Fe^{total} concentrations at Cwm Rheidol.

In near-neutral and alkaline waters, i.e. Cwmystwyth, significant diurnal variations were expected, with the exception of Fe, with metal concentrations decreasing during the day and increasing at night, inversely correlated with diurnal changes in pH and water temperature. These diurnal variations may be attributed to the reversible pH- and temperature-controlled sorption reactions between the water column and the stream bed and biological uptake (Gammons *et al.*, 2005; Nimick *et al.*, 2005). At Cwmystwyth, however, no diurnal variation occurred in any of the elements.

Changes in the following parameters have been used to explain diurnal variations: (a) variations in stream flow caused by snowmelt, floodplain evapotranspiration and by the addition of groundwater, either causing a dilution or increase in concentrations (Sullivan *et al.*, 1998; Nimick *et al.*, 2003); and (b) variations in pH, temperature and light effecting sorption reactions, biotic uptake, precipitation and dilution (Fuller and Davis, 1989; Jones *et al.*, 2004; Nimick *et al.*, 2005). The lack of changes in these parameters described can explain the absence of diurnal cycles in the elements. The sample at Cwmystwyth was taken ~2 m from the adit entrance; therefore there will not have been sufficient time for the reactions detailed in (b) to occur and cause the element concentrations to vary.

Nimick *et al.* (2005) determined that the maximum and minimum concentrations within the diurnal variations occurred at about the same time regardless of the season or flow conditions. For example, if considering the minimum and maximum Fe^{total} concentrations at Cwm Rheidol during the diurnal and seasonal variation studies, the range in the diurnal variation (9.6–12.6 mg/L) is very small compared with that of the seasonal variation (2.1–21.1 mg/L), and therefore providing that the samples are collected at approximately the same time errors introduced into the data set should be minimised. The mine drainage waters/water courses were samples to determine the seasonal variation as part of a route; therefore they were collected at approximately the same time on every trip. It is important to recognise that diurnal variations studies have been conducted in major streams/rivers by previous authors, not in mine drainage adits and therefore other unknown factors may influence the composition of the mine drainage.

4.7 Summary

This study has shown that despite the mines being closed and abandoned for over 100 years there is still a legacy of metal-rich spoil tips and contaminated drainage waters. Chemical weathering of the host rocks and ore minerals leads to the release of elements into the aqueous environment. The drainage waters are predominantly circum-neutral; contain little Fe (<1 mg/L), because there is limited pyrite and/or marcasite within the ore bodies; but the waters contain a number of metals at elevated concentrations, especially Zn, Cd and Pb. The majority of sampled waters were taken directly from the mine adits and once the adit water mixed with the receiving water course, the EQS may be met. Two receiving water courses were sampled to determine whether this is the case and both the Afon Llywernog and the Nant Silo fail EQS for Pb (an annual average of 4 µg/L dissolved Pb). This research has demonstrated that mine water has a dramatic effect on the receiving water courses and causes many of these streams and rivers to fail water quality standards set by the EU, especially Zn, Cu, Pb and a large number of mines fail EQS for Cd.

Seventeen waters were sampled (15 mine drainage waters and two receiving water courses) between January 2004 and January 2006. Samples were collected fortnightly

during 2004 and monthly during 2005. The waters were collected to determine the element concentrations and to ascertain whether any seasonal variations occurred. The element concentrations within mine drainage waters vary to different degrees and sometimes contrasting ways, for different groups of elements (Neal *et al.*, 1990). Element concentrations are variable throughout the year, although they do not necessarily show a seasonal variation. The seasonal variation trends vary for different elements and at different mines, with the minimum and maximum concentrations occurring at different times of the year; for example, the maximum Cd concentration typically occurred in June-July, but at Cwmystwyth occurred in September-October. The seasonal variation is not consistent between the two sampling years, for example, at Cwmystwyth, Ca was relatively constant in 2004, but showed a more pronounced variation in 2005. However, Zn at Cwm Rheidol showed a pronounced seasonal variation in 2004, but was more or less constant in 2005.

In general, Bwlch, Cwm Rheidol, Cwmystwyth, Frongoch and Wemyss are the most severely contaminated of the seventeen mine drainage waters/water courses sampled (contain the highest concentrations of SO₄, Mn, Fe, Co, Ni, Zn, Cd, Ba and Pb) and these mines show greater seasonal variation than the other mine drainages/water courses. The majority of those elements that show a seasonal variation increase to a maximum in summer caused by limited dilution, increased oxidation of the host rock and ore minerals in the warmer, drier conditions and an increased water-rock interaction time. Zinc, Cd and Pb tend to increase in the winter, which may be related to increased oxidation in the summer creating easily soluble sulphate salts, which are mobilised by the increasing rain in the autumn or the increased, slightly acidic, rain encouraging the dissolution of the minerals. The concentration of elements within the mine drainage or water course and when the maximum and minimum concentrations occur indicates that that weathering and removal rates differ relative to the element and no single reaction or explanation can describe all of these variations (Neal *et al.*, 1990). At a minimum, the waters need to be sampled in the summer (June–July) and winter (December–January) to get the range of element concentrations. Samples were taken every 30 minutes at Cwm Rheidol and Cwmystwyth to determine whether any variations occurred over a 24 hour period. At Cwm Rheidol only Fe showed a diurnal variation with concentrations increasing slightly during the night; the other elements measured at Cwm Rheidol and all the elements measured at Cwmystwyth did not show any diurnal variation.

Sampling occurred at more or less the same time of day for each sample period so any sampling errors should be minimised.

The composition of the sampled water can be derived through any number of gas, water and rock interactions (Fairchild *et al.*, 2000). To determine absolutely the source of the elements contained within the mine drainage/water course further studies are required, for example to describe the weathering intensity or loss of material (Bluth and Kump, 1994). The additional measurements of the following parameters would be interesting to try and constrain the source of the elements within the mine drainage waters and water courses, but they are well beyond the scope of this thesis, where the primary objective of this section is to detail the range of concentrations of relevant elements and when they occur. The additional information required may include:

- * the discharge of the mine drainage waters and water courses - to take into account the losses through infiltration, evaporation, transpiration, and additions to the discharge by snowmelt from rainfall.

- * the alkalinity of the mine drainage waters and water courses – to determine the capacity of the solution to react with and neutralise acids; commonly reported as an equivalent amount of CaCO₃ (Hem, 1985)

- * Underground mine workings can be extremely complex and because accurate maps were not kept, the extent of them is rarely known (National Rivers Authority, 1994). The hydrological residence time of the water within the mine would be useful for providing an estimation of the contact time between water, wall rock and ore minerals, this can be achieved through tracer tests (see Williams *et al.*, 1993), although it would be difficult to spike every water input to the mine.

- * The concentration of elements derived from the atmosphere and precipitation; for example Hren *et al.* (2007) determined that 30 % of the Na in the lower Brahmaputra River was derived from marine sources and Mortattia and Probst (2003) estimated that 13.8 % of Na was contributed by the atmosphere to the Amazon River, once the corrections had been made for atmospheric input, Mortattia and Probst (2003) attributed all the Na and K from silicate rock weathering.

- * The concentration of elements supplied by shallow and deep groundwater would be required for those mines where the water samples were taken directly from the adit (Neal *et al.*, 1990; Land *et al.*, 2000). The chemistry of the soil pore water (Land *et al.*, 2000) would be desirable, as flow increases the contribution from the soil also increases

and could therefore have a significant impact on the chemistry of the waters (Neal *et al.*, 1990).

* The concentration of a number of additional solutes should be monitored, including HCO_3 and Si as these elements can be used to investigate chemical weathering as they provide an indication of the weathering sequence and are not influenced by human activities (Bluth and Kump, 1994); net alkalinity and silica can be used to determine the rate and intensity of chemical weathering (Drever and Zobrist, 1992; Palmer and Edmond, 1992).

* Determining the Sr isotope ratio can give an indication of the amount of Sr from silicates with a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio typically indicating silicate weathering (Wadleigh *et al.*, 1985; Krishnaswami *et al.*, 1992; Blum *et al.*, 1998; Jacobson *et al.*, 2002).

Many of the element concentrations occurring in the mine drainage waters and water courses exceed the limits set by the EU EQS and therefore to comply with the 'good chemical and ecological status' require by the EU's WFD, remediation of these waters is required. Variations in element concentration occur on a seasonal and diurnal timescale and understanding this variability is vital for planning a remediation strategy for point source mine drainages. The options available for the remediation of mine waters are explored in the next chapter.

CHAPTER 5:

Bioremediation

Research addressing metal mine drainage has generally focussed on acidic and/or Fe-rich waters, for example Younger (1995), Nordstrom *et al.* (2000) and papers within Jambor *et al.* (2003). The mine waters within this study are slightly acidic to circum-neutral and non-ferrous (see Chapter 4) and can not be remediated using conventional acid mine drainage techniques such as Fe-oxidation (Nengovhela *et al.*, 2004); forced Fe precipitation (Hedin *et al.*, 1994; Cravotta *et al.*, 1999) or by passing the mine drainage waters through wetlands (Wieder, 1994; Wiseman and Edwards, 2004; Woulds and Ngwenya, 2004). There are, however, a number of remediation techniques that are commonly used for treating industrial wastewaters which may be applicable to the treatment of neutral mine drainage.

5.1 Conventional techniques

The main conventional treatment techniques which are used to treat waste waters are described below, though the application of these technologies is sometimes limited because of technical and economic challenges.

* *Chemical oxidation-reduction* where pollutants are converted into less hazardous forms. Oxidation may occur through the addition of potassium permanganate, hydrogen peroxide, hypochlorite or chlorine gas; and reduction may be caused by the addition of Na, SO₂, FeSO₄ or sulphite salts (Mulligan *et al.*, 2001).

* *Chemical precipitation* is one of the most widely used methods for removing metals from chemically complex solutions (Lehmann *et al.*, 1999; Lee and Davis, 2001) where metal recovery is not a consideration (Dean *et al.*, 1972; Gupta *et al.*, 2001). Metals are usually forced to precipitate by the addition of Ca-, Na- or K- hydroxide (Aderhold *et al.*, 1996; de França *et al.*, 2002).

* *Solvent extraction* is used to recover a metal from wastewater by the addition of an organic reagent. The reagent converts the metal into a form which is soluble in an appropriate organic solvent. An immiscible solution is mixed with the wastewater and

then the two phases are separated. The metal-containing phase can then be acid washed to remove the metal, which can then be recovered (Dean *et al.*, 1972).

* *Electrochemical methods* involving the removal of metal from a solution for recycling or for resale. Electrodeposition may recover the metals using insoluble anodes. Acidic solutions produced from cleaning Cu with H₂SO₄ may be remediated by electrowinning; the Cu is deposited onto Cu cathode and the free H₂SO₄ is regenerated. The electrolyte from the electrodeposition cells, after minor adjustments can be recycled to the cleaning operation. The remediation can be profitable with the sale of the recovered metal and the reuse of the electrolyte (Dean *et al.*, 1972).

* *Ion exchange* where ions are exchanged between a solid substrate (usually a resin) and a solution. Numerous ion exchange resins are available and some are designed to remove specific metals (Aderhold *et al.*, 1996). There are numerous advantages to using ion exchange, including the effective removal of low metal concentrations (Huang and Wu 1975 cited in Fiol *et al.*, 2003), the production of a pure effluent; the resins can be regenerated and may be reused hundreds of times and metal recovery may be possible (Volesky, 1990; Aderhold *et al.*, 1996), though some ion exchange resins may not be selective enough for this to occur (Valdman and Leite, 2000).

* *Membrane processes* including osmosis, reverse osmosis, dialysis or electrodialysis are only found occasionally in specialised applications (Aderhold *et al.*, 1996) such as the desalting brackish waters, seawater desalinisation, food production and waste water treatment (Patterson and Minear, 1973; Kuyucak, 1990). Membrane processes use a pressure differential across semi-permeable membranes which allow varying molecular sizes through the membrane pores.

* *Evaporation* has been primarily used for the recovery of a product (Patterson and Minear, 1973), though it is of limited use because of high capital and operational costs, energy intensiveness and sludge production (Volesky, 1990; Aderhold *et al.*, 1996; Kuyucak, 1990).

* *Cementation* allowing a metal-rich solution to contact with an appropriate scrap metal or metal powder, for example, contacting a Cu-rich solution with scrap Fe to allow the cementation of Cu; if the Fe dissolves in an acidic solution, the Fe is precipitated out of solution (with any residual Cu) by the addition of lime (Dean *et al.*, 1972).

There are, however, many disadvantages to using the above techniques, which frequently make them unsuitable for use in mine water treatment schemes. They have high capital

and operational costs, especially ion exchange resins and evaporation techniques (Volesky, 1990; Kuyucak, 1990; Fiol *et al.*, 2003) and electrochemical methods are dependent on energy prices (Patterson and Minear, 1973; Aderhold *et al.*, 1996). Chemical oxidation/reduction and precipitation techniques require additional chemicals and this further increases the cost, especially where the chemicals can not be recovered and re-used (Volesky, 1990; Aderhold *et al.*, 1996; Valdman and Leite, 2000). Many are only effective for high concentrations of metals, for example, solvent extraction is only economical when concentration are >1 g/L (Kratochvil *et al.*, 1997; Valdman and Leite, 2000); when metal concentrations are <100 mg/L these processes are less effective, therefore increasing the cost (de Carvalho *et al.*, 1994; Kapoor and Viraghavan, 1995; Williams and Edyvean, 1997b) especially where element concentrations are required to meet EQS or drinking water standards (Namasivayam and Yamuna, 1995). Chemical precipitation and evaporation produce large quantities of low-volume, metal-rich sludge which requires disposal (Volesky, 1990; Kratochvil *et al.*, 1997; Eccles, 1999). The problems caused by sludge include: increasing costs of disposal, instability of the sludge; the potential addition of chemicals to produce a more dense sludge and the long term environmental consequences (Lehmann *et al.*, 1999; Valdman and Leite, 2000). Waste waters are often highly varied (containing organics, complexing agents and alkaline earth metals) and the presence of these substances can hinder the remediation process (Patterson and Minear, 1973; Aderhold *et al.*, 1996); ion exchange resins are susceptible to chemical oxidation, fouling by organics, precipitates and can be affected by the presence of Ca and Mg ions (Kuyucak, 1990) and particles in solution (Volesky, 1990); membrane processes can become unstable in alkaline and acidic conditions and may be fouled by particles, organic and inorganic species (Volesky, 1990; Kapoor and Viraraghavan, 1995; Kuyucak, 1990).

There is therefore a necessity to develop a new remediation technology which has low capital and operating costs; does not produce any sludge; is effective at treating waters with metal concentrations <100 mg/L and is not compromised by additional substances within the water. The new technology may either replace the above technologies or act as a 'polisher' operating at the end of the above methods to further improve the water quality.

5.2 Adsorption

An alternative remediation method for low metal concentration waste waters is via sorption-based processes (Park *et al.*, 2004a). Adsorption is the accumulation of ions (gaseous or aqueous) onto the surface of a solid material (called an adsorbent). Absorption, however, is the accumulation of ions within the mass of the solid as opposed to on its surface (Alexander, 1999; Nigro *et al.*, 2002). As mentioned above, low concentrations of metals (<100 mg/L) are very difficult to remove from wastewaters and adsorption is one of the few alternative remediation techniques which can be used in this situation (Huang and Huang, 1996); it can also be used where metals can not be removed using conventional techniques (Mohan and Singh, 2002). Adsorption is a well established and very effective technique for treating both domestic and industrial waste waters (Gupta *et al.*, 2001; Aksu *et al.*, 2002a). The adsorption process allows flexible use of equipment and it is a relatively simple method for removing impurities from aqueous or gaseous media (Aderhold *et al.*, 1996).

Adsorbents have a porous surface structure and therefore a high surface area (Aderhold *et al.*, 1996); and include fly ash (Panday *et al.*, 1985), ion exchange resins, zeolite (Suh and Kim, 2000), magnesite, titanium dioxide, hydrotalcite, goethite and ferric hydroxide (Lehmann *et al.*, 1999). One of the most widely used adsorbents is activated carbon (Kuyucak, 1990; Lehmann *et al.*, 1999; Suh and Kim, 2000; Mohan and Singh, 2002) which is effective at removing low concentrations of metals from wastewaters (Patterson and Minear, 1973) as well as trace organics such as colour, toxic or mutagenic compounds (Suzuki, 1997). Once the adsorbent becomes saturated, the ions can be removed and the activated carbon regenerated so that it can be used again which increases its cost effectiveness (Kuyucak, 1990). Regeneration (chemical or thermal) is expensive, impractical on a large scale (Aksu *et al.*, 2002a) and causes a reduction in the uptake capacity and a loss in weight, which has implications for the cost of the process (Kuyucak, 1990). The major disadvantage of these adsorbents is that they are expensive (Won *et al.*, 2004; Kapoor and Viraraghavan, 1995; Gupta *et al.*, 2001) therefore limiting their use in developing countries (Panaday *et al.*, 1985) and on a large-scale for waste water remediation (Lee and Davis, 2001); therefore a low-cost alternative to activated carbon is required (Gupta *et al.*, 2001). Of all the adsorbent materials examined, biological material

is thought to be the cheapest and most environmentally friendly option, with biomass being abundant and available (Park *et al.*, 2004a).

5.3 Biosorption

Biosorption is a specific example of adsorption which has gained increasing importance since the 1980s (Bakkaloglu *et al.*, 1998) and has since gained increasing attention (Aderhold *et al.*, 1996). Biosorption is the general term used to describe the removal of metals, and related elements or compounds from solution by biological materials (Gadd, 1990; 1993a); such materials include both plant biomass and animal derived materials (Wilde and Benemann, 1993; Stirk and van Staden, 2002; Fiol *et al.*, 2003). Biosorption is the passive sorption and complexation of metals by non-viable biomass (i.e. dead biomass); whereas bioaccumulation is the accumulation of metals by viable biomass (i.e. living biomass) and includes biosorptive mechanisms, together with metabolism dependent intracellular accumulation and bio-precipitation mechanisms (Eccles, 1995; Kapoor and Viraraghavan, 1995). It has long been known that biological materials can accumulate metal ions, often to many times the concentration in the surrounding environment. This has led to the increase in using biotechnological methods for metal removal and recovery from a number of metal-bearing wastewaters (Wilson and Edyvean, 1993a; Schiewer and Volesky, 1995; Volesky and Holan, 1995).

Biosorption offers many advantages over conventional treatment techniques making it competitive. The main advantage is that it has low operating costs (Marques *et al.*, 2000; de Franca *et al.*, 2002) and low material costs, using either naturally abundant biomasses or waste products from industry (Schiewer and Volesky, 1996; Kratochvil and Volesky, 2000). Biosorption is a rapid method of removing metal ions from waste waters, especially when concentrations are <100 mg/L (when conventional techniques are inefficient and costly) and EQS and drinking water standards may be achieved (de Carvalho *et al.*, 1994; Schiewer and Volesky, 1995; 1996; Davis *et al.*, 2003); only ion exchange can compete regarding residual metal concentration (Wilde and Benemann, 1993). Biosorption by non-viable biomass can also have the ability to adjust easily to changes in the physico-chemical characteristics of the waste water. Biosorption can tolerate changes in solution pH (can occur over pH range between 3 and 9), temperature (between 4 and 40 °C) and metal

concentrations (Kuyucak, 1990; Wilde and Benemann, 1993). Other advantages of biosorption, compared to other remediation techniques, include the minimal production of sludge (Kratochvil and Volesky, 1998a; Choi and Yun, 2004) and the biosorption process tends not to be affected by the presence of Ca, Mg, other metals, suspended solids and organics in solution when compared to ion exchange and reverse osmosis (Wilde and Benemann, 1993). The regeneration of the biosorbent and possible metal recovery from the eluant (the solution used to desorb the metals) is possible (Cruz *et al.*, 2004).

5.4 Biosorbents

Many different types of biological and biologically derived materials have been examined to determine their suitability as biosorbents (Edyvean *et al.*, 1997; Hashim and Chu, 2004). Amongst the biomasses studied are bacteria or microbes (Muraleedharan *et al.*, 1991; Alexander, 1999; Goyal *et al.*, 2003), fungi (Tobin *et al.*, 1994; Kapoor and Viraraghavan, 1995; Huang and Huang, 1996; Gadd, 1993b; 2001), yeasts (Simmons *et al.*, 1995; Bustard and McHale, 1998; Marques *et al.*, 2000) and microalgae (Wilde and Benemann, 1993; Veglio and Beolchini, 1997). One of the most promising biomass types is algae (Kuyucak, 1990; Figueira *et al.*, 2000) and this has been chosen for further study within this thesis.

The ideal biosorbent should fulfil the following criteria after Muraleedharan *et al.* (1991); Stirk and van Staden (2000) and Vieira and Volesky (2000). The biosorbent should be low cost, readily available and re-useable; have a rapid and efficient uptake; it should have a particle size and mechanical strength suitable for use under continuous flow conditions; the separation of the biosorbent from solution should be rapid, efficient and cheap; the biomass should show a high selectivity; regeneration should be metal-selective and economically feasible; and the biosorbent should be in a physical state that can be used.

5.4.1 Viable or non-viable?

Viable biomass can accumulate metals by both passive and active processes (Ramelow *et al.*, 1992) and therefore may exhibit a wider range of accumulation mechanisms than non-viable materials. Accumulation mechanisms include transport, synthesis of intracellular and extracellular metal binding proteins, extracellular precipitation and complex formation as a result of metabolite excretion (Gadd, 1990; Banks, 1997). There are, however, many

practical limitations to using viable biomass including: the need to maintain living organisms (Yun *et al.*, 2001) (expensive and difficult) because they require an energy source in the form of an organic substrate (Muraleedharan *et al.*, 1991), a nutrient supply (Wilson and Edyvean, 1993a; Aderhold *et al.*, 1996; Park *et al.*, 2005) and a habitable environment; i.e. stable pH and temperature and low metal concentrations (Muraleedharan *et al.*, 1991; Cruz *et al.*, 2004; Park *et al.*, 2004b; 2005). The amount of metal uptake by the viable biomass is affected by the age and physiological state (Volesky, 1990) and once saturation occurred the biomass may not be easily separated from the wastewater (Park *et al.*, 2004b; 2005) therefore requiring the use of flocculants (Bakkaloglu *et al.*, 1998; Matis *et al.*, 2003). After separation, the regeneration process requires the use of either alkali or acid solutions which would possibly kill the biomass (Muraleedharan *et al.*, 1991). The major advantage of using non-viable biomass is that it may accumulate metals to a similar or greater extent than viable biomass because the cell changes that occur positively affect biosorption (Kuyucak and Volesky, 1988a; Nourbaksh *et al.*, 1994); large quantities are readily and economically available (Cruz *et al.*, 2004); it can be stored for long periods by drying or preservation in formaldehyde and the use of non-viable microorganisms represents a reduced health risk if utilising potentially pathogenic strains (Brady *et al.*, 1994).

5.4.2 Alternative waste biomass

Waste biomass is an obvious source of biosorbents as they are produced in large quantities (Stirk and van Staden, 2000), are low cost (Williams *et al.*, 1998) and with the regeneration and recycling of the biomass offer a competitive alternative to conventional remediation techniques (Bakkaloglu *et al.*, 1998). They also help to solve the processor's problem of waste disposal. The use of waste biomass means that the material does not have to be collected and prepared to a state where it can be used (although some minor pre-treatment may be required), which reduces the cost, time and effort required. For example, the use of genetically modified and specifically grown biomass (for example, fungi) which requires cultivation in a growth medium (Kuyucak and Volesky, 1988b; Park *et al.*, 2005) before it can be killed and used as a biosorbent. The bulk production costs of specifically cultured algae and fungi have been determined to be between £2000 and £10000 per tonne (Wang and Chen, 2009).

Biomass wastes which have been studied include ricebran (Verma and Rehal, 1994); seafood processing waste sludge (Lee and Davis, 2001); sewage sludge and paper mill waste (Lister and Line, 2001); waste biogas slurry (Namasivayam and Yamuna, 2005); sewage sludge (Gould and Genetelli, 1978a; 1978b; Artola and Rigola, 1992; Aksu *et al.*, 2002a; 2002b); olive mill residues (Pagnanelli *et al.*, 2002a); maple sawdust (Yu *et al.*, 2003); and biomass derived from several strains of lichen, sphagnum (peat) moss and water hyacinth root (Yao and Ramelow, 1997).

A biosorbent has the features of an ion exchange resin or activated carbon (Veglio and Beolchini, 1997; Chang and Hong, 1994 cited in Atkinson *et al.*, 1998). Biosorption is a rapid physico-chemical process and the term biosorption does not take into account the mechanistic details of the metal removal (Gadd, 1990).

5.5 Biosorption mechanisms

The biosorption of metals from waste waters is based on a number of different mechanisms that differ quantitatively and qualitatively depending on the type of biosorbent used, the origin of the biosorbent and its processing (Volesky and Holan, 1995). The mechanisms include chemisorption by ion exchange, complexation, coordination, chelation and physical adsorption and micro-precipitation; oxidation/reduction reactions may also occur (Kuyucak and Volesky, 1988b; Volesky, 2003). Any one or a combination of the mechanisms can occur (Vieira and Volesky, 2000). Although numerous types of materials have the ability to remove metals, the specific interactions between the metal ion and the biosorbent are difficult to determine, understand and describe (Veglio and Beolchini, 1997; Ramelow *et al.*, 1992). For example, the inorganic deposition and precipitation can not be estimated (Kuyucak and Volesky, 1989c), the biosorption mechanisms are not readily predictable or constant (Wilson and Edyvean, 1993a) and metal ions seem to be removed by different mechanisms in different biomasses (Goyal *et al.*, 2003).

Ion exchange

Metal uptake by biomass is not a simple physical adsorption process (Yin *et al.*, 2001). Biosorption is an ion exchange process where the metal ion in solution is exchanged for a counter ion (either an H⁺ ion or a previously sorbed metal ion) attached to the surface of

the biosorbent (Eccles, 1999; Romero-Gonzalez *et al.*, 2001). Ion exchange has been identified as the key mechanism for metal removal (Kuyucak and Volesky, 1989a; Figueria *et al.*, 2000; Cossich *et al.*, 2002).

A linear relationship was noted between the exchange of Ca ions with Co onto *Ascophyllum nodosum* (Kuyucak and Volesky, 1989a) with Cd on dealginated seaweed (Romero-Gonzalez *et al.*, 2000) and with Ni on *Ecklonia maxima*, alginate fibres and dealginated seaweed (Williams and Edyvean, 1997a). Both *Sargassum* and *Gelidium* species released low concentrations of total alkaline earth ions, but had a high uptake capacity of Cd suggesting that there is more than one biosorption mechanism operating in the two biomasses (da Costa and de França, 1996).

Complexation

Complexation is the formation of a species by the association of two or more species, when one of the species is a metal ion, a metal complex is formed (Volesky, 2003). The negative charge of the functional groups on the algal surface results in electrostatic interactions and the co-ordination between the metal ions and the adsorbent surface (Malik *et al.*, 2002). Yun and Volesky (2003) determined that the binding mechanism for the carboxyl group on the surface of *Sargassum polycystum* was ion exchange, whereas the phosphonate group was most likely to bind metal ions by a complexation reaction. The binding of Cu^{2+} , U^{6+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Cr^{6+} and Cd^{2+} is thought to involve the complexation of the metal ion with ligands on or in the cell wall (Greene *et al.*, 1986; Darnall *et al.*, 1986 cited in Kuyucak and Volesky, 1989c). Crist *et al.* (1994) noted the importance of complexation with carboxyl groups in *Vaucheria* freshwater algae. Carboxyl groups have the ability to complex metals (especially transition metals and Al); the complexation is strong when two adjacent functional groups on a single molecule co-ordinated with a cation and forms a chelate (Drever, 1997). Metal chelates are metal complexes where an organic compound is bound to a metal ion by at least two available sites (Volesky, 2003). Chelation by carboxyl and phenolic functional groups is the major mode of metal complexation (Stumm and Morgan, 1996).

Co-ordination

The central metal ion of a complex is bound to its neighbours by covalent bonds resulting from accepting an electron pair from each non-metal atom (Volesky, 2003).

Physical adsorption

Physical adsorption is associated with the weak forces of attraction such as Van der Waal's forces (Drever, 1997; Romero-Gonzalez *et al.* 2001; Davis *et al.*, 2003). Adsorption occurs when the metal ions are held by forces from an adjacent surface (the biosorbent) (Coulson and Richardson, 1991), for example, by positively charged ions being held by the negative charge of the biomass functional groups (Kuyucak and Volesky, 1988a). Additional chemical forces may also adsorb ions to the biomass surface and involve the sharing or exchange of an electron, which is restricted to one layer, though additional layers of ions may be physically adsorbed onto the surface; the number of layers is restricted by the size of the pores (Coulson and Richardson, 1991). Electrostatic interactions have been proposed for the adsorption of Co to biosorbents (Kuyucak and Volesky, 1988b) and have been demonstrated to be responsible for Cd adsorption by marine algae (Holan *et al.*, 1993) and anionic Au species by *Sargassum natans* (Kuyucak and Volesky, 1988a). These forces are only weak and can easily be reversed (Coulson and Richardson, 1991).

Micro-precipitation

The removal of metals from solution may also involve their precipitation onto the surface of the biomass by a chemical reaction between the metal ion and the surface of the biosorbent (Veglio and Beolchini, 1997; Alexander, 1999). The precipitation of a metal may occur when the solubility of the metal ion reaches its limit and may take place in or on the biosorbent (not necessarily in the bulk of the solution) by a change in pH or by materials from the biosorbent (Volesky, 2003). The precipitation may be dependent or independent of metabolic activity (Veglio and Beolchini, 1997). Metabolically produced SO_4^{2-} , S^{2-} , oxalic acid, HPO_4^{2-} may form an insoluble salt or complex such as sulphides, carbonates, oxides, oxalates or phosphonates (Beveridge, 1990; Remacle, 1990 both cited in Volesky, 2003) and H_2S producing micro-organisms may precipitate insoluble metal sulphides in and around the cell surface (Gadd, 1990). Holan *et al.* (1993 cited in Veglio and Beolchini, 1997) proposed that micro-precipitation could greatly contribute to Cd biosorption by marine algae.

Redox reactions

Redox reactions can also occur resulting in the immobilisation of the metal (Volesky, 2003), for example Cr^{6+} to Cr^{3+} (Gadd, 2004); at pH values <2 , the major removal mechanism for Cr^{6+} was a redox reaction by non-viable fungal biomass (Park *et al.*, 2005) and *Ecklonia maxima* (Park *et al.*, 2004a; 2004b).

The biosorption of metals to a viable biosorbent is a two-stage process. The first is a rapid (passive) uptake which is thought to be physical adsorption and ion exchange occurring at the cell surface (Nourbakhsh *et al.*, 1994; Fiol *et al.*, 2003; Goyal *et al.*, 2003). The second stage is a slower process (active) where additional metals are bound and metabolically controlled diffusion into the cell occurs (Xue *et al.*, 1988; Donmez *et al.*, 1999; Goyal *et al.*, 2003). The slower stage mechanisms could also be the same as occurs on the cell surface (Crist *et al.*, 1990). The biomass used within this thesis is non-viable and therefore only the first process will occur.

5.6 Factors affecting biosorption

There are many factors that affect biosorption including temperature, pH, the contact time between the biomass and the solution, the weight of biomass contacted with the solution, the combination of metals in solution, whether the biomass has been subjected to any pre-treatment and whether or not the biomass has been immobilised.

5.6.1 Temperature

The temperature of the adsorption system can significantly affect the binding of the metal ion to the surface of the biosorbent (Edyvean *et al.*, 1997). Most authors have found that temperature fluctuations between 5 °C and 35 °C do not affect the uptake capacity of the biomass (Volesky and Holan, 1995; Edyvean *et al.*, 1997; Tobin, 2001). However, increases in uptake capacity with an increase in temperature have been noted in *Sargassum* species seaweeds with an increase in adsorption from 20 °C to 40 °C (Cossich *et al.*, 2002) and from 25 °C to 55 °C (Cruz *et al.*, 2004). The binding of Cr^{6+} onto *Ecklonia* showed a significant increase when the temperature was increased from 5 °C to 45 °C (Park *et al.*, 2004a). At temperatures <10 °C, the uptake capacity and rate of Cr^{3+} adsorption to *Halimeda opuntia* was reduced (Kuyucak and Volesky, 1988c); >60 °C the uptake capacity

of the biomass began to decrease and the biomass surface began to change; and >80 °C the uptake capacity was considerably reduced and biomass began to lose its granular form and coagulate making the solid-liquid separation slower and more difficult (Kuyucak and Volesky, 1989a).

Barrow (1992 cited in Nimick *et al.*, 2003) determined that the adsorption of cations, for example, Mn, Zn and Cd onto hydrous metal oxides and organic substrates such as biofilms is an endothermic process and therefore favours an increase in temperature and conversely, the adsorption of anions is an exothermic process and favours a decrease in temperature. Alhakawati and Banks (2004) also noted an increase in Cu uptake with temperature to immobilised *Ascophyllum nodosum* and suggested that this could indicate that the adsorption process was partially chemical in nature. Higher temperatures will increase the kinetic energy of the metal ions facilitating the binding of the metal to the biosorbent surface (Goyal *et al.*, 2003).

5.6.2 pH

The biosorption of metal ions is highly pH dependent (Yao and Ramelow, 1997) and pH is one of the most important factors controlling biosorption (Wilde and Benemann, 1993). Generally, the optimum pH for biosorption is between 3 and 7 (Edyvean *et al.*, 1997; Tobin, 2001; Cruz *et al.*, 2004) though increasing pH may cause an increase in cation adsorption and a decrease in anion adsorption (Nimick *et al.*, 2003). Yun and Volesky (2003) and Choi and Yun (2004) noted that uptake increased with an increase in pH, for example, Kuyucak and Volesky (1989a) found that Co uptake was lower at pH 2 than at pH 4 and Yin *et al.*, (2001) found uptake was negligible when the pH was less than 1.5. Acidic conditions can cause an increase in uptake capacity of some metals that form anionic complexes (Kuyucak and Volesky, 1989a), for example, Au uptake onto *Sargassum natans* (Kuyucak and Volesky, 1989a) and *Gracilaria conferta* (Ramelow *et al.*, 1992). A decrease in pH also facilitates the removal of dyes (for example, Reactive Orange 16) with negligible uptake occurring under neutral pH values (Won *et al.*, 2004). The carboxyl and sulphate functional groups on the biomass surface are acidic; at low pH the groups are protonated and are therefore less available for the binding of cationic metal ions; at increased pH values the groups become deprotonated (negatively charged) and more available to metal ion binding (Ramelow *et al.*, 1992; Cruz *et al.*, 2004). At low pH

values the protons compete with metal ions for the binding sites (Hashim and Chu, 2004), this competition has been modelled by Schiewer and Volesky (1995; 1996; 1997a; 1997b). Most researchers conduct biosorption experiments at pH values less than 7 to prevent the precipitation of insoluble metal hydroxides (Kuyucak and Volesky, 1989a; Tobin, 2001; Cruz *et al.*, 2004). If the precipitation of metal hydroxides occurs then the interpretation of the experimental results can be very difficult (Alkahawati and Banks, 2004); although the removal of metals will be increased, it can not be attributed to biosorption (Tobin, 2001) therefore making true biosorption studies impossible (Cruz *et al.*, 2004). Where a system occurs where the removal of metals from wastewater is required then in addition to biosorption, the precipitation of metals is advantageous (additional chemicals are not required to maintain the pH of the system) especially when considering circum-neutral waters. The precipitated metals would then be removed when filtering through the biosorbent.

5.6.3 Contact time

The length of time for which the solution is in contact with the biosorbent is critical to the design and economics of an adsorption system (Edyvean *et al.*, 1997). If the uptake is fast, then the solution only requires a short contact time between solution and the biosorbent, which has economic advantages (Stirk and van Staden, 2000) allowing a shallower biosorbent contact bed to be used in column applications (Kuyucak and Volesky, 1988c) and more waste water may be treated. The contact time required for the biosorption process to reach an equilibrium uptake can vary between a few minutes and several days. Williams and Edyvean (1997a) found that alginate fibres removed >90 % Ni within two minutes and Romero-Gonzalez *et al.* (2001) found that >91 % of Cd was removed by DS within the first five minutes. Most authors, however, have found that >90 % of metal ion removal takes between 10 minutes and a few hours; this is compared to activated carbons which can take between several hours to several days to reach equilibrium (Chen and Wang, 2001). Kuyucak and Volesky (1988a) studied Co uptake by *Ascophyllum nodosum* and found that the 100 mg/L Co was removed within 10 minutes and 600 mg/L Co within 20 minutes (Kuyucak and Volesky, 1989a), though uptake of 100 mg/L Au by *Sargassum natans* took around two hours to reach equilibrium. The pH of the biosorption process can also alter the time taken to reach equilibrium, for example, the removal of 100 mg/L Cr⁶⁺ by 5 g/L *Ecklonia* species occurred in 12 hours at pH 1, around 120 hours at pH 3 and

around 500 hours at pH 5 (Park *et al.*, 2004a). The time taken for equilibrium uptake to occur depends upon the type of biomass (number and type of functional group present on the surface), the size and form of the biomass, the physiological state of the biomass (viable or non-viable; free or immobilised) and the metal ion involved (Cossich *et al.*, 2002).

The uptake of metal ions generally follows a pattern of very rapid uptake in the first few minutes followed by a slower uptake until equilibrium is reached (Cossich *et al.*, 2002; Choi and Yun, 2004; Cruz *et al.*, 2004) i.e., a fast then slow process (Yin *et al.*, 2001). Crist *et al.* (1988; 1990) noted that the fast uptake was caused by a surface reaction and the slower uptake to equilibrium was caused by the diffusion of protons into the cell. There are four main rate-limiting steps: 1) the mass transfer of the metal ion from the solution to the boundary film; 2) the mass transfer of the metal ions from the boundary film to surface of the biosorbent; 3) the sorption of the metal ions onto the binding sites (functional groups); and 4) the diffusion of the metal ion into the surface of the biosorbent. The first and second steps are external mass transfer resistance steps which depend on factors such as the homogeneity of the solution and the agitation. The third step is assumed to be very rapid and not limited and the fourth step is an intraparticle diffusion resistance step (Yu *et al.*, 2003).

5.6.4 Weight of biomass

The weight of biomass in contact with the solution influences the amount and specific metal ion uptake. The weight of biomass determines the number of binding sites or surface area available to the metal ions in solution, Yu *et al.* (2003) found an increase in Cr removal with an increase in the weight of maple sawdust (from 1 g to 5 g) contacted with the metal laden solution for 24 hours. Experiments conducted by Williams and Edyvean (1997b) show that when dealginated seaweed was reacted with 50 mL of 1, 5 or 10 mg/L Ni solution for 24 hours, the lowest residual metal concentration was achieved by 0.05 g (weights from 0.05 g to 0.5 g were tested); with increasing biomass weight, the residual metal concentration increased as well. However, when the Ni concentration increased to 100 g/L a weight of 0.05 g gave the highest residual metal concentration in solution, a result of the biomass becoming saturated; and with increasing biomass weight the residual metal concentration within the solution decreased. The decreased adsorption with

increased biomass weight within the 1, 5 and 10 mg/L Ni solution may be caused by crowding effects. These effects may obscure or make temporarily unavailable the active biomass sites therefore when the cells attach to each other by electrostatic interactions the available surface area in contact with the solution is reduced (Kapoor and Viraraghavan, 1995; Williams and Edyvean, 1997b).

5.6.5 Metals in solution

Wastewaters are complex, containing a mixture of elements. The uptake capacity of the biomass may be affected by the presence of additional ions and their concentration.

Adsorption of Zn or Cu onto Kelpack waste (Nigro *et al.*, 2002) and Zn, Cu and Ni adsorption onto *Ascophyllum nodosum* (Bakkaloglu *et al.*, 1998) was little affected by the presence of anions such as Cl^- , NO_3^- , SO_4^{2-} , acetate or cations such as Na, K, Mg; though the presence of Ca significantly reduced the uptake of Cd onto *Sargassum bacularia* (Hashim and Chu, 2004). Kuyucak and Volesky (1989a) found that the presence of most additional ions in solutions (Ca, Cu, Ni, Zn, Cr, Pb, UO_2^{2+} , NO_3^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-}) had a negative effect on the uptake capacity of Co with NO_3^- having the greatest negative effect (reducing Co uptake by ~35 %); K, however, had a positive effect. The additional ions suppress biosorption as a result of an increased electrostatic charge or by competition with the sorption of the metal of interest (Volesky, 2003).

5.6.6 Pre-treatment

Biosorbents have been subjected to a range of chemical and physical pre-treatments in an attempt to increase their biosorption capacity or physical performance (Tobin *et al.*, 1994; Edyvean *et al.*, 1997). Pre-treatment of the biomass often increases the uptake when compared to untreated biomass (Zhao *et al.*, 1994). Various biosorbents have been subjected to treatment with $\text{Ca}(\text{NO}_3)_2$, Na_2SO_4 , HCl, HNO_3 , NaOH, EDTA, sodium lauryl sulphate detergent, hot water and acetone (Ramelow *et al.*, 1992; Zhao *et al.*, 1994; Yao and Ramelow, 1997; Bakkaloglu *et al.*, 1998) and all treatments showed an increased in uptake capacity when compared to the untreated biomass.

Sodium hydroxide was the most effective treatment (Zhao *et al.*, 1994; Yao and Ramelow, 1997) and Yin *et al.* (2001) determined that $\text{Ca}(\text{NO}_3)_2$ treatment of *Laminaria japonica*

increased uptake capacity by ~30 %. Ramelow *et al.* (1992) found that HCl and HNO₃ treatment slightly increased uptake capacity of *Gracilaria conferta* and *Sargassum* species, but greatly reduced the uptake capacity of *Ecklonia bicyclis*. Kuyucak and Volesky (1989c) pre-treated *Ascophyllum nodosum* with various solutions and found that acid treatments caused a reduction in the weight of the biomass and Co uptake capacity of the biomass occurred with a release of ionic species (especially Ca) into solution, the destruction of alginate chains and simultaneous hydrolysis of the polysaccharides. Alkali treatment caused a 68 % loss in Co uptake capacity and only minor changes are seen when using KSCN and a methanol-chloroform solution (Kuyucak and Volesky, 1989c); acetone and hot water were the least effective (Zhao *et al.*, 1994; Yao and Ramelow, 1997). The contact time between the pre-treatment solution (15 to 60 minutes) and the biomass and the temperature (25 to 60 °C) at which the process occurs did not have any effect on the pre-treatment process (Zhao *et al.*, 1994). Pre-treating the biosorbent is used as a method of attaching various ions (for example, protons with treatment by HCl or HNO₃, or Ca or Na by treatment with Ca(NO₃)₂ or NaOH) to the surface of the biosorbent, which are then released (exchanged) during biosorption of metal ions (Figueira *et al.*, 2000; Volesky, 2003).

The pre-treatment process has not only been used for the increase in biosorption uptake. Exposure of the biomass to a solution containing Ca may convert the seaweed's alginate to an insoluble form therefore minimising weight loss especially during regeneration. Bakkaloglu *et al.* (1998) used formaldehyde to prevent the growth of other microorganisms; pre-treatment may exert a cleansing effect removing extracellular material, soluble polysaccharides and water-insoluble substances therefore exposing a greater surface area which is available for biosorption (Zhao *et al.*, 1994; Edyvean *et al.*, 1997).

5.6.7 Immobilisation

Alhakawati and Banks (2004) noted that to use biosorbents as a commercial product it is generally accepted that the biosorbent must be immobilised. For example, the US Bureau of Mines immobilised biomass in porous polysulfone beads (BIO-FIX beads) and this has been field tested at four sites (Jeffers *et al.*, 1993). The disadvantage of using free biomass (especially microbial biomass) is that they have a small particle size, low mechanical strength and the separation of liquid and biomass is difficult, providing a limited choice of

treatment plants that can be successfully used. Immobilisation of the biomass provides several advantages: the production of the required particle size, increased mechanical strength, a higher biomass loading with minimal clogging, viable cells may have an increased metal tolerance, the immobilised biomass is easier to handle and is stable and allows the successive use and regeneration of the biomass without loss of performance similar to ion exchange resins and activated carbon (Kuyucak, 1990; Gadd, 1990; 2004; Veglio and Beolchini, 1997; Tobin, 2001; Alhakawati and Banks, 2004).

The main methods of immobilising biomass are: a) adsorption on inert supports i.e. micro-organisms are grown as a film on a support surface such as activated carbon, coal, sand or foam particles; b) entrapment on a polymeric matrix such as Ca-alginate, polyacrylamide, polysulfone, polyethylenimine and polyhydroxyethylmethacrylate; c) covalent bonds to vector compounds i.e. a carrier, the most common being silica gel; and d) cross-linking the biomass to form a stable cellular aggregate (Veglio and Beolchini, 1997). In general, the immobilised biomass should have the same particle size (1-3 mm) as a conventional adsorbent (Williams *et al.*, 1996; Volesky, 2003). The biomass can be entrapped using natural or synthetic gels; carrageenan and Ca-alginate are commonly used in live cell systems (Chen and Wang, 2001; Tobin, 2001). Other materials used include polyacrylamide, polyhydroxyethylmethacrylate, polysulfonate (Veglio and Beolchini, 1997), polyethylenimine (Valdman and Leite, 2000), a polyvinyl butyral based polymer (MOWITAL[®] B30H) (Aksu *et al.*, 2002a); polyvinyl alcohol (Hashim *et al.*, 2000) and polyurethane foam (Alhakawati and Banks, 2004). Storey *et al.* (1990 cited in Alhakawati and Banks, 2004) reported that the immobilised material is covalently attached to the polymers during the process of polymerization.

Once immobilised, the biomass may be further cross-linked to introduce more chemical groups (Valdman and Leite, 2000). Cross-linking acts to reinforce the biomass by bridging/binding of the molecules of the biomass (Volesky, 2003). Common cross-linking agents include: formaldehyde (de Carvalho *et al.*, 1994; Schiewer and Volesky, 1996; Chong and Volesky, 1995 cited in Alhakawati and Banks, 2004), formaldehyde-urea mixture, sulfone, glutaraldehyde, glutaric dialdehyde and divinylsulfone (Veglio and Beolchini, 1997 Tobin, 2001; Volesky, 2003).

The disadvantage of using immobilised biomass is that the biosorption process is not as rapid as when using free biomass. The reduced biosorption rate may be caused by mass transfer resistance within the particle (Veglio and Beolchini, 1997; Tobin, 2001; Alhakawati and Banks, 2004). Once the biomass has been immobilised there is a decrease in the surface area, and therefore the number of binding sites, available for the metal ions to sorb to (Schiewer and Volesky, 1995; Volesky, 2003), for example immobilised biomass reached equilibrium uptake in 320 minutes as opposed to 90 minutes for free biomass (Alhakawati and Banks, 2004). Depending on the material used to immobilise the biomass the mechanical properties could be lost, it may easily disintegrate and the chemicals used may damage the biomass or cause the loss of its sorption capabilities (Volesky, 2003). The use of immobilising chemicals may prohibitively increase the cost of the biosorbent (Volesky, 2003) though generally immobilisation does not require much support material (Kuyucak, 1990). For a low cost method of immobilising biomass, Williams *et al.* (1996) sandwiched dealginated seaweed between two layers of linseed fibre (a lower affinity biosorbent) thereby avoiding some of the disadvantages described above.

5.7 Seaweed

The metal content of seaweeds was first determined when edible seaweeds were analysed (McHugh, 2003). Ions from seawater are concentrated both actively and passively by the algae and the concentration in the thallus is taken to reflect the concentration in the surrounding seawater (Lobban and Harrison, 1994); the concentration varies, especially in large brown seaweeds, according to geographic source and sometimes their proximity to industrial wastewaters; therefore seaweeds have often been used as biological monitors of metal pollution (McHugh, 2003). For example, *Ascophyllum nodosum* was used to estimate pollution in the Norwegian Ffjords (Haug *et al.*, 1974) and to monitor marine pollution along the Atlantic coast on the Canada/USA border (Woolston *et al.*, 1982). Volterra and Conti (2000) determined that the *Laminariales* and *Fucales* seaweed species are relevant in biomonitoring studies in the Mediterranean and other regions. The ability of the seaweed to take up metals has been developed using seaweeds to remove metals from wastewaters (da Costa and de França 1996; Edyvean *et al.*, 1997; McHugh, 2003).

Research by numerous authors (Zhao *et al.*, 1994; Edyvean *et al.*, 1997; Figueria *et al.*, 2000; Nigro *et al.*, 2002) shows that selected species of seaweeds possess the ability to adsorb both a large range and concentration of metals from solution. Seaweeds are ubiquitous and abundant within the world's oceans, and are therefore readily available and inexpensive for use as biosorbents (Bailey *et al.*, 1999; Schiewer, 1999; Yun and Volesky, 2003) and in many cases show a greater adsorption capacity than that of the inorganic adsorbents mentioned above.

Selected species of marine algae show a greater adsorption capacity than commercial ion exchange resins (Lee *et al.*, 2000) and activated carbon (da Costa *et al.*, 1996). Kuyucak and Volesky (1988a) showed that *Ascophyllum nodosum* exhibited better uptake capacity than cation (Duolite C20) and anion (IRA 400) exchange resins, and activated carbon; and that uptake by the green algae *Halimeda opuntia* was ten times that of activated carbon. Kumar and Kaladharan (2006), however, found the biosorptive capacities of seaweeds, activated carbon and natural zeolites are comparable to those of synthetic ion exchange resins. Matheickal *et al.* (1997 cited in Yu *et al.* 1999) studied various bacteria, fungi, yeast, freshwater and marine algae and found the uptake capacity of brown seaweeds to be much higher than other biomasses, activated carbon and natural zeolites; and that the uptake capacity was comparable to that of ion exchange resins. The biological adsorbents show better uptake capacities than commercial ion exchangers or activated carbon because they comprise of a variety (rather than limited numbers) of weakly acidic and basic functional groups (Eccles, 1999; Yun and Volesky, 2003) that have a high selectivity and capacity for divalent ions even at low concentrations (Lee *et al.*, 2000).

Functional groups

Variations in metal sorption capacity between different seaweed species suggest the presence of different types of binding sites (functional groups) on the cell walls (Ramelow *et al.*, 1992). The functional groups in cell walls of seaweeds and seaweed derived materials are responsible for metal ion sorption and exchange (Romero-Gonzalez *et al.* 2001). These functional groups include carboxyl, imidazole, sulphhydryl, amino, phosphate, sulphate, thioether, phenol, carbonyl amide and hydroxyl groups (Kuyucak and Volesky, 1988b; Williams and Edyvean, 1997a; Marques *et al.*, 2000). The carboxyl and sulphate functional groups are acidic and are protonated at low pH values (Schiewer and Wong, 2000); as pH increases the protons dissociate from the surface of the seaweed

leaving a net negative charge and therefore the seaweed's surface acts as a cation exchanger adsorbing cations from the surrounding environment (Lobban and Harrison, 1994). In addition to these functional binding groups, polysaccharides often have ion exchange properties (Nourbakhsh *et al.*, 1994). The presence of a functional group on the biomass surface does not assure the availability of it as a sorption site (Zouboulis *et al.*, 1999), it depends on the number of sites; the accessibility and availability of the site; and binding strength between metal and the site (Vieira and Volesky, 2000), with different ions displaying affinities for the various functional groups (Stirk and van Staden, 2000).

Carboxyl groups have been determined to be the main binding site in seaweeds (Schiewer and Wong, 2000; de Franca *et al.*, 2002; Park *et al.*, 2004b; Kratochvil and Volesky, 1998a) and sulphate groups are of secondary importance (Schiewer and Wong, 2000). The presence of carboxyl groups in various biosorbents has been determined by:

- 1) Potentiometric titrations (Malik *et al.*, 1999; Figueira *et al.*, 2000; Yun *et al.*, 2001; Romero-Gonzalez *et al.*, 2001; Yun and Volesky, 2003; Park *et al.*, 2004b).
- 2) Esterification of the biomass using acidic methanol and propylene oxide. Malik *et al.* (1999) found that Cu sorption decreased by up to 70 % in non-viable *Ascophyllum nodosum* and by 30 % in both *Ascophyllum nodosum* and *Lessonia flavicans* dealginated seaweed (though after a second 48 hour treatment period up to 70 % of the binding sites were reduced); Romero-Gonzalez *et al.* (2001) found that esterification reduced Cd binding to dealginated seaweed by 17-95 %. Gardea-Torresday *et al.* (1990) esterified five algal species and found that although Cu and Al binding decreased, there was an increase in Au binding suggesting that the carboxyl group had a negative effect on Au binding.
- 3) Fourier Transform Infra Red spectrometry (FT-IR) (Fourest and Volesky, 1996; Kiefer *et al.*, 1997; Romero-Gonzalez *et al.*, 2001).
- 4) ^{113}Cd nuclear magnetic resonance (NMR) was used to determine that carboxylate was the most likely functional group responsible for metal uptake in *Stichococcus bacillaris* (a unialgae culture) (Majidi *et al.*, 1990).
- 5) Drake *et al.* (1996) used Eu^{3+} and UO_2^{2+} luminescence to determine that amine and carboxyl groups were responsible for Cd binding to *Datura innoxia* (*D. innoxia* belongs to the plant family Solanaceae (for example, potatoes and tobacco)).

Seaweeds include unicellular, multicellular, microscopic and macroscopic red (Rhodophyta), green (Chlorophyta) and brown (Phaeophyta) algae (Lobban and Harrison,

1994). Studies of various red, green and brown seaweed species have been conducted by Kuyucak and Volesky (1989c), Jalali *et al.* (2002) and Hashim and Chu (2004) who found that brown seaweeds adsorbed Co, Pb and Cd more effectively than green or red seaweeds, though Lee *et al.* (2000) found that chromate was most effectively adsorbed by red seaweeds. Brown seaweeds have been proven to be highly effective, reliable and predictable in the removal of metal ions (for example, Pb, Cu, Cd and Zn) from solution (Davis *et al.*, 2003). The cell wall plays an important role in the biosorption of the metals (Crist *et al.*, 1988) and Kuyucak and Volesky (1988a; 1989c) have shown by electron microscopy that Co adsorbed by non-viable *Ascophyllum nodosum* is contained within the cell wall.

Algal cell walls

Algal cell walls are made up of multilayer parallel cellulose microfibrils (usually cellulose, but xylans and mannans also occur), proteins and lipids in an amorphous polysaccharide matrix (Chapman, 1970; Lobban and Harrison, 1994; Lodeiro *et al.*, 2005). The matrix polysaccharides include alginate, fuciodan (10-20 % of the alginic acid), agar and carageenan. Fucoidan occurs in the fronds of *Laminaria digitata*, *Ascophyllum nodosum* and *Macrocystis* (Chapman, 1970). Alginate is the major structural polysaccharide of brown algae and constitutes 14-40 % of the seaweed (dry weight) (Chapman, 1970). The alginate is made up of linear block co-polymer of D-mannuronic acid residues (M) and L-guluronic acid residues (G) linked by 1,4 glycosidic bonds (Indergaard and Skjåk-Bræk, 1987); alternating MG segments also occur (Lobban and Harrison, 1994; Kuyucak and Volesky, 1989a). The chemical structure of the alginate varies from species to species and this is reflected in the M/G ratio; for example, *Ascophyllum nodosum*: 1.10-1.85, *Laminaria digitata*: 1.16-1.63, *Macrocystis pyrifera*: 1.02-1.56, *Undaria pinnatifida*: 1.45-2.65 (McHugh, 2003). Those with a higher proportion of G (i.e. a low M/G ratio) have a greater affinity for Ca^{2+} and other divalent metals than those with a higher proportion of M (Lobban and Harrison, 1994; Volterra and Conti, 2000). The guluronic acid residue has a zig-zag structure which can accommodate the divalent metals more easily (Lobban *et al.*, 1985 cited in Figueira *et al.*, 2000).

The chemical composition not only depends on the species of seaweed, but also on the season (the alginate content is at a maximum in *Laminaria digitata* from September to October and at a maximum on *Laminaria hyperborea* in February), habitat, depth, state of

development and on the part of seaweed in question (Percival and McDowell, 1967; Chapman, 1970). In *Laminaria* species the stipes (M/G ratio of 0.3-0.65) have a higher M/G ratio than the fronds (M/G ratio of 1.28-1.35) (McHugh, 2003), and new blades have a higher M/G ratio than old blades (Chapman, 1970; Indergaard and Skjåk-Bræk, 1987).

Although seaweed and alginate show a high capacity for the adsorption of metals, there are disadvantages to using these materials as biosorbents: alginate is very expensive, particularly in an easily useable form (fibrous) and therefore it is not economical to use, except for highly critical occasions (Edyvean *et al.* 1997). Another major concern of using alginate to remove metals from wastewater is that it may not be effective for the removal of Zn, as the alginate polymer is extruded in a Zn solution and actually releases Zn into the effluent (Aderhold *et al.*, 1996; Williams and Edyvean, 1997b). Dried seaweeds and alginate absorb water when in contact with aqueous solution (Chapman, 1970) and may swell to twenty times their initial size and release a gelatinous material (Stirk and van Staden, 2000). This swelling and gel release cause problems in process systems, for example, a pressure drop through a column system and problems with filtration and analysis (Aderhold *et al.*, 1996; Edyvean *et al.*, 1997). Release of seaweed constituents also occurs when the seaweed, for example, *Ecklonia* species is contacted with solutions of low pH (Yun and Volesky, 2003; Park *et al.*, 2004a).

The alginate present within the seaweeds has been determined to be responsible for the majority of metal binding (Fourest and Volesky, 1996; Schiewer and Volesky, 1997a; de Franca *et al.*, 2002; Hashim and Chu, 2004; Lodeiro *et al.*, 2005). Kuyucak and Volesky (1989c) examined the adsorption capacity for Co of Na-, K-alginate and NH_4^+ -alginate and found they adsorbed ~35 % more than untreated *Ascophyllum nodosum*. De Carvalho *et al.* (1994), however, determined that the alginates do not contain the main or only chemical sites responsible for metal biosorption onto *Ascophyllum nodosum*.

A number of authors have determined the adsorption capacity of dealginated seaweed (DS) (the cell wall material remaining after the alginate has been removed) and have found that although the alginate possesses a higher adsorption capacity than the DS, DS is comparable or superior to the native biomass (Williams and Edyvean, 1997b; Aderhold *et al.*, 1996; Edyvean *et al.*, 1997). Waste from the production of Kelpack (seaweed concentrate used as a fertiliser) has also been shown to be comparable or superior to its parent seaweed

(*Ecklonia* species), especially for Cu adsorption. The Kelpack is extracted from the *Ecklonia* by a cell burst process (Stirk and van Staden, 2000; Nigro *et al.*, 2002). The production process of both dealginated seaweed and Kelpack waste opens up the structure of the seaweed and exposes the binding surfaces in the inner surfaces of the cell wall, therefore the ratio of cell wall per unit weight is greater than that of the parent material and this is advantageous to the biosorption process (Edyvean *et al.*, 1997; Stirk and van Staden, 2000).

5.8 Dealginated seaweed

5.8.1 Alginate production process

Before World War II seaweeds were used as fertiliser or as animal fodder by people living by the coast. From the late 1940s the principal use of harvested seaweed was the production of alginate, although it was used to some extent during World War I; the 1950s saw the introduction of liquid fertilisers from seaweed, with seaweed no longer directly used for fertiliser or animal fodder (Kain and Dawes, 1987). In 2003, the total annual use by the global seaweed industry was ~8 million tonnes at an estimated production value of almost \$6 billion (McHugh, 2003). Approximately one million tonnes of wet seaweed are harvested per year to produce 55,000 tonnes of agar, alginate and carageenan (McHugh, 2003) with *Laminaria*, *Ecklonia*, *Durvillea* and *Ascophyllum* species being the richest source of alginate (Chapman, 1970).

Production of alginate

There are limited details on the commercial production of alginate, the species of seaweed used (or number of species) and the seaweed source or species available in the open literature (Percival and McDowell, 1967; Chapman, 1970; Williams and Edyvean, 1997a). The removal of alginate from seaweed is a relatively simple process; since the alginate can be made soluble by treating the seaweed with Na₂CO₃ and the resulting Na-alginate can easily be extracted from the solid residue. The following stages describe the process.

The seaweed may be harvested from the sea either by harvesting by hand, after it has been brought onshore by the tidal current; via a mechanical arm and hook (scobidou) which is lowered into the seaweed forest, rotated to wrap the seaweed around it and then raised into

the boat; by mechanically cutting and collecting the seaweed; or by trawling the seabed and collecting the seaweed, which allows sand and carbonate particles (for example, corals or bryozoa) to be collected as well (McHugh, 1987; 2003). The seaweed is then chopped, which allows the chemicals to easily penetrate the seaweed more thoroughly and quickly (the size reduction is also advantageous for the transportation of the material). Alginic acid is present within seaweed mainly as the Ca-salt, though Na-, K- or Mg- salts may also occur. The Ca- and Mg-salts do not dissolve in water and therefore need to be converted into Na-salts (i.e. Na-alginate) (McHugh, 1987).

The seaweed is treated with alkali (usually Na_2CO_3) and ion exchange occurs between the Ca and the Na which causes the cells to swell and lose their shape (Chapman, 1970). This process is more efficient if the seaweed is first treated with dilute acid, which also removes some of the water soluble salts, mannitol, laminarian, fucoidan and some phenolic compounds (colouring materials). The acid treatment does not remove all of the phenolic compounds, therefore the seaweed may then be treated with formaldehyde and the liquid is then removed. The alginate is then converted into its soluble form by the use of Na_2CO_3 so that it can be separated from the residual seaweed. This process can be used to control the viscosity of the product. The alginate is separated from the seaweed by flocculation. The clarified liquid is removed, although the process may be repeated to gain a higher grade product. The liquid is then filtered. The Na-alginate needs to be recovered in its solid form; evaporation is not practical as the solution is too dilute. The Na-alginate is converted to fibrous Ca-alginate by the addition of CaCl_2 , which can then be easily separated from the solution and washed. The Ca-alginate can be converted to alginic acid by the addition of dilute HCl or H_2SO_4 ; but both the alginic acid and Ca-alginate require converting back into Na-alginate later on in the process. If the seaweed has not been pre-treated with acid and formaldehyde or the colour is not satisfactory, then the alginate is bleached using a Na-hypochlorite solution (McHugh, 1987). The Ca-alginate is then converted into fibrous alginic acid by the addition of dilute acid, for example HCl (Chapman, 1970). Some Ca may be left within the alginate to increase the viscosity. The alginic acid then needs to be dewatered and converted back into Na-alginate using a solid alkali (usually Na_2CO_3) with water or alcohol as a solvent. The Na-alginate is then dewatered and dried (McHugh, 1987). Other extraction processes are described in Chapman (1970) and further process details are given in McHugh (1987). Sodium-alginate is the primary alginate used, though small quantities of alginic acid and the ammonium-,

Ca-, K- and triethanolamine-salts are produced by treating the alginic acid with the appropriate base (McHugh, 1987).

Uses of alginate

The use to which alginic acid is put depends upon which salt the alginic acid is converted to. Alginic acid is important in its own accord as it can absorb 200-300 times its own weight in water. Sodium-, K- and Na-salts all readily dissolve in water and form an extremely thick or viscous solution; divalent ions generally produce gels, the forming ability dependent on the ion used; and the addition of metals, for example Hg, Be, Cu and Co gives a water-insoluble plastic material which can be moulded when damp and sets hard when dry.

The extensive use of alginates is based upon their numerous properties: 1) the formation of viscous solutions at relatively low concentrations; 2) their behaviour as polyelectrolytes in solution; 3) the ability to form gels (the hardness of which is dependent on the proportion of M and G segments in the alginate, a high proportion of G forms harder alginates and the gels are weaker if there is a high proportion of M segments); 4) the formation of films on surfaces; 5) the formation of films and fibres; and 6) their base exchange properties (Percival and McDowell, 1967; McHugh, 1991). The uses of alginates are extensive and include textiles (thickening agents in print pastes); paper products; adhesives; within the paint industry; water-insoluble substances such as tar products, petrol, oil and disinfectants; cosmetics (hairspray, creams, shaving foam, shampoo); car polishes; insecticides; production of waterproof cloth (tents and wagon covers); plastics; rubber. In food production, alginate has a wide range of uses including as a thickener in sauces, syrups, pie fillings, jam; as a smoother in ice cream, artificial creams and many semi-solid products; to stabilise beer foam and suspend solids in fruit drinks. Alginate also has uses in medicine and dentistry including pharmaceutical preparations, lubricating jellies, pills, dental moulds and models, slimming pills and as a water softener (Percival and McDowell, 1967; Chapman, 1970; McHugh, 1987).

The production of agar, alginate and carageenan from around one millions tonnes of wet seaweed per year means that there is a large amount of waste material being produced, which at the moment, has no existing market value and consequently causes a disposal problem for the alginate industry (Aderhold *et al.*, 1996). This waste material is

dealginated seaweed (DS) which comprises of the cell wall material of the seaweed and ~1 % alginic acid (Romero-Gonzalez *et al.*, 2001).

5.8.2 Sources

Two different sources of DS have been investigated in this thesis: 1) supplied by International Speciality Products (ISP) from a seaweed processing plant in Girvan (Scotland); referred to as Girvan; and 2) supplied by Algavi (France) from the Danisco processing company; referred to as Algavi.

Girvan DS is obtained from the treatment of predominantly *Ascophyllum nodosum* (knotted wrack) as well as seaweed imported from around the world, including *Macrocystis pyrifera*, *Lessonia flavicans*, *Durvillea potatorum*, *Laminaria hyperborea* (Edyvean *et al.*, 1997). Danisco harvests mainly *Laminaria* species off the coast of Brittany between May and October. *Laminaria digitata* is the main seaweed used because of its high alginic acid content (the complex polysaccharide on which alginate is based) (www.danisco.com). The Algavi DS used within this thesis is wholly derived from *Laminaria digitata*.

Two different dealginated seaweed sources were used because at the start of the project 50 kg of Girvan DS was obtained and it was anticipated that this supply would be available for the duration of the project. However, when further supplies (~1000 kg) were required the ISP processing plant had changed their processing procedure and no longer separated and dried the material. The waste is now disposed of as wet slurry and pumped into the sea via a long-fall pipe; therefore it was no longer available in large quantities and as a result an alternative supplier had to be found.

5.8.3 Physical and chemical properties of the raw material

Appearance

The two DS are very different in both appearance and behaviour. The Girvan DS is a granular brown material; whilst that from Algavi is a dusty, grey-green powdery material which contained sand and carbonate particles, (see Figure 5.1 a and b). The variations between the two DS may represent either differences in 'parent' seaweeds or the processing technique employed to remove the alginate.

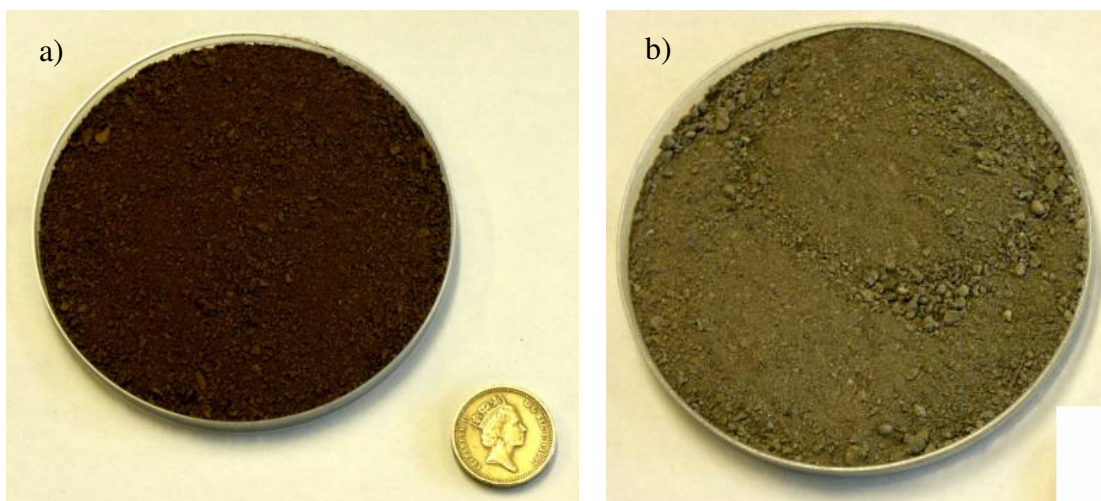


Figure 5.1. Dealginated seaweed: a) Girvan DS and b) Algavi DS.

Physical properties

The grain size distribution of the two materials (Figure 5.2 a and b) is very different. The Girvan DS is dominated by particles ~ 0.2 mm, whereas the Algavi DS is dominated by particles ~ 0.1 mm. The very fine nature of the Algavi DS renders the material much less permeable to water and in its raw state it does not easily mix with water; as such the use of Algavi DS as a biosorbent is not practical.

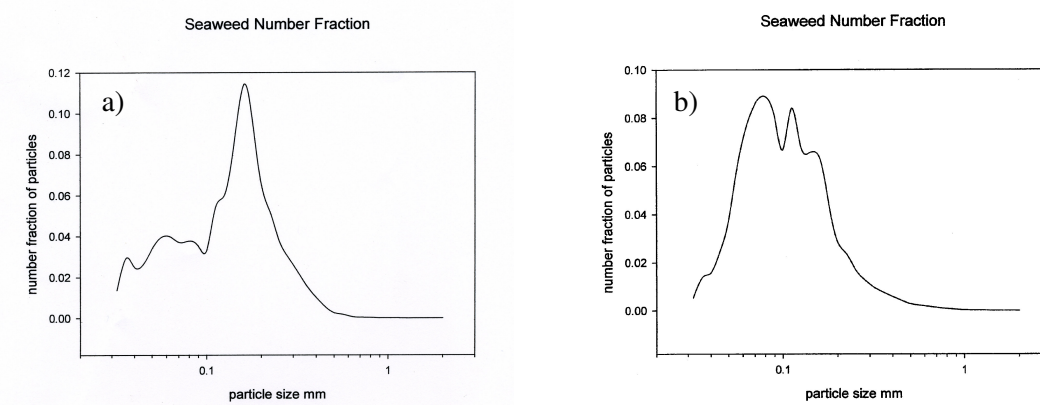


Figure 5.2. Grain size distribution: a) Girvan DS and b) Algavi DS.

Solution pH

When 0.5 g DS was mixed with 20 mL of distilled water (pH ~ 6.5) the Girvan DS produced a circum-neutral/mildly alkaline solution (pH 7.6) while the Algavi DS produced a solution pH of >12 . This may suggest that once the seaweed has been treated with Na_2CO_3 to remove the alginic acid the Algavi DS is not washed before disposal. The Girvan DS does not require any pre-treatment before it can be used as a biosorbent because

of its larger grain sizes and the production of a circum-neutral solution when mixed with water. The Algavi DS, however, requires pre-treatment before it can be used as a biosorbent: a) to remove the large quantities of fine material so as to improve its ability to mix with water and allow water to permeate through a bed of the DS; and b) to reduce the alkalinity of the DS which would increase the ability of the material to adsorb metal ions from mine drainage waters (see Chapter 5.6.6).

5.8.4 Treatment of Algavi DS

Removal of fines

The fines were removed from the Algavi DS by first dry sieving the material through a 0.18 mm mesh sized nylon bag (produced by Mike Reynolds Industrial Fabrics) placed in a sealed container to contain the DS dust or by 'windsifting' (which separates and collects the DS into fractions <0.2 mm and >0.2 mm); the DS was then wetted and the fines washed through the 180 µm nylon bag, although it was impossible to remove all of the fines. The fines were collected and stored for use in later experiments.

Acidification

After the fines were removed from the Algavi DS, the residual DS was treated with ~10 % HCl (v/v) to reduce the alkaline solution produced by the material when contacted with water. The DS was placed into a large container, mixed with tap water and ~10% HCl (v/v) was added; the material was frequently agitated with a drill-powered paint-stirrer and the pH of the solution was checked. The excess solution was occasionally removed and poured through the 0.18 mm bag, which also acted to remove more of the fines, and the collected DS was placed back into the container and an additional 10 % HCl (v/v) was added. This procedure was repeated until the solution was stable at pH 4 for ~1 hour. Acidification, although adding to the cost of producing the biosorbent, may increase the metal uptake capacity (Choi and Yun, 2004). The acidification of the DS converts the acidic groups of the seaweed's polysaccharides to the hydrogen form i.e. saturated with protons (Malik *et al.*, 1999; Schiewer and Wong, 2000; Choi and Yun, 2004) and removes excess Na-, K-, Mg- and Ca-salts (Romero-Gonzalez *et al.*, 2001) to activate the binding sites (Kapoor and Viraraghavan, 1998), therefore increasing the adsorption capacity of the DS. The DS mix was then filtered through the 0.18 mm bag to remove the excess acid solution, rinsed with tap water and then dried (see below) to produce an Algavi DS still

containing some carbonate (referred to as Algavi_(c)). The subscript (c) denotes that the Algavi DS still contains some carbonate particles.

Carbonate removal

The wild seaweed used to produce the Algavi DS is collected by specialised boats (www.dansico.com) and although the exact collection method is not known, it is speculated that the seaweed is removed from close to the seabed as the DS also contains ~10-15 % by weight of sand and small (1-5 mm sized) CaCO₃ particles which appear to be derived from corals and bryozoa. These were removed by placing the unacidified, >0.18 mm DS in a large container with copious amounts of tap water, agitating and allowing the carbonate to settle out, removing the less dense DS from the top. The DS was then acidified, as above, sieved to remove the excess water and dried. This produced a second form of Algavi DS (referred to as Algavi_(f)) so that the effects that carbonate has on biosorption can be examined. The subscript (f) denotes that the Algavi DS is carbonate-free.

Drying

Once the fines were removed and the DS acidified, the DS was then dried. Drying the DS meant that it could be stored for long periods and was in the same state as the dry 'untreated' Girvan DS. The DS was spread out in a thin (about one cm) layer on trays and placed in an oven at 50 °C for two to three days, with the DS being mixed daily until dry and granulated, see Figure 5.3.

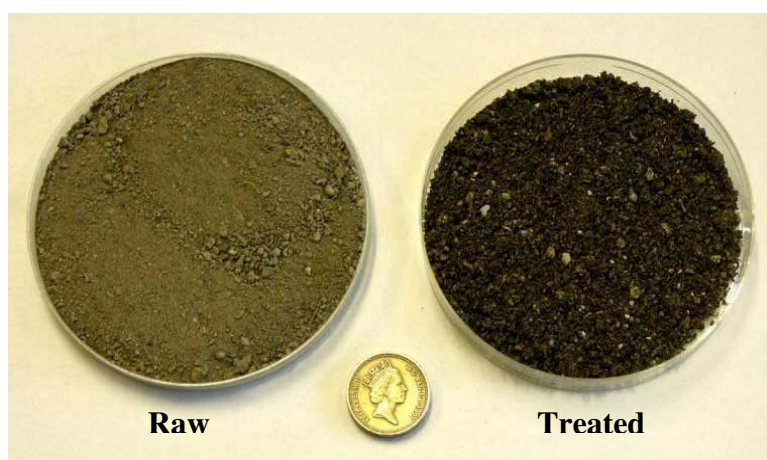


Figure 5.3. Comparison between raw and treated Algavi_(c) DS

Thermal drying may cause degradation of the cellular structure of the DS and may negatively affect the biosorption characteristics of the DS (Malik *et al.*, 1999). Malik *et al.* (1999) compared adsorption after the material had been subjected to thermal drying and freeze drying and they found there to be no difference; although thermal drying >60 °C did cause some loss of biosorption capacity, Park *et al.* (2004b) also found that thermally treating *Ecklonia maxima* at 60 or 100 °C caused a 76 % reduction in carboxyl groups, which caused a decrease in removal rate and efficiency. Nigro *et al.* (2002), however, subjected *Ecklonia maxima*, *Laminaria pallida* and Kelpack waste to various drying and rehydration regimes and found that air and oven drying (at 85 °C) did not improve adsorption of Cu, Zn and Cd by *Ecklonia maxima* and *Laminaria pallida*, and produced only a slight increase in Kelpack waste (oven drying was more effective than air drying), though the drying and rehydration of the seaweeds did improve adsorption. Williams and Edyvean (1997b) also found that biosorption improved if the biomass (various seaweeds and their derivatives) were first pre-soaked in distilled water. The major advantage of drying the material is that it has a longer shelf-life and transport costs are reduced. Atkinson *et al.* (1998) determined that 55 % of the final cost of using activated sludge as a biosorbent was transport. Drying the material therefore reduced transport costs, making the materials more economical to use.

The treatment of the Algavi DS affects the surface area, which may influence its adsorption characteristics. The surface areas of various adsorbents are given in Table 5.1. The Algavi DS has a greater surface area than the Girvan DS and the additional acid-washing and drying that the Algavi DS was subjected may have contributed to this increase. The carbonate contained with the Algavi_(c) DS must contribute to the surface area of the material. However, when compared to other adsorbents in the literature, the DS has a very low surface area, and is more comparable to that of *Ecklonia maxima*.

Table 5.1. Surface area of various adsorbents

Biosorbent	Surface area (m ² /g)	Remarks
Girvan DS	0.98	This study
Algavi _(c) DS	2.8	This study
Algavi _(f) DS	1.2	This study
Activated carbon	≥1000	Park <i>et al.</i> , 2004b
KAU(ini)	1191	steam activate carbon from fruit stones ¹
KAU-2.7	1150	acid oxygenation of activated carbon ¹
KAU-1.8	949	carbon oxygenation of activated carbon ¹
PGP	279	carbon containing phosphorous heteroatoms ¹
PFB1	257	fungal based biosorbent ¹
<i>Ecklonia maxima</i>	<0.08	Park <i>et al.</i> , 2004b

¹Malik *et al.*, 2002

5.8.5 Surface Properties

To determine the functional groups present on the surface of the DS, the three DS types were analysed using a Fourier Transform-Infra Red spectrometer (FT-IR) (Perkin-Elmer Spectrum-One FT-IR spectrophotometer) at the University of Sheffield within the range 450-4000 cm⁻¹. The infra red (IR) spectra of most materials contains a large number of peaks which are produced by the energy exchange of molecules excited by the absorbance of the IR. The IR spectrum produced is thought of as a unique physical property and is characteristic of that molecule. FT-IR determines the wavenumbers (number of waves per cm) simultaneously (opposed to classical ‘dispersive’ IR spectroscopy where the wavelengths were measured one after another) using interferometric modulation of the radiation, which produces an interferogram. The interferometer encodes the initial frequencies in a form that can be read by the instruments detector, which observes all the frequencies at the same time. The interferogram is then recalculated using algorithms and the Fourier Transform instrument is a means of separating the individual frequencies to create the IR spectra. FT-IR has a number of advantages, including: 1) it is non-destructive, 2) numerous materials in most phases (solid or liquid) under very different physical and chemical conditions can be analysed, and 3) little or no sample preparation (Naumann *et al.*, 1991; Coates, 2000).

The FT-IR spectra for Algavi_(c), Algavi_(f) and Girvan DS (displayed in Figure 5.4) show that there are numerous peaks, indicating that the material is very complex in nature. The assignment of the peaks is shown in Table 5.2. Alginic acid has been displayed as a

comparison. There are occasions, however, where the peaks representing the functional groups do not occur in the quoted ranges; this may be caused by the influence of other functional groups within a molecule, the impact of preferred spatial orientations and both chemical and physical environmental effects on the molecule (Coates, 2000). The Girvan DS has a similar spectrum to the Algavi DS and neither DS shows similarities to the alginic acid. The DS types share some of the functional groups, but there are a few that only occur in the Girvan DS, for example, peaks occur at 764 cm^{-1} (C-H bending), 1482 cm^{-1} (carbonate ion) and 1243 cm^{-1} (skeletal C-C stretching). Coates (2000) suggested that if a broad peak occurred between 3600 and 3250 cm^{-1} then the material was dominated by hydroxyl or amino groups; and that adsorption at the low end of the range (i.e. $<1700\text{ cm}^{-1}$) then the material probably contained an amide or a carboxyl (carboxylic acid salt) group. Won *et al.* (2004) noted that a peak between 3600 and 3200 cm^{-1} and peaks at 1652 cm^{-1} and 1233 cm^{-1} were indicative of carboxyl groups. When comparing the Algavi_(c) and Algavi_(f) spectra it can be seen that while most of the carbonate has been removed in the Algavi_(f) sample some still remains.

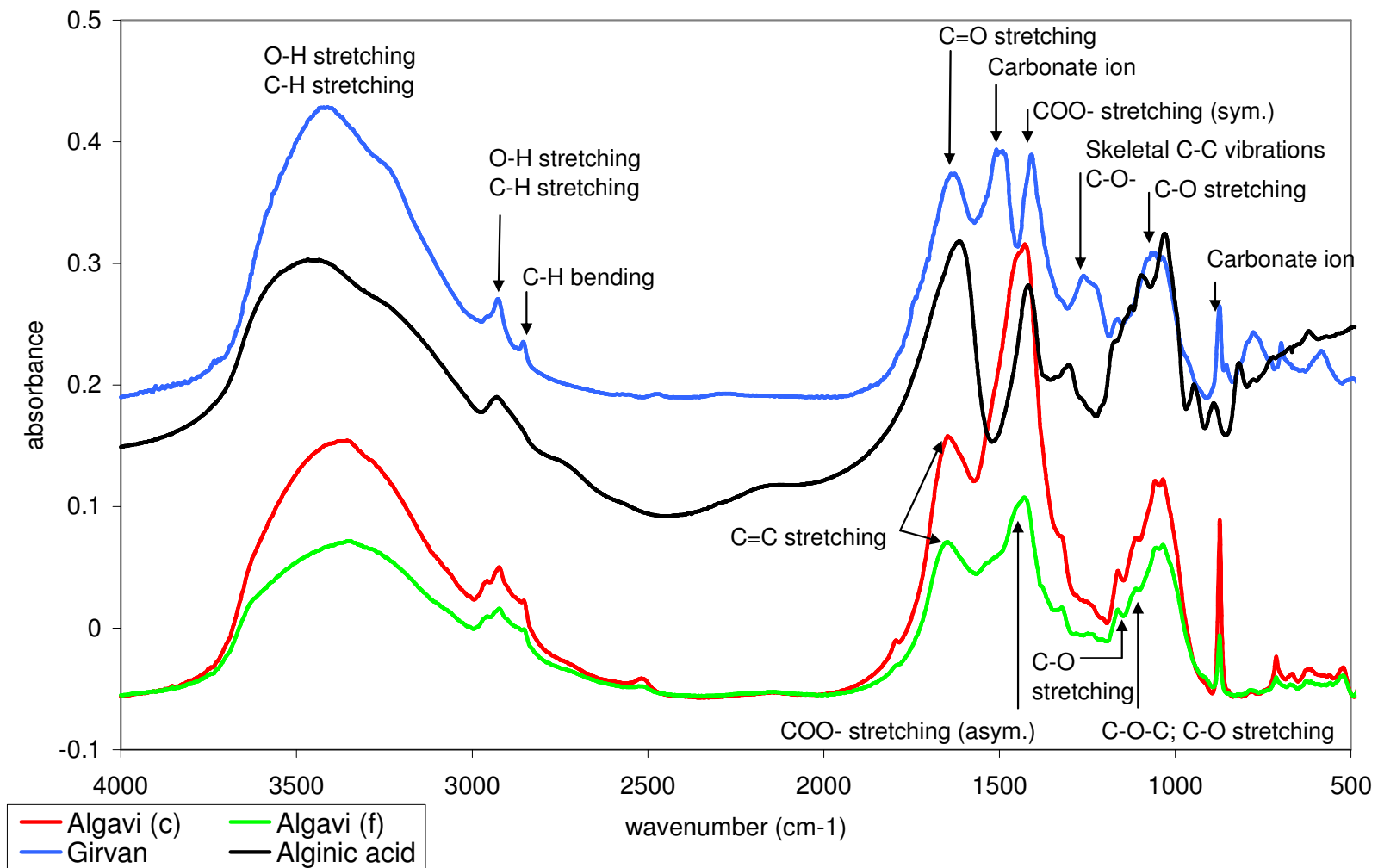


Figure 5.4. FT-IR spectra of Algavi_(c), Algavi_(f), Girvan DS and alginic acid.

Table 5.2. Assignment of infrared absorption bands for Algavi_(c), Algavi_(f), Girvan DS and alginic acid.

Composed from Coates (2000) and Romero-Gonzalez *et al.* (2001)

Wavenumbers in parentheses are those of mannuronic acid-rich calcium alginate (Dupuy *et al.*, 1994 cited in Romero-Gonzalez *et al.*, 2001)

Wavenumber (cm ⁻¹)	Functional group
3570 – 3200	O-H (hydroxyl group; H-bonded OH stretching)
3500 – 3000	O-H stretching C-H stretching
Broad peak ~3350 ¹	Existence of bonded hydroxyl group (3320-3380)
Broad peak ~3440 ⁴	Stretching mode of OH, CH, NH
2935 - 2915	C-H stretching (2924 – CH group ¹)
2922 ⁴	Stretching mode of the aromatic and aliphatic C-H groups
2892 (2904)	O-H stretching C-H stretching
2865 – 2845	C-H bending
1820 – 1770	Carbonyl compound group frequencies
1680 – 1620	C=C stretching
1623 ⁴	Carboxylate RCOO ⁻
1620 ^{1,2}	C=O stretching
1605 (1609)	COO ⁻ stretching (asymmetric)
1490 – 1410	Carbonate ion
1413 (1420)	COO ⁻ stretching (symmetric)
1350 – 1260	O-H (primary or secondary, OH in-plane bend)
1267 ⁴	Aromatic C, C-O stretching
~ 1250	C-O- (Epoxy and oxirane rings)
1246	Skeletal C-C vibrations
~ 1350 – 1000	Skeletal C-C vibrations
1168	Skeletal C-C vibrations; secondary amine; C-N stretching
1159	C-C, C-O and C-C-C stretching
~ 1150	C-O (tertiary alcohol; C-O stretching); P=O stretching ¹
1150 – 1050	C-O-C (alkyl-substituted ether; C-O stretching)
1056	O-H bending
~ 1050	C-O (primary alcohol; C-O stretching)
1140 - 1070	C-O-C (cyclic ethers; large rings; C-O stretching)
1136	Skeletal C-C vibrations; secondary amine; C-N stretching
1038	Skeletal C-C vibrations; primary amine; C-N stretching
890 – 800	C-O- (Epoxy and oxirane rings)
890 – 820	C-O-O-C (peroxides; C-O-O stretching)
868	C-C-O; C-O-C
880-860	Carbonate ion
770-730 ³	C-H bending

¹ – Yun *et al.*, 2001

² - 1620 wavenumber indicates the presence of the amid I band which is caused by the combination of double-bond stretching vibrations (mainly C=O stretching) and hydrogen bonding (Grasdalen *et al.*, 1981)

³ – Naumann *et al.*, 1991

⁴ – Gibert *et al.*, 2005a

5.9 Desorption

When the biosorbent is saturated with metal ions, the metals can be removed (desorbed) to allow the re-use of the biomass. If a biosorbent can only be used for one adsorption cycle before it has to be disposed of, it makes the process labour intensive and uneconomical (Nigro *et al.*, 2002) therefore desorption and the subsequent regeneration of the biosorbent are cost-effective steps of the biosorption process (Kuyucak and Volesky, 1988c; Kuyucak, 1990; Stirk and van Staden, 2002). The major cost factor in the use of any biosorbent is not the uptake capacity of a single exposure, but the uptake capacity over the lifetime of the biosorbent i.e. the number of adsorption/desorption cycles that the biosorbent can withstand without structurally deteriorating or losing its biosorption capacity (Edyvean *et al.*, 1997). The desorption process is dependent on the adsorption system and may not be applicable to multicomponent systems where the metal ions are strongly adsorbed to the biosorbent (Suzuki, 1997).

Processes which allow the non-destructive recovery and allow the biomass to be regenerated for further use are very appealing (Banks, 1997) and can be simple and inexpensive; if non-destructive recovery can not occur then the biomass may be incinerated to obtain a highly metalliferous ash (Kuyucak and Volesky, 1988c; Pagnanelli *et al.*, 2002a). The adsorption of metals is often reversible by simple physico-chemical methods and can be achieved by the use of an appropriate elution solution capable of effectively stripping the metal from the biomass and bringing it into solution (Veglio and Beolchini, 1997). Of major importance is the volume of desorbing solution (eluant) used to remove the metals; the smaller the volume used the more concentrated the metals will be and therefore providing a greater possibility of recovering the metals and re-using the biosorbent; though the volume has to be large enough to provide a maximum solubility for the desorbed metal. Also, if the metals are removed from the biomass it can then be more easily disposed of than if it remains loaded with metals (Banks, 1997; Edyvean *et al.*, 1997; Kuyucak and Volesky, 1989b). It is desirable to remove the metals without damaging the biosorbent, which would occur through the use of concentrated acids, so that the biomass can be used for subsequent adsorption cycles (Gadd, 1990; Suzuki, 1997). Effective desorption eluants can be proton exchangers (for example, mineral acids), complexing agents or may contain competing ions. The pH of the eluant solution

influences the mechanism of proton exchange and is an important factor in the desorption of metal ions (Stirk and van Staden, 2002).

Kuyucak and Volesky (1989b) determined that almost all eluant solutions performed better when the solution was acidic and optimum desorption occurred at pH 2-3 when desorbing metals such as Co, Cu, Zn and Pb. Numerous eluting solutions have been used with varying degrees of success, including acids: HCl, HNO₃, H₂SO₄, acetic acid, lactic acid; salts: NaHCO₃, NaCl, NaOH, Na₂SO₄, CaCl₂, K₂CO₃; and chelators: EDTA, Na₂EDTA. Stirk and van Staden (2002) found that HCl, HNO₃ and H₂SO₄ could remove >80 % of the Cd sorbed onto *Ecklonia maxima* and Kelpack waste; Aldor *et al.* (1995 cited in Stirk and van Staden, 2002) determined that HCl was the most effective desorbing eluant and Jeffers *et al.* (1993) determined H₂SO₄ to be the most effective eluant (>90 % metal removed after a 15 minute contact time) and gave the added advantage of the matrix being compatible with the subsequent processing of the metal-rich eluant by chemical precipitation, evaporation and solvent extraction. Kuyucak and Volesky (1989b) used CaCl₂ at pH 2-3 to desorb over 96 % of the Co adsorbed onto *Ascophyllum nodosum* and although NaCl and CaCl₂ desorbed the metals from the biomass some colouration occurred in the solution (Stirk and van Staden, 2002). Sodium hydroxide, NaHCO₃, Na₂SO₄, K₂CO₃, EDTA and Na₂EDTA were not effective at desorbing the metals (Mattuschka and Straube, 1993; Bakkaloglu *et al.*, 1998; Stirk and van Staden, 2002) with 0.2M EDTA retaining 10-15 % of the Cd adsorbed onto *Laminaria japonica* (Yin *et al.*, 2001).

The temperature effect on the desorption process and the speed of desorption is not significant (Kuyucak and Volesky, 1988c; 1989b), but contact time is very important. The less time the biomass is in contact with the eluant, the quicker the biomass can be reused. Stirk and van Staden (2002) found that using 0.1M HCl was advantageous, as equilibrium was reached in 30 minutes; Kuyucak and Volesky (1989b) found that over 80 % of Co was desorbed in 30 minutes from *Ascophyllum nodosum*, but equilibrium was reached in less than one hour.

Metals such as Au, Ag and Hg may still be strongly bound at acidic pH values. Gold and Hg may be selectively removed using mercaptoethanol and U may be desorbed using carbonate and/or bicarbonates, though a carbonate eluant may affect the biomass structure (Gadd, 1990). Lee *et al.* (2000) found that Cr was desorbed from *Pachymeniopsis* species

(red algae) most effectively using 1N HCl or NaOH and that as pH increased the desorption became more effective and Kuyucak and Volesky (1988a) desorbed Au using 0.1M thiourea and 0.02M ferric ammonium sulphate solution at pH 5. Following desorption of the metals from the biomass, the biomass has to be regenerated (reactivated) for successful use in subsequent biosorption cycles (Kuyucak, 1990), for example, by contacting the biomass with a Na₂CO₃ solution to neutralise the acid and to provide Na⁺ ions for use in ion exchange (Jeffers *et al.*, 1993).

There are disadvantages to regenerating the adsorbent/biosorbent, including the loss of biomass weight and sorption capacity. Kuyucak (1990) noted that after every regeneration step, activated carbon lost ~10 % of its weight and ~15 % of its adsorption capacity. The use of different solutions causes different losses in weight, for example, elution by SO₄²⁻ (pH 5.2) and KSCN (pH 2.5) caused an 11 % loss and CaCl₂/HCl caused only a 6 % loss (Kuyucak and Volesky, 1989b). The process of desorption can also cause damage to the biosorbent, for example the removal of metals from Kelpack waste caused structural damage (Stirk and van Standen, 2002) and Kuyucak and Volesky (1989b) noted that using an alkaline eluant solution caused the deformation of *Ascophyllum nodosum*. The structural damage and loss of the biosorbent will add costs to the process (Kuyucak, 1990).

With the regeneration of the biosorbent, multiple adsorption/desorption cycles may be conducted. Kuyucak and Volesky (1989b) reused *Ascophyllum nodosum* for five cycles and found that the loss of weight was less than 10 % (6 % in the first cycle); Chu *et al.* (1997) used *Sargassum baccharia* for five cycles and after the fifth cycle the Cd uptake had reduced by 44 %. Volesky *et al.* (2003) found that *Sargassum filipendula* could be used for ten cycles when desorbed with pH 3 CaCl₂ with only a 30 % loss of weight; though da Costa and de França (1996) found that the adsorption capacity of *Sargassum* (sample BS1) did not decrease over ten adsorption/desorption cycles. Alhakawati and Banks (2004) attributed the weight loss to the leaching of the alginate from the seaweed. The loss of alginate could be minimised by cross-linking the biomass before use (see Chapter 5.6.7). Aderhold *et al.* (1996) and Williams *et al.* (1997) found that DS could be used for numerous cycles without a loss of sorption capacity; DS was contacted with 10 mg/L Cu, Cd and Ni solution for 24 hours, then filtered and contacted again with the metal-laden solution. After eleven cycles almost all Cu, ~3 mg/L Ni and ~7 mg/L Cd was still being removed and saturation of the DS had not yet occurred.

Metal recovery may then occur from the metal-rich effluents through the use of Mg oxides (producing ~0.4 kg of precipitate per ~3800 L of wastewater), evaporation (producing ~1.3 kg of residue per ~3800 L of wastewater) (Jeffers *et al.*, 1993) or electrolysis. Butter *et al.* (1998) used an electrolyte as an eluant to remove Cd from *Streptomyces* and then recovered the Cd by a rotating cell cathode to produce Cd powder and a Cd depleted electrolyte which was recycled. Bolger and Szlag (2002) used a combination of electrodeposition and electrowinning to recover the Ni from a simulated electrolytic wastewater.

5.10 Summary

The use of conventional techniques for the removal of metal ions from waste waters has several disadvantages and therefore a novel technique is required. Biosorption is the removal of metals, and related elements or compounds from solution by biological materials. Numerous types of biomass have been researched for their uptake capacity and seaweed was determined to be the most promising. Seaweeds possess the ability to remove a large range and concentration of metals from solution and in many cases outperform activated carbon and ion exchange resins. The alginate within the seaweed was thought to be responsible for the majority of the metal removal, though numerous authors have shown that the alginate free (dealginated) seaweed has a comparable or superior sorption capacity when compared to native biomass. There is an extensive alginate extraction industry processing about one millions tonnes of wet seaweed per year; therefore there is a large amount of dealginated seaweed available.

Two different DS sources were considered (Girvan processes mainly *Ascophyllum nodosum* along with other seaweed species and Algavi processes *Laminaria* species) and three DS samples were prepared (Girvan; Algavi containing carbonate (Algavi_(c)) and carbonate-free Algavi (Algavi_(f))). The following chapter will determine the capability of the three DS to adsorb metals from a number of mine drainage waters, which were investigated in Chapter 4.

CHAPTER 6:

Laboratory Scale Experiments

To be successfully used as a biosorbent for the removal of metals from waste waters, the adsorption capacity of the dealginated seaweed (DS) needs to be quantified. The adsorption behaviour of DS was characterised through a series of laboratory experiments using both real (collected directly from the mine adit) mine waters. These experiments were designed to take into account a number of important and interrelated factors: the contact time required between DS and solution to allow biosorption to occur; the physico-chemical conditions of the mine waters and the concentration and composition of the mine waters. The aim was to assess the adsorption capacity of the DS with a range of different mine water types, as described in Chapter 4.4.

6.1 Methodology

The experiments were conducted in two stages: batch and column experiments. In the batch experiments a measured amount of DS was weighed into an Erlenmeyer flask (flask volume dependent on the experiment, but typically 250 mL) and a volume of mine water added, placed on a reciprocal shaker and reacted for a defined length of time. The DS weight, solution volume and reaction times of the experiments were dependent on the experiment being conducted and the conditions were controlled so that only one parameter was changed in any one set of tests. The solution was then filtered through a Whatman[®] number 1 filter paper and the filtrate was collected in new low density polyethylene bottles. The solution pH was measured before addition to the DS and after filtration; the filtrate was then acidified with a few drops of 50 % HNO₃ (v/v). The initial solution and the filtrate were analysed by ICP-MS, except Ca, Mg, Na, K and Zn, which were analysed using AAS. All experiments were conducted at room temperature, to mimic the variable conditions experienced within a field treatment system; though biosorption is not affected at temperatures between 10 and 35 °C (Aderhold *et al.*, 1996).

The batch tests consisted of four different experiments. The first three experiments were conducted using real and synthetic mine drainages. The first experiment was to determine the length of time necessary for metal ions to be removed from solution. 0.5 g (± 0.0005 g) DS was reacted with 50 mL of solution for varying times (2, 5, 10, 15, 30, 60, 120, 180, 360, and 1440 minutes). The length of time the adsorption takes is dependent on the transport to the adsorbent surface, the transport within the adsorbent and the time taken to adsorb to the surface. The second and third set of experiments were designed to determine the capacity of the DS to adsorb metals; the second set of experiments reacted varying weights (0.1, 0.25, 0.5, 0.75, 1 g ± 0.0005 g) of DS with 50 mL of solution for 30 minutes; and the third set reacted 0.5 g (± 0.0005 g) of DS with varying volumes (50, 100, 150, 200, 250, 500, 1000 mL) of solution for 30 minutes. The final set of experiments was conducted using single and mixed element solutions and also determined the adsorption capability with 0.5 g (± 0.0005 g) of DS reacted with 50 mL of solution for 30 minutes; the only varying factor is the concentration and mixture of metals in solution. Concentrations ranged from 1 mg/L to 100 mg/L of Zn, Cd and Pb in single element solutions and mixed element solutions, for example 1 mg/L each of Zn, Cd and Pb (a total of 3 mg/L).

When the batch experiments were completed, column experiments were designed to simulate the flow of mine drainage through a bed of DS. The batch experiments are ideal for providing optimum adsorption of metals from mine drainage as the experiments are constantly agitated and the DS is free to contact with the solution; they are unlikely, however, to describe the conditions found within a treatment system.

6.1.1 Mine drainage

During the first three experiments a number of mine waters were used, including mine waters collected directly from the mine adit (Bwlch and Esgair Hir) and prepared synthetic mine waters (Bwlch and Cwm Rheidol). Bwlch mine water is circum-neutral (pH ~ 6.4), has a high concentration of several elements, especially Zn (median concentration between 2004 and 2006 was 28.4 mg/L) and Cd (median concentration between 2004 and 2006 was 57.9 $\mu\text{g/L}$) and provides an excellent short-term test for the DS. Cwm Rheidol also has high concentrations of contaminants, especially Mn, Co, Ni and Cu (median concentrations between 2004 and 2006 were 392 $\mu\text{g/L}$, 36 $\mu\text{g/L}$, 64 $\mu\text{g/L}$ and 61 $\mu\text{g/L}$ respectively), but a lower pH (~ 3.4). Esgair Hir mine water was also used as it contains much lower

concentrations of elements and is more typical of mine drainage found in mid-Wales. Experiments were conducted using both real and synthetic Bwlch mine water to allow comparison between the real mine water containing the whole suite of elements and the synthetic mine drainage containing solely contaminant metals (with a minor concentration of Na, from the NaOH used to adjust the pH). Two synthetic Cwm Rheidol waters (one at pH 3.3 and one at pH 6.6) were prepared to determine the effect that pH has on adsorption. Zinc, Cd and Pb are the main elements investigated within this chapter as they are present within the mine drainage and are a major cause of the waters failing EQS, see Chapter 4.4.

'Real' mine drainage

Large volumes (25 L) of Bwlch and Esgair Hir mine waters were collected directly from the adit. The waters were stored in new high density polyethylene 25 L containers, which had been rinsed with 10 % HNO₃ (v/v), left to stand overnight, rinsed three times with MilliQ water and then rinsed three times with the mine water prior to collection. The real mine waters are referred to as either Bwlch mine water or Esgair Hir mine water.

Synthetic mine drainage

Synthetic mine drainages were prepared for Bwlch and Cwm Rheidol mimicking the concentrations found in the mine drainage (Table 6.1) but containing no major cations (Ca, Na, K and Mg) or Fe in the Cwm Rheidol waters, so the adsorption behaviour of the DS can be determined with respect to the contaminant metals alone. The synthetic mine drainage is distinguished from the real mine water by referring to it as synthetic Bwlch mine water or synthetic Cwm Rheidol mine water.

Table 6.1. Synthetic mine water composition.

Concentrations displayed in µg/L.

Element	Bwlch mine water	Cwm Rheidol mine water
Co	40	80
Ni	50	100
Cu	140	200
Zn	40,000	20,000
Cd	100	60
Pb	1300	1100

The synthetic mine waters were prepared using the relevant dilutions of 1000 µg/mL stock solutions (provided by the Aldrich Chemical Company); except Zn where the relevant weight of ZnSO₄·7H₂O (BDH Chemicals Ltd, Poole) was weighed and added to the solution. The solutions were produced in 25 L batches, using MilliQ water, in the containers which had been acid-washed and rinsed as above. The pH was adjusted as required, with the addition of either 0.1 M/L H₂SO₄ or 0.1 M/L NaOH; the synthetic Bwlch mine water was adjusted to ~pH 6.6 and the Cwm Rheidol mine waters were adjusted to ~pH 3.3 and ~pH 6.6.

The containers of mine drainage were mixed thoroughly before use. At the same time as the mine drainage was decanted from the 25 L container for use in the experiments, a sample was taken, acidified and analysed to provide an accurate initial composition to take into account any metal precipitation or adsorption onto the storage container that occurred.

6.1.2 Isotherms

The results of biosorption experiments are usually presented in the form of either Langmuir or Freundlich isotherms, which can only reflect the influence of metal concentration on the uptake of one metal (de Carvalho *et al.*, 1994; Namasivayam and Yamuna, 1995; Schiewer, 1999; Park *et al.*, 2004b); very few authors have modelled the interaction of two or three metals (Schiewer and Volesky, 1996; Pagnanelli *et al.*, 2002b; Antoniadis and Tsadilas, 2007); and it is rare to find published data using real wastewater (Jeffers *et al.*, 1993). Sorption isotherms are constructed by studying equilibrium batch sorption behaviour for different biosorbents; they are convenient for determining the maximum uptake and they are also used for systemising data at high concentrations (Crist *et al.*, 1994; Figueria *et al.*, 1997; Park *et al.*, 2004b). Displaying experimental results using isotherms has a number of disadvantages: important parameters such as pH, ionic strength and the presence of other metals are not taken into consideration (Schiewer, 1999) and they do not apply to the chemical processes involved (Crist *et al.*, 1994) i.e. an understanding of the biosorption mechanism is not provided (Park *et al.*, 2004b). The Langmuir isotherm model assumes that the metal ion binds to free binding sites on the surface of the biosorbent rather than by ion exchange (Schiewer, 1999) and therefore the model can not accurately describe the metal binding process and numerous authors have determined that metal binding to seaweed and its derivatives primarily occurs by ion

exchange (Kuyucak and Volesky, 1989a; Figueria *et al.*, 2000; Cossich *et al.*, 2002). The experiments within this thesis were not conducted at a constant pH and therefore isotherms can not be modelled (Veglio and Beolchini, 1997). The results of these experiments are presented as the percentage of metal removed from solution, which is considered more appropriate and informative (Zouboulis *et al.*, 1999).

6.2 Adsorbent type

Two different types of DS were used during these experiments: Algavi and Girvan. The Algavi DS was further divided into that containing CaCO_3 (Algavi_(c)) and that which was CaCO_3 -free (Algavi_(f)), see Chapter 5.8. The three DS differ with respect to the parent seaweed species, surface area and grain size distribution; which may alter the adsorption capacity of the DS. The experiments were conducted using 0.5 g of DS reacted with 50 mL of Bwlch mine water for varying lengths of time (from two minutes to a maximum of 1440 minutes). The full set of results can be seen in Appendix 6.

6.2.1 Algavi_(c) DS v Algavi_(f) DS

Batch experiments were performed comparing Algavi_(c) and Algavi_(f) to determine whether the presence of CaCO_3 affects the amount of adsorption that occurs. Although Algavi_(c) has had the majority of the CaCO_3 removed and has been thoroughly acid washed it still contains a small amount of CaCO_3 (see FT-IR spectra in Chapter 5.8.5). Figures 6.1 a), b) and c) show the removal of Zn, Cd and Pb from Bwlch mine water over time.

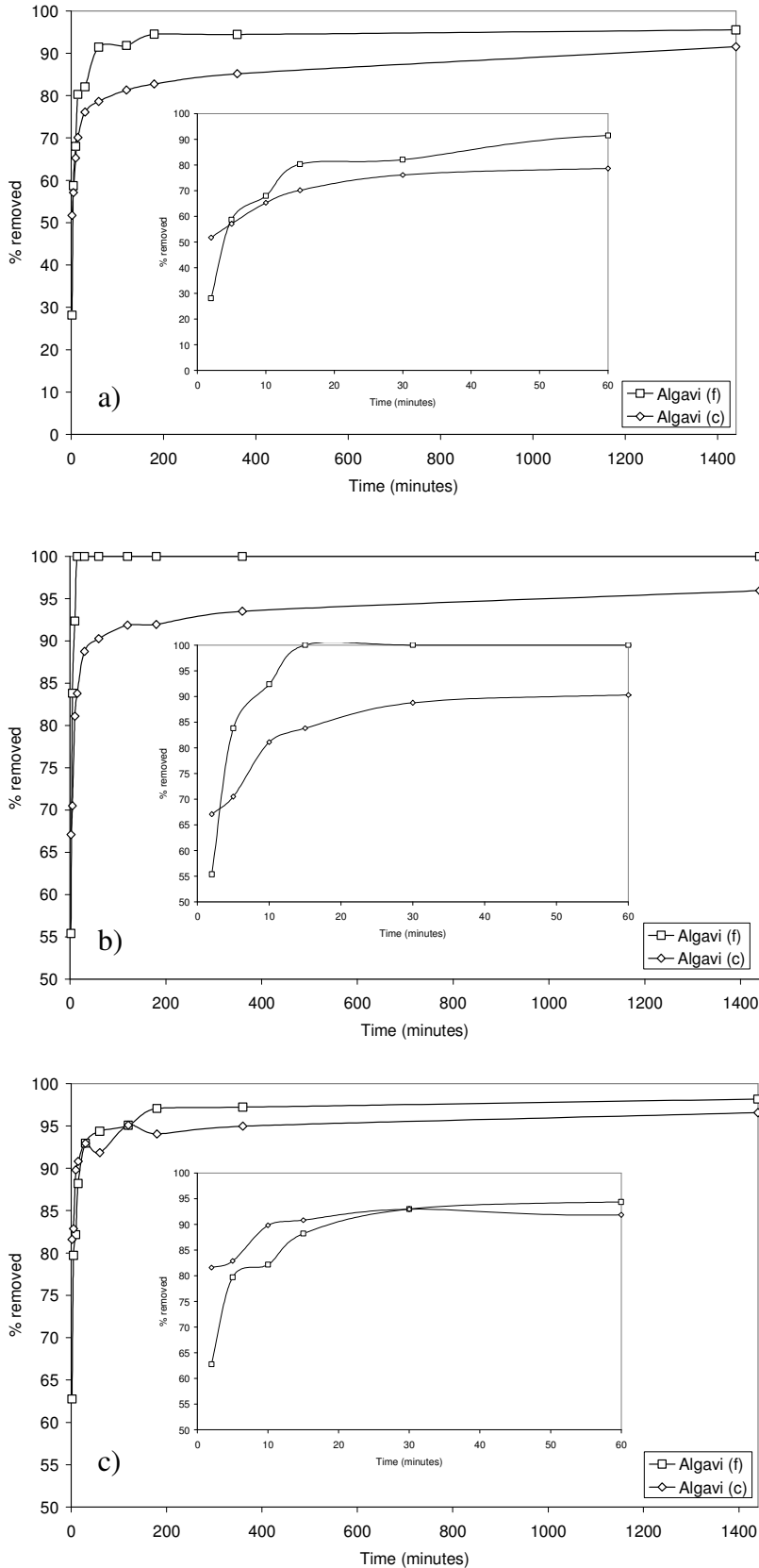


Figure 6.1. Adsorption of: a) Zn, b) Cd and c) Pb by 0.5 g Algavi_(c) and Algavi_(f) DS from Bwlch mine water over 1440 minutes. Inset: first 60 minutes.

Initial concentrations of Zn: Algavi_(c) 35.2 mg/L and Algavi_(f) 25.5 mg/L; Cd: Algavi_(c) 66.4 µg/L and Algavi_(f) 68.4 µg/L; and Pb Algavi_(c) 621 µg/L and Algavi_(f) 744 µg/L.

Algavi_(f) typically removed a greater amount of Zn than Algavi_(c), though the initial reaction (after two minutes) showed that Algavi_(c) adsorbed more (52 % compared with 28 % adsorbed by Algavi_(f)). The amount adsorbed by Algavi_(f) increased very quickly from 28 % after two minutes to 59 % after five minutes (compared to Algavi_(f) which only increased from 52 % to 57 %). After 2 minutes, Algavi_(c) also removed a greater amount of Cd, though after this Algavi_(f) removed a greater amount. After a 15 minute reaction time, Algavi_(f) DS had removed all of the Cd in solution (initial concentration: 68.4 µg/L), whereas Algavi_(c) had only removed 83.8 µg/L. After 1440 minutes, Algavi_(c) had removed 96 %. The presence of CaCO₃ does not make a significant difference to the amount of Pb removed from solution. After two minutes, a greater concentration of Pb is removed by Algavi_(c) (> 80 %) than Algavi_(f) (60 %), and this trend continues until 30 minutes, when both the Algavi DS adsorbed ~95 %; after 120 minutes of contact time the Algavi_(f) adsorbs a slightly higher percentage of Pb than Algavi_(c).

6.2.2 Girvan_(r) DS v Girvan_(a) DS

The Algavi experiments above, show that acid washing the DS has a positive effect on the uptake capacity of the DS, therefore Girvan DS was also subjected to acid washing; subscript (r) denotes the untreated Girvan DS and subscript (a) denotes the acid-washed Girvan DS. The adsorption of Zn, Cd and Pb from Bwlch mine water are shown in Figures 6.2 a), b) and c).

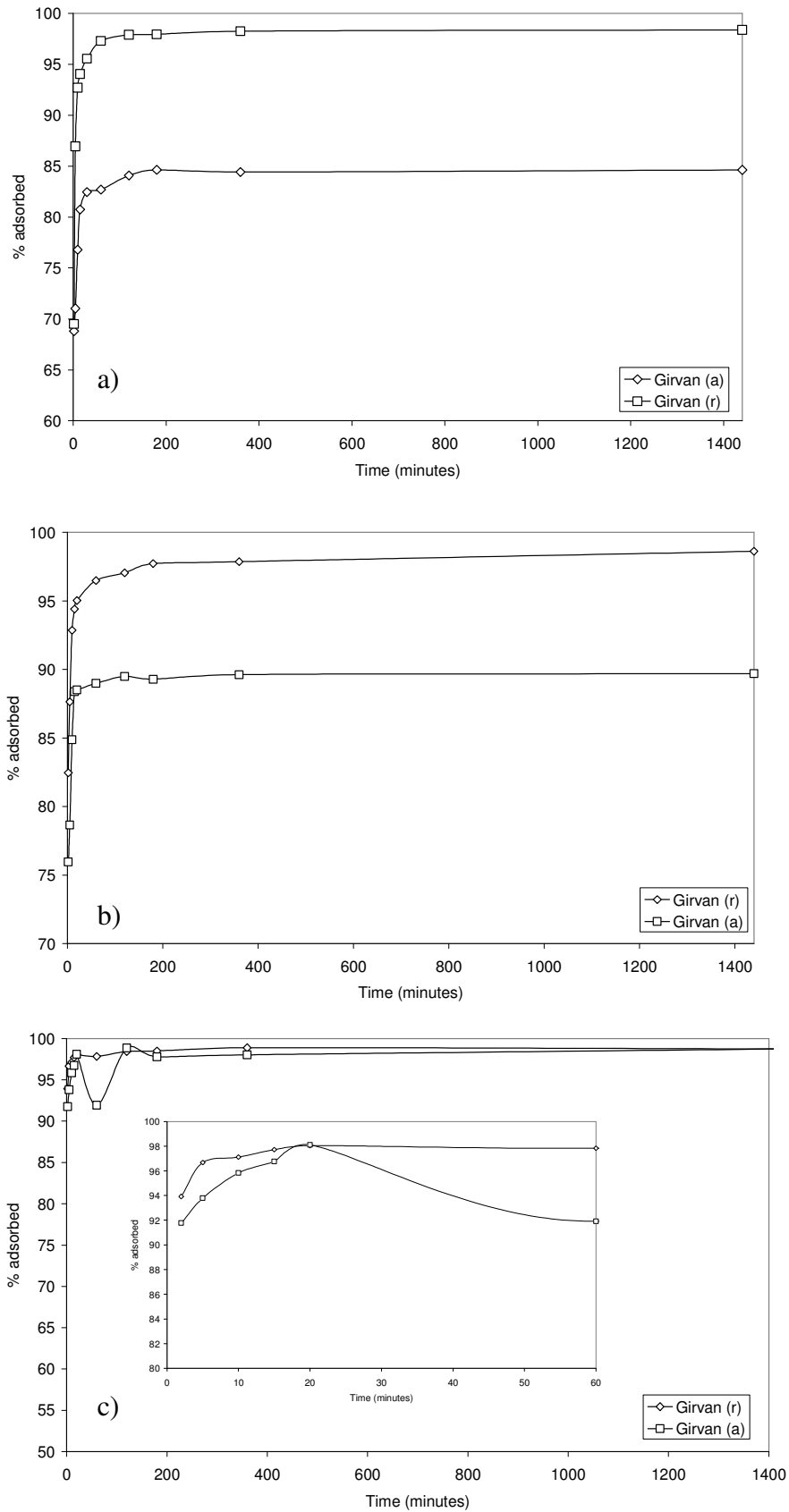


Figure 6.2. Adsorption of: a) Zn, b) Cd and c) Pb by 0.5 g Girvan_(r) and Girvan_(a) DS from Bwlch mine water over 1440 minutes.

Initial concentrations of Zn: Girvan_(r) 37.4 mg/L and Girvan_(a) 35.2 mg/L; Cd: Girvan_(r) 55 µg/L and Girvan_(a) 66.4 µg/L and Pb: Girvan_(r) 742 µg/L and Girvan_(a) 621 µg/L

Contrary to the Algavi results, Girvan_(a) typically adsorbed less Cd and Zn than Girvan_(r). After two minutes both Girvan DS adsorbed the same amount of Zn (~70 %), but after this Girvan_(r) adsorbed a greater amount than Girvan_(a); after 30 minutes Girvan_(r) adsorbed 95 % Zn compared to Girvan_(a) which only removed 82 %. Girvan_(r) also removes a greater amount of Cd, after 2 minutes Girvan_(a) removed 76 % and Girvan_(r) removed 82 %; after 60 minutes the removal by Girvan_(a) was stable at ~91 % whereas the removal by Girvan_(r) was stable at ~98 % after 120 minutes. Lead, however, showed more or less the same affinity for both Girvan_(r) and Girvan_(a); the decrease in the amount of Pb adsorbed by Girvan_(a) at 60 minutes (from 98 % to 92 %) was probably caused by analytical error.

6.2.3 Algavi_(f) DS v Girvan_(r) DS

The difference in adsorption capacity between Algavi_(f) DS and Girvan_(r) DS for Zn, Cd and Pb is shown in Figures 6.5, 6.6 and 6.7. Only the first 120 minutes have been displayed as after this the percentage removed was more or less stable.

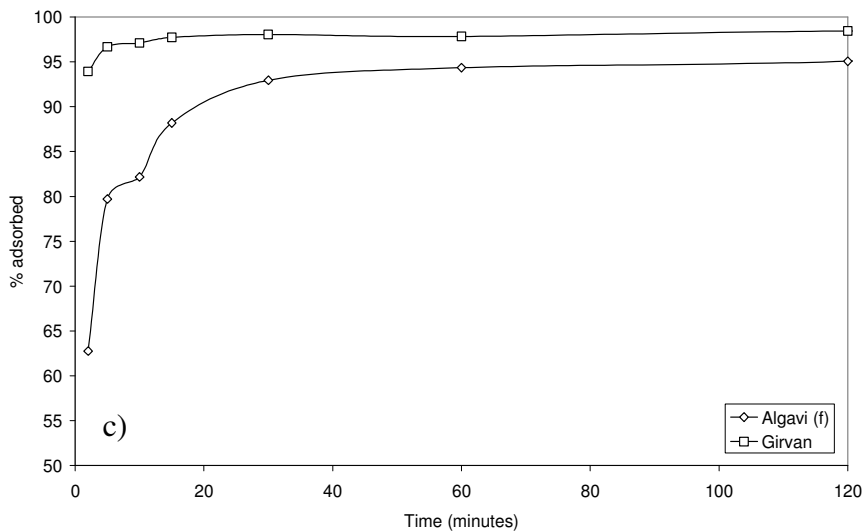
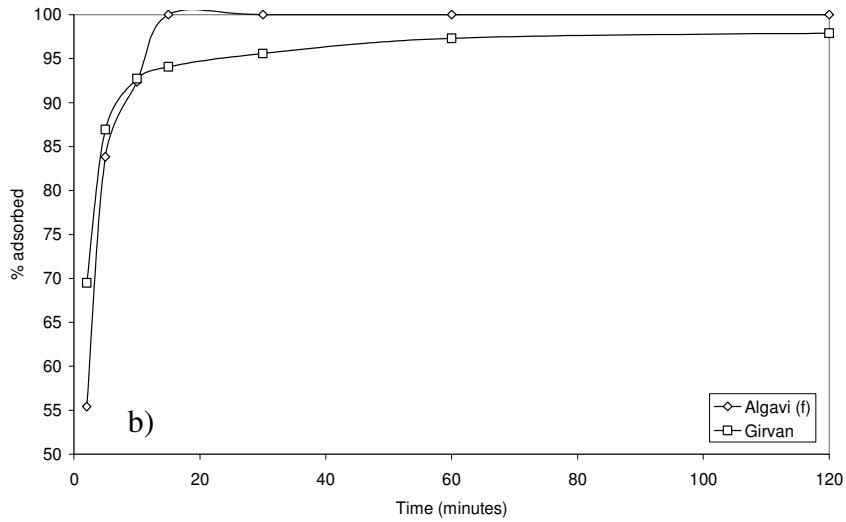
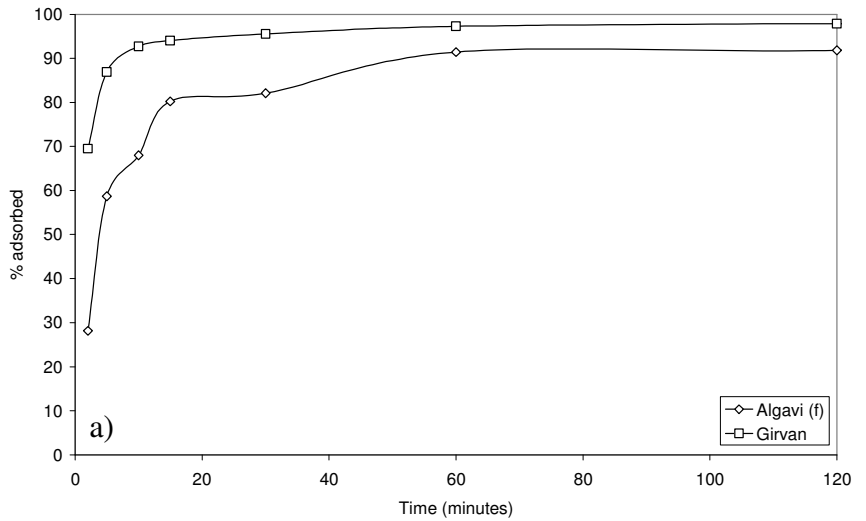


Figure 6.3. Adsorption of: a) Zn, b) Cd and c) Pb by 0.5 g Algavi_(f) and Girvan_(r) DS from Bwlch mine water over 120 minutes.

Initial concentrations of Zn: Algavi_(f) 25.5 mg/L and Girvan_(a) 37.4 mg/L; Cd: Algavi_(f) 68.5 µg/L and Girvan_(a) 55 µg/L; and Pb: Algavi_(f) 744 µg/L and Girvan_(a) 742 µg/L.

Girvan DS adsorbed a greater amount of Zn and Pb than Algavi DS, for example after 30 minutes 96 % Zn and 98 % Pb had been removed by the Girvan DS and only 82 % Zn and 93 % Pb using Algavi DS. For the first 15 minutes Girvan DS adsorbed more Cd from solution than Algavi DS, but after this Algavi adsorbed a greater amount. Girvan DS also required less time to remove >90 % of the element in question; Girvan DS required ten minutes to remove >90 % of the Zn compared to 60 minutes for the Algavi DS and two minutes to remove >90 % of the Pb in comparison to 30 minutes for the Algavi DS. In contrast, both DS required ten minutes to remove over 90 % of the Cd.

During the experiments the pH of the filtrate did not remain below pH 7, therefore metal removal by biosorption alone was not measured, some metal removal by precipitation may also have occurred, see Chapter 5.6.2. Permitting the pH to increase above 7 is advantageous from an application perspective as it may enhance metal immobilisation and removal, and increase the apparent overall metal removal from solution (Zouboulis *et al.*, 1999). In a low cost, low technology treatment plant it would not be economical to continuously monitor and adjust the pH (using expensive chemicals), especially when a pH change may be advantageous.

6.3 Batch experiments

Despite Girvan DS having the greatest adsorption capacity of the three DS examined above; Algavi_(f) DS is going to be considered in more detail because there were problems obtaining large quantities of Girvan DS.

6.3.1 Contact time

Varying the contact time between the DS (0.5 g) and Bwlch mine water (50 mL) provides an indication of the length of time necessary for biosorption to occur. Time is a very important factor when designing a treatment plant, as the time taken for adsorption to occur determines the treatment plant size and volume of liquid that can be treated. The results for the adsorption of Zn, Cd and Pb from Bwlch mine water are shown in Figure 6.8. The results shown here are similar to those gained from using synthetic Bwlch, Cwm Rheidol pH 3.3, Cwm Rheidol pH 6.6 and Esgair Hir mine water, the results of which are discussed below.

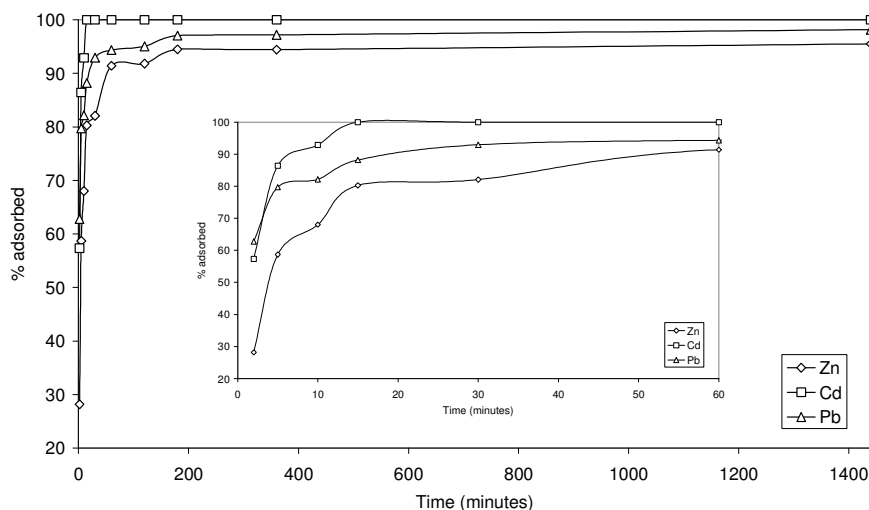


Figure 6.4. Adsorption of Zn, Cd and Pb from Bwlch mine water by Algavi_(D) DS over 1440 minutes. Inset: first 60 minutes.

Initial concentration of Zn: 25.5 mg/L, Cd: 68.5 µg/L and Pb: 744 µg/L.

The elements are rapidly adsorbed with >25 % of the Zn, >55 % Cd and >65 % Pb removed after only two minutes. The majority of the uptake occurred within 15 minutes with >80 % Cd, Zn and Pb being removed; after this rapid uptake, the rate slowed down and >90 % of Pb and Cd were removed after 30 minutes, after ~60 minutes the removal rate for Cd was more or less stable and after 180 minutes for Zn and Pb. The inset of Figure 6.8 shows that after 30 minutes an insignificant increase in the amount of adsorption occurred; as a result of these findings a 30 minute contact time was used in all experiments (with the exception of the time experiments); there seems to be little advantage in contacting the biomass and solution for longer.

The Esgair Hir mine water contains the lowest concentration of metals, which when compared to the other studied mine waters, shows the lowest metal adsorption over time, see Figure 6.9. The removal rate of Pb from the Esgair Hir mine water does not follow the fast/slow adsorption rate typical of the other mine waters, but increased steadily over time before reaching 100 % removal after 1440 minutes (24 hours). The lower metal adsorption from low metal concentration mine waters is also shown in Figure 6.10; with greater adsorption occurring with increasing initial metal concentrations. Lead removal is only shown at 2, 30 and 1440 minutes to display the increasing removal with increasing initial concentrations.

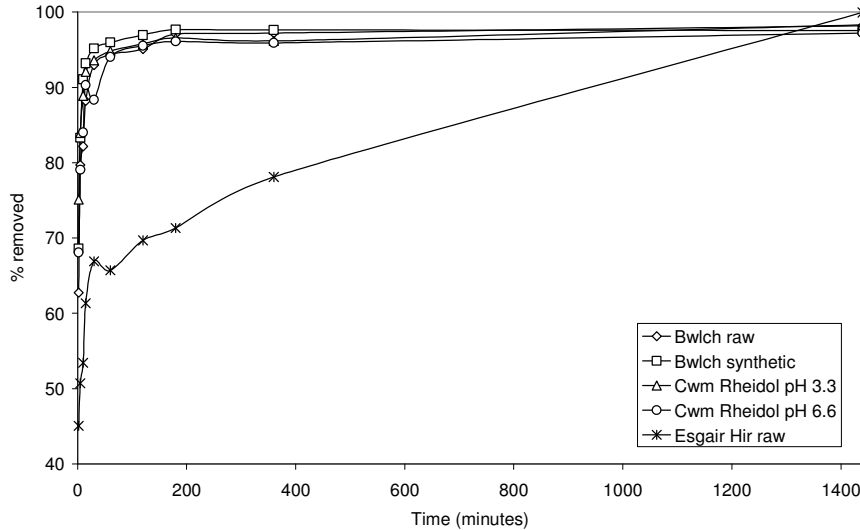


Figure 6.5. Adsorption of Pb from various mine waters by 0.5 g Algavi_(t) DS over 1440 minutes.

Initial concentrations of Pb: Bwlch 744 µg/L; synthetic Bwlch 2216 µg/L; Cwm Rheidol pH 3.3 1687 µg/L; Cwm Rheidol pH 6.6 1418 µg/L; Esgair Hir 26 µg/L

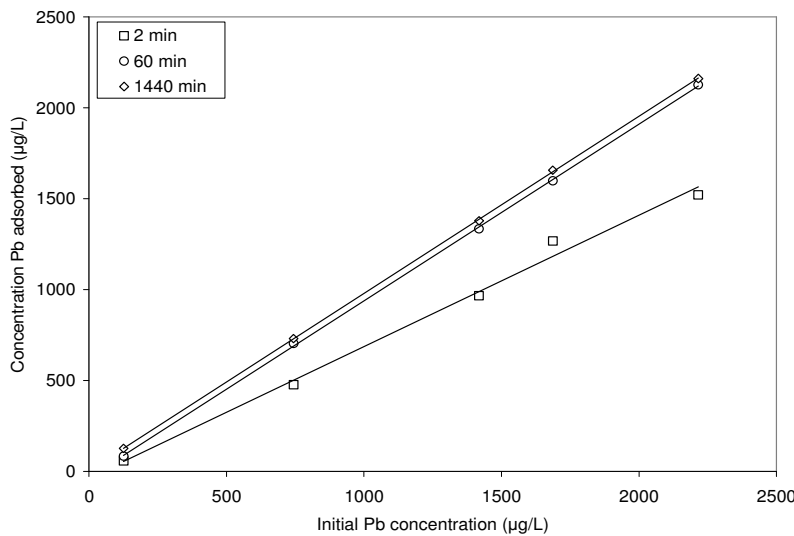


Figure 6.6. Adsorption of Pb from mine waters with different initial concentrations by 0.5 g Algavi_(t) DS at 2, 60 and 1440 minutes.

Initial concentrations of Pb: Esgair Hir 126 µg/L; Bwlch 744 µg/L; Cwm Rheidol pH 6.6 1418 µg/L; Cwm Rheidol pH 3.3 1686 µg/L; and synthetic Bwlch 2216 µg/L.

Bwlch v Synthetic Bwlch mine water

Experiments were conducted using Bwlch and synthetic Bwlch mine waters to determine whether the presence of major cations (Na, Mg, K and Ca) in the waters affected the adsorption by Algavi_(t) DS. The adsorption of Zn is compared in Figure 6.11; there was minimal difference between the adsorption from the Bwlch or synthetic Bwlch mine water,

despite the different initial concentrations, see Table 6.2. Cadmium and Pb show a similar pattern to Zn and are therefore not shown.

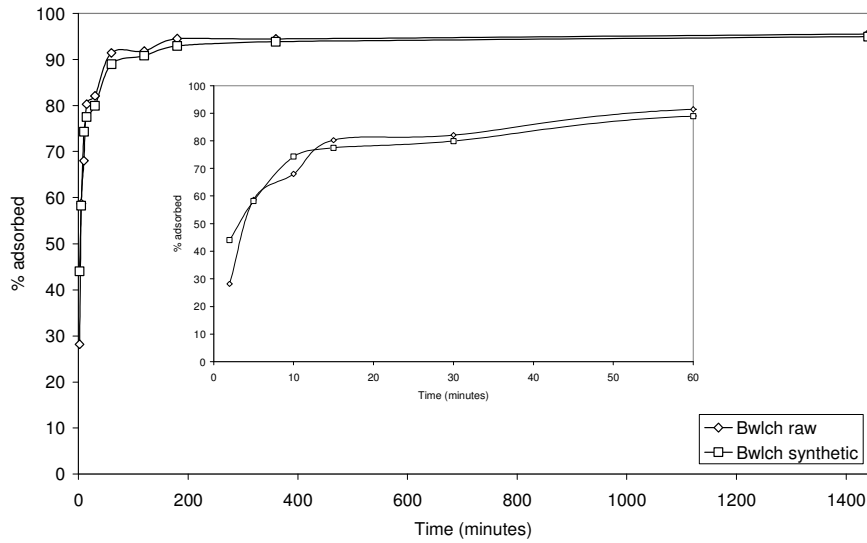


Figure 6.7. Adsorption of Zn from Bwlch and synthetic Bwlch mine waters over 1440 minutes. Inset: first 60 minutes.

Initial concentration in solution: Bwlch mine water 25.5 mg/L and synthetic Bwlch mine water 43.7 mg/L.

Table 6.2. Bwlch and synthetic Bwlch mine water element concentrations.

	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Co µg/L
Bwlch	8.9	8.6	3.7	33.2	14.8
Bwlch Synthetic	6.0	0.0	0.0	0.1	51.3
	Ni µg/L	Cu µg/L	Zn mg/L	Cd µg/L	Pb µg/L
Bwlch	84.8	35	25.5	68.5	744
Bwlch Synthetic	80.2	144	43.7	141	2216

Cwm Rheidol pH 3.3 v Cwm Rheidol pH 6.6

The effect of pH on adsorption was determined by reacting waters with a similar chemistry, but different pH values with Algavi_(f) DS, see Table 6.3. The adsorption of Zn from synthetic Cwm Rheidol mine waters at pH 3.3 and pH 6.6 is shown in Figure 6.12 and the pH of the mine waters does not make a significant difference to the adsorption of metals from solution. Cadmium and Pb show a similar pattern and are therefore not shown.

Table 6.3. Synthetic Cwm Rheidol pH 3.3 and 6.6 mine water element concentrations.

	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Co µg/L
pH 3.3	0.0	0.0	0.0	0.1	92.3
pH 6.6	7.0	0.0	0.0	0.0	86.6
	Ni µg/L	Cu µg/L	Zn mg/L	Cd µg/L	Pb µg/L
pH 3.3	203	271	21.9	80.2	1687
pH 6.6	213	257	21.5	67.6	1418

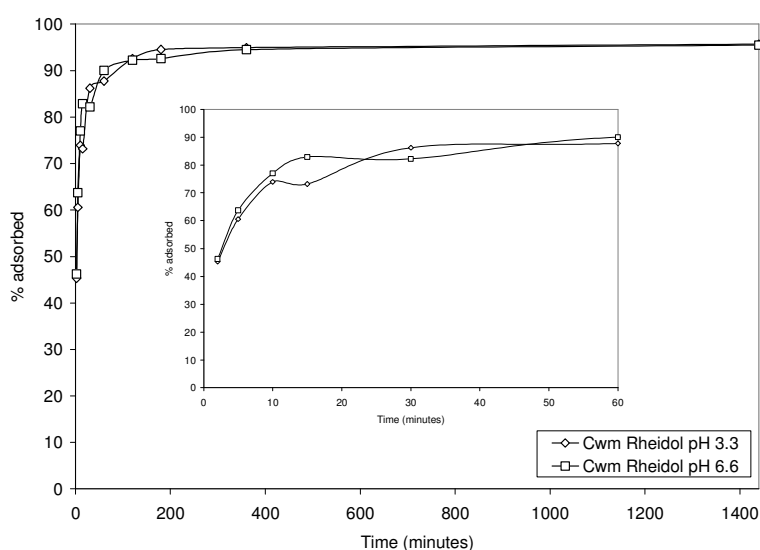


Figure 6.8. Adsorption of Zn from Cwm Rheidol mine waters at pH 3.3 and pH 6.6 over 1440 minutes. Inset: first 60 minutes.
Initial concentrations of Zn: Cwm Rheidol pH 3.3 21.9 mg/L and Cwm Rheidol pH 6.6 21.5 mg/L.

6.3.2 Weight of biomass

To determine the adsorption capacity of the DS, varying weights (0.1, 0.25, 0.5, 0.75 and 1.0 g) were contacted with 50 mL of Bwlch mine water for 30 minutes. The removal of metal ions adsorbed was over 50 % using only 0.1 g DS, see Figure 6.13, with >50 % of Zn and >80 % Cd and Pb being removed using only 0.1 g. The amount removed generally increased with an increasing weight of DS until no further adsorption occurred.

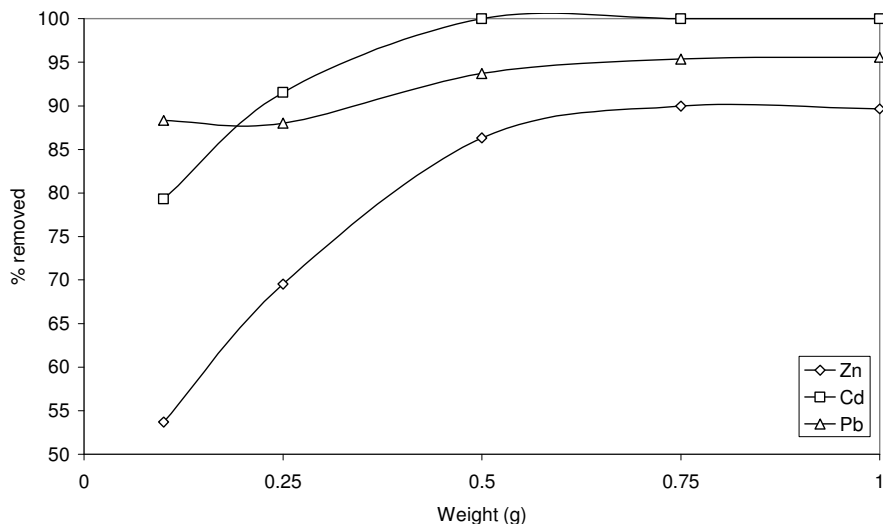


Figure 6.9. Adsorption of Zn, Cd and Pb from 50 mL Bwlch mine water with varying weights of Algavi_(f) DS.

Initial concentration of Zn 25.5 mg/L, Cd 68.5 µg/L and Pb 744 µg/L.

The removal of Zn increased from 53 % removal using 0.1 g DS to 90 % using 1 g DS; though after 0.5 g DS no further significant increase in adsorption occurred (Zn removal increased from 86 to 90 % from 0.5 g and 1 g, respectively). Lead, however, was adsorbed at more or less the same percentage independent of the weight of DS used, i.e. 88 % was adsorbed reacting only 0.1 g and ~ 94 % was adsorbed using 0.5g and above. The removal of Cd increased with DS weight until 0.5 g when all of the Cd in the Bwlch mine water had been removed from solution; therefore no additional Cd could be removed. This pattern was also seen using the synthetic Bwlch, Synthetic Cwm Rheidol (at pH 3.3 and 6.6) and raw Esgair Hir mine waters.

An increase in the weight of DS within the experiments also produced an increase in the concentration of major ions in solution, especially Ca, see Figure 6.14. The concentration of released major cations was calculated by subtracting the concentration in the initial mine waters from that of the experiment filtrate. The release of Ca was effectively linear, i.e. 0.5 g Algavi_(f) DS released ~50 mg/L Ca and 1 g Algavi_(f) released ~100 mg/L. This may suggest that the Ca is present on the surface of the DS; during the alginate removal process, the seaweed is known to undergo a Ca-dewatering process (Williams and Edyvean, 1997a) and therefore the increase of Ca in the filtrate may be a simple wash off from the surface. When 1 g Algavi_(f) DS was reacted with Bwlch and Cwm Rheidol pH 6.6 mine waters, lower than expected concentrations were released (when compared to the

other mine waters). The release of Na, Mg and K with increasing weights of Algavi_(f) are shown in Figure 6.15; larger concentrations of Na and Mg are released than K, the concentration of Na increased from 3.4 mg/L (released from 0.1 g) to 5.5 mg/L (released from 1 g), whereas K only increased from 0.2 mg/L (from 0.1 g DS) to 0.8 mg/L (from 1 g).

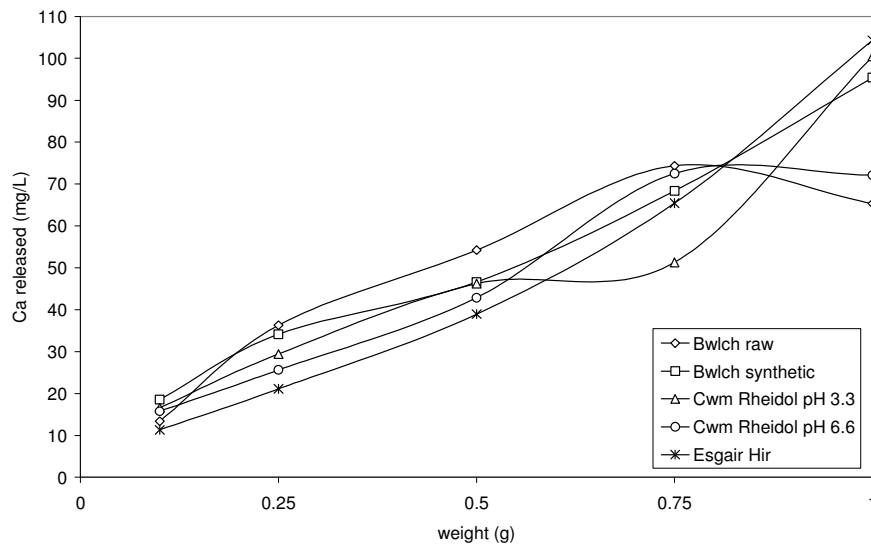


Figure 6.10. Concentration of Ca (mg/L) released from varying weights of Algavi_(f) DS when reacted with 50 mL of mine water.

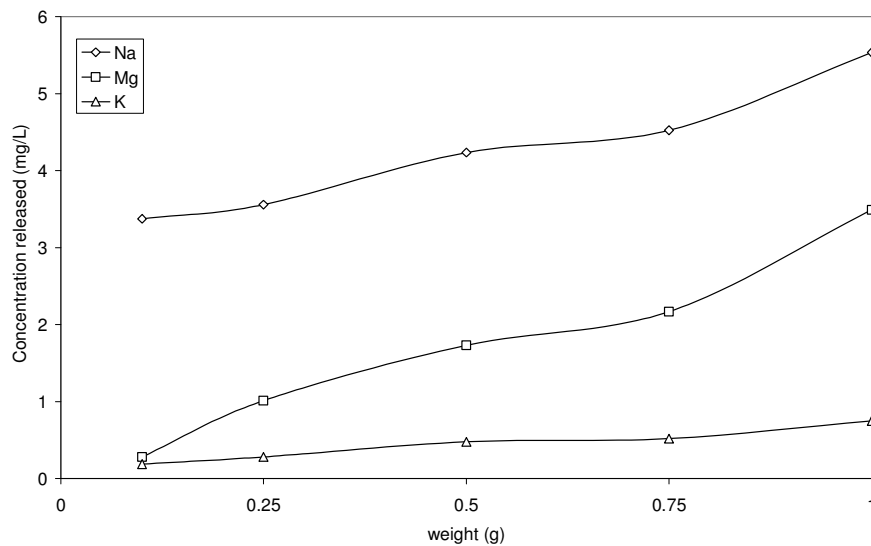


Figure 6.11. Concentration of Na, Mg and K (mg/L) released by varying weights of Algavi_(f) DS using 50 mL synthetic Bwlch mine water.

6.3.3 Volume

Increasing the volume of solution (50, 100, 150, 200, 250, 500 and 1000 mL) reacting with 0.5 g Algavi_(f) for 30 minutes also provides information regarding the capacity of the DS. The DS reaches its adsorption capacity when no further increase in adsorption occurs, see Figure 6.16. The Cd adsorption capacity of the DS was reached after reaction with 500 mL of Bwlch mine water, after which no further adsorption occurred, neither Zn nor Pb had reached adsorption capacity and were still being removed from solution. The total mg removed from Bwlch mine water was calculated by:

$$\left[\left(\frac{a(\text{mg/L})}{1000} \right) \times b \right] - \left[\left(\frac{c(\text{mg/L})}{1000} \right) \times d \right] \quad (6.1)$$

Where:

- a: initial concentration of the mine water (mg/L);
- b: volume (mL) of the initial mine water sample, i.e. 50 mL;
- c: concentration (mg/L) of the filtrate; and
- d: volume (mL) of the filtrate collected.

The weight of adsorbed metal from the various mine waters is shown in Table 6.4. Within the mine waters studied, the concentration of Pb adsorbed continued to increase with increasing volumes of mine water i.e. increasing mg of Pb (with the exception of Esgair Hir mine water) therefore suggesting that saturation of the DS had not occurred. The adsorption of Zn by 0.5 g Algavi_(f) DS ceased after 500 mL using synthetic Bwlch mine water (after adsorbing 6.2 mg Zn) and Cwm Rheidol pH 6.6 mine water (after adsorbing 4 mg Zn). Only a small amount of Cd was adsorbed before saturation of the DS occurred; saturation did not occur when the DS was reacted with either synthetic Bwlch or Cwm Rheidol pH 3.3 mine water.

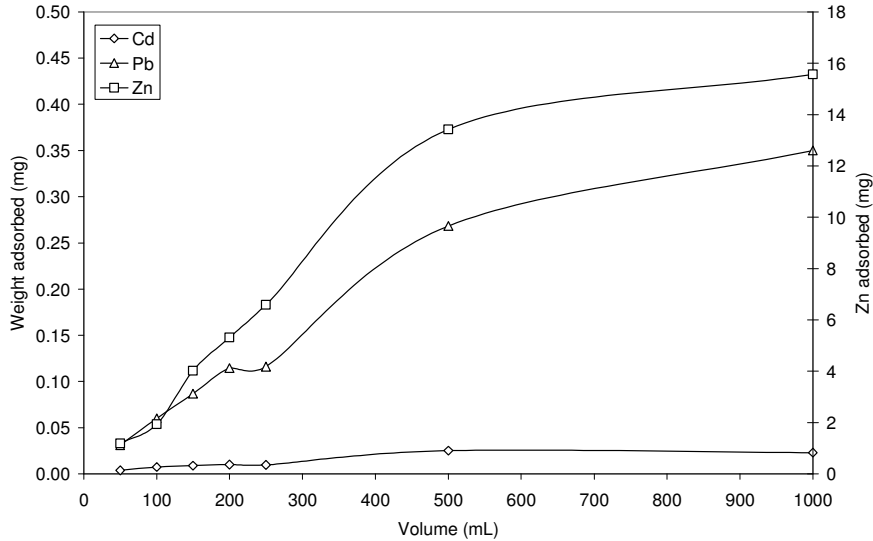


Figure 6.12. Weight of Zn, Cd and Pb adsorbed from Bwlch mine water by 0.5 g Algavi_(f) DS. Initial concentration of Zn 27.9 mg/L, Cd 76.7 µg/L and Pb 667 µg/L.

Table 6.4. Weight of Zn, Cd and Pb adsorbed by 0.5 g Algavi_(f) DS from various mine waters. Value in parentheses denotes the volume after which no further adsorption occurs.

		Zn (mg)	Cd (mg)	Pb (mg)
Bwlch	Initial concentration	27.9 mg/L	76.7 µg/L	667 µg/L
	Weight adsorbed	15.6 mg	0.03 mg (>500 mL)	0.35 mg
Synthetic Bwlch	Initial concentration	43.7 mg/L	141 µg/L	2216 µg/L
	Weight adsorbed	6.2 mg (>500 mL)	0.05 mg	1.2 mg
Cwm Rheidol pH 3.3	Initial concentration	21.9 mg/L	80.2 µg/L	1687 µg/L
	Weight adsorbed	3.1 mg	0.23 mg	0.9 mg
Cwm Rheidol pH 6.6	Initial concentration	21.5 mg/L	67.6 µg/L	1418 µg/L
	Weight adsorbed	4 mg (>500 mL)	0.02 mg (>500 mL)	0.8 mg
Esgair Hir	Initial concentration	0.94 mg/L	1.66 µg/L	126 µg/L
	Weight adsorbed	0.4 mg	0.0003 mg (>500 mL)	0.01 mg (>200 mL)

6.3.4 Concentration

The final set of experiments varied the element concentration in 50 mL of solution contacting with 0.5 g of Algavi_(f) DS for 30 minutes. These experiments show the adsorption of Cd, Zn and Pb when reacted with a solution of a given concentration. Single element solutions were prepared containing 1, 5, 10, 25, 50, 75 and 100 mg/L of Zn, Cd and Pb. To determine whether the presence of other elements in solution affected the amount of adsorption mixed element solutions were prepared i.e. containing 1 mg/L of Zn, Cd and Pb (total element concentration of 3 mg/L). A 1000 mg/L standard of Zn, Cd and Pb was prepared using $\text{ZnSO}_4 \cdot \text{H}_2\text{O} \cdot 7\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ and $(\text{PbNO}_3)_2$ respectively. The required solutions (1, 5, 25, 50, 75 and 100 mg/L) were then prepared by the necessary dilutions of the standard. For a complete set of results see Appendix 7.

The concentrations adsorbed from single metal and mixed metal solutions are shown in Figure 6.17; the concentrations have been displayed in mM/g to provide a more accurate comparison between the metals. The presence of additional elements in solution did not affect the amount of adsorption that occurred; though there was a small reduction in Zn adsorption (above an initial concentration of ~25 mg/L/~0.38 mM/L Zn) in the presence of Cd and Pb (Figure 6.17 a).

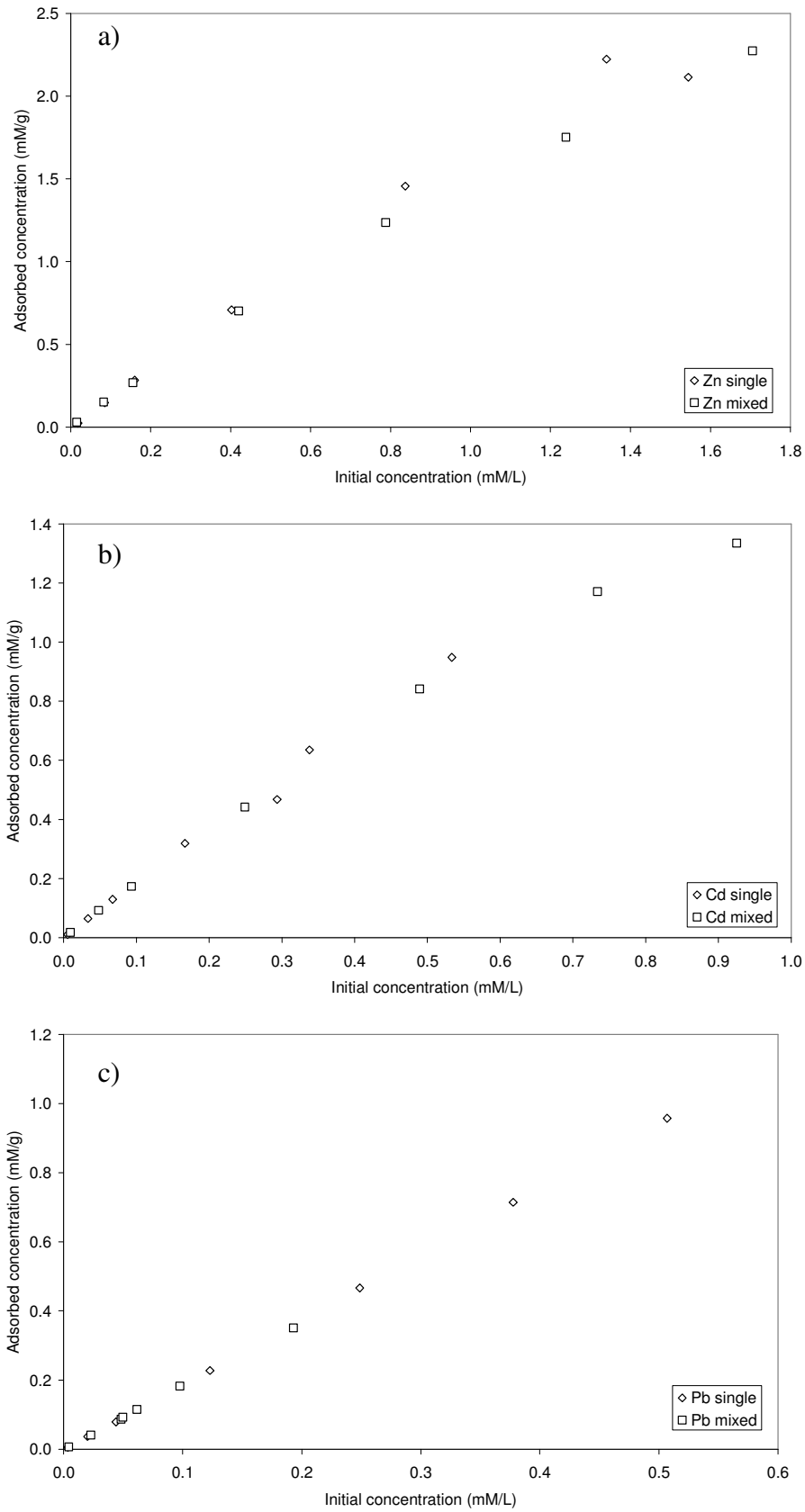


Figure 6.13. Concentration of: a) Zn, b) Cd and c) Pb (mM/g) adsorbed onto 0.5 g Algavi_(f) DS in both single and mixed metal solutions.

6.3.5 Ion exchange

Ion exchange has been identified as the main mechanism for metal removal by biosorbents (Schiewer and Volesky, 1996; Kratochvil and Volesky, 1998a; Figueria *et al.*, 2000; Cossich *et al.*, 2002). If the DS is acting as an ion exchange material, then as the metal ion in question is adsorbed then another ion should be released. Calcium was analysed to determine whether the release of this ion was related to the adsorption of the metal ion, (after Crist *et al.*, 1990; Williams and Edyvean, 1997a; Kuyucak and Volesky, 1989c). The adsorption of Zn, Cd and Pb with the simultaneous release of Ca is shown in Figure 6.18; the full data set is shown in Appendix 7.

As the concentration of adsorbed metal increased, the concentration of Ca released into solution also increased therefore suggesting an exchange of ions. It is important to note that there is a significant Ca concentration release even by low metal ion concentration solutions (i.e. the 1 mg/L solution); the Ca concentration increased from ~0.03 mg/L in the initial solution to ~48 mg/L in the filtrate after a 30 minute reaction time. This suggests that there is a release of Ca irrespective of whether any metals are present in solution; this is supported by the release of ~35 mg/L Ca when 0.5 g Algavi_(f) DS was reacted with 50 mL MilliQ water for 30 minutes. This ~35 mg/L Ca released has been taken into consideration when determining the amount of Ca released from the interaction with the metal solutions (Figure 6.18) i.e. the ~35 mg/L Ca has been subtracted from the Ca concentration within the filtrate. The correlation between the metal ion adsorbed and the Ca released show more or less a straight line relationship (Ca and Zn: $r = 0.96$; Ca and Cd: $r = 0.92$; Ca and Pb: $r = 0.84$).

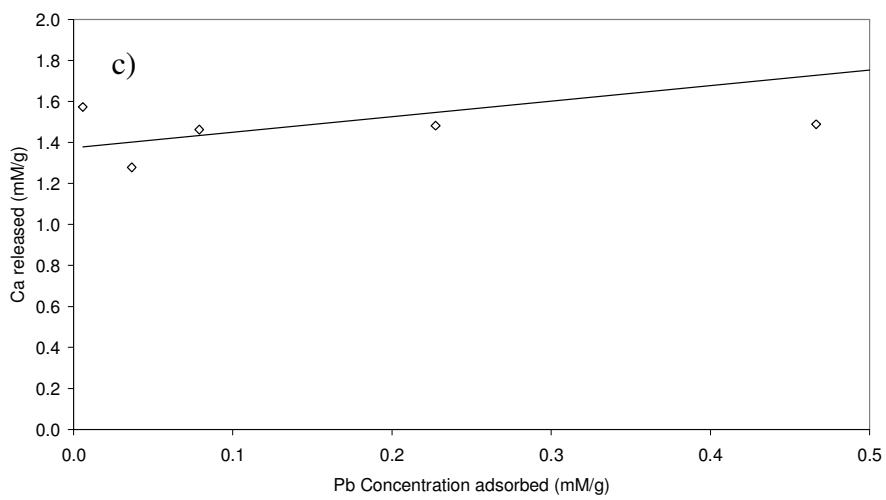
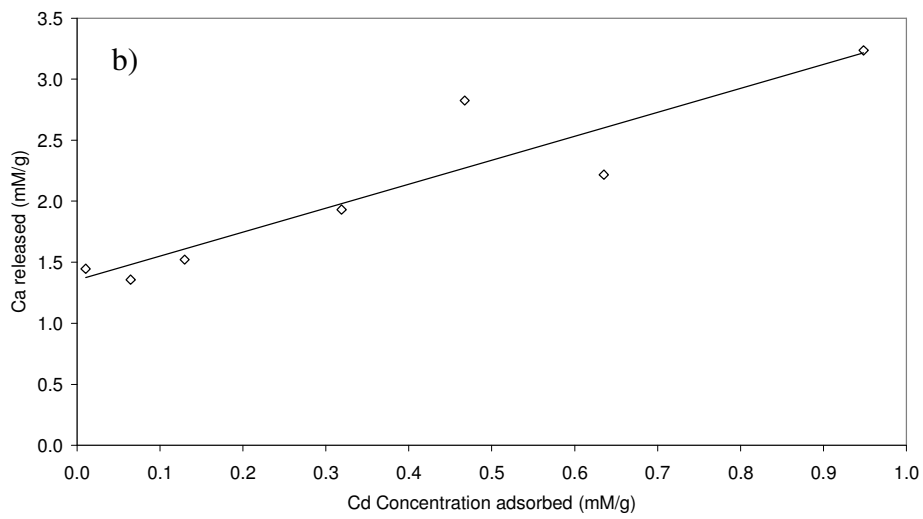
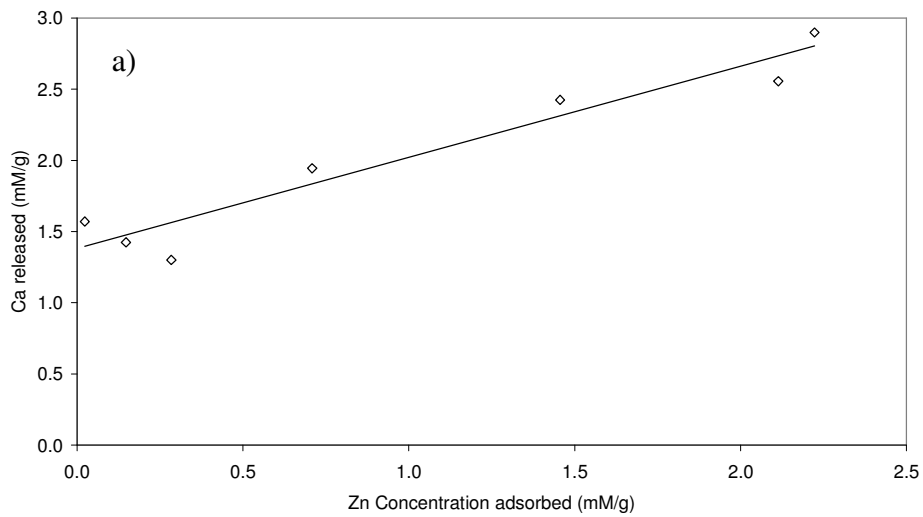


Figure 6.14. Relationship between: a) Zn, b) Cd and c) Pb adsorption and Ca release (mM/g) in single metal solutions by 0.5 g Algavi_(f) DS.

6.4 Column experiments

Column experiments were conducted to simulate the flow of solution through a bed of biosorbent, as may be used in a treatment plant. Standard chromatography columns (20 mm internal diameter, 200 mm length) were used, with a sinter glass disc at the base (porosity of 200-250 μm). On top of the sinter glass disc a layer of glass wool was placed to prevent the DS from blocking the pores of the sinter glass, 2.5 g of Algavi_(c) DS was placed into the column and then another layer of glass wool, to constrain the DS. The column was then filled with MilliQ water to saturate the DS and equilibrate the DS with the water. A reservoir (500 mL) was then placed on top of the column to seal the column, filled with Bwlch mine water and kept at a constant level throughout the experiment. The Bwlch mine water was gravity fed through the column and the flow was controlled via taps on both the reservoir and at the base of the chromatography column. The experiment was designed to allow a flow of ~ 7 mL per minute. The water was collected in 10 mL aliquots and then acidified using a few drops of 50 % HNO_3 (v/v). The initial Zn concentration in the Bwlch mine water used in this experiment was 36 mg/L and, in total, 1500 mL flowed through the bed of DS. Only Zn was determined, as large concentrations occurred in the waters and the concentration could be easily and quickly determined by AAS. During the experiment the flow through the DS bed decreased, see Figure 6.19, which may have been caused by the compaction of the DS or the slight swelling of the DS; because of the restricted nature of the column experiments this decrease in flow over time is not likely to be seen in a large bed of the DS, such as might be found in a fixed bed treatment system. The full set of results is presented in Appendix 8.

The concentration of Zn in solution after flowing through the DS bed (the effluent) is shown in Figure 6.20. The Zn concentration increased in the effluent as the volume of raw Bwlch mine water through the DS bed increased. The weight of Zn adsorbed onto the 2.5 g Algavi_(c) DS is shown in Figure 6.21 and as the volume of Bwlch mine water through the DS bed increased so does the weight of Zn retained on the DS. Given that the initial concentration of Zn in the raw Bwlch mine water was 36 mg/L, the total amount of Zn that flowed through the DS bed was 56 mg (initial concentration divided by 1000 to give the weight per mL, then multiplied by the volume of solution which flowed through the column) and over 40 mg Zn had been retained by the DS; therefore the DS had adsorbed

1.6 % of its own weight in Zn and because the DS had not saturated (after 1500 mL raw Bwlch mine water had flowed through 2.5 g Algavi_(f) DS) this value is likely to increase.

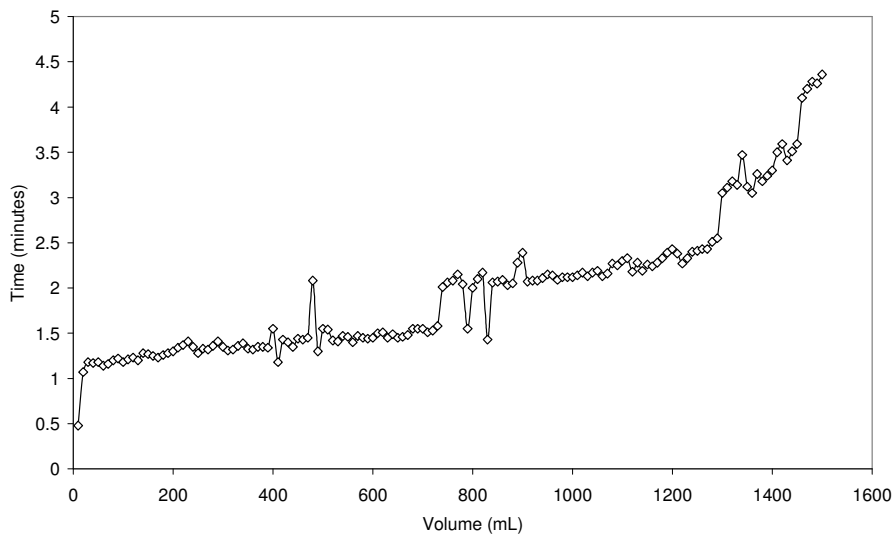


Figure 6.15. Time taken for 10 mL of Bwlch mine water to flow through 2.5 g bed of Algavi_(e) DS.

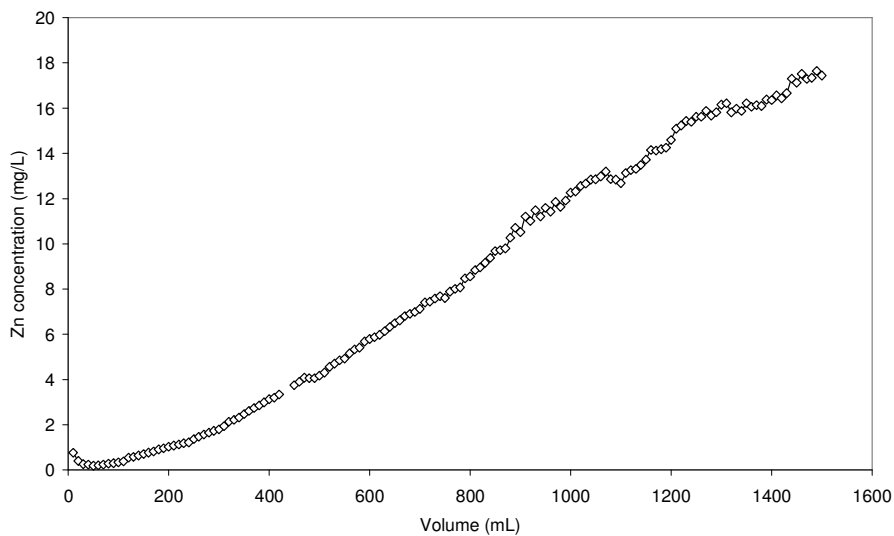


Figure 6.16. Concentration of Zn in the effluent after Bwlch mine water has flowed through a bed of 2.5 g Algavi_(e) DS. Initial concentration of Zn is 36 mg/L.

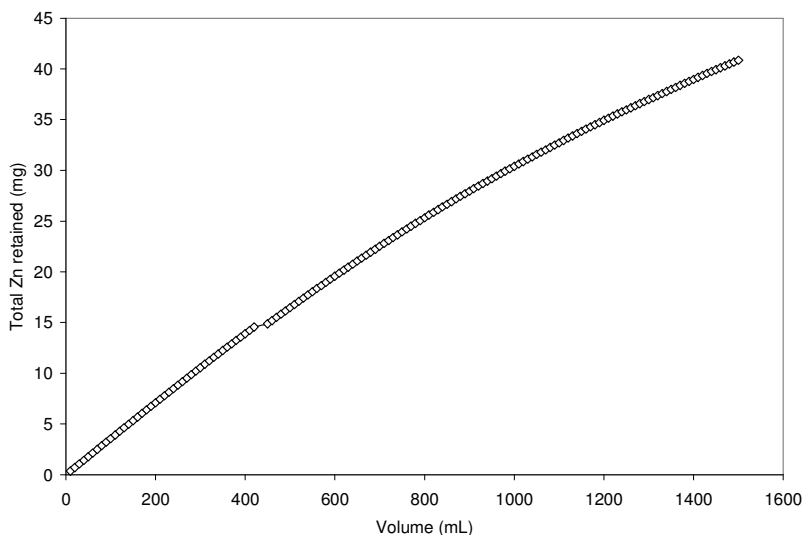


Figure 6.17. Total weight of Zn retained in 2.5 g Algavi_(c) DS from Bwlch mine water. Initial concentration of Zn is 36 mg/L.

6.5 Desorption experiments

To increase the cost-effectiveness of the biosorption process (Chu *et al.*, 1997), once the DS is saturated with metals, the metals may be removed (desorbed) from the DS thereby allowing the DS to be re-used. Although desorption of metals from the DS was not part of the initial aim of the thesis, a basic ‘test’ experiment was conducted to see whether the desorption of metals from DS was possible. A column (40.8 mm internal diameter) was loaded with 2.5 g Algavi_(c) DS, which had been previously saturated with Zn (unknown concentration); then increasing volumes of 0.1 M HCl (unknown flow rate) was passed through the column of DS. The eluant (the 0.1 M HCl solution after it had flowed through the saturated DS) was collected in 25 mL aliquots and analysed for Zn using AAS. Only the Zn concentration was determined because of the high concentrations and the ease and speed of analysis. Hydrochloric acid was chosen as it has been used by numerous authors (for example, Awadalla and Pesic, 1992; Chu *et al.*, 1997; Hashim *et al.*, 2000; Fiol *et al.*, 2003; Senthilkumar *et al.*, 2007) to desorb metals from various biomass types. Within these papers, the usual desorption method is to contact the acid with the saturated biosorbent in a vessel (such as an Erlenmeyer flask), though a column experiment was chosen for this experiment.

The desorption of Zn from the DS is shown in Figure 6.22 and the full set of results is shown in Appendix 9. The concentration of Zn within the eluant increased with the

volume of HCl flowing through the bed, a dramatic increase was seen after ~250 mL and after 500mL the concentration removed started to decrease. There was also a sharp increase after the DS was left overnight (~15 hours) before the continuation of the flow of HCl through the bed of DS, the concentration released continued to decrease and after 1500 mL little further Zn was released. This basic desorption experiment shows that the Zn adsorbed onto the DS can successfully be removed, the major disadvantage is the large volume of acid taken to remove the majority of the Zn. The complete removal of the Zn does not occur because the DS within the column was not fully saturated with HCl, some air pockets still occurred; this is the advantage of contacting the DS with the HCl in an Erlenmeyer flask and placing it on a reciprocal shaker (as in the batch experiments) as the DS is fully contacted with the acid.

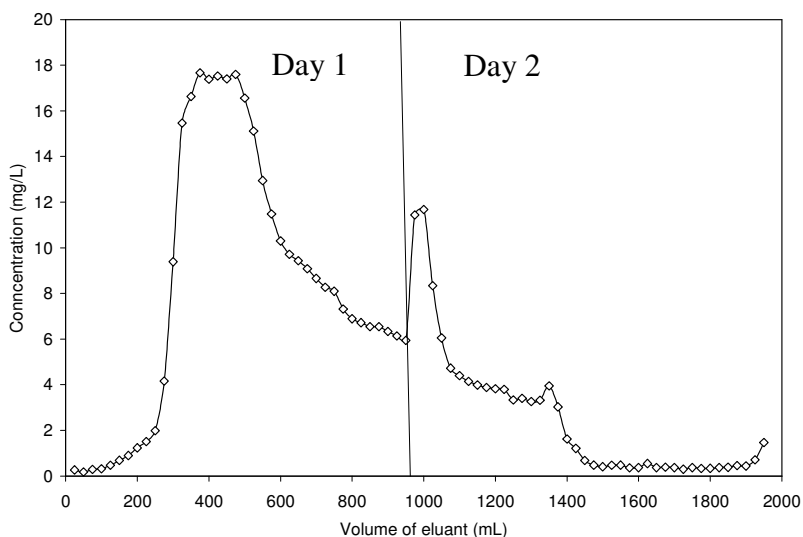


Figure 6.18. Removal of Zn from 2.5 g *Algavi*_(c) DS with increasing volumes of 0.1 M HCl.

The aim of desorption is to remove the metals from the biosorbent using the smallest volume of liquid possible. As detailed in Chapter 5.9, the smaller the eluant volume the more concentrated the metals are in solution thereby providing a greater possibility of subsequent metal recovery. Greater desorption may occur when a more concentrated acid solution is used, but care has to be taken so that the biosorbent is not damaged resulting in the loss of biosorption capacity when the biosorbent is re-used. Kuyucak and Volesky (1989b) determined that optimum desorption occurred when the eluant was between pH 2 and 3.

6.6 Discussion

6.6.1 Adsorbent type

Algavi_(c) v Algavi_(f)

The increased adsorption capacity of Algavi_(f) DS was not a result of an increased surface area, as Algavi_(f) has a smaller surface area than Algavi_(c) (1.23 m²/g and 2.79 m²/g respectively); as both DS were subjected to the same preparation and drying methods and stored in the same way, this also could not have affected the observed differences. The greater adsorption capacity of Algavi_(f) DS may have been caused by the more thorough acidification of the Algavi_(f) DS; the CaCO₃ present within the Algavi_(c) DS acted to neutralise a significant proportion of the acid, without the acid activating the binding sites on the DS surface. The more thorough acidification of Algavi_(f) removed a greater concentration of Ca and Na from the DS surface, therefore making a larger number of binding sites available for the metals ions to adsorb to. The increased metal removal by Algavi_(f) may also result from the acid washing removing some of the carbonate particles and sand, therefore in the 0.5 g DS sample, the Algavi_(f) is likely to contain a greater proportion of DS than the Algavi_(c) sample. The amount of Pb adsorbed by the DS was little affected by the presence of CaCO₃ and this may indicate that the DS has a greater affinity for this metal or that Pb is adsorbed via a different mechanism.

Girvan_(r) v Girvan_(a)

Contrary to the Algavi results, the acid washed Girvan DS (Girvan_(a)) typically adsorbed less Cd and Zn than the untreated Girvan DS (Girvan_(r)). Ramelow *et al.* (1992) determined that acid washing affected various seaweed species in different ways: pre-treating *Gracilaria conferta* and *Sargassum* species with HCl positively affected uptake capacity, but greatly reduced the uptake capacity of *Ecklonia bicyclis*. Kuyucak and Volesky (1989c) found that the uptake of Co by *Ascophyllum nodosum* was reduced by 74 % and 81 % by pre-treating the seaweed with dilute and concentrated acids respectively. The Girvan DS had already been dried before delivery and therefore the pre-treatment and subsequent drying (to produce Girvan_(a)) may have adversely affected the uptake capacity; i.e. by removing a proportion of the finer DS particles. Malik *et al.* (1999) found that thermal drying >50 °C may cause degradation of the seaweed's cellular structure. The varying uptake capacities of the two Girvan DS may also have been caused by the

differences in surface area or the number and availability of functional groups present on the surface.

Algavi v Girvan

Girvan DS has a greater adsorption capacity than Algavi DS. The surface area of the DS was not a controlling factor as Algavi DS has a larger surface area (Algavi_(f): 1.23 m²/g; Algavi_(c): 2.79 m²/g) than the Girvan DS (0.98 m²/g) and potentially possesses a greater number of functional groups (assuming that the cell wall structure of the two DS are similar); therefore the Algavi DS should removed a greater amount of metals, but this does not occur. The two DS are derived from different seaweed species: Algavi is purely derived from *Laminaria digitata* and Girvan is mostly derived from *Ascophyllum nodosum* with minor amounts of *Macrocystis pyrifera*, *Lessonia flavicans*, *Durvillea potatorum* and *Laminaria hyperborea*. Many authors have determined that various seaweed species have different adsorption capacities (Kuyucak and Volesky, 1989c; Jalali *et al.*, 2002; Hashim and Chu, 2004) and the experiments within this chapter have confirmed that these differences in adsorption capacity may still be seen in the DS, even after aggressive chemical treatment (to produce the DS and acidify the Algavi DS before use).

The differences in adsorption capacity within experiments using the same DS may be caused by the varying proportions of different seaweed species used to produce the DS (for the Girvan DS) and which part of the seaweed was used (for the Algavi DS). The differing adsorption capacity of the varying seaweed species may be caused by the difference in the composition of the alginate within the cell walls (Hamdy, 2000). Romero-Gonzalez *et al.* (2001) noted that DS (supplied by FMC BioPolymer AS, Norway) contained ~1 % alginate, which is made up of mannuronic (M) and guluronic (G) residues (Indergaard and Skjåk-Bræk, 1987). The seaweed species contain varying M/G ratios, for example *Ascophyllum nodosum*: 1.10-1.85, *Laminaria digitata*: 1.16-1.63, *Macrocystis pyrifera*: 1.02-1.56, and *Undaria pinnatifida*: 1.45-2.65 (McHugh, 2003). Those seaweeds with a higher proportion of G (i.e. a lower M/G ratio) have a greater affinity for Ca²⁺ and other divalent metals than those with a higher proportion of M (Lobban and Harrison, 1994; Volterra and Conti, 2000; Kumar and Kaladharan, 2006). The alginate remaining within the DS may cause differences in the uptake capacity; though Malik *et al.* (1999) determined that metal adsorption does not occur because of the residual alginate within the DS.

The Girvan DS was used as received (i.e. the DS was not sieved or acid washed before use) and the majority of the particles were >0.2 mm though some smaller particles also occurred; whereas the Algavi DS had been sieved and washed so that the particle size was mainly >0.18 mm; therefore the greater variation in particle size of the Girvan DS may have increased its uptake capacity. Bakkaloglu *et al.* (1998) noted that larger particles were more effective at removing Zn than powdered biomass. The presence of binding sites on the surface of the biomass allows seaweeds to be effective metal biosorbents (Vijayaraghavan and Yun, 2008); varying functional groups and their availability may cause the differences in uptake capacity between the two DS (Ramelow *et al.*, 1992). The FT-IR spectra of the two DS (Chapter 5.8.5) show that they contain varying functional groups; the Girvan DS may contain a greater number of functional groups that are more available; to confirm this, the number of sites may be determined using potentiometric titrations (detailed in Figueira *et al.*, 2000; Yun *et al.*, 2001; Yun, 2004). Different production methods may have been used to extract the alginate from the parent seaweed (Chapter 5.8.1) and this may also have altered the uptake capacity of the DS.

6.6.2 Time experiments (Algavi_(f) DS)

The majority of adsorption occurred within 15 minutes with >80 % Zn, Cd and Pb removed from solution, which is comparable to that determined by Kuyucak and Volesky (1989a); after this rapid uptake the rate slowed down and after ~60 minutes the removal of Cd was stable (~180 minutes for Zn and Pb) when using Bwlch mine water. This fast-slow adsorption has also been seen by numerous authors (Xue *et al.*, 1988; Chen and Wang, 2001; Yu *et al.*, 2003; Kumar and Kaladharan, 2006); Volesky and Holan (1995) and Yu *et al.* (2003) determined that this was caused by a fast surface adsorption and after saturation of the surface, the removal rate slows down as the metal ions diffuse to binding sites within the interior of the biosorbent particle.

Increased metal adsorption with increasing concentration

Esgair Hir contains the lowest concentration of metals of all the mine water studied and shows the lowest adsorption, in agreement with Puranik *et al.* (1999) who found that metal adsorption increased with an increased initial metal concentration. The lower metal adsorption may be caused by Fe interference (the concentration was not measured during the experiments but the average concentration of the Esgair Hir mine drainage was 0.43

mg/L between January 2004 and 2006). Kuyucak and Volesky (1989a) found that the presence of Fe caused a slight decrease in the adsorption capacity of Co by *Ascophyllum nodosum*, though Figueria *et al.* (1997) determined that the presence of Fe severely affected the uptake of Cd onto *Sargassum* species, with the effect of the Fe decreasing with increasing Cd concentrations.

The time required to achieve maximum adsorption is critical to the design of a treatment plant, with a rapid process being more likely to be considered for an industrial scale-up. A fast biosorption process will affect the volume that it is possible to treat (Williams and Edyvean, 1997b). The majority of adsorption occurs within 15 minutes and in a real treatment situation it has to be taken into consideration whether there are any additional advantages in contacting the biosorbent for a longer reaction period (i.e. 60–120 minutes to achieve over 90 % adsorption) therefore being able to remove an increased amount of metals from a smaller volume of waste water; or whether to treat a larger volume of solution but producing an effluent with a slightly higher metal concentration. In this case, the treatment plant may require a second treatment stage further decreasing the element concentration, especially when EQS concentrations are sought. As mentioned above, lower adsorption occurs with lower initial metal concentrations, therefore lower concentrations entering the second treatment plant will be more difficult to remove; this may have design implications for the treatment plant i.e. a larger treatment plant may be required containing a larger amount of biosorbent or a longer contact period between the DS and the waste water.

Bwlch v Synthetic Bwlch mine water

The experiments showed that the additional presence of Mg, K and Ca in the Bwlch mine water did not adversely affect the metal adsorption (when compared to the adsorption of metals from Synthetic Bwlch mine water); this was also found by Choi and Yun (2004) and Hashim and Chu (2004) who determined that concentrations of K up to 11 g/L and Mg up to 1.3 mg/L did significantly effect metal ion uptake. Therefore, the relatively low concentrations of Na, Mg, K and Ca contained within the Bwlch mine water should not cause a reduction in metal adsorption. Numerous authors, however, determined that the presence of Ca (de Franca *et al.*, 2002; Schiewer and Volesky, 1997b) and Na (Schiewer and Wong, 2000; Fiol *et al.*, 2003) in solution reduced the metal uptake by various biosorbents.

Cwm Rheidol pH 3.3 v pH 6.6

No significant differences in the adsorption capacity of Algavi_(f) DS was found when it was reacted with acidic and circum-neutral synthetic Cwm Rheidol mine waters. This is comparable to findings by Wilson and Edyvean (1993a), Williams and Edyvean (1997b) and Romero-Gonzalez *et al.* (2000) who determined that DS adsorbs metals over a wide pH range (between 2 and 7).

6.6.3 Weight experiments (Algavi_(f) DS)

The increasing weight of biomass increased the amount of Zn, Cd and Pb removed from solution. Over 79 % of the Cd had been removed from Bwlch mine water using only 0.1 g DS and had been completely removed (to below detection limit) by 0.5 g DS. The amount of Zn and Pb removed increased with increasing weight, though after 0.5 g (to a maximum of 1 g) no significant increase in metal removal occurred. This increase in removal with increasing biomass weight could be related to the increase in major cation release with increasing biomass weight, for example, 0.5 g DS released ~50 mg/L Ca and 1 g DS releases ~100 g DS. These findings are in direct contrast to Williams and Edyvean (1997b) who found that concentrations of residual metals in solution (from an initial Ni concentration of 100 mg/L) increased with an increasing weight of biomass. This decrease in removal with increasing biomass weight was attributed to crowding effects, where the active sites on the biomass became obscured or temporarily unavailable to metal binding. Wilson and Edyvean (1993a) and Williams and Edyvean (1997b) both concluded that the optimum biomass loading was between 0.1 and 0.5 g per 50 mL of solution with metal concentrations less than 100 mg/L. The low DS weight required for optimal adsorption has major advantages if it were to be used in as a remediation method, because the cost (and size) of the treatment plant is reduced.

6.6.4 Concentration experiments (Algavi_(f) DS)

The presence of additional metals (Cd and Pb) slightly affected the uptake of Zn, but additional metals in solution did not affect the uptake of Cd and Pb. Chen and Wang (2001) found that competition effects were important for Zn, but less significant for Cu and Pb. Aderhold *et al.* (1996) found that the presence of additional metals (within two- and three-metal solutions) at 10 mg/L did not significantly affect the uptake capacity and Wilson (1993 cited in Aderhold *et al.*, 1996) found that no competition between metals

occurred at concentrations ≤ 100 mg/L. Antoniadis and Tsadilas (2007) also found that the suppressive affect of additional metals in solution was only evident at higher concentrations. At low metal concentrations equilibrium had not been reached and therefore little competition between the ions occurred; competition between the metals only occurs when binding sites are saturated (Aderhold *et al.*, 1996; Antoniadis and Tsadilas, 2007). Many authors (da Costa *et al.*, 1996; Lister and Line, 2001), however, have found that additional metals in solution decreased the uptake of the individual metal, with the additional metals in solution competing for the limited number of binding sites, thus reducing uptake (da Costa *et al.*, 1996; Kumar and Kaladharan, 2006).

Metal affinity

The above experiments have shown that metal ions are not adsorbed at the same rate or in the same concentrations, with DS showing a greater tendency to adsorb $Pb > Cd > Zn$ with increasing concentrations (also seen in Algavi_(c) and Girvan DS). This order is in agreement with other biosorbents, including paper mill waste, sewage sludge (Lister and Lime, 2001), *Rhizopus arrhizus* and *Sargassum fluitans* (Suh and Kim, 2000). Most authors have also found that Pb is more strongly adsorbed than either Cd or Zn (Mattuschka and Straube, 1993; Wilson and Edyvean, 1993a; Kuyucak and Volesky, 1988c; Bustard and McHale, 1998; Romero-Gonzalez *et al.*, 2000) and that Cd is more strongly adsorbed than Zn (Schiewer and Volesky, 1996; Kratochvil and Volesky, 2000; Valdman and Leite, 2000; Nigro *et al.*, 2002). Metal ions show different affinities for varying functional groups and therefore there will be a certain degree of metal selectivity by the biosorbent (Stirk and van Staden, 2000; Volesky, 2001; Ramelow *et al.*, 1992).

When considering metal adsorption, the hard/soft, acid/bases theory (Pearson, 1963) has to be taken into consideration (Muter *et al.*, 2002). Pearson's classification divides elements into three main groups on the basis of the element's chemical co-ordination characteristics: Class A (hard ions) include Na, Mg, K and Ca which preferentially form complexes with ligands, which have O₂ as donor atoms (known as hard ligands) such as OH⁻, SO₄²⁻, NO₃⁻ and carboxylates by ionic forces; Class B (soft ions) include Cu, Hg and Cd which preferentially form complexes with ligands of decreasing electro-negativity (soft ligands) by covalent forces; and borderline (or intermediate) ions include Co, Ni, Zn and Pb which have both class A and B properties (Pearson, 1963; Tsezos *et al.*, 1996; Jeon *et al.*, 2002; Muter *et al.*, 2002). According to Pearson's theory, the carboxyl functional groups (which

are the main functional groups responsible for the metal adsorption onto the DS) are classified as hard ligands, which should prefer hard ions. However, the hard ions (Na, Mg, K and Ca) were not adsorbed from solution; Zn and Pb are intermediate ions and Cd is a soft ion; therefore the high selectivity of these ions can not be explained the hard/soft, acid/base theory. The affinity of a metal to the biosorbent may be controlled by the element's atomic weight, atomic number, ionic radius, electro-negativity, hydraulic radius and its co-ordination number (Kuyucak and Volesky, 1988b; Volesky and Holan, 1995; Figueira *et al.*, 2000; Jeon *et al.*, 2002). The affinity of the metal to the biomass was found to increase with atomic weight (Figueira *et al.*, 2000), atomic number (Volesky and Holan, 1995) and ionic radius (Kuyucak and Volesky, 1988b) and this confirms the findings of these experiments. Malik *et al.* (2002) determined that electrostatic interactions between Pb ions and carbonyl-oxygen atoms (in the un-dissociated carboxylic group) may be responsible for the greater selectivity of Purolite C104 (exchange resin); therefore an adsorbent with an increased amount of carbonyl-oxygen atoms may have a preference for Pb.

6.6.5 Ion exchange

The release of ~35 mg/L Ca from 0.5 g Algavi_(f) when reacted with 50 mL MilliQ water showed that the high initial release of Ca must be a simple release of Ca, rather than via ion exchange; as mentioned above, the seaweed within the alginate production process is known to undergo a Ca-dewatering process (Williams and Edyvean, 1997a). The concentration of Ca released into solution is also dependent on how thoroughly the DS had been washed, with both water and dilute acid. The straight line relationship between the metal adsorbed and the Ca released is also shown by Kuyucak and Volesky (1989c), Crist *et al.* (1990), Williams and Edyvean (1997a), and Romero-Gonzalez *et al.* (2001). If the relationship is not 1:1 then other metal removal mechanisms may be responsible (Choi and Yun, 2004) which may include complexation, physical adsorption or micro-precipitation (see Chapter 5.5).

6.7 Summary

Batch experiments determined that the three DS have different adsorption capacities, with Girvan DS adsorbing a greater amount of metals than Algavi_(f), which in turn adsorbs more

than Algavi_(c). The surface area of the DS does not control the amount of biosorption that occurs. The species of seaweed that the DS is derived from is likely to have a greater control, with the surface of the DS containing different numbers, types and availability of functional group. The particle size of the DS and the chemical and physical treatment of the DS may also have an affect. Acid washing Algavi DS increased the amount of biosorption that occurred, though it has the opposite effect on Girvan DS. This result is very positive because the untreated Girvan DS has the greatest adsorption capacity and does not require time-consuming and costly pre-treatment.

Algavi_(f) was used for the remaining experiments because of difficulties in obtaining large quantities of Girvan DS. Over 90 % of Zn, Cd and Pb adsorption occurred within 30 minutes of contact between the DS and mine water, therefore subsequent experiments were run for 30 minutes. The adsorption showed a fast uptake and as the surface sites become saturated the removal rate slowed down as the metal ions diffuse into the interior of the biosorbent. Neither additional metal ions in solution nor the solution pH (comparing similar mine waters with a pH of 3.3 and 6.6) caused a reduction in the adsorption capacity of the DS. The optimum weight of DS was 0.5 g for 50 mL experiments and an increase in weight of DS used did not significantly increase the concentration of metals removed from solution. The DS does not have the same affinity for the different metals with Pb being preferentially adsorbed followed by Cd and then Zn; this may be caused by the relative atomic mass and radius. The metal removal is mainly an ion exchange phenomenon as when metal ions are adsorbed and Ca is released. There is, however, a release of Ca ions when the DS is contacted with MilliQ water, caused by the washing off of the Ca from the DS (a result of a Ca-dewatering process in the alginate processing industry). The Ca release and metal adsorption is not a 1:1 relationship and therefore additional removal mechanisms may also be occurring.

These experiments show that DS fulfils the criteria required for it to be suitable for use as a biosorbent, i.e.:

- low cost material and readily available;
- a fast removal rate;
- requires a low biomass weight to achieve optimum metal ion removal;
- it can remove low concentrations of metals (<100 mg/L);

- it does not require additional chemicals (other than washing with dilute acid);
- sludge, which would require disposal, is not produced;
- the presence of additional metals and major cations do not reduce the uptake capacity;
- the metal ions can be desorbed from the biomass using dilute HCl; and
- the larger size of the DS particles means that it can be easily separated from solution.

The ability of the DS to remove metals in a real treatment situation is explored in the subsequent chapters.

CHAPTER 7:

Mid-Wales Field Trials

There has been a great deal of research focussing on the biosorption phenomenon, but the majority of this has been laboratory based (Butter *et al.*, 1998; Gadd, 2001). The use of dealginated seaweed (DS) as a biosorbent has previously been only applied within a laboratory environment (Aderhold *et al.*, 1996; Williams and Edyvean 1997a; 1997b; Malik *et al.*, 1999; Esteves *et al.*, 2000; Romero-Gonzalez *et al.*, 2000; 2001). These papers have shown the adsorption mechanisms and the maximum adsorption capacity of the DS, but such experiments are difficult to extrapolate to actual applications within real treatment situations (Wilde and Benemann, 1993). Within a real treatment situation the biosorbent has to deal with varying metal concentrations; combinations of metals and organic materials; water and air temperature variability and changing pH values. Within this research the demonstration scale treatment plants will determine the durability of the biomass i.e. whether it degrades over time and whether it is subject to algal, bacterial or fungal growth, as well as proving the adsorption technique in a real mine water remediation situation.

Despite the evident potential of biosorption and the increase in published research on biosorption, there has been little or no exploitation in an industrial context and the few commercial applications that have been developed have had only limited success (Butter *et al.*, 1998; Gadd, 2008). The commercial biosorbents which have been developed include:

1) AMT-Bioclaim™ (Brierley, 1990 cited in Gadd, 1990; Kuyucak, 1990; Veglio and Beolchini, 1997; Edyvean *et al.*, 1997; and Volesky, 2003) where biomass *Bacillus subtilis* (by-product from a fermentation process) was been subjected to heat and alkali treatment (a strong caustic solution), immobilised using polyethyleneimine and glutaraldehyde, dried and then sieved. The material is suggested for use in packed beds or fluidised pulsed beds (for larger flows) and it is claimed to be capable of removing >99 % of Au and Cu in solution.

2) AlgaSORB™ where *Chlorella vulgaris* (freshwater algae) can effectively remove metals from dilute solutions (1-100 mg/L) to <1 mg/L; Ca and Mg within the waters do not affect the sorption capacity (Kuyucak, 1990).

3) BIO-FIX using immobilised biomass in polysulfone. The types of biomass used include sphagnum moss, algae, bacteria and aquatic flora (Veglio and Beolchini, 1997; Stirk and van Staden, 2000).

Two other commercial biosorbents are MetaGeneR and RAHCO Bio-Beads which have been shown to be effective for removing the metals from electroplating and mining waste waters (Atkinson *et al.*, 1998). The limited success of these biosorbents is caused by the competition with ion exchange media (Gadd, 2004), i.e. the cost, specificity and robustness when compared to ion exchange resins, activated carbon and other remediation systems (Edyvean *et al.*, 1997; Eccles, 1999).

In this study a series of treatment plants were deployed into the field to assess the behaviour of DS in real treatment situations. The treatment plants were deployed at Bwlch, Esgair Hir and Alltycrib to determine the metal removal characteristics when treating varying flows of mine water of differing composition (i.e. Zn, Cd, Pb and Fe concentrations) using the three types of DS described in Chapters 5.8.3 and 5.8.4. Mine drainage waters from Bwlch were used as they are circum-neutral and contain high concentrations of Zn (~25 mg/L), Cd (~60 µg/L) and Pb (~700 µg/L). The high Zn concentration is likely to saturate the DS in a short time period therefore providing a short-term test. Esgair Hir and Alltycrib were chosen to provide a longer-term indication of the DS behaviour as they contain lower metal concentrations than Bwlch and are more typical of mine drainage in mid-Wales. Both mine waters contain similar concentrations of metals, though Esgair Hir contains minor concentrations of Fe (<1 mg/L) and Alltycrib has a higher total organic carbon content (15.7 mg/L) than either Bwlch or Esgair Hir (3.7 mg/L and 5.5 mg/L respectively). In this chapter the performance of each of the field trials is described and then an interpretation of each system is presented.

7.1 Dealginated seaweed treatment plant

The treatment plant was designed to allow a 15 minute contact time between the DS and the mine drainage water (designed by the Chemical and Process Engineering Group at the University of Sheffield as part of the BIOMAN project). The treatment plant was built using low cost, easily available materials which could be obtained from DIY stores and

plumbing merchants. The 1 L/minute treatment plant used a Titan Plastech 4 Gallon/18 Litre capacity polypropylene feed and expansion cistern suitable for cold water storage tank (approximately 30 cm wide, 30 cm depth and 44 cm long). The treatment plant consists of two tanks, which stack one inside the other, see Figure 7.1 and 7.2. The base of the inner tank is perforated with 1.5 cm diameter holes to allow the mine water to flow into the outer tank. At the base of the inner tank is a sheet of perforated stainless steel with 4 mm diameter holes, covered with a nylon mesh (0.18 mm pore size) and then ~2 kg DS (dry weight); the DS is then sandwiched with an upper layer of nylon and stainless steel mesh. The mesh contains the DS and disperses the mine water to inhibit the formation of flow paths through the DS bed. Before entry into the plant, the mine drainage water is collected in a reservoir at Bwlch (Figure 7.3) or a header tank at Alltycrib or Esgair Hir (see Figure 7.4); this water is then piped (via a length of reinforced PVC pipe, internal diameter 30 mm) into the treatment tank. The flow rate is controlled via an inflow control which is set between horizontal (preventing the majority of the mine water entering the treatment plant) and vertical (allowing the majority of the mine water to enter the treatment plant). The mine water enters the treatment plant through a distribution pipe, which disperses the mine water through a series of small holes. A head of water is kept above the DS; any excess water flows back into the water course. When the mine water passed through the DS bed it collected in the outer tank, and eventually overflows, via an outlet pipe, back into the water course. The angle of the outflow pipe also controlled the head of water above the DS and the residence time of mine water within the system.

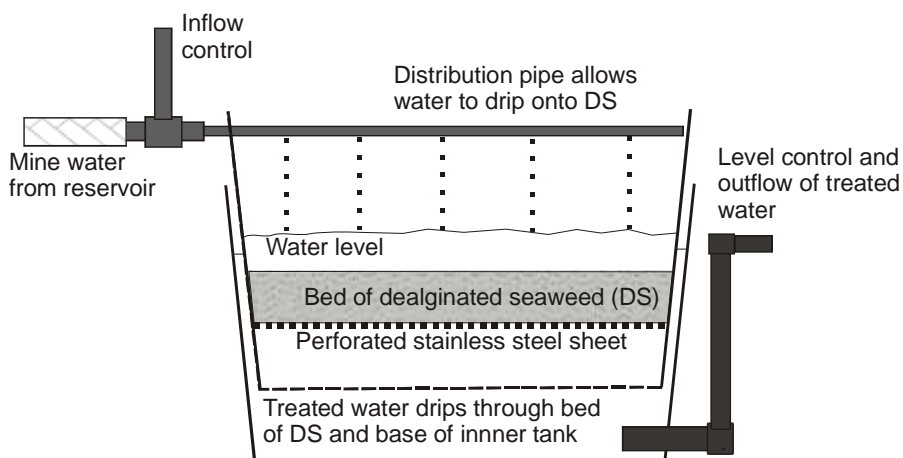


Figure 7.1. Schematic of the 1 L/minute treatment plant.

From: Pearce *et al.*, 2007

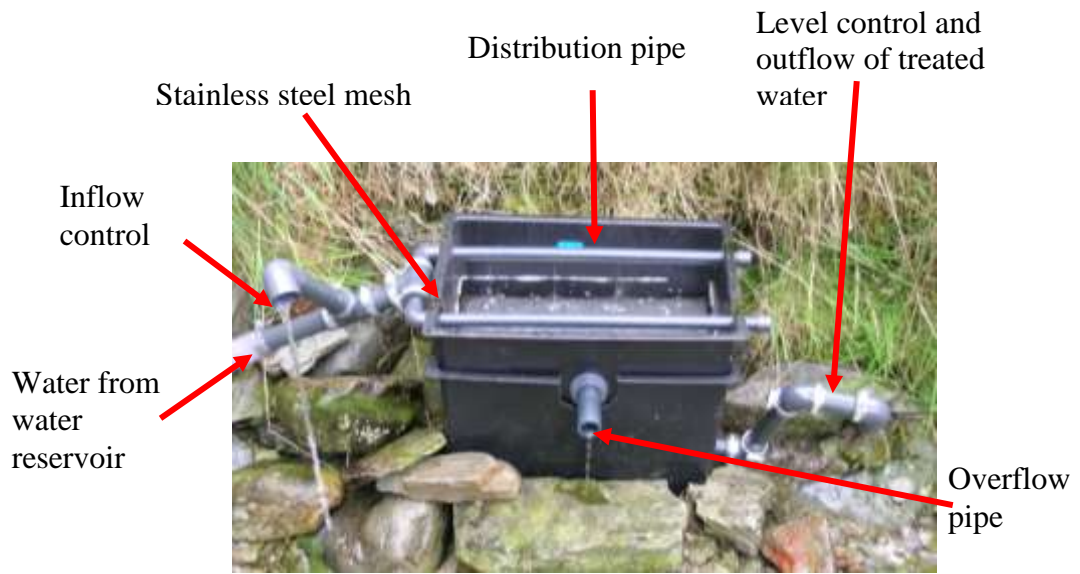


Figure 7.2. 1 L/minute treatment plant at Bwlch.

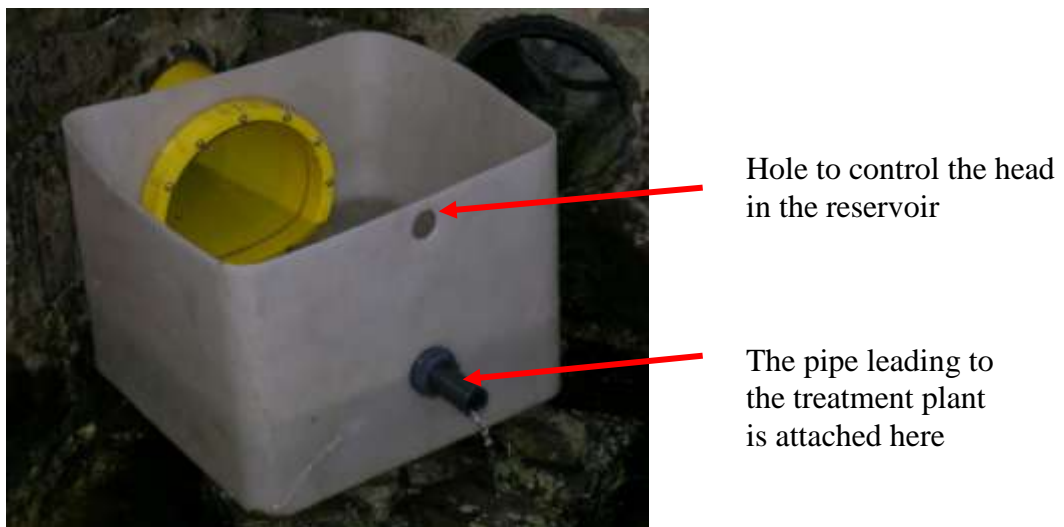


Figure 7.3. Water reservoir at Bwlch.



Figure 7.4. Header tank at Esgair Hir.

Once the treatment plant was installed, the flow was allowed to stabilise for ~20 minutes before the first sample was taken. Normally, three samples were taken of the inlet and outlet waters within the first hour of operation, samples were then collected once a day until adsorption ceased. The waters were sampled and analysed according to the methods given in Chapter 3. The full set of results is presented in Appendix 10. Once the DS within the treatment plant ceased to adsorb any of the studied metals, the treatment plant was removed from the field, the DS bed was removed and the treatment plant was thoroughly washed, acid rinsed and air-dried before being re-deployed at another site.

7.1.1 Dealginated seaweed digestion

Once the treatment plant was removed from the field, cores were taken through the DS bed to determine the distribution of metal ions and major cations through the core. The cores, typically ~100 mm in thickness, were divided into ~1 cm thick sections and digested as follows:

- Dry at 70 °C.
- Weigh into labelled Erlenmeyer flasks.
- Add 100 mL 10 % HNO₃ (v/v), cover with a watch glass and heat at 60-70 °C overnight.
- Increase heat to 110-120 °C for a few hours.
- Remove watch glass and allow to evaporate.
- Add 20 mL concentrated HNO₃, swirl, cover and heat to 110-120 °C overnight until brown fumes are produced.
- Remove from the heat and allow to cool, add 2 mL 100 volumes H₂O₂.
- Heat to 100 °C.
- Repeat the above two steps until the solution is clear, if this does not occur add 20 mL aqua regia (15 mL concentrated HNO₃ and 5 mL concentrated HCl), heat to 150°C and leave overnight. Remove from the heat and add 5 mL 100 volume H₂O₂, make up to 100mL with MilliQ water and leave at 150 °C overnight.
- Remove from heat and allow to cool.
- Filter through a Whatman[®] number 1 filter paper into a 250 mL volumetric flask and make up to volume with MilliQ water.

Any insoluble residues that remain after the solution has been filtered are most likely to be hydrated silicates (which are soluble in hydrofluoric acid) (Edginton *et al.*, 1970). The full set of results are shown in Appendix 11.

The concentrations of elements within each core are displayed as the total of weight of each element within each layer i.e. if the treatment plant contained 3 kg DS at a depth of ~100 mm and then the core was divided into 10 mm sections each section layer would contain 0.3 kg. The total weight of the element within each 10 mm layer was calculated by:

$$a - b \left(\frac{vol}{wt_d} \right) * wt_l \quad (7.1)$$

Where:

a = the element concentration in the digested solution (μm)

b = concentration in the blank sample (μm)

vol = volume of the sample (i.e. 250 mL)

wt_d = weight of the digested DS (g)

wt_l = weight of the DS layer in the treatment plant (kg)

7.2 Bwlch 1 L/minute

A 1L/minute treatment plant (see Figure 7.5), containing ~3 kg Algavi_(c) DS (dry weight) was deployed at Bwlch (see Figure 7.6) between the 13th September and 4th October 2005. The removal of Zn, Cd, Ba and Pb from Bwlch mine drainage water is shown in Figures 7.7 and 7.8, a negative percentage indicates the metal ions are being released back into solution.

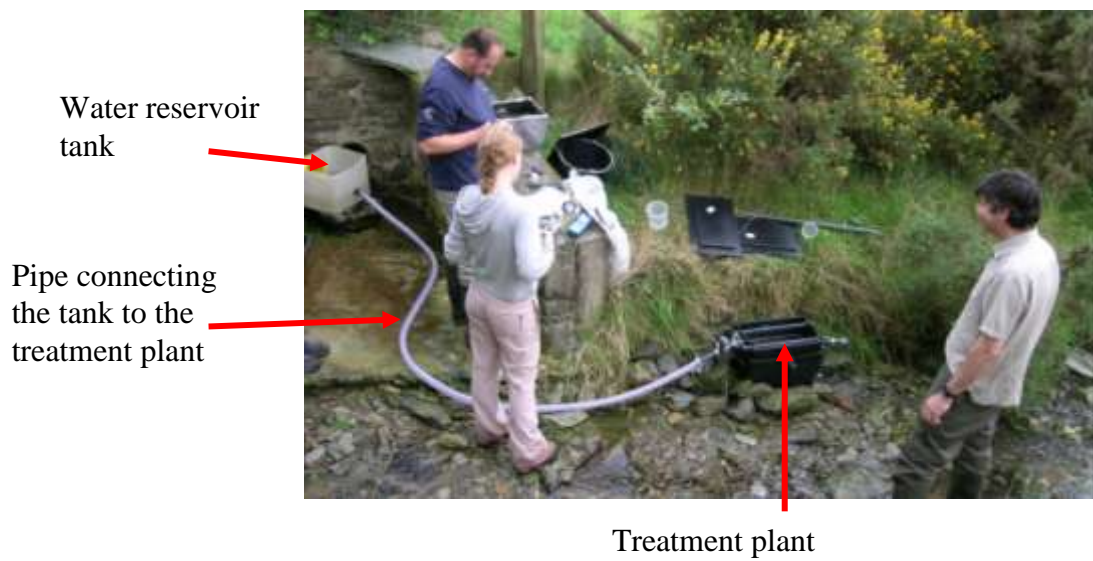


Figure 7.5. Bwlch treatment plant set-up.

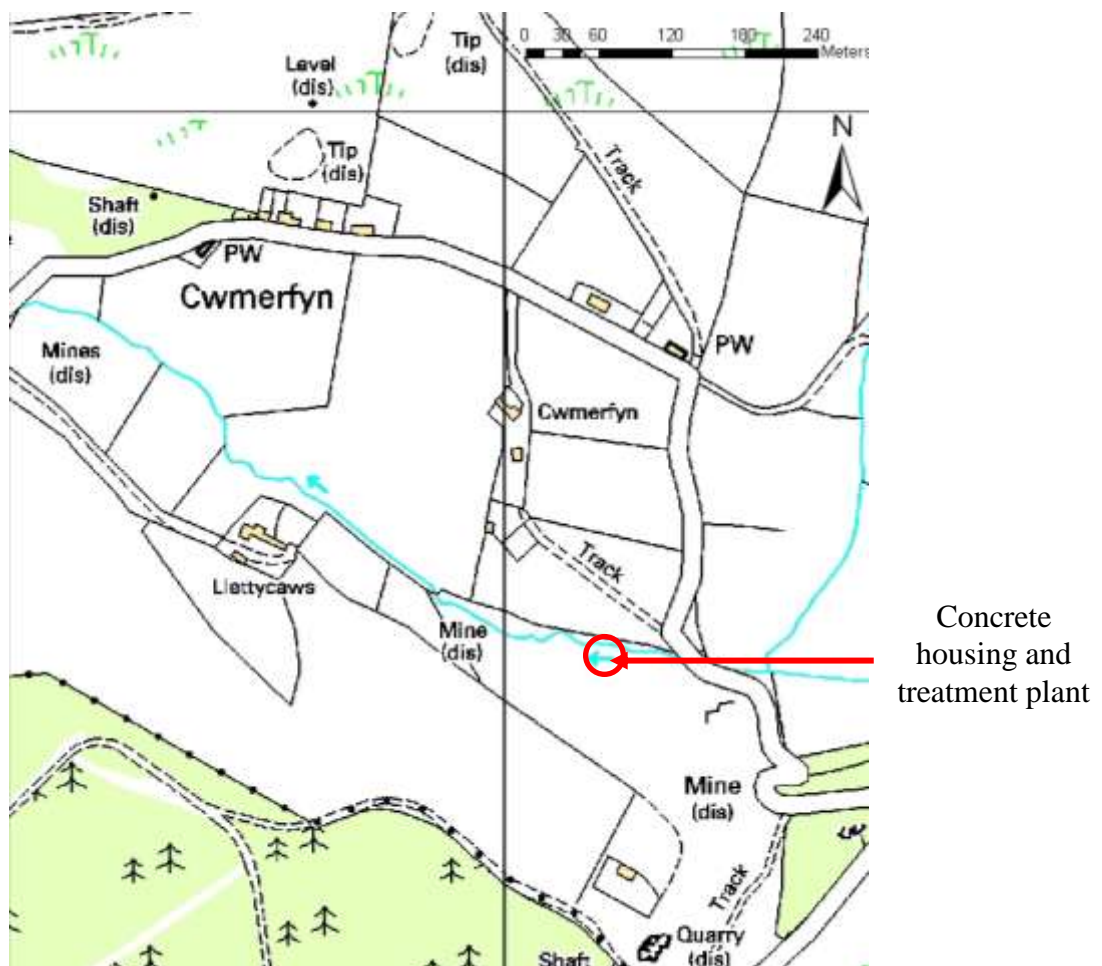


Figure 7.6. Location of the Bwlch treatment plant.

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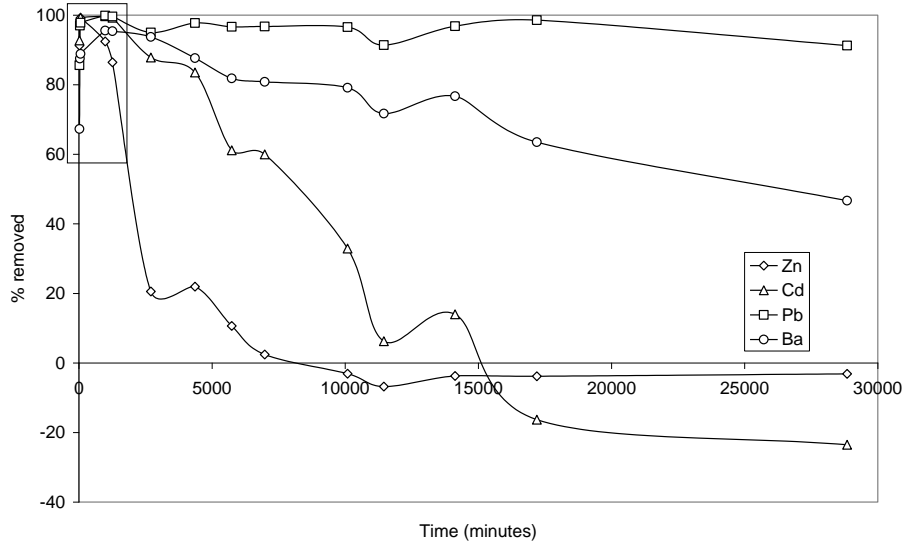


Figure 7.7. Removal of Zn, Cd, Ba and Pb from 1 L/minute Algavi_(c) DS treatment plant at Bwlch. Average inlet concentration: Zn ~25 mg/L, Cd ~64µg/L, Ba ~24 µg/L and Pb ~700 µg/L. The highlighted area is enlarged below.

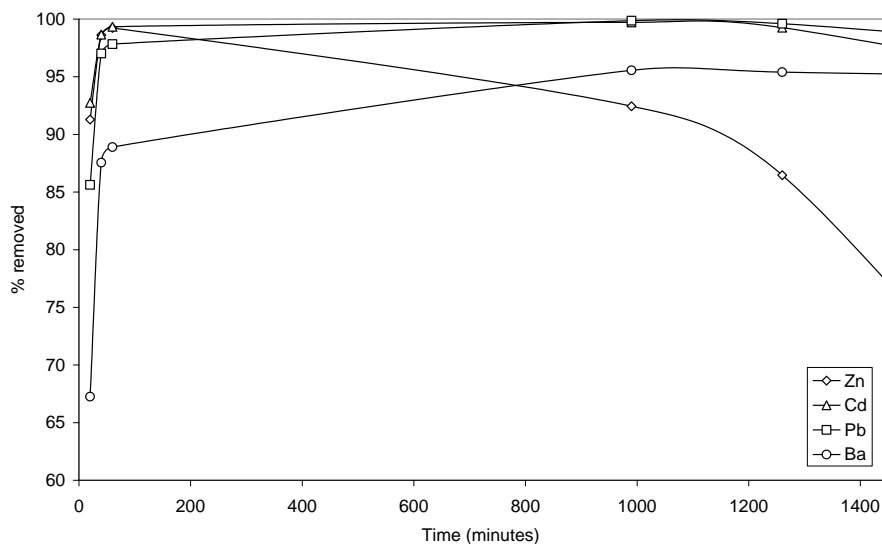


Figure 7.8. Removal of Zn, Cd, Ba and Pb from 1 L/minute Algavi_(c) DS treatment plant at Bwlch during the first 1440 minutes (24 hours). Average inlet concentration: Zn ~25 mg/L, Cd ~64µg/L, Ba ~ 24 µg/L and Pb ~700 µg/L.

During the first hour of operation the metal removal increased and Cd, Zn and Pb peaked at ~98 %, but only ~90 % Ba was removed; the removal of Ba then increased and peaked at ~95 % after 990 minutes (~16 hours). After the first hour the removal of Zn started to decrease, though after 24 hours the DS bed still removed over 75 %; Zn ceased to adsorb after ~ 8000 minutes (~5 days) and then the Zn began to be released back into solution. The DS continued to adsorb ~98 % of Cd until ~1260 minutes (21 hours) after which the Cd removal started to decrease; when the DS becomes saturated with Zn ~52% Cd was

still being removed, Cd ceased to be adsorbed after ~15500 minutes (~11 days) then Cd started to be re-released. Barium also continued to be adsorbed (~95 %) until ~1260 minutes (21 hours) when the removal started to decline. Lead continued to be removed at >90 % for the duration of the field trial (~20 days). At the end of the field trial (after ~20 days) neither Ba nor Pb have reached saturation and >45 % Ba and >90 % Pb was still being removed. At this stage ~28845 L of Bwlch mine water had been treated.

The high removal seen for Zn, Cd and Pb within the first hour of treatment plant operation could be the result of ion exchange reactions in which Ca and Mg are replaced. This is illustrated in Figure 7.9 which shows that Mg and particularly Ca ions are at a higher concentration in the outflow than in the inflow. Calcium showed the largest increase in concentration (from 39 mg/L to 136 mg/L); after 4360 minutes (~73 hours) the release of Ca from the DS was more or less constant at ~8 mg/L. Magnesium showed a large increase in concentration, increasing from ~11 mg/L to ~43 mg/L, the released concentration then decreased and after ~2700 minutes (~2 days) the concentration was equal to that entering the treatment plant. The concentration of Na was more or less constant throughout the trial (at ~8 mg/L) though the first sample (at 20 minutes) showed a slight increase to ~12 mg/L; the same was true for K, which showed a slight increase in the first sample from ~4 mg/L to ~6 mg/L. The continued adsorption of Pb, and to a lesser extent Ba, may be caused by these metal ions exchanging with the Ca released from the DS and/or by the Ba and Pb exchanging with Zn and Cd causing these to be re-released into solution.

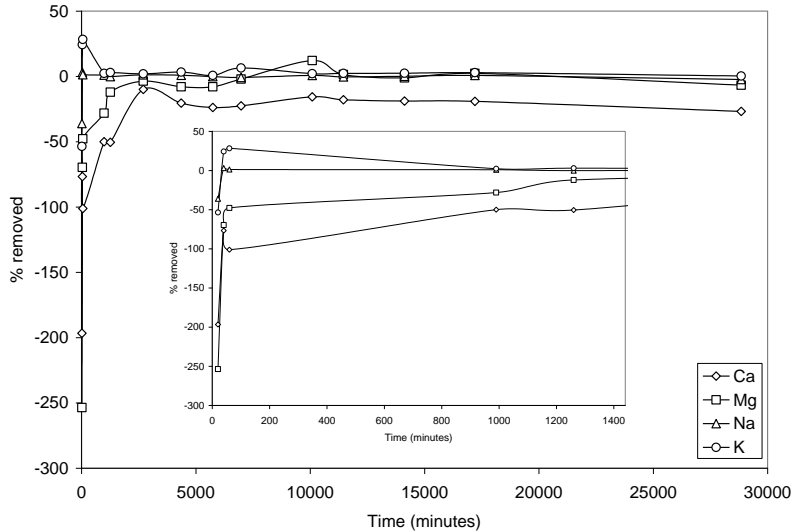


Figure 7.9. Removal of Ca, Mg, Na and K by 1 L/minute treatment plant at Bwlch using Algavi_(c) DS. Inset: first 24 hours.

Average inlet concentration: Ca ~39 mg/L, Mg ~11.3 mg/L, Na ~8 mg/L and K ~3.8 mg/L.

7.2.1 Bwlch 1L/minute DS core (Algavi_(c))

Once the treatment plant was removed from the field, two cores were taken through the DS bed (one in the centre and one at the edge) to determine the location of elements through the core, see Figure 7.10. Significant differences in the amounts of elements between the outer and inner cores may indicate that the mine water had taken a preferential flow path through the bed; the difference between the cores was minimal and therefore an average amount is shown. The DS bed was divided into 10 mm sections and digested as detailed in Chapter 7.1.1; the amount of elements in each of these layers (calculated using equation 7.1) are shown in Figures 7.11 and 7.12; the calculation assumes that no loss of DS occurs during the operation of the treatment plant.



Figure 7.10. The core taken from the Bwlch 1 L/minute Algavi_(c) DS bed.

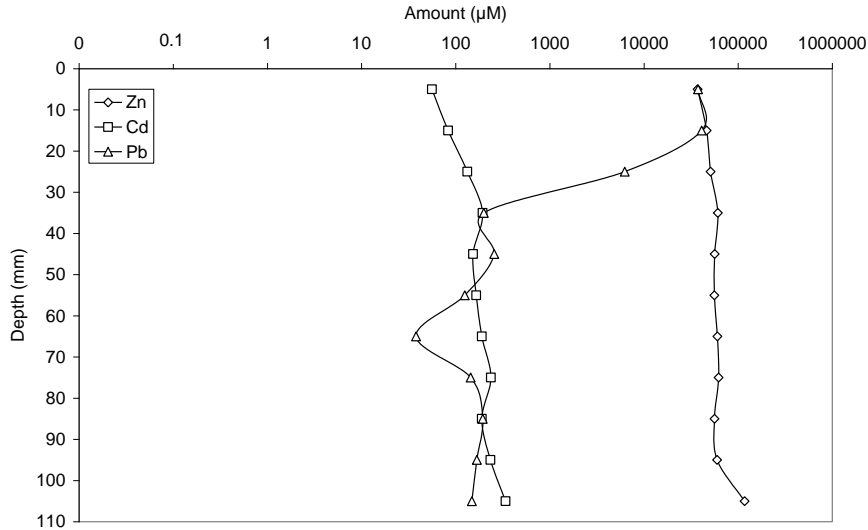


Figure 7.11. Amount of Zn, Cd and Pb (μM) within each 10 mm layer through the Algavi_(c) DS bed of the Bwlch 1L/minute treatment plant.

The marker is placed in the centre of the layer i.e. the marker at 5 mm represents the amount of the layer 0-10 mm. Note the logarithmic scale.

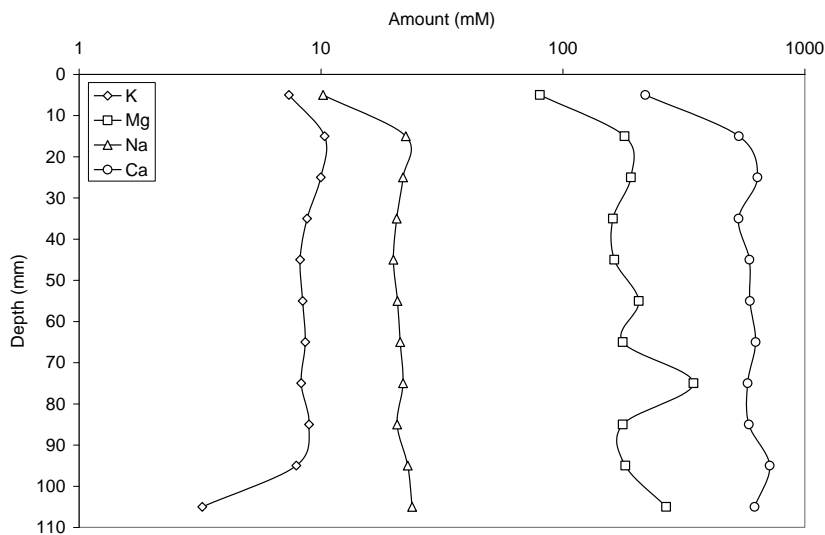


Figure 7.12. Amount of K, Mg, Na and Ca (mM) within each 10 mm layer through the Algavi_(c) DS bed of the Bwlch 1L/minute treatment plant.

The marker is placed in the centre of the layer i.e. the marker at 5 mm represents the amount of the layer 0-10 mm. Note the logarithmic scale.

The concentration of Zn and Cd contained within the DS core was relatively constant, with a slightly higher amount in the lower 10 mm; Pb, however, was concentrated within the top 20 mm. In the top 20 mm of the core, Pb and Zn had a 1:1 relationship and in the lower 80 mm Pb and Cd had a 1:1 relationship. Typically, throughout the core Zn and Cd have a ~336:1 relationship (calculated by dividing the average Zn (μM) in each core layer by the average Cd (μM) in each layer). The concentration of K, Mg, Na and Ca was relatively constant through the DS bed, although slightly lower amounts occurred within the top 10

mm and lower amounts of K also occurred within the bottom 10 mm. The amounts of Ca and Mg within the core were higher than the amounts of Na and K. The maximum amount (μm) of element within each 10 mm layer of the DS bed (~ 0.27 kg, dry weight) provides an indication of the effective capacity of the DS. The maximum amount removed from the Bwlch mine water was $\sim 56506 \mu\text{M}$ Zn, $\sim 187 \mu\text{M}$ Cd and $\sim 39226 \mu\text{M}$ Pb which equates to 13.7 mg/g (metal/DS), 0.08 mg/g and 30 mg/g (respectively), therefore the DS has twice the adsorption capacity for Pb than Zn.

7.3 Esgair Hir 1 L/minute

The 1L/minute treatment plant, containing ~ 2 kg of Algavi_(c) DS (dry weight), was deployed at Esgair Hir between the 17th October 2005 and 21st December 2005. The Esgair Hir mine drainage waters contain lower concentrations of metals than Bwlch mine drainage with minor amounts of Fe (< 1 mg/L) which is a sufficient concentration to produce ochre staining on the bed of the mine outflow. The mine water was not collected directly from the adit (see Figure 7.13), but a mine water collector tank was placed ~ 55 m down stream. The water was piped under the track into a header tank (see Figure 7.14) which fed the treatment plant, with the excess water flowing back into the stream.

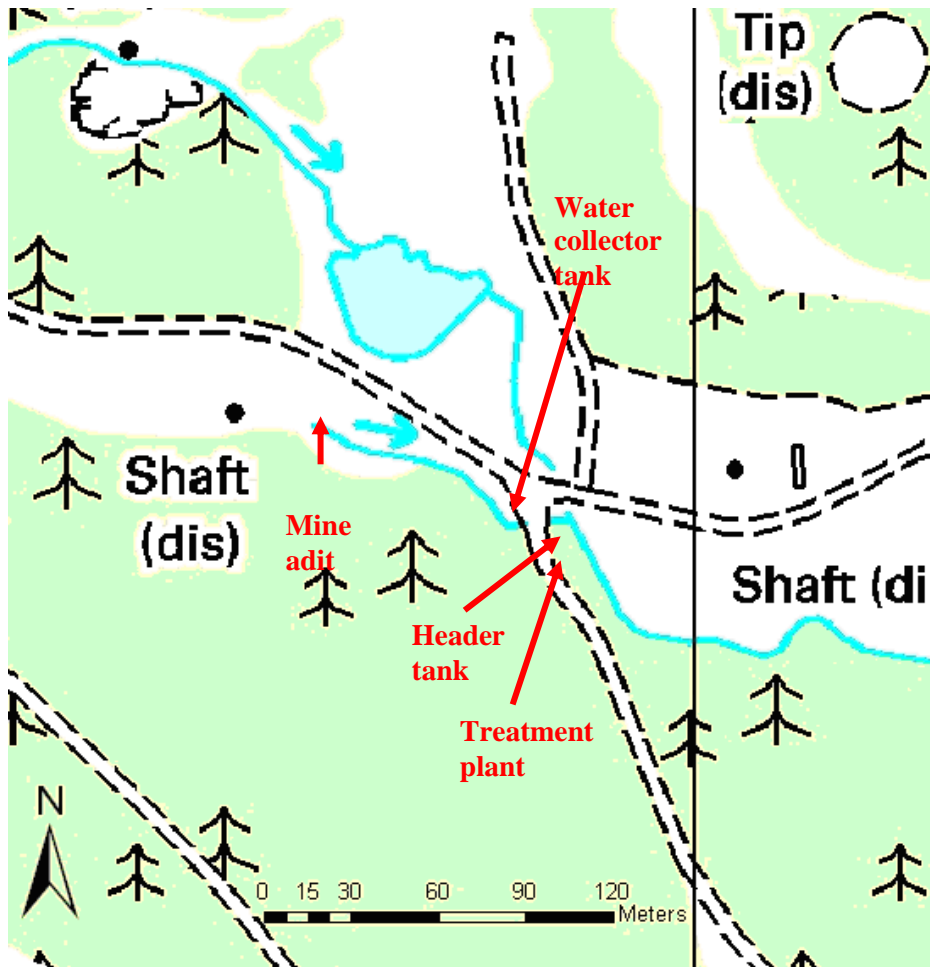


Figure 7.13. Location of the Esgair Hir treatment plant.
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Figure 7.14. Header tank for the Esgair Hir treatment plant.

The flow of mine drainage water through the DS bed was not constant over the trial period. Even though the waters contained only minor amounts of Fe (average inlet concentration during the trial was 0.19 mg/L), the Fe precipitated out of solution blocking the distribution pipe holes and coated the top of the DS bed and stainless steel mesh, see Figure 7.15a and b. After seven days the flow decreased from 1 L/minute to 0.3 L/minute; washing off the Fe from the stainless steel and plastic mesh did not increase the flow through the DS bed. The DS bed, therefore, had to be stirred by suspending the material in mine water and then allowing the DS to settle onto the mesh at the base of the tank; the ochre coating was removed and the flow reinstated.

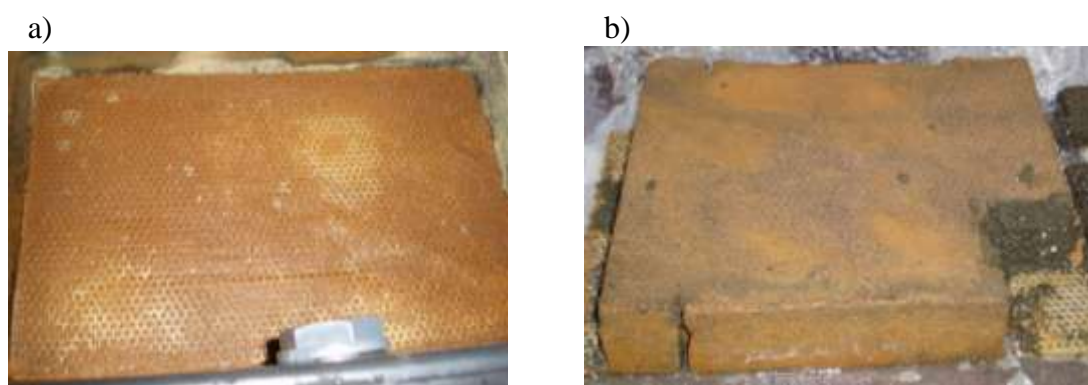


Figure 7.15. Treatment plant after removal from Esgair Hir: a) stainless steel mesh and b) dealginated seaweed.

The removal of the metals from Esgair Hir mine drainage was effective after just 5 minutes of operation (when the first sample was taken), see Figure 7.16a and b, with 48 % Zn, 67 % Cd and 75 % Pb removed from the first sample. Metal adsorption increased, peaked and was more or less constant until the DS bed was stirred (after ~15 days of operation) with ~80 % Zn, 80–100 % Cd and 80–90 % Pb being removed. After the DS had been stirred the adsorption decreased dramatically, with Zn and Pb decreasing from ~75 % removal before the DS was stirred to ~40 % 20 minutes after the DS had been stirred and then settled; after an hour adsorption increased and ~80 % of Zn and Pb was removed. Cadmium was released into solution after stirring (adsorption decreased from 96 % to -35 %) though an hour after stirring, adsorption had increased to ~70 %. After the DS bed had been stirred, it did not regain the adsorption levels measured before stirring. The adsorption then decreased, as did the flow rate and therefore the DS had to be stirred again (after ~29 days of operation); as before, the removal increased, decreased and finally after two months of the treatment plant ceased to adsorb any metals. Iron also followed the same pattern of decreasing removal after each stirring (though the concentrations were

much more variable). Over 40 % of Fe was removed after the first 5 minutes with an average of 67 % (39–100 %) before the DS bed was stirred; a large release of Fe then occurred after which the removal increased to ~66 % before the DS was again stirred and Fe was no longer removed.

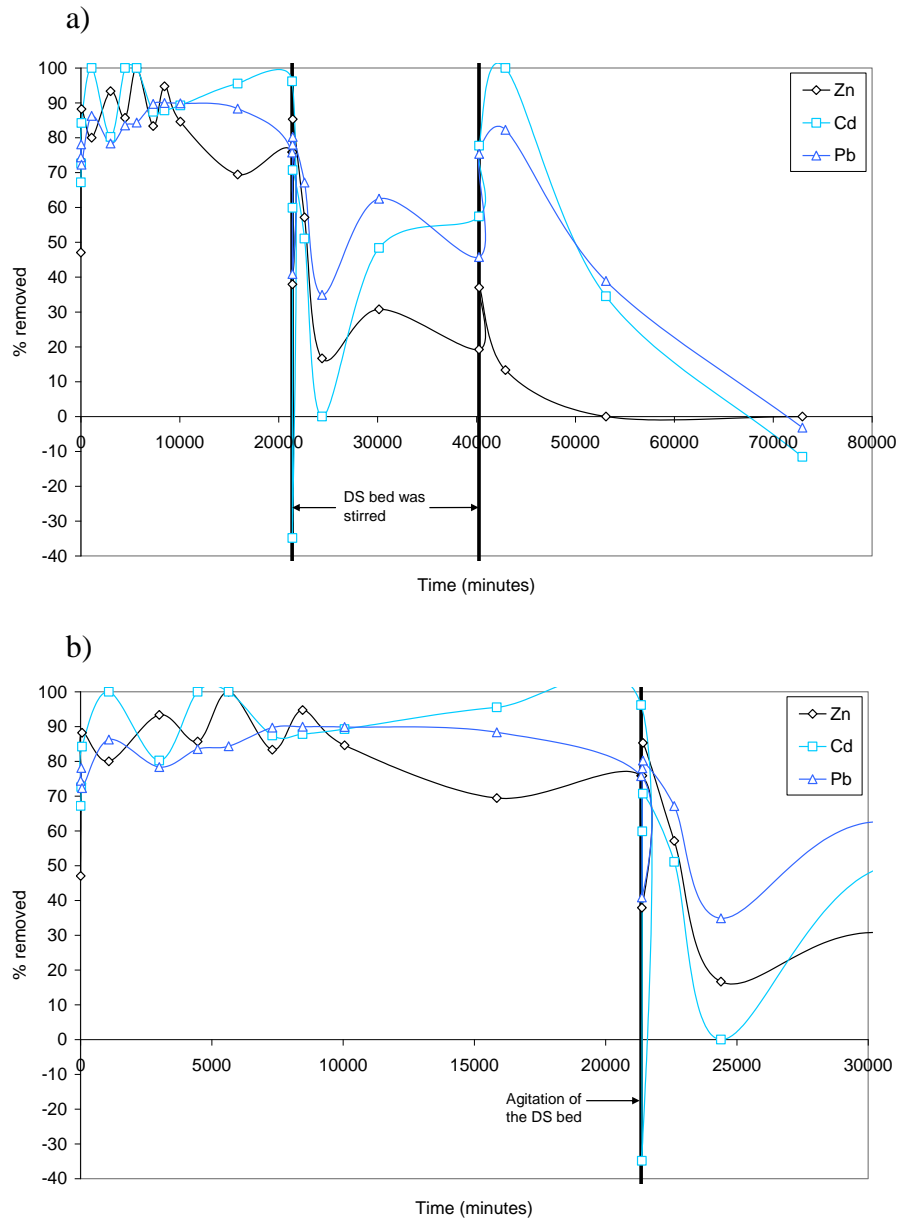


Figure 7.16. Removal of Zn, Cd and Pb by 1 L/minute treatment plant at Esgair Hir: a) over the duration of the field trail and b) first 30,000 minutes.

Black vertical lines at 21355 and 40245 minutes mark when the DS bed was stirred to remove the Fe coating. Average inlet concentration: Zn ~0.23 mg/L, Cd ~1.23 µg/L and Pb ~144 µg/L.

An increase in Na, K and Mg concentration occurred during the first hour or so of operation at Esgair Hir, caused by the wash off of the cations from the DS, see Figure 7.17. Over 39 mg/L of Ca was released after 30 minutes of operation, the amount of Ca released

then decreased and after 3000 minutes (~2 days) the concentration in the outlet water was ~9.5 mg/L. After the DS bed had been stirred, the Ca concentration in the outlet water decreased to ~6 mg/L, after the second stirring the concentration decreased again and after two months of operation the concentration in the outlet water was stable at ~3 mg/L. Even after two months of operation Ca was still being released from the treatment plant, possibly caused by the dissolution of the carbonate particles within the DS bed. The concentration of Na, Mg and K in the outlet water soon returned approximately to the same as entering the treatment plant; Na within 30 minutes; Mg concentration returned to more or less the inlet concentration after 1800 minutes (~30 hours), and K after 3000 minutes (~2 days). After stirring the DS within the treatment plant a minor decrease in concentration occurred (within analytical error) which may have been caused by the adsorption of a small amount of Na, K or Mg.

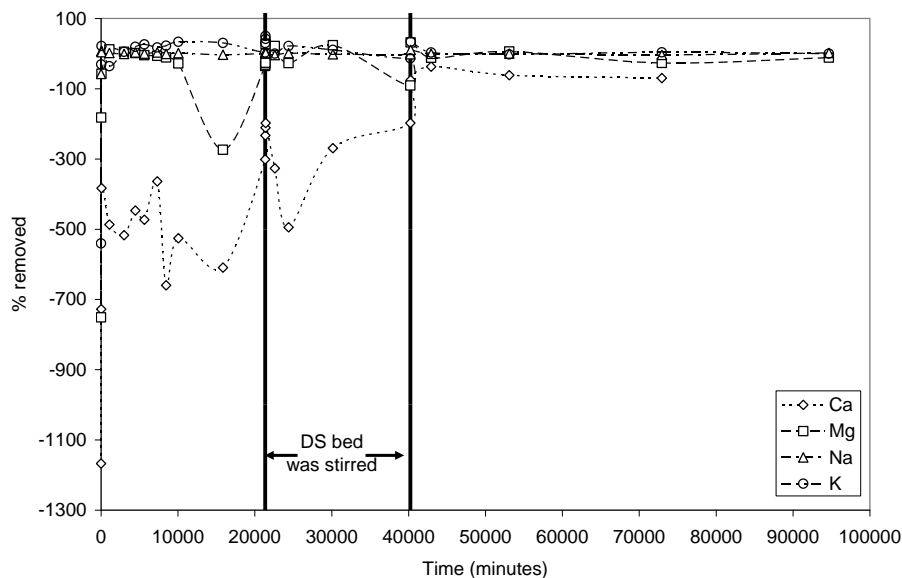


Figure 7.17. Removal of Ca, Mg, Na and K by 1 L/minute treatment plant at Esgair Hir using Algavi_(c) DS. Black vertical lines at 21355 and 40245 minutes mark when the DS bed was stirred to remove the Fe coating. Average inlet concentration: Ca ~1.85 mg/L, Mg ~1.7 mg/L, Na ~5.4 mg/L and K ~0.29 mg/L.

7.3.1 Esgair Hir 1 L/minute DS core (Algavi_(c))

Once the Esgair Hir treatment plant was removed from the field, the DS bed was cored and digested as detailed in Section 7.1.1. The amount of elements through the core of the DS bed is shown in Figure 7.18. The amounts (mM) of Na, K and Zn through the DS core were variable, but have an approximate 1:1:1 relationship. All the analysed elements show a lower amount in the upper 10 mm, then variable amounts throughout the rest of the bed. The effective capacity (the maximum amount adsorbed by a 10 mm layer of DS (0.286

kg)) is ~12.4 mM which gives 2.8 mg/g (Zn/DS), which is much lower than that found in the Bwlch Algavi_(c) core (13.7 mg/g).

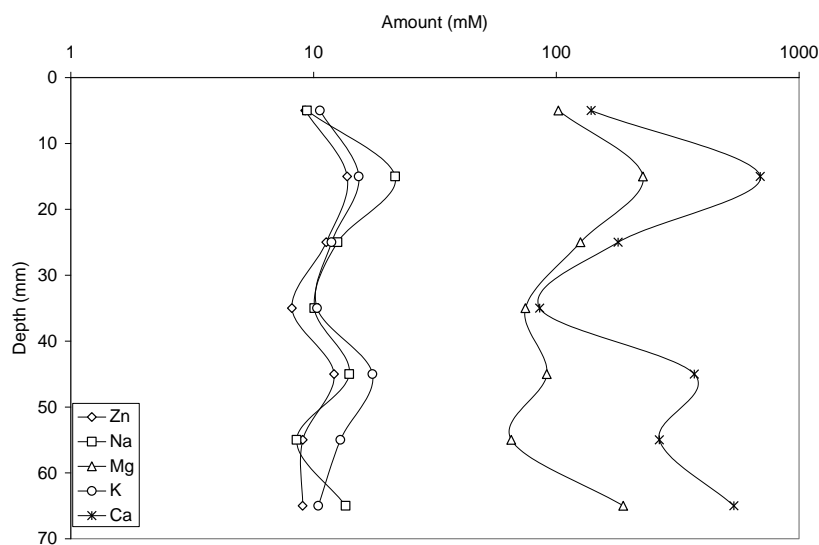


Figure 7.18. Amount of Zn, Na, Mg, K and Ca (mM) within each 10 mm layer through the Algavi_(c) DS bed of the treatment plant.

The marker is placed in the centre of the layer i.e. the marker at 5 mm represents the amount of the layer 0-10 mm. Note the logarithmic scale.

7.4 Esgair Hir 1 L/minute (carbonate sand)

The 1 L/minute treatment plant was again deployed at Esgair Hir, containing ~9.2 kg carbonate sand, between 25th April 2006 and 9th May 2006. Carbonate sand was used to determine whether the metal removal was caused by a mechanical filtering effect associated with Fe precipitation (with simultaneous sorption or co-precipitation of additional metals). The sand was rinsed to remove dust and small particles and used in the treatment plant in the same way as the DS. As with the above DS treatment plant the distribution pipe holes and the top of the bed was soon coated with Fe, see Figure 7.19, even though the average Fe concentration throughout the trial was <0.1 mg/L. This Fe coating caused the flow through the treatment plant to decrease from 1 L/minute to ~0.5 L/minute after two days. Significant metal removal only occurred within the first hour of operation, see Figure 7.20, after which an average of ~10 % Zn and ~20 % Pb was removed until ~18660 minutes (~13 days) when Pb started to be released back into solution.



Figure 7.19. Sand bed from the 1 L/minute Esgair Hir treatment plant after 15 days.

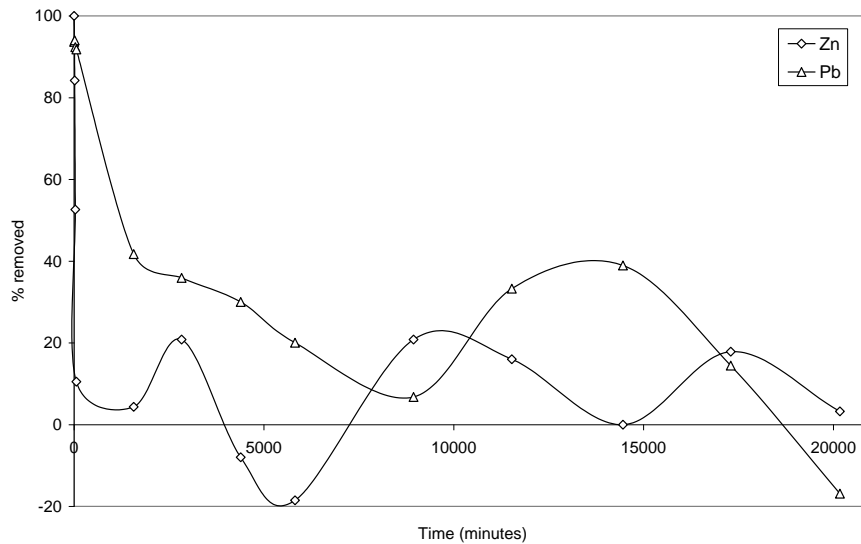


Figure 7.20. Removal of Zn and Pb from the 1 L/minute carbonate sand treatment plant at Esgair Hir.

Average inlet concentration: Zn ~0.3 mg/L and Pb ~62 µg/L.

The concentration of Ca and Mg increased in the outlet waters (Ca increased from 2.8 mg/L to 8.8 mg/L and Mg increased from ~2.3 mg/L to 4.3 mg/L) until ~30 minutes, after which the outlet concentration was approximately the same as the inlet water. Sodium and K concentrations (Figure 7.21) were not affected by flowing through the bed of carbonate sand and concentrations were approximately the same in the inlet and outlet waters.

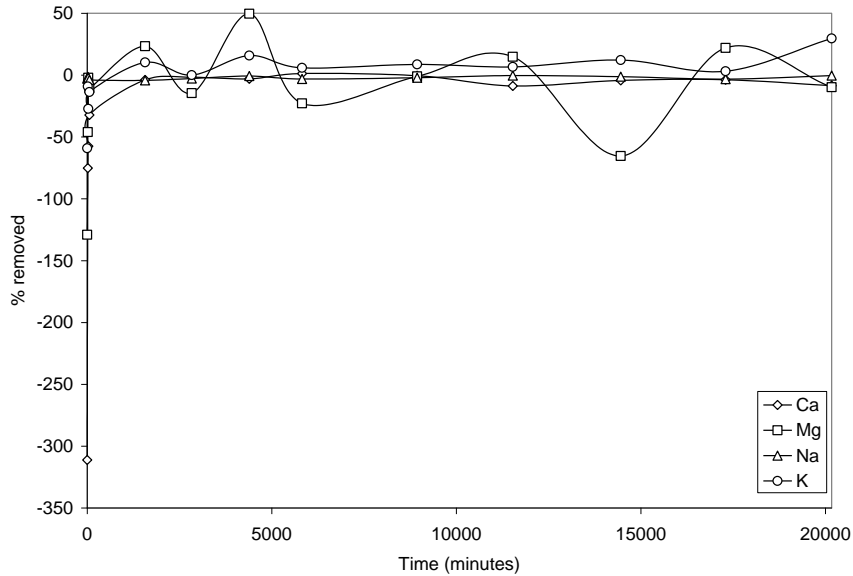


Figure 7.21. Removal of Ca, Mg, Na and K from the 1 L/minute carbonate sand treatment plant at Esgair Hir.

Average inlet concentration: Ca ~2.8 mg/L, Mg ~2.3 mg/L, Na ~5.7 mg/L and K ~0.3 mg/L.

7.4.1 Esgair Hir 1 L/minute core (Carbonate sand)

Once the treatment plant was removed from the field, the carbonate sand bed was removed divided into 20 mm sections (0-20 mm, 20-40 mm and 40-60 mm) and digested using HCl. The amounts within each 20 mm layer are shown in Figure 7.22 with Zn and Cd approximately constant throughout the bed; higher amounts of Fe and Pb occurred in the upper 20 mm of the carbonate sand bed. The effective capacity (the maximum amount of element removed by a 20 mm layer of DS (3.01 kg)) of the carbonate sand was ~10,374 μM Fe, ~1044 μM Zn, ~1.73 μM Cd and ~379 μM Pb, which gives a removal of ~0.19 mg Fe per g of carbonate sand, 22.6 $\mu\text{g/g}$ Zn, 0.1 $\mu\text{g/g}$ Cd and 25.9 $\mu\text{g/g}$ Pb. The relationship between Zn and Cd in the Algavi_(c) DS core at Bwlch (1 L/minute) was ~520:1 (calculated using the average amount (μm) of Zn and Cd in each 20 mm layer).

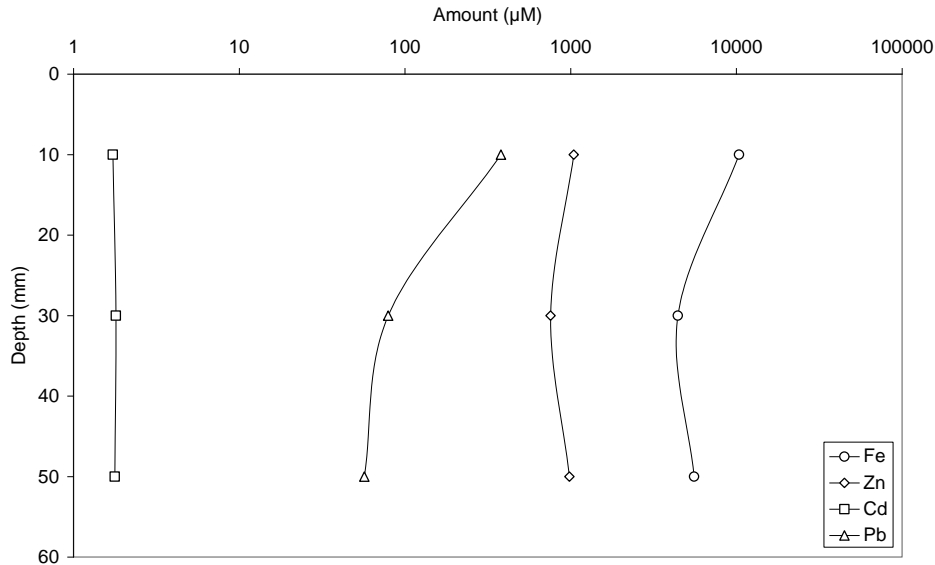


Figure 7.22. Amount of Fe, Zn, Cd and Pb (μM) within each 20 mm layer through the carbonate sand core from the Esgair Hir 1 L/minute treatment plant. The marker is placed in the centre of the layer i.e. the marker at 10 mm represents the amount of the layer 0-20 mm. Note the logarithmic scale.

7.5 Alltycrib 2 L/minute.

The treatment plant was re-designed to treat 2 L/minute; the plant is essentially two 1 L/minute treatment plants side by side within a larger outer tank (approximately 58 cm wide, 53 cm deep and 74 cm long), see Figure 7.23. The distribution pipe allowed 1 L/minute to flow into each half of the treatment plant. This trial was the first to use carbonate-free Algavi DS (Algavi_(f)) and each treatment plant was filled with ~2 kg (dry weight). The treatment plant was deployed at Alltycrib and operated between the 8th and 28th June 2006. The treatment plant was not placed at the entrance to the adit but where the pipe emerged from under the road, see Figure 7.24, allowing easier collection of the mine water. The water emerging from the pipe was funnelled into a pipe which led into the 'header' tank, the water then flowed into the treatment plant (Figure 7.25).

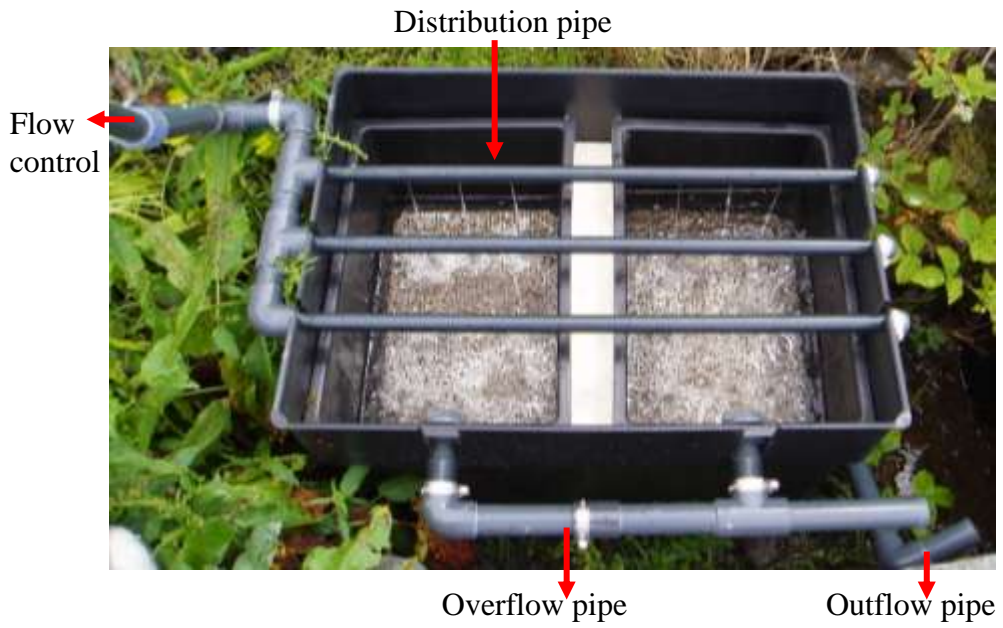


Figure 7.23. 2 L/minute treatment plant at Alltycrib.

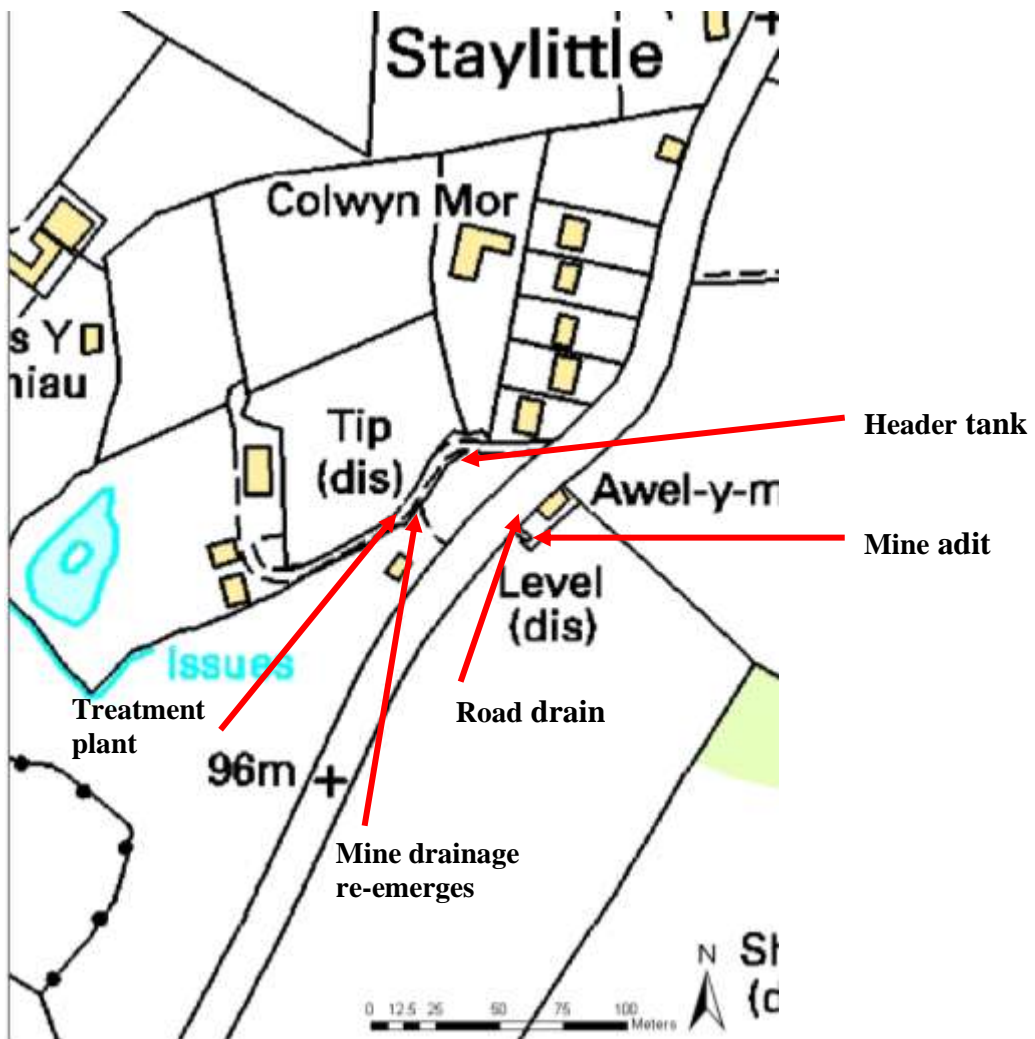


Figure 7.24. Location of the Alltycrib treatment plant.

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Figure 7.25. Alltycrib treatment plant

The removal of Zn, Cd and Pb from the 2 L/minute treatment plant is shown in Figure 7.26. The removal of Zn and Pb was ~80 % for the first hour of operation, the removal increased to a maximum of 90–95 % between 1620 and 3120 minutes (27 and 52 hours) after which the removal started to decrease, with a steady decrease until ~12600 minutes (~9 days) when Zn removal ceased and the Zn started to desorb. A greater percentage of Zn was removed than Pb until 4030 minutes (~67 hours); however, Pb continued to be removed at between 70-90 % until the removal started to decrease after ~15990 minutes (~11 days). During the trial period, Pb did not reach saturation, although removal could not have continued for much longer. Cadmium was removed at ~100 % until 18705 minutes (~13 days) when the adsorption started to decrease; both the Cd concentration in the inlet and outlet waters were nearing or below the detection limit of the ICP-MS and

therefore it is difficult to make definitive remarks about the performance of the system for this element.

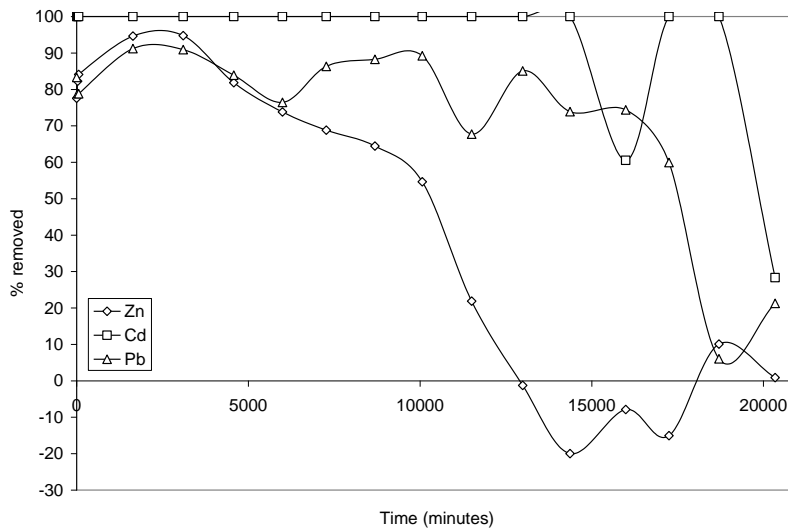


Figure 7.26. Removal of Zn, Cd and Pb from the 2 L/minute Algavi_(t) (carbonate free) DS treatment plant at Alltycrib.

Average inlet concentration: Zn ~1 mg/L, Cd ~1.5 µg/L and Pb ~130 µg/L.

As with the treatment plants deployed at Bwlch and Esgair Hir (discussed above), a large increase in Ca, Mg, and Na concentration occurred in the first waters flushed through the treatment plant; even though the majority of CaCO₃ grains had been removed in the pre-treatment process. The concentration of K was not affected by passing through the bed of Algavi_(t) DS (Figure 7.27). In the first waters leaving the treatment plant, the Ca concentration increased by 216 mg/L, Mg by 21 mg/L and Na by 204 mg/L. After 30 minutes, the Mg concentration returned to more or less the same as in the inlet water. The Ca and Na concentrations in the outlet waters then decreased; after 1640 minutes (~27 hours) the concentrations released from the DS were more or less stable at ~13 mg/L and ~9 mg/L (respectively). The Na concentration returned to that of the inlet water after 17250 minutes (~12 days), but ~2 mg/L Ca was still being released. In the first trial conducted at Bwlch the treatment plant continued to release Ca for the duration of the trial (~ 20 days), whereas this trial did not show the same pattern.

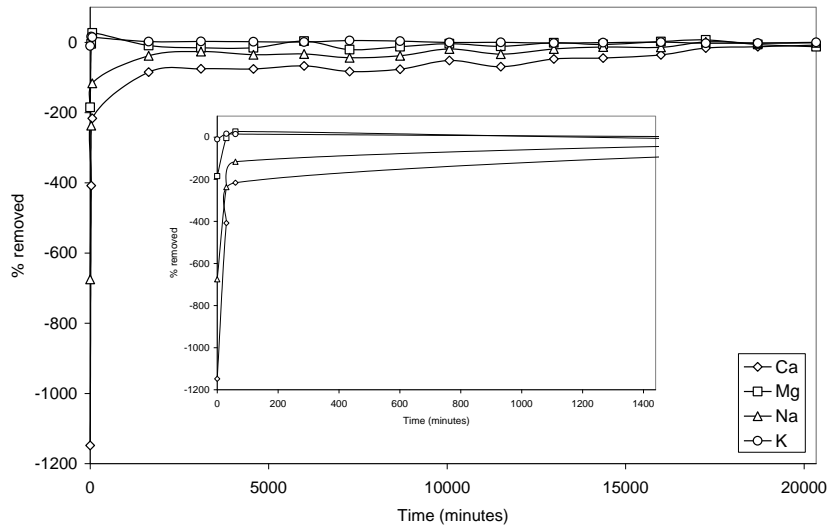


Figure 7.27. Removal of Ca, Mg, Na and K by the 2 L/minute Algavi_(t) DS treatment plant at Alltycrib. Inset: first 24 hours.

Average inlet concentration: Na ~33 mg/L, K ~4.3 mg/L, Mg ~11.4 mg/L and Ca ~21.4 mg/L.

The main problem that occurred at Alltycrib was that leaves and other organic matter blocked the pipe that led from the header tank to the treatment plant and the distribution pipes, this meant that the flow through the DS was reduced and the pipes had to be cleared of debris before the flow could continue at 2 L/minute.

7.6 Bwlch dual 1 L/minute

The treatment plant used at Alltycrib was modified so that the two 1 L/minute treatment plants could be separately operated, to provide a direct comparison between the two plants, see Figure 7.28. A divider (heavy duty pond liner) was fitted in the centre of the large, outer tank to separate the two DS beds. As the large outer tank was initially designed to remove all the water that passed through the two DS beds, a second outflow pipe was added so that each 1 L/minute DS tank had a separate outflow. The advantage of operating two treatment plants simultaneously is that they are subject to identical conditions, for example, changes in mine water chemistry, water and air temperature, flow conditions and other such variables.



Figure 7.28. Dual treatment plant at Bwlch.

The laboratory batch experiments within Chapter 6 determined that the Girvan DS had a greater adsorption capacity than Algavi_(f) DS. To determine whether this difference in adsorption capacity could also be seen when the DS is in contact with metal-rich water for a longer period (i.e. which of the DS showed the greatest adsorption capacity over time), 2 kg (dry weight) of Algavi_(f) DS was placed into one half of the treatment plant and 2 kg (dry weight) of Girvan DS was placed into the other. The Algavi_(f) DS was mostly carbonate free and had been subjected to acid washing and drying; the Girvan DS, however, was used as received (i.e. it had not been subjected to any pre-treatment).

The dual treatment plant was deployed at Bwlch between the 10th and 24th October 2006. Previous field trials showed that the most dramatic changes in outlet concentration occurred within the first few hours of operation; therefore samples were simultaneously taken from both Algavi_(f) and Girvan DS outlet pipes every 15 minutes for two hours, then every 30 minutes for the next five hours, and then daily. After the first seven days, the mine drainage had ceased to flow through the bed of Algavi_(f) DS; the cause of the cessation is unknown, so both treatment plants were drained and then re-filled. The plants were left to equilibrate for ~20 minutes before the sample was taken, after which the flow through the treatment plant was more or less stable throughout the trial. The removal of Zn, Cd and Pb is shown in Figures 7.29, 7.30 and 7.31a and b, with Girvan DS having a

higher adsorption capacity than Algavi_(f) DS; a pattern which is comparable to the laboratory experiments.

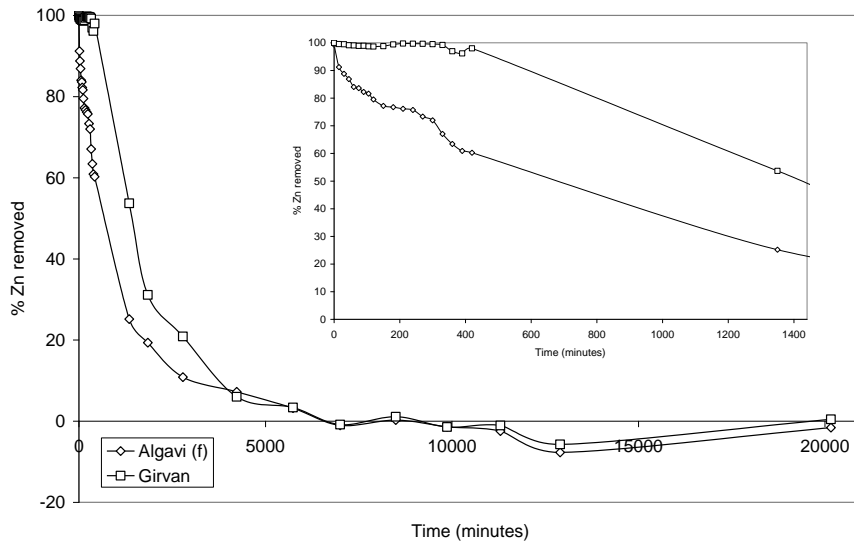


Figure 7.29. Removal of Zn from the Algavi_(f) and Girvan DS 1 L/minute dual treatment plant at Bwlch. Inset: first 24 hours.
Average inlet concentration: Zn ~28 mg/L.

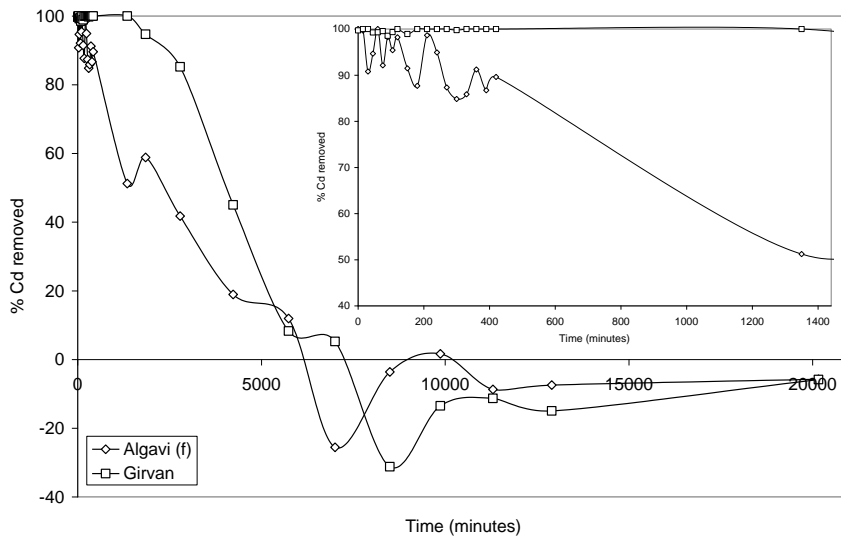


Figure 7.30. Removal of Cd from the Algavi_(f) and Girvan DS 1 L/minute dual treatment plant at Bwlch. Inset: first 24 hours.
Average inlet concentration: Cd ~60 µg/L.

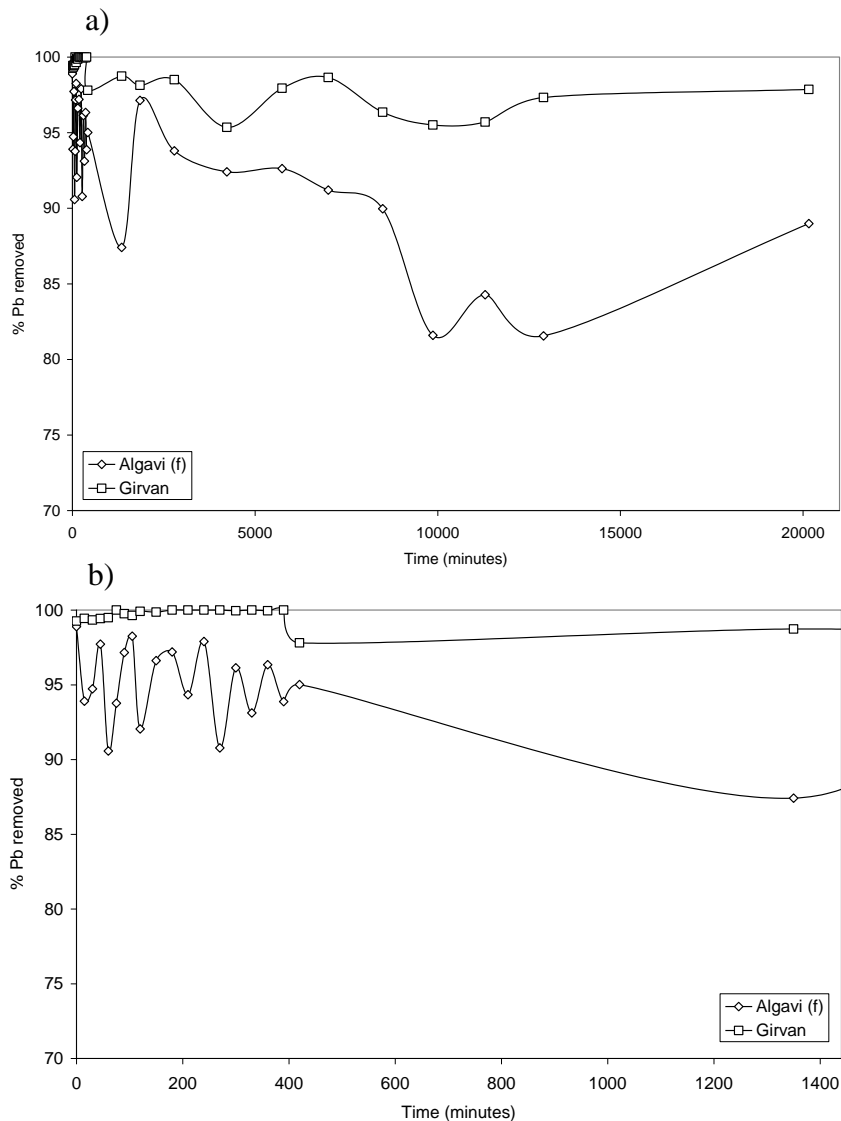


Figure 7.31. Removal of Pb from the Algavi_(f) and Girvan DS 1 L/minute dual treatment plant at Bwlch: a) whole trial period and b) first 1440 minutes.
Average inlet concentration: Pb ~890 µg/L.

Both DS removed >90 % of Zn from the Bwlch mine water after 15 minutes, after this the removal by the Algavi_(f) DS decreased and after seven hours only 60 % was adsorbed. Girvan DS, however, continued to remove Zn at 98–100 % until seven hours after which the removal started to decrease. Interestingly both the Algavi_(f) and Girvan DS ceased to adsorb Zn at exactly the same time (~110 hours); however, the total weight of Zn removed by the Girvan DS was greater than that removed by the Algavi_(f) DS (after 110 hours the Girvan DS had removed ~48 g and Algavi_(f) DS had removed ~31 g Zn from the Bwlch mine water). The removal of Cd showed a similar result with a greater amount being removed by Girvan DS, adsorbing ~100 % until 24 hours after which the removal decreased; compared to the Algavi DS which adsorbed between 85–100 % until seven hours when the removal started to decrease. Girvan DS ceased to adsorb Cd after five days

and Algavi_(f) DS after about four days. Neither DS saturated with Pb, Algavi_(f) DS removed Pb at ~95 % until after ~24 hours when the removal started to decrease, though adsorption was still >80 %; Girvan DS adsorbs Pb at over 99 % until 390 minutes (6.5 hours) when the adsorption slightly decreases, but over 95 % was still being removed.

Large concentrations of Ca were released from the two DS (Figure 7.32) though a higher concentration was released from the Girvan DS. After 15 minutes of operation the Algavi_(f) DS released 6 mg/L Ca, after which the concentration released decreased and after ~150 minutes the inlet and outlet concentrations were more or less the same. The Girvan DS released 12.5 mg/L Ca into the outlet water after 15 minutes, the concentration slowly decreased and the inlet and outlet concentrations were approximately the same after ~4230 minutes (~70 hours). As with the previous treatment plants, the release of Ca into the mine water is important for interpreting the adsorption characteristics of the two types of DS. The very first samples collected from the Girvan and Algavi_(f) DS treatment plant (the first flush of water through the treatment plant), showed that minor concentrations of Na, Mg and K were released from Girvan DS (not shown on the graph). However, both DS adsorb Na, Mg and K until the concentration was more or less the same in the inlet and outlet waters. Up until 120 minutes, more Mg was adsorbed by Algavi_(f) DS, after which more Mg was removed by Girvan DS; after 1350 minutes (~22 hours) the Mg concentration in the outlet water was more or less the same as the inlet water (Figure 7.33). Minor concentrations of Na and K were adsorbed by the two DS; after ~150 minutes the inlet and outlet concentration of K were more or less the same and throughout the operation of the treatment plant the outlet concentration was no more than 0.25 mg/L different to that of the inlet concentration.

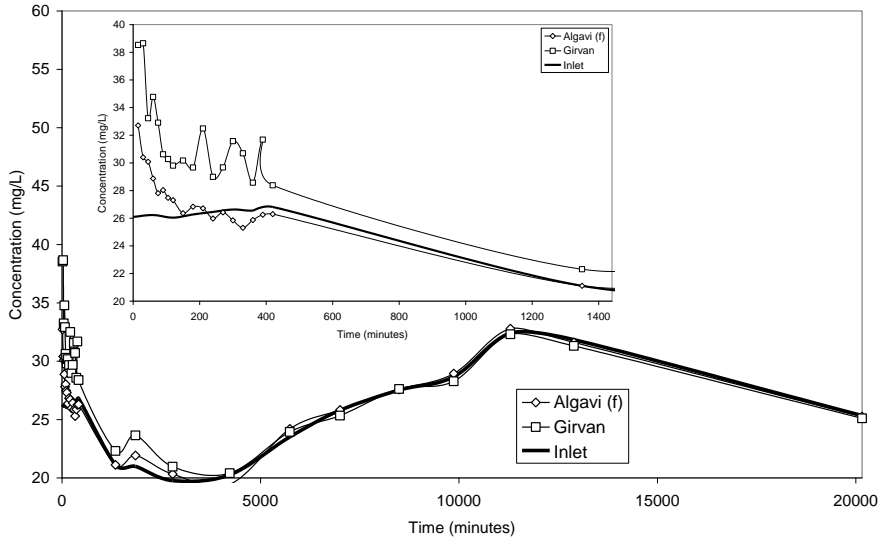


Figure 7.32. Concentration of Ca in the inlet and outlet waters of the Algavi_(f) and Girvan DS 1 L/minute treatment plant at Bwlch. Inset: first 1440 minutes (24 hours).

Please note the different concentration scales on the two graphs.

Average inlet concentration: Ca ~26 mg/L

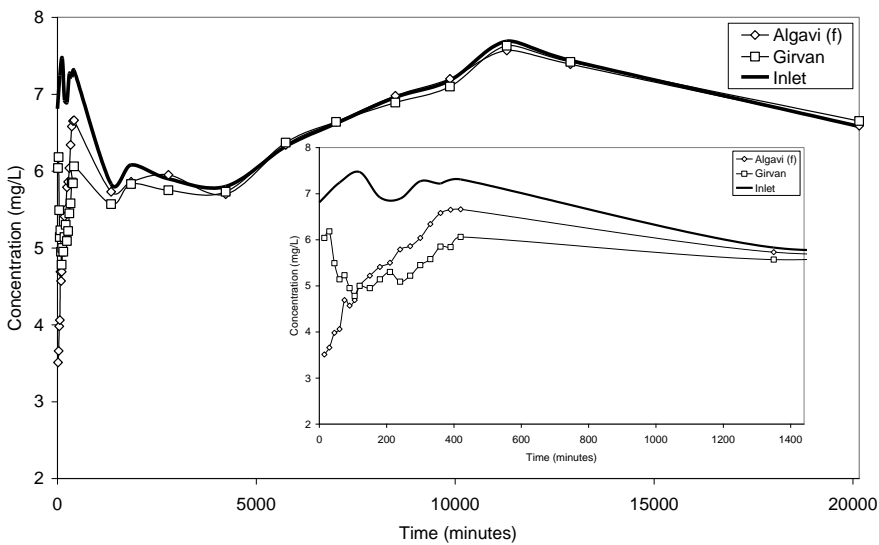


Figure 7.33. Concentration of Mg in the inlet and outlet waters of the Algavi_(f) and Girvan DS 1 L/minute treatment plant at Bwlch. Inset: first 1440 minutes (24 hours).

Average inlet concentration: Mg ~6.8 mg/L

These results show that the Girvan DS was more efficient at removing metals and that both DS types have an affinity for Pb ions. The total concentration of Zn, Cd and Pb removed from solution may be calculated by:

$$C_i - C_o * T + C_{i-1} - C_{o-1} - C_1 - C_o * T/2 \quad (7.2)$$

Where:

C_i = inlet concentration at a certain sample time (mg/L)

C_o = outlet concentration at a certain sample time (mg/L)

T = time that the treatment plant had been in operation when the samples were taken (minutes)

C_{i-1} = inlet concentration at the previous sample time (mg/L)

C_{o-1} = outlet concentration at the previous sample time (mg/L)

The concentration removed between each sample is calculated per minute, and then added to the concentration removed between the samples, the $T/2$ assumes that the concentration decreased (or increased) linearly between the samples. This calculation is applied until the end of the trial period to take account of the concentration of elements desorbed from the DS. The total amount removed from solution by the Algavi_(f) and Girvan DS is compared in Table 7.1; Girvan DS adsorbed a greater weight of metals than the Algavi_(f) DS, especially Zn, with the Girvan adsorbing almost twice as much as Algavi_(f) DS. As neither the Algavi_(f) nor the Girvan DS had saturated with Pb, the adsorbed weight shown was likely to increase; conversely, the weight of Zn and Cd was likely to decrease with continued desorption from the DS.

Table 7.1. Weight of Zn, Cd and Pb removed per kg (dry weight) of Algavi_(f) and Girvan DS at the Bwlch dual 1 L/minute field trial after 14 days.

	Zn (g)	Cd (g)	Pb (g)
Algavi _(f) DS	9.0	0.04	7.65
Girvan DS	20.2	0.06	8.45

7.6.1 Bwlch dual 1 L/minute DS cores (Algavi_(f) and Girvan)

Once the dual treatment plant was removed from the field, each of the DS beds was segmented and digested following the methods detailed in Section 7.1.1. Only the amounts of Cd and Pb were analysed; the amount of Zn within the core may be estimated by multiplying the amount of Cd by 300 (the ratio of Zn:Cd in the Algavi_(c) 1 L/minute treatment plant at Bwlch). Figure 7.34 shows that the amounts of Zn, Cd and Pb were variable through the DS beds; though the amount of Cd (and therefore Zn) was approximately constant through the bed (the amount slightly increased between 10-20 mm

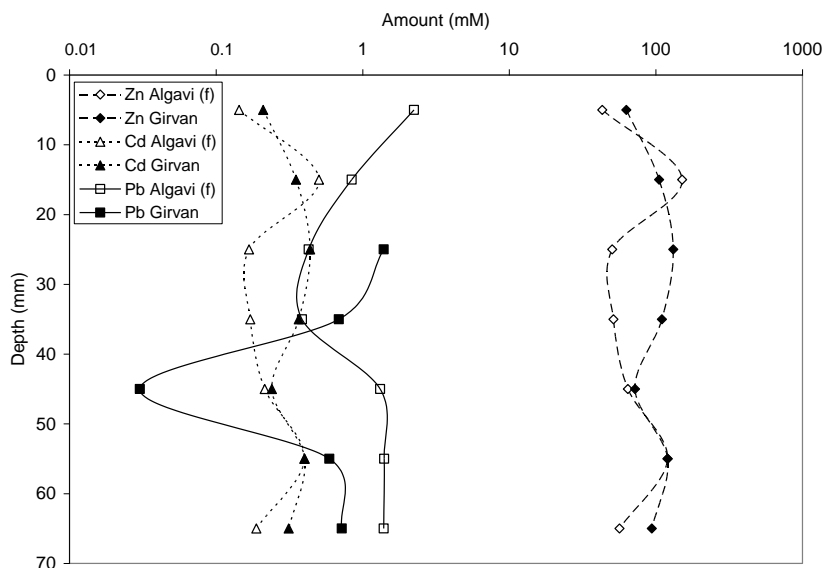


Figure 7.34. Amount of Zn, Cd and Pb (mM) within each 10 mm layer through the Algavi_(f) and Girvan_(r) DS core from the Bwlch dual 1 L/minute treatment plant.

The marker is placed in the centre of the layer i.e. the marker at 5 mm represents the amount of the layer 0-10 mm. Note the logarithmic scale.

and 50-60 mm). The amount of Pb was very variable with depth through the two DS cores and Pb could not be detected in the upper 20 mm of the Girvan DS core. If the above data is compared to that of the 1 L/minute Algavi_(c) core digestion, then the upper 20 mm of the core should contain a high concentration of Pb, which the above Girvan DS core does not. This discrepancy is most likely to have been caused by the high concentration of Pb saturating the ICP-MS detector causing the Pb concentration to be measured inaccurately. The effective capacity (maximum amount of metal removed by a 10 mm layer of DS (Algavi_(c): 250 g and Girvan: 286 g)) of the Algavi_(f) and Girvan DS for Cd, Zn and Pb is shown in Table 7.2.

Table 7.2. Effective capacity of Algavi_(f) and Girvan DS at Bwlch

	Zn	Cd	Pb
Algavi _(f) DS	71692 µM (16.4 mg/g DS)	239 µM (0.09 mg/g DS)	1587 µM (1.2 mg/g DS)
Girvan DS	99411 µM (22.7 mg/g DS)	331 µM (0.13 mg/g DS)	848 µM (0.6 mg/g DS)

7.7 Bwlch 10 L/minute

A larger treatment plant was designed, see Figure 7.35 and 7.36a, to treat 10 L/minute and was filled with wet Algavi_(f) DS (~20 kg dry weight) and deployed at Bwlch between the 7th and 23rd November 2006. The treatment plant was essentially the same design as the smaller treatment plants, although there was only one tank (approximately 53 cm wide, 48 cm deep and 142 cm long) and the DS was sandwiched between nylon and stainless steel mesh which was kept level and supported by stainless steel pillars. The larger treatment plant required a much larger quantity of DS and therefore to save time (drying and granulating the DS) the DS was left wet and placed into the treatment plant as a slurry, see Figure 7.36b. The treatment plant was placed at the same location as the previous Bwlch trials, though after three days the flow of mine drainage through the plant was only ~2.5 L/minute and therefore the plant was moved further downstream to increase the head of water thereby increasing the flow through the plant (to ~7.5 L/minute).

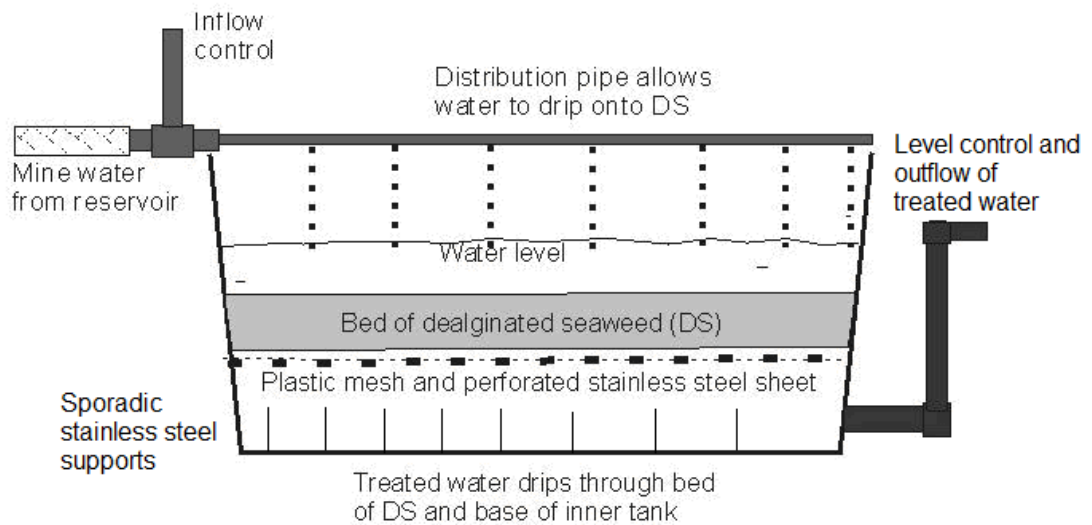


Figure 7.35. Schematic of the 10 L/minute treatment plant.

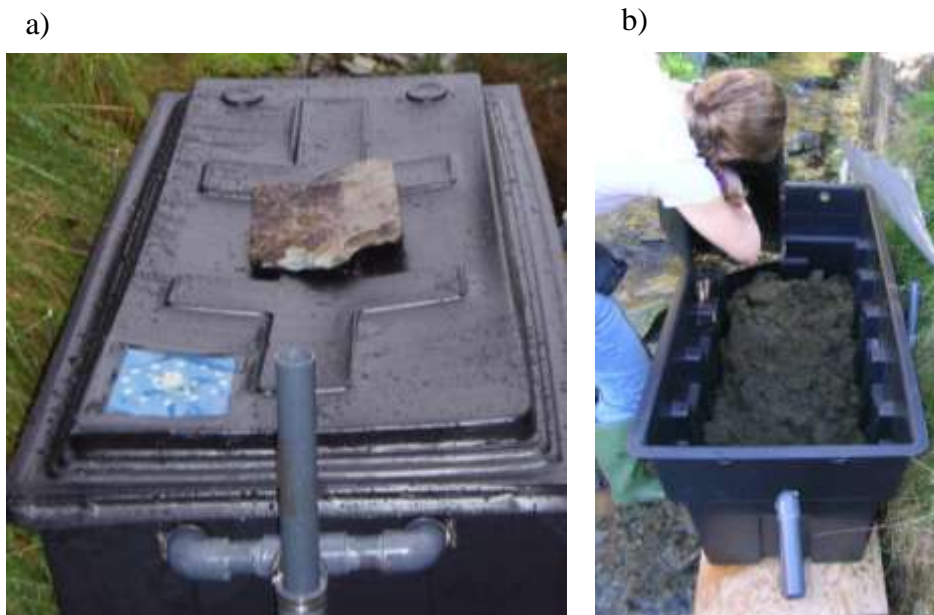


Figure 7.36. 10 L/minute treatment plant at Bwlch: a) treatment plant with lid to prevent precipitation from entering the plant and b) adding the wet DS into the treatment plant.

The removal of Cd and Pb from the mine drainage by the 10 L/minute treatment plant was poor (see Figure 7.37) especially when compared to the removal achieved by the smaller treatment plants (discussed above). The metal removal peaked after 15 minutes of operation at ~70 % and then started to decrease; Cd ceased to be adsorbed after only 730 minutes (~12 hours) and Pb after 890 minutes (~15 hours). When the treatment plant was moved further downstream after three days of operation, it was noted that small channels had formed around the edge of the DS bed allowing the mine drainage to flow directly into the base of the treatment plant, with minimal contact with the DS. The DS was being eroded from the channel into the base of the treatment plant which made this problem worse. When the treatment plant was moved, the DS was stirred to try and re-establish the flow through the DS bed, but this did not occur; though immediately after stirring the removal of Pb increased for a short time (~1 hour), before decreasing again. The development of channels within the DS bed did not occur in the smaller treatment plants because the systems had a much better support at the base of the DS bed. The larger treatment plant also had a higher flow rate entering the treatment plant and a greater head of water above the DS bed. Another major factor was that the DS was added to the 10 L/minute treatment plant wet and in the smaller treatment plants the DS was added as a dry granular material; which swells slightly on contact with water effectively ‘sealing’ the treatment plant, therefore allowing greater contact between the mine drainage and the DS. When wet DS was used in the 10 L/minute treatment plant, channels formed rapidly and

the mine drainage was not thoroughly contacting the DS, therefore offering little or no potential for the removal of metal ions from the mine drainage.

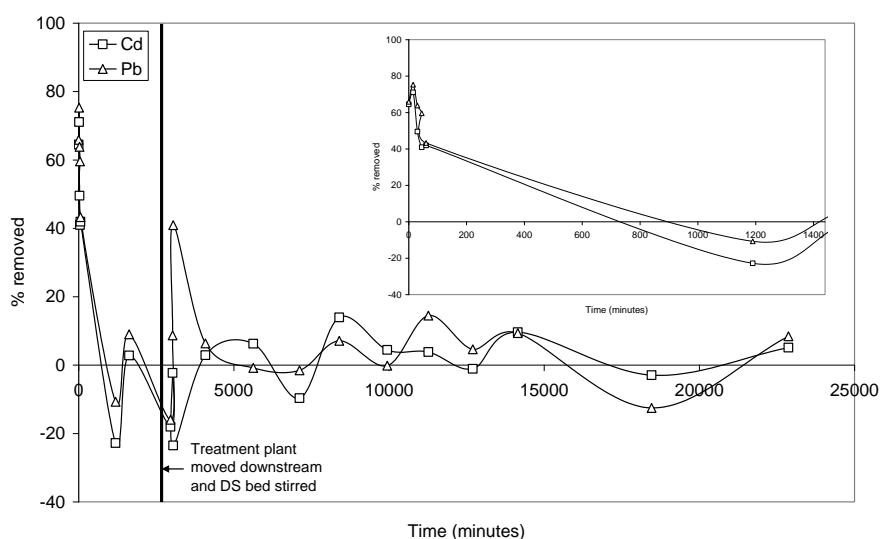


Figure 7.37. Removal of Cd and Pb by the Algavi_(f) DS 10 L/minute treatment plant at Bwlch. Inset: first 24 hours.

The vertical line marks when the treatment plant was moved and the DS bed was stirred. Average inlet concentrations: Cd ~71 µg/L and Pb ~1080 µg/L.

7.8 Capacity of the dealginated seaweed

The effectiveness of the different treatment plants may be evaluated by comparing the amounts of metals removed. The total amount of metals removed during the operation of the treatment plant (Table 7.3) can be calculated using equation 7.2; the equation assumes a constant flow rate (for example, at 1 L/minute) and that no DS had been lost during the treatment plant operation. The amount of metal removed from the mine drainage may then be compared to the amount of metals removed which has been calculated from the digestion of the DS core (equation 7.1).

The amounts removed from the mine drainage water and the digestion of the treatment plant bed confirms that the adsorption capacity is $\text{Algavi}_{(c)} > \text{Girvan} > \text{Algavi}_{(f)} > \text{carbonate sand}$ (on a dry weight basis). When the amount of metal removed as a percentage of the amount of DS (or carbonate sand) within the treatment plant is considered, the adsorption capacity is $\text{Girvan} > \text{Algavi}_{(c)} > \text{Algavi}_{(f)} > \text{carbonate sand}$. When comparing the two methods for calculating the amount of metals removed, the metal removed, generally, is higher when calculated from the mine drainage water than the core

Table 7.3. Amount of Zn, Cd, Pb and Fe removed from solution at Bwlch calculated from the area under the adsorption curve and from the digestion of the DS core.

Values in parentheses indicate the amount of metal adsorbed as a percentage of the DS (dry weight).

	Zn (g)	Cd (g)	Pb (g)	Fe (g)
Bwlch 1 L/minute (~3 kg Algavi_(c) DS)				
Treatment plant	50.6 (1.69 %)	0.35 (0.01 %)	18.5 (0.62 %)	n.a.
Core	43.4 (1.45 %)	0.22 (0.01 %)	17.8 (0.59 %)	n.a.
Esgair Hir 1 L/minute (~2 kg Algavi_(c) DS)				
Treatment plant	5.32 (0.27 %)	0.05 (0.003 %)	5.72 (0.29 %)	n.a.
Core	4.75 (0.24 %)	0.02* (0.001%)	n.a.	n.a.
Esgair Hir 1 L/minute (~9.2 kg Carbonate sand)				
Treatment plant	0.37 (0.04 %)	0.0005 (5 x 10 ⁻⁵ %)	0.33 (0.04 %)	n.a.
Core	0.18 (0.02 %)	0.0006 (7 x 10 ⁻⁵ %)	0.11 (0.01 %)	n.a.
Alltycrib 1 L/minute (~2 kg Algavi_(f) DS)				
Treatment plant	8.44 (0.42 %)	0.03 (0.002 %)	1.93 (0.1 %)	n.a.
Bwlch dual 1 L/minute (~2 kg Algavi_(f) DS)				
Treatment plant	18.0 (0.90 %)	0.08 (0.004 %)	15.3 (0.77 %)	n.a.
Core	37.5* (1.88 %)	0.22 (0.01 %)	1.66 [#] (0.08 %)	n.a.
Bwlch dual 1 L/minute (~2 kg Girvan DS)				
Treatment plant	40.3 (2.02 %)	0.12 (0.006 %)	16.9 (0.85 %)	n.a.
Core	45.5* (2.28 %)	0.26 (0.01 %)	0.71 [#] (0.04 %)	n.a.
Bwlch 10 L/minute (~20 kg Algavi_(f) DS)				
Treatment plant	n.a.	0.04 (0.0002 %)	1.07 (0.005 %)	n.a.

n.a. = not analysed

* = estimated (using a Zn: Cd ratio of 300:1)

[#] = unreliable value (reasoning detailed above)

digestion. The greater calculated metal removed from the mine drainage water may have been because the equation used (7.2) assumes that the concentration decreased linearly between samples and that the flow rate is constant and this may not be the case. However, in the dual treatment plant, the amounts are higher when calculated using the DS core digestion. The higher amount of Zn in the dual DS cores may be explained as the value was calculated by multiplying the Cd value by 300 (the approximate ratio of Zn:Cd in the Bwlch 1 L minute Algavi_(c) core). The extremely low Pb values determined from the dual treatment plant DS cores are clearly incorrect; these low values may have been caused by analytical error i.e. the Pb concentration within the digested core may have been very high and saturated the ICP-MS detector and caused the Pb concentration to be measured inaccurately.

The removal of metals by weight is typically $Zn > Pb > Cd$ by the DS or carbonate sand; where the Pb has saturated the material within the treatment plant more Pb is removed than Zn (for example, at Esgair Hir using Algavi_(c) DS). When carbonate sand was used at Esgair Hir the amount of Pb and Zn removed (calculated using the mine drainage water results) were similar. Lead, however, had not saturated the DS within the Bwlch 1 L/minute (Algavi_(c), Algavi_(f) and Girvan) and at Alltycrib. Therefore, the amount removed would have increased if the trial had continued, conversely the amount of Zn and Cd would have decreased as these metals would continue to be desorbed from the DS.

7.9 Discussion

7.9.1 Bwlch 1 L/minute DS core (Algavi_(c))

In the top 20 mm of the core, Pb and Zn have a 1:1 relationship and in the lower 80 mm Pb and Cd have a 1:1 relationship. These 1:1 relationships that occur between the Pb and Zn and the Pb and Cd suggest that similar processes are affecting the metals, not necessarily that direct ion exchange occurs between the metals. Typically, the Zn and Cd have a ~336:1 relationship (calculated dividing the average Zn amount (μm) in each 10 mm layer by the average Cd amount (μm) in each layer), indicating that the DS preferentially adsorbed Cd from the mine water (the Zn:Cd ratio of the Bwlch mine water was ~400:1). The increased amount of Pb in the upper 20-30 mm, and the low amount in the lower section of the core, suggested that the DS bed was not saturated with Pb (within the field

trials the DS bed continues to remove >90 % of the Pb, see Figure 7.7); it may be assumed that only ~25 % of the DS bed was been saturated. This implies that the DS bed could have continued to adsorb Pb for another ~60 days (until, in total, ~ 100,000 L Bwlch mine water had flowed through the DS bed); the Zn and Cd would continue to desorb and be released back into solution.

The DS core contains higher amounts of Ca and Mg than Na and K, which is expected as carbonate grains were contained within the Algavi_(c) DS. The lower amounts contained within the upper 10 mm may have been caused by the dissolution of the carbonate grains and their subsequent wash out of the DS bed or the exchange of Pb for Ca and/or Mg.

7.9.2 Esgair Hir 1 L/minute DS core (Algavi_(c))

There are higher amounts of Ca and Mg than Na and K within the Algavi_(c) core which was deployed at Esgair Hir, which is consistent with the Algavi_(c) containing carbonate grains which have been dissolved. In this trial the Algavi_(c) DS was stirred on two occasions (after ~15 and ~29 days of operation) in an attempt to restore water flow through the system. If any patterns of element distribution did exist within the DS bed, as seen at the Bwlch trial, then these patterns would have been destroyed by the stirring.

7.9.3 Esgair Hir 1 L/minute (carbonate sand)

Significant removal of Zn, Cd and Pb only occurred during the first hour of operation of the 1 L/minute carbonate sand treatment plant. Metal removal may have been caused by the co-precipitation of the metals at the same time as the Fe ochre or the adsorption of the metals onto the surface of the carbonate sand until the active sites become saturated.

The Zn:Cd ratio of the carbonate sand core was ~524:1 (calculated using the average Zn and Cd amount (μm) in each 20 mm layer); the Zn:Cd ratio of Esgair Hir mine water was ~575:1, therefore Cd was preferentially adsorbed, compared to Zn. There were increased amounts of Fe and Pb (compared to Zn and Cd) within the upper 20 mm of the core suggesting that the carbonate sand bed was not saturated with these metals, even though when the treatment plant was removed from Esgair Hir Pb was being re-released into solution. The high Fe and Pb in the top 20 mm may indicate that the Pb is associated with the ochre which precipitated onto the top of the carbonate sand bed (shown in Figure 7.19).

The high Pb adsorption onto ochre is expected, given the pH (average inlet pH was ~5.7), the model sorption curves showing the sorption of metals onto Fe oxides produced by Dzombak and Morel (1990) and Ponthieu *et al.* (2006) suggests that a greater amount of Pb will be adsorbed at a lower pH than Zn and Cd.

7.9.4 Esgair Hir treatment plant (DS v carbonate sand)

The two treatment plants operated at Esgair Hir may be compared to determine whether the metal removal from the mine drainage is a product of metals co-precipitating with Fe or sorbing onto the Fe and subsequently filtering out of solution or via biosorption onto the DS. The two treatment plants contained the same depth of material (~7 cm) and the Fe and Zn concentration within the mine water was similar (~0.15 mg/L Fe and ~0.24 mg/L Zn). The removal of Zn by the DS and carbonate sand is shown in Figure 7.38. Only the first 14 days are shown (the DS plant operated for 66 days and the carbonate sand plant operated for just over 14 days) and the Algavi_(c) DS removed >80 % of the Zn throughout the 14 days, whereas the Zn removal by carbonate sand was >50 % during the first 30 minutes of operation and then rapidly decreased. After the first hour, Zn removal was variable between 20 % and -20 %. This behaviour was displayed until the treatment plant had been operating for 14 days. The variability may have been caused by the low Zn concentrations nearing the detection limit of the AAS. After 20160 minutes (14 days) the total Zn removed from the mine drainage by 2 kg Algavi_(c) DS was 3.6 g Zn and only 0.37 g Zn was removed by the carbonate sand bed. The removal of Pb by Algavi_(c) DS was higher than the removal by the carbonate sand, see Figure 7.39. The Algavi_(c) DS continued to remove Pb at >80 % over 14 days, whereas the removal by carbonate sand decreased from >91 % in the first hour of operation to <40 % after 1570 minutes (~26 hours); the carbonate sand finally ceased to remove Pb after ~18660 minutes (~13 days). Therefore, the main metal removal mechanism was metal adsorption to the DS, rather than co-precipitation with the Fe and subsequent filtration onto the bed.

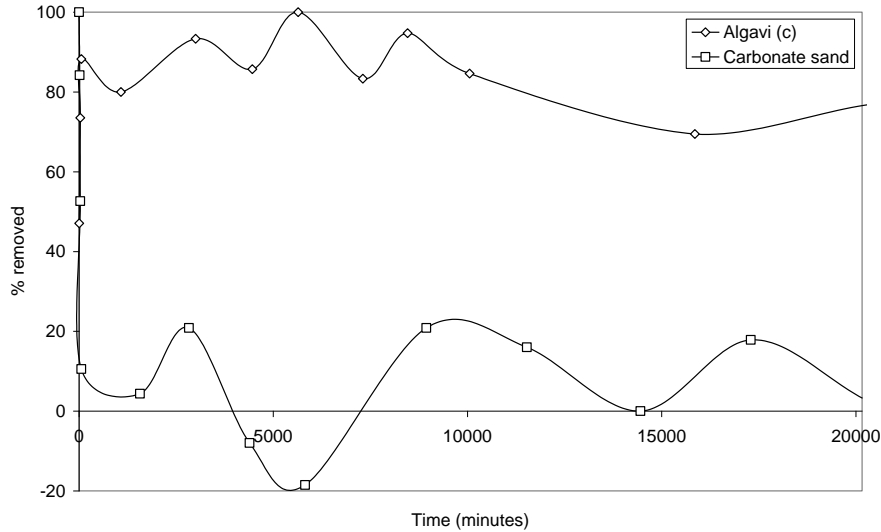


Figure 7.38. Removal of Zn by 2 kg Algavi_(c) DS and 9.2 kg carbonate sand at Esgair Hir. Average inlet Zn concentration ~0.24 mg/L

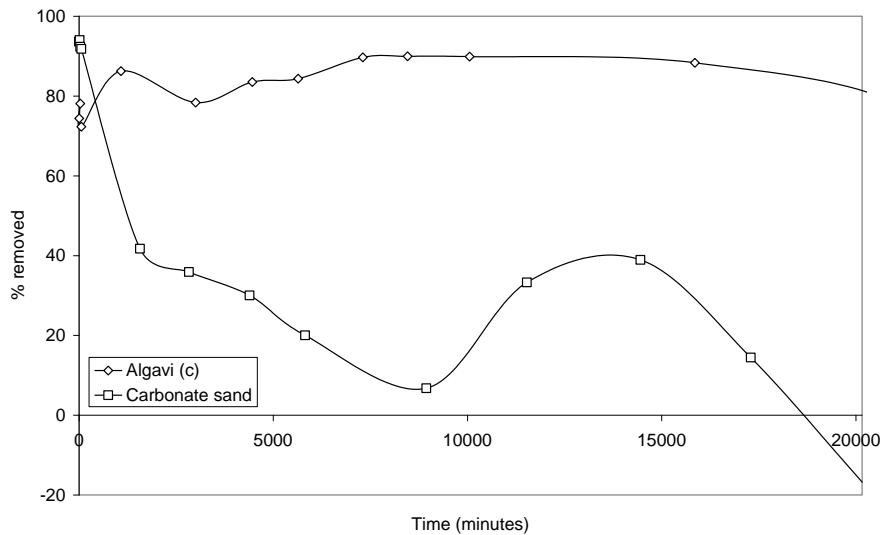


Figure 7.39. Removal of Pb by 2 kg Algavi_(c) DS and 9.2 kg carbonate sand at Esgair Hir. Average inlet Pb concentration ~104 µg/L

7.9.5 Bwlch 1 L/minute dual treatment plant (Algavi_(f) v Girvan DS)

The differences in adsorption capacity may be caused by:

- the different seaweed species used to produce the DS (Girvan is mostly *Ascophyllum nodosum* with additional seaweed species and Algavi is purely *Laminaria digitata*);
- the pre-treatment of the DS before use (detailed in Chapter 5.8.3 and 5.8.4), Algavi DS has been subjected to acid washing and thermal drying which may be detrimental to the adsorption capacity of the DS (see Chapter 6.6.1);

- the two DS may contain different types of functional groups or contain varying numbers and availability of binding sites; or
- the concentration of cations (Ca, Mg, Na and K) released from the DS.

7.9.6 Bwlch 1 L/minute treatment plant (Algavi_(c) v Algavi_(f) DS)

The results gained from the dual treatment plant meant that a comparison could be made between the two Algavi DS (both treatment plant were operated at Bwlch between September and October); it has to be noted that there are different inlet concentrations (Table 7.4), different weights of DS were initially added to the treatment plant (~3 kg (dry weight) of Algavi_(c) DS was used in the first Bwlch treatment plant and 2 kg (dry weight) of Algavi_(f) DS was used within the dual treatment plant at Bwlch) and the field trials operated for different lengths of time (the first trial operated for 20 days and the dual treatment plant operated for 15 days).

Table 7.4. Chemical composition of Bwlch mine water during the Algavi_(c) and Algavi_(f) DS field trials. Average concentrations during the trials are shown.

	Ca (mg/L)	Zn (mg/L)	Cd (µg/L)	Pb (µg/L)
Algavi _(c) DS	40	28	60	887
Algavi _(f) DS	26	25	64	696

The amount of DS within the treatment plant will affect the flow through the DS bed and therefore the contact time between the mine water and the DS. Laboratory experiments (Chapter 6.2) show that the metal adsorption capacity is greater using Algavi_(f) than Algavi_(c) DS. In a real treatment situation however Algavi_(c) DS was more effective at removing metals from mine water than Algavi_(f); Table 7.5 shows the total amount of metals removed by the bed of DS. The comparison between the adsorption of Zn is shown in Figure 7.40 (Cd and Pb show similar results and are therefore not shown).

Table 7.5. Weight of Zn, Cd and Pb removed per kg (dry weight) of Algavi_(c) and Algavi_(f) DS during the Bwlch 1 L/minute field trials.

	Zn (g)	Cd (g)	Pb (g)
Algavi _(f) DS	9.0	0.04	7.6
Algavi _(c) DS	16.9	0.12	6.2

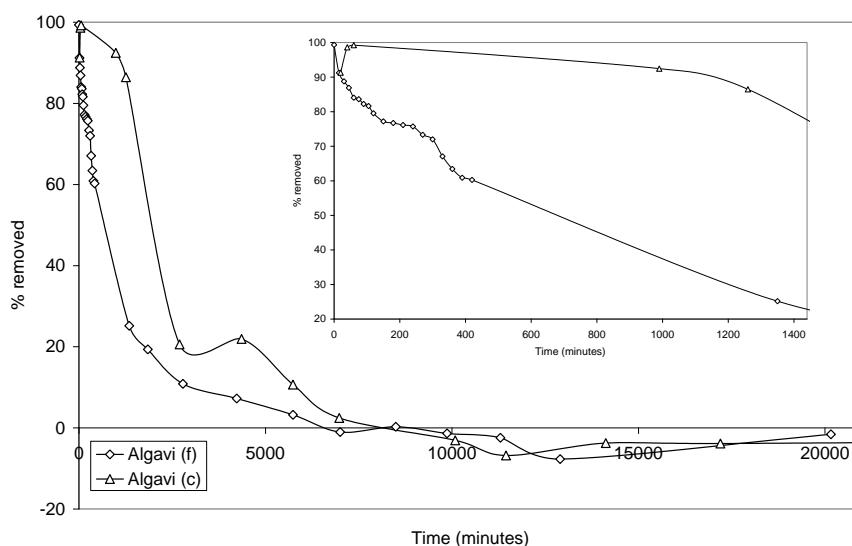


Figure 7.40. Removal of Zn by the 1 L/minute treatment plant containing 2 kg Algavi_(f) and 3 kg Algavi_(c) DS at Bwlch. Inset: first 24 hours.

Average inlet concentrations of Zn: Algavi_(c) ~25 mg/L and Algavi_(f) ~28 mg/L.

The two DS influence the concentration of major cations within the outlet waters in different ways. Calcium was released from both Algavi DS (Figure 7.41), although Algavi_(c) released a larger concentration; after ~240 minutes the Ca concentration in the treatment plant effluent was more or less the same as the inlet concentration. Algavi_(c) continued to release Ca into solution and after 4360 minutes (~72 hours) ~5 mg/L was continuously released into solution. The greater increase in Ca concentration at the start of the trial and the sustained release of Ca caused the pH of the outlet water of the Algavi_(c) treatment plant to be higher than the Algavi_(f) outlet water, see Figure 7.42. The higher concentration of carbonate within the water may assist in the precipitation of metal carbonates which would then filter out via the DS bed and remove a greater concentration of metals. Algavi_(f) tended to remove Na, Mg and K from solution until the inlet concentration was more or less the same as the outlet concentration which occurred in an

hour, 2700 minutes (45 hours) and 1850 minutes (~31 hours) respectively. $\text{Algavi}_{(c)}$ initially released Na and Mg from the DS, after ~40 minutes they were removed from solution and after 2700 minutes (45 hours) and 1850 minutes (~31 hours) respectively the inlet concentration was more or less the same as the outlet concentration. $\text{Algavi}_{(f)}$ did not release K and instead adsorbed it until, as with the $\text{Algavi}_{(c)}$ DS, the concentration was not affected.

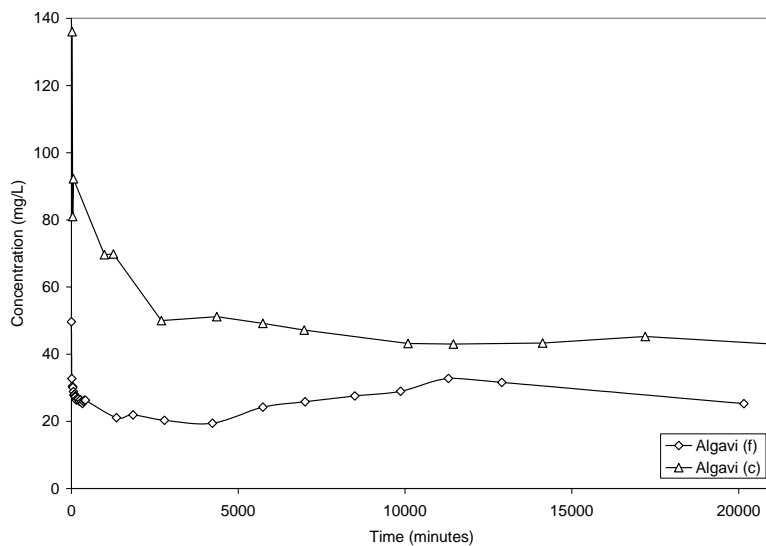


Figure 7.41. Ca in the outlet water of the $\text{Algavi}_{(c)}$ and $\text{Algavi}_{(f)}$ DS 1 L/minute treatment plant at Bwlch.
Average inlet Ca concentrations: $\text{Algavi}_{(c)}$ 40 mg/L; $\text{Algavi}_{(f)}$ 26 mg/L.

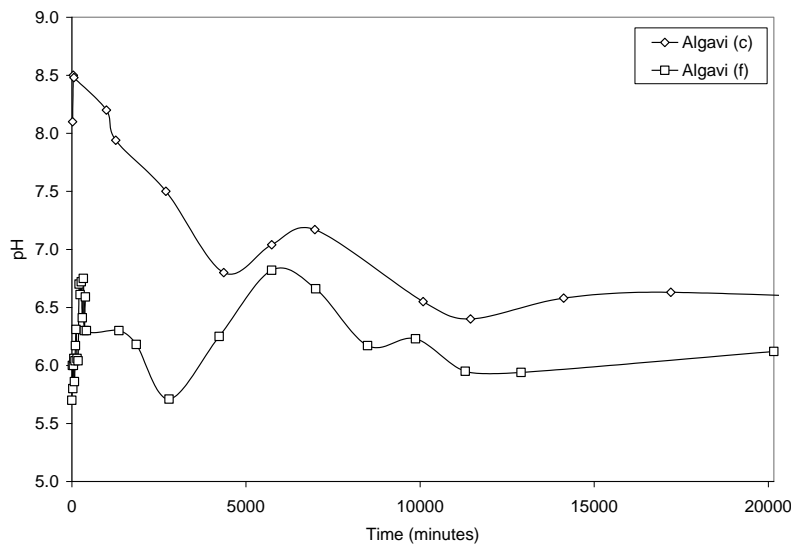


Figure 7.42. pH of the outlet water from the $\text{Algavi}_{(c)}$ and $\text{Algavi}_{(f)}$ DS treatment plant.
Average inlet pH: $\text{Algavi}_{(c)}$ 6.8; $\text{Algavi}_{(f)}$ 6.2.

Activity diagrams of selected samples collected from both Algavi treatment plants (the average inlet waters, 60 minutes, 4360 minutes from the Algavi_(c) treatment plant and 4230 minutes from the Algavi_(f) treatment plant) were calculated to determine whether the removal of metals from the mine drainage water could be attributed to the precipitation of metals carbonates. Within the samples, Pb always occurs within the PbCO₃ field predicting that the metal should precipitate out of solution; Figure 7.43 shows the average inlet waters for the Algavi_(f) treatment plant. The speciation of Zn differs between the Algavi_(f) and Algavi_(c) inlet waters. The inlet waters entering both the Algavi_(f) and Algavi_(c) treatment plant are nearing the boundary between Zn²⁺ and smithsonite (ZnCO₃) fields, see Figure 7.44a and b. The waters exiting the Algavi_(f) treatment plant does not fall into the smithsonite field (Figures 7.45a and 7.46a), therefore any metal removal that occurs is most likely primarily caused by Zn adsorption by DS. The waters exiting the Algavi_(c) treatment plant, however, are closer to the smithsonite field (Figure 7.45b and 7.46b) and it is more likely that metal carbonate precipitation is occurring removing the metal from the mine water. This may help to explain why increased amounts of Zn are removed by the Algavi_(c) DS (see Figure 7.40) because the Zn is removed by both adsorption and precipitation processes.

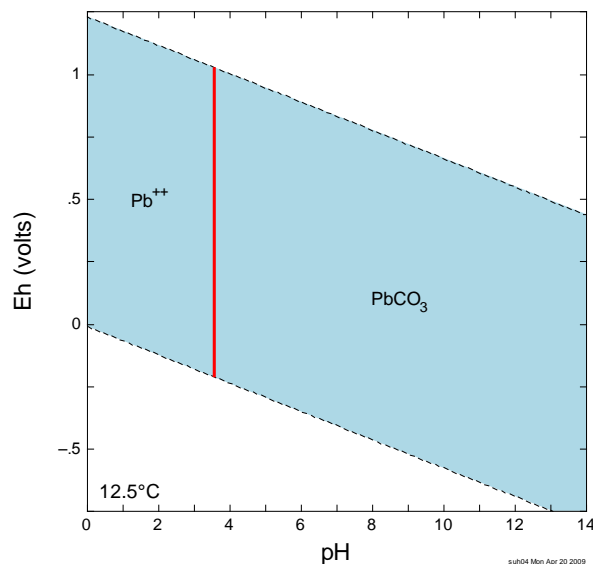


Figure 7.43. Pb activity diagram for the average inlet waters for the Algavi_(f) DS treatment plant. Average inlet parameters: pH 6.24, Eh 0.11 V, Ca 25.7 mg/L and Pb 887 µg/L.

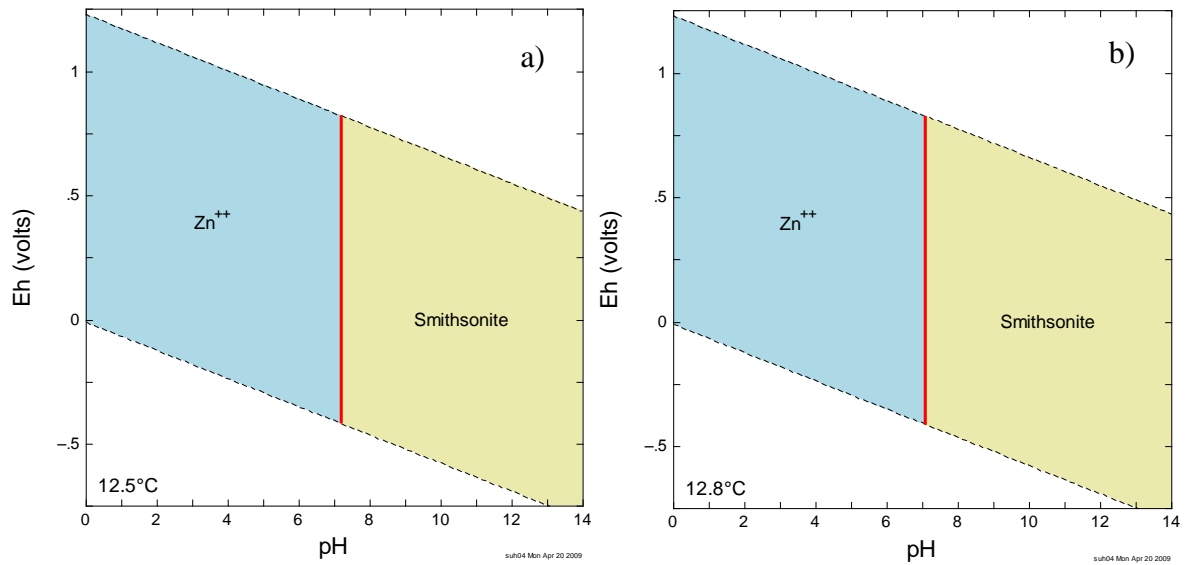


Figure 7.44. Zn activity diagrams for the average inlet waters to the Bwlch 1L/minute treatment plants containing: a) Algavi_(f) DS and b) Algavi_(c) DS. Average inlet parameters for Algavi_(f): pH 6.4, Eh 0.08 V, Ca 25.7 mg/L and Zn 27.7 mg/L; and Algavi_(c): pH 6.8, Eh 0.17 V, Ca 39.7 mg/L and Zn 25.4 mg/L.

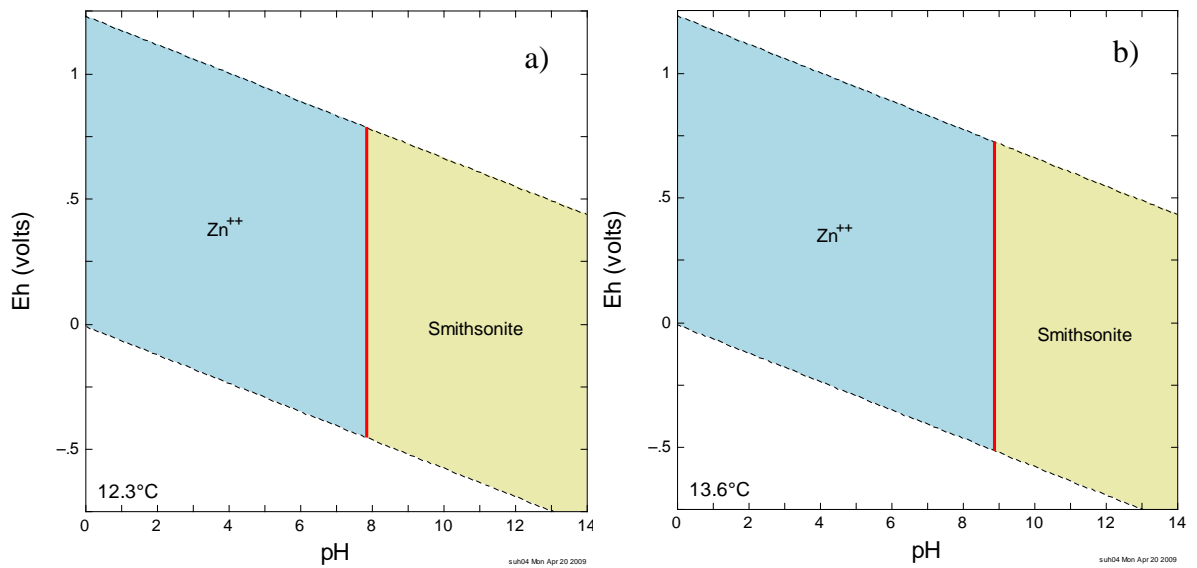


Figure 7.45. Zn activity diagrams at 60 minutes for the Bwlch 1 L/minute treatment plants containing: a) Algavi_(f) DS and b) Algavi_(c) DS. Inlet parameters at 60 minutes for Algavi_(f): pH 6.1, Eh 0.05 V, Ca 28.9 mg/L and Zn 4.78 mg/L; and Algavi_(c): pH 8.5, Eh 0.03 V, Ca 92.2 mg/L and Zn 0.21 mg/L.

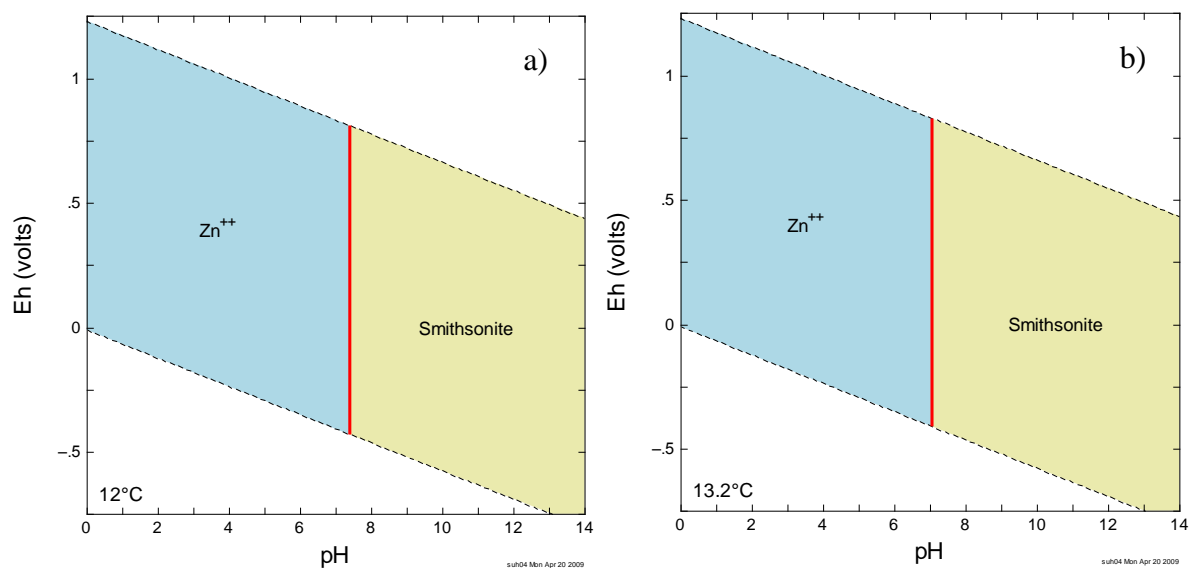


Figure 7.46. Zn activity diagrams for the Bwlch 1 L/minute treatment plants containing: a) Algavi_(f) DS at 4230 minutes and b) Algavi_(c) DS at 4360 minutes. Inlet parameters for Algavi_(f) at 4230 minutes: pH 6.3, Eh 0.10 V, Ca 19.5 mg/L and Zn 20.9 mg/L; and Algavi_(c) at 4360 minutes: pH 6.8, Eh 0.20 V, Ca 51.2 mg/L and Zn 20.1 mg/L.

The laboratory experiments (Chapter 6) showed that Algavi_(f) DS had a greater adsorption capacity than Algavi_(c) DS. Algavi_(c) DS has a larger surface area (2.79 m²/g compared to Algavi_(f), which has a surface area of 1.23 m²/g) and has a greater adsorption capacity; therefore it may be assumed that metal ions required longer than 24 hours (maximum contact time of the laboratory experiments) to diffuse into the interior of the particle. Algavi_(f) was also subjected to a more thorough water- and acid-washing and this may have removed a greater concentration of major cations from the DS surface which made them less available for ion exchange with the metal ions; H⁺ ions from the acid used, however, are available for exchange.

7.10 Summary

These field trials have successfully demonstrated that DS is an effective and rapid material for the removal (adsorption) of metal ions from circum-neutral mine drainage. The trials have provided more relevant detailed information on the adsorption characteristics of the DS in a real treatment situation and shown the differences in adsorption when using different DS types and different preparation methods. The DS has proven that it is a durable biosorbent to use (the DS did not degrade when left in the field for a number of weeks) and it is advantageous that biosorption can occur even in variable water

temperatures, the sampled waters varied between 6 and 23 °C (expected to be lower at night).

The Bwlch field trials were designed to quickly test the adsorption capacity of DS to its limit. The first 1 L/minute treatment plant contained ~3 kg (dry weight) Algavi_(c) DS and operated for 20 days, Zn saturation was reached after ~5 days and Cd saturation after ~11 days. Saturation was not reached for Pb and analysis of the DS bed showed that the Pb was concentrated in the top 20-30 mm of the bed and therefore the DS could continue to adsorb Pb from the mine water until ~100,000 L had flowed through (~60 days). This trial showed that DS had a very high affinity for Pb > Cd > Zn; the preference of the DS for Cd rather than Zn was also shown by the digestion of the DS core, the Zn:Cd ratio within the core was ~336:1 (average amount (µm) within each 10 mm DS layer) and within the Bwlch mine water was ~400:1 (average inlet concentration in mg/L). Once the Zn and Cd have saturated the DS, they are desorbed and re-released back into solution. During all the field trials large concentrations of Na, K, Mg and Ca were washed off the DS into solution in the first hour of operation and ion exchange may have occurred between these major cations and metal ions.

The mine drainage at Esgair Hir contains much lower concentrations of metals than Bwlch and therefore the treatment plant should not saturate as quickly as at Bwlch. The 1 L/minute treatment plant contained ~2 kg Algavi_(c) DS (dry weight) and operated for 66 days. The lengthy operation time proves that the DS is stable (i.e. not coated by algal growth nor does it degrade) and does not require constant operator involvement. The waters at Esgair Hir contained minor concentrations of Fe (an average of 0.2 mg/L during the trial period) and this had a major impact on the operation of the treatment plant. The Fe precipitated as ochre blocking the holes in the distribution pipe and coated the upper plastic and stainless steel mesh and the top of the DS bed. The precipitated ochre dramatically decreased the flow of mine water through the bed and impeded the adsorption of metals onto the DS. The DS bed had to be stirred to remove the Fe coating and increase the flow through the bed; stirring initially caused a large release of the metals, then the removal returned to about the same as it was before the bed was stirred. Stirring decreased the amount of metals which were retained within the treatment plant; this illustrates that a filter bed treatment plant is preferable to a stirred tank treatment system. To optimise the flow of the mine drainage through the treatment plant, Fe would need to be removed from

the mine water before it entered the treatment plant; for example by aerating the mine drainage to precipitate Fe or by passing the mine drainage through a sand bed. The deployment of a treatment plant containing carbonate sand at Esgair Hir proved that the metal removal was not purely a mechanical filtering effect, but caused by adsorption onto the DS. The digestion of a core of the carbonate sand showed a Zn:Cd ratio of ~524:1 and confirmed the adsorption preference of the DS of Pb > Cd > Zn (the Zn:Cd ratio of the Esgair Hir mine water was ~575:1). The initial removal of Fe followed by metal removal from mine drainage water is discussed in the next chapter.

A larger 2 L/minute treatment plant (containing ~4 kg (dry weight) Algavi_(f) DS) was deployed at Alltycrib to determine whether the treatment plant could be successfully scaled up. Zinc saturated the DS after ~9 days, but by the end of the trial (21 days) neither Cd nor Pb had saturated, proving that the treatment plant can be successfully scaled up. There were problems with organic matter blocking the inlet pipes and the distribution pipe holes, which would need to be removed to ensure the successful operation of the treatment plant if deployed in a similar organic-rich environment.

The 2 L/minute treatment plant was divided (with two outlet pipes) so that two 1 L/minute treatment plants could be operated simultaneously to directly compare two DS types (Girvan and Algavi_(f)). The field trials confirmed the results of the laboratory experiments that the Girvan DS has a greater capacity for the adsorption of metals. In addition, it is advantageous that the Girvan DS requires little or no pre-treatment; unfortunately this is no longer available in large quantities, as the processor now disposes of its DS via a long-fall pipe directly into the sea. If the treatment plants were deployed on a large enough scale it may be economic to acquire large quantities of the wet DS (before disposal into the sea) and prepare it using specialist drying equipment before use in the treatment plant. The dual treatment plant also allowed comparison between the Algavi_(c) and Algavi_(f) DS and contrary to the laboratory experiments the Algavi_(c) DS has a greater adsorption capacity than either Algavi_(f) or the Girvan DS (a direct comparison trial between the two Algavi DS would be required to prove this). It is interesting to note that all three DS saturate with Zn at more or less the same time (~5 days) although different amounts of metals are removed from the mine waters. These field trials have proved that the greatest adsorption of metal ions is achieved through the use of Algavi_(c) though using this DS on a large scale would require a rapid and effective method to remove the fines before the DS is washed

and acid-washed to pH 4-5. The acquisition of large quantities of the Girvan DS would most likely still be more economic as little or no pre-treatment is required.

The 10 L/minute treatment plant was not successful at removing large quantities of metals from the Bwlch mine water, but it highlighted problems that need to be addressed. In future large-scale treatment plants, a number of modifications are required to optimise metal ion removal. A more robust treatment plant is required to provide a more solid base to the bed of DS that would prevent the buckling of the perforated stainless steel sheet (i.e. an improved separation of the DS bed and the treated water); at present the steel sheet and DS bed is supported by a number of stainless steel pillars. A design similar to the 1 and 2 L/minute treatment plants (i.e. an inner and outer tank) may be more suitable. If the design remained unchanged, more frequent pillars would be required, plus a closer fit between the sides of the treatment plant and the stainless steel and nylon mesh (to prevent the loss of the DS from around the edges of the DS bed into the base of the tank and thus the development of preferential flow paths). This 10 L/minute trial also highlighted the need for the DS to be added to the plant in its dry, granulated form so that on contact with the mine water it could swell and effectively seal the treatment plant.

The effectiveness of the different treatment plants can be evaluated by comparing the amounts of metals removed within the trial period (including the amount desorbed from the DS). The calculated amount of metals removed shows that the Algavi_(c) DS has the highest adsorption capacity, followed by the Girvan DS and then the Algavi_(f) DS; from Bwlch mine water the Algavi_(c) DS adsorbed 50.6 g of Zn, Girvan adsorbed 40.3 g of Zn and the Algavi_(f) DS adsorbed 18 g of Zn. However, when the amount of metal removed as a percentage of the weight of DS or carbonate sand used within the treatment plant was compared the Girvan DS has the highest adsorption capacity (2.02 %) followed by Algavi_(c) (1.69 %) then Algavi_(f) (0.90 %).

The amount removed by the DS or the carbonate was typically Zn > Pb > Cd; this occurred when the treatment plant has not saturated with Pb; therefore if the treatment plant was operational for a longer period, the amount of Pb removed by the DS would increase. Conversely, the additional operating time would decrease the amount of Zn and Cd within the DS as it was desorbed back into solution. Where the DS had been saturated with Pb (in the Algavi_(c) 1 L/minute treatment plant at Esgair Hir), the amount of Pb removed (5.72 g

or 0.29 %) was slightly higher than that of Zn (5.32 g or 0.27 %). Typically the amount removed from the mine water when calculated by the removal of the metal from the mine water and from the digestion of the core was similar.

To determine the efficiency of the 1 L/minute treatment plant to remediate a different mine drainage, it was taken to the Libiola mine in Italy. The mine waters of the Libiola mine are acidic, Fe- and metal-rich.

CHAPTER 8:

Remediation of acidic mine drainage

Acid mine drainage (AMD) is the most widespread and challenging problem faced when remediating past and present mining activities (Volesky, 2003). Worldwide, acidic and metal-rich drainage from coal- and metal-mines poses a serious threat to the environment (Powell, 1988; Desbarats and Dirom, 2005), with Benner *et al.* (1999) estimating the cost of remediation to be billions of pounds.

The effects of AMD on the aquatic environment are dependent on the quality of the mine drainage, quality of the receiving waters and the amount of dilution that occurs. There are numerous deleterious effects of AMD, many of which are potentially serious (Glover, 1975) and pose a threat to human health, the environment (Alpers *et al.*, 1994) and cause the waters to fail EQS. The acidity of the drainage lowers the pH of the receiving waters making it corrosive to pipelines and equipment, toxic to fauna and flora and therefore unable to support life (Maree *et al.*, 2004a; Kim and Chon, 2001). The high metal concentrations (either in dissolved or particulate form) contained within AMD can disperse once the drainage waters enters the receiving waters (Salomons, 1995). High concentrations of suspended solids are associated with AMD which may have a significant effect on fish, including the production of excess mucus and the formation of deposits within the gills (Kelly, 1988).

Acid mine drainage is characterised by orange Fe^{3+} flocs (ochre) which are predominately Fe-oxyhydroxide precipitates that are deposited on the stream bed and on spoil tips (Fuge *et al.*, 1994; White, 2000). In reality, ochres are complex and contain a number of Fe-oxyhydroxides, hydroxysulphates and various partially hydrolysed forms; they form as the AMD becomes neutral with the critical pH for Fe^{3+} being 4.3 (Kelly, 1988). As pH increases, the Fe^{3+} precipitates out of solution and forms colloids, precipitates or heavier amorphous flocs (Kelly, 1988; National Rivers Authority, 1994). These ochres have a high visual impact on the receiving water course and may smother the stream bed and fauna, preventing photosynthesis, therefore, having a detrimental impact on the local ecology. Ochre may also sorb and co-precipitate additional metals which increase the effects on

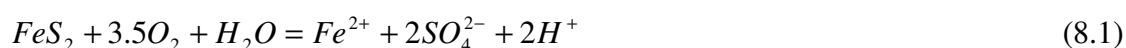
flora and fauna and on the water quality (National Rivers Authority, 1994; Younger, 1997; White, 2000). As little as 1 mg/L Fe in a stream causes a visible impact on the receiving water course (Glover, 1975).

This chapter discusses the remediation of acidic Fe-rich mine drainage waters, providing a contrast to the circum-neutral Fe-poor mine drainage waters of mid-Wales discussed in earlier chapters. The acid mine drainage of the Libiola mine in North West Italy was chosen as it provides a direct contrast to the mine drainage of mid-Wales, climatically, geologically and hydrochemically.

8.1 Acid Mine Drainage

Drainage waters associated with the extraction of Fe-containing metal- and coal-mines are commonly acidic and metal-rich and are a serious, persistent environmental pollution problem which occurs worldwide (Förstner and Kersten, 1988; Kim and Chon, 2001); it is regarded as the principal problem associated with mining sulphide ore deposits (Doyle, 1990). Ore deposits containing pyrite commonly produce acidic drainages caused by the exposure of the sulphide minerals to oxic conditions and their subsequent dissolution, though some types are more susceptible than others (Förstner and Kersten, 1988; Kelly, 1988; Salomons, 1995; Stumm and Morgan, 1996; Drever, 1997; Langmuir, 1997). Mining exposes pyrite to both air and water and as soon as it is exposed the mineral begins to oxidise (Glover, 1975). The Fe-sulphides may be continuously or sporadically exposed to air in the near-surface levels and in deeper workings the minerals may be below the water table therefore limiting the exposure to O₂ (Pentreath, 1994).

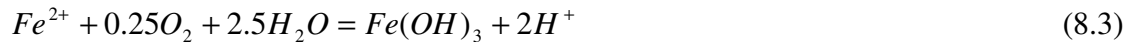
When pyrite is exposed to air the following stoichiometric reactions characterise the oxidation of pyrite (Stumm and Morgan, 1996; Drever, 1997; Langmuir, 1997, Faure, 1998):



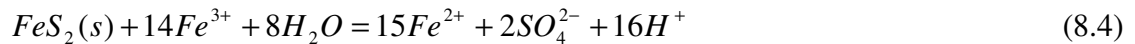
The sulphide in pyrite oxidises to sulphate and releases Fe²⁺ and H⁺ ions.



If there is enough O₂ present in solution the Fe²⁺ will oxidise into Fe³⁺ and some acidity is consumed (Banwart and Malmström, 2001); this oxidation also occurs as the solution emerges from underground (low O₂ concentration and the Fe²⁺ is in solution) and mixes with the atmosphere and oxygenated water (Pentreath, 1994).



Fe²⁺ oxidises to ferric oxide and forms insoluble ferric hydroxides and more H⁺ ions are released. Between pH of 4 and 7, Fe³⁺ tends to precipitate.



Fe²⁺ can be an oxidising agent for the pyrite itself, where there is a limited supply of O₂, generating predominantly Fe²⁺ in solution, and releasing additional H⁺ ions (Förstner and Wittmann, 1979; White, 2000; Banwart and Malmström, 2001).

Acidity generated by pyrite oxidation may occur seasonally where the water table occurs close to the ground surface. Within the unsaturated zone pyrite is oxidised in the absence of O₂ to form Fe-hydroxysulphates; when the water table rises the dissolution of the hydroxysulphates occurs and then after the water table falls fresh pyrite surfaces are exposed for oxidation. This cycle means that it is possible for flooded mine workings to generate acid for decades, if not centuries (Younger, 1997).

Pyrite oxidation rate

There are many factors which determine the rate of pyrite oxidation including: chemical parameters (pH, temperature, O₂ concentrations and availability within the atmosphere and in solution); the concentration and chemical activity of Fe³⁺ (Pentreath, 1994; Salomons, 1995); the morphology of the mineral (Pentreath, 1994); and the reactive surface area of the exposed mineral (Glover, 1975; Salomons, 1995). Finer grained minerals, although having a larger surface area which should promote reactions, may limit O₂ diffusion and therefore act as a limiting factor (Salomons, 1995).

Bacteria

At pH values between 4.5 and 7, the rate of Fe²⁺ to Fe³⁺ oxidation is relatively fast (Nordstrom, 1982 cited in Nimick and Moore, 1991), but below pH 3.5 the rate is very slow (Merefield, 1995). The rate of chemical oxidation of Fe²⁺ may be catalysed by the presence of suspended solids (Maree *et al.*, 1997 cited in Maree *et al.*, 2004a) or by the presence of bacteria (Förstner and Wittmann, 1979; Singer and Stumm, 1970 cited in Stumm and Morgan, 1996; Kim and Chon, 2001; Nengovhela *et al.*, 2004) as they derive their metabolic energy by using O₂ to oxidise Fe²⁺ to Fe³⁺ (Rimstidt *et al.*, 1994). In acidic conditions Fe-oxidising bacteria may speed up the reaction by $\leq 10^6$ times (Merefield, 1995; Langmuir, 1997) and S- and O₂-oxidising bacteria may encourage ≥ 200 times more Fe to be released from pyrite than when bacteria is absent (Karamenko, 1969 cited in Langmuir, 1997).

The role of bacteria in AMD formation has been extensively studied (Glover, 1975) and many species have been found to have a direct role. The most common bacteria are *Thiobacillus ferrooxidans* (Fe- and S-oxidising bacteria) and *Thiobacillus thiooxidans* (S-oxidising), although there are numerous other bacteria (Förstner and Kersten, 1988; Doyle, 1990; Roane *et al.*, 1996); Nordstrom and Southam (1997, cited in White, 2000) found 22 species associated with mine waters and pyrite oxidation. These bacteria are most active in an acidic environment and therefore once the acidity is produced, the production of acid rapidly increases and is very difficult to stop (Doyle, 1990; Drever, 1997). Bacteria may also play a role in the precipitation of Fe oxyhydroxides as well as their decomposition (Faure, 1998).

Additional metals

Acidic FeSO₄ solutions are strong oxidants which attack other metal-sulphide minerals such as galena and sphalerite (Förstner and Kersten, 1988; Doyle, 1990; Rimstidt *et al.*, 1994; Drever, 1997) and minerals within the associated country rock and gangue minerals (for example, the Al in aluminosilicates) (Sullivan and Yelton, 1988 cited in Kim and Chon, 2001; Howell and Bruce, 1995). Therefore, AMD usually contains high concentrations of other metals (Förstner and Kersten, 1988; Doyle, 1990; Drever, 1997).

8.2 Remediation methods

The main problem of AMD is that once acid generation processes have started they tend to worsen and are very difficult to stop (Doyle, 1990). AMD may be released for many decades, even centuries, after a mine has been abandoned (Doyle, 1990; Wood *et al.*, 1999 cited in Younger, 2000b). AMD remediation is difficult as each individual mine has its own characteristic drainage i.e. a particular pH, conductivity and the combination and concentration of metals; a result of specific weathering reactions and pyrite oxidation kinetics (Doyle, 1990; Batty and Younger, 2004). Once AMD is produced often all that can be done is to prevent air and water contacting with the pyrite within the mine or spoil tips; or if this is impractical then the mine drainage can be remediated either actively or passively (Glover, 1975; Doyle, 1990; Burke and Banwart, 2002).

The main objective of AMD remediation is the neutralisation of the mine drainage and the removal of Fe and associated metals, as precipitates (Hedin *et al.*, 1994; Pentreath, 1994; Drever, 1997). Active remediation methods require the continuous addition of chemicals and use of artificial energy sources for pumping and aeration to achieve lower metal concentrations (Burke and Banwart, 2002). Passive treatment systems avoid continuous input of chemicals or energy for equipment operation and use natural biochemical processes (Batty and Younger, 2004). All passive methods, however, require some maintenance during their lifetime (Burke and Banwart, 2002). There are numerous remediation methods and each method is appropriate for an individual mine water dependent on the specific hydraulic circumstances, the volume of mine water, and the type and concentration of elements present (Gazea *et al.*, 1996; Younger, 2000b). The selection of which remediation method is most suitable for a particular mine drainage is dependent on a number of technical and economic considerations (Coulton *et al.*, 2003). AMD may be treated to comply with EQS, but this may markedly increase the cost of remediation, making it uneconomical (Glover, 1975).

The enduring nature of AMD means that any remediation method is likely to be exceedingly costly, both in terms of capital and operating costs (Doyle, 1990). Within the UK, the entry of “*poisonous, noxious or polluting matter of solid waste*” into controlled waters from abandoned mines is not controlled by law (section 89 of the Water Resources

Act, 1991) and therefore any costs derived from the remediation of an AMD source or polluted stream become a public responsibility and expense (Ziemkiewicz *et al.*, 2003).

8.2.1 Prevention

Preventing the formation of AMD is preferable to remediating the resultant drainage and spoil tips, especially for new mines or new spoil tip management facilities (Doyle, 1990). Prevention is relatively simple, either the source of drainage can be removed or air and water can be excluded to prevent pyrite oxidation (Glover, 1975; Doyle, 1990). Although pyrite oxidation can not be prevented during the active phase of mining, there are several methods for minimising oxidation when parts, or the whole, of the mine have been abandoned (Glover, 1975), including flooding the mine, capping the mine area and spoil tips and diversion of local water courses.

If a mine is completely flooded (either naturally once pumping ceases or artificially), the rate of oxidation is reduced with limited availability of free O₂ (Glover, 1975; Doyle, 1990; Salomons, 1995; Drever, 1997; Langmuir, 1997); Younger (1997) noted that pyrite oxidation in flooded coal fields was negligible. Hydraulic seals may be constructed to prevent waters leaving the mine and are often a highly cost-effective method of reducing the AMD from some sites. There are, however, many associated problems including: 1) it is nearly impossible to seal every mine exit, especially in old mines; 2) sealing a lower adit may cause the drainage to flow out of a higher adit (Doyle, 1990), which may be highly acidic and metal-rich because of previously formed oxidation products (for example, H₂SO₄ and FeSO₄) being brought into solution (Glover, 1975; Pentreath, 1994); and 3) the seal may leak and/or fail leading to extensive and widespread seepages of AMD (Doyle, 1990; Alpers *et al.*, 2003; Csővári *et al.*, 2007).

Mine spoil tips are often covered with an impermeable cap to prevent water and air infiltration, although this is not always practical (Doyle, 1990; Alpers *et al.*, 2003). Materials used as an impermeable cap include plastic or tar (often only a temporary solution); well compacted spoil (more efficient and permanent) or alternating layers of clay, gravel and topsoil covered in vegetation (to prevent erosion of the surface) (Glover, 1975; Salomons, 1995). To exclude water from entering a mine it may be possible to seal surface fissures, adits, and shafts; but the prevention of strata water entering the mine is

expensive and potentially dangerous (Glover, 1975). To reduce water infiltration into spoil tips, drainage ditches may be constructed around the tips and surface water diverted (Doyle, 1990).

If pyrite oxidation can not be prevented then basic material may be added into the mine creating moderate pH values, which may reduce the oxidation rate; though the quantity of material is difficult to predict because of the variable nature of pyrite oxidation (Doyle, 1990). Bactericides have also been investigated to reduce the microbial pyrite oxidation though the effect is only temporary as the bactericides are subject to degradation (Salomons, 1995).

8.2.2 Active Remediation

Ferruginous discharges from abandoned mines might best be treated by active methods on a decadal scale (Younger, 1997; Banwart and Malmström, 2001). Active remediation is usually achieved by oxidation (by chemical means or physical aeration), the addition of alkaline chemicals to precipitate metals in their insoluble form, followed by the settlement of these precipitates prior to discharge of the metal-poor drainage (Wieder, 1994; Younger *et al.*, 2002). Other (often more expensive) methods include: bacterial sulphate reduction, reverse osmosis, flash distillation, freezing, ion exchange and solvent extraction (Glover, 1975; Younger, 2000a).

Active remediation is not applicable to all ferruginous mine drainages, it is usually only used for long-term mine discharges and waters that are difficult to treat by passive methods (Burke and Banwart, 2002; Batty and Younger, 2004; Coulton *et al.*, 2003). Active methods are associated with high capital and operating costs (Wieder, 1994; Lee *et al.*, 2000; Burke and Banwart, 2002); including the installation of treatment plants with various agitators, precipitators, clarifiers and thickeners; plant operation and maintenance; the constant supply of reagents; and disposal of the resulting sludge (Gazea *et al.*, 1996; Ziemkiewicz *et al.*, 2003; Maree *et al.*, 2004a).

Addition of alkali chemicals

The alkali chemicals used to treat AMD include CaCO_3 , NaOH , Ca(OH)_2 , CaO , Na_2CO_3 , NH_3 , or MgO (Skousen *et al.*, 1990 cited in Hedin *et al.*, 1994; Gazea *et al.*, 1996; Burke

and Banwart, 2002). The addition of alkali chemicals aims to raise the solution pH; encourage metal adsorption onto solids (including clays, organic matter, carbonates, and hydrous Fe and Mn oxides) within the water column; increase the rate of Fe^{2+} oxidation; and the precipitation of metals (Hedin *et al.*, 1994; Salomons, 1995; Gazea *et al.*, 1996; Burke and Banwart, 2002; Coulton *et al.*, 2003). The adsorbed and precipitated metals are then removed either in a settlement pond (Ziemkiewicz *et al.*, 2003) or by liquid-solid separation in a clarifier (Coulton *et al.*, 2003). Each metal species has an optimum pH at which maximum removal is achieved and either a multi-stage treatment can be used where each metal is removed at its optimum pH, or a single pH is used which allows the removal of the majority of the metals (Coulton *et al.*, 2003).

The selection of alkali chemical depends upon the cost, the handling equipment and the volume used (Coulton *et al.*, 2003); care has to be taken as chemicals may be expensive, potentially dangerous and may lead to highly alkaline water when improperly used (Hedin *et al.*, 1994). On a purely costs basis, lime or quicklime (CaO) is the cheapest, followed by hydrated lime (Ca(OH)_2); both chemicals may be added directly to the mine water, though it is common practice to make a slurry containing 5-10 % hydrated lime (Coulton *et al.*, 2003). Lime is the preferred chemical to use because of its high reactivity, abundance and cost-effectiveness when treating highly metalliferous drainage (Kuyucak, 2002; Coulton *et al.*, 2003; Maree *et al.*, 2004b). The precipitation of metal oxyhydroxides is rapid and produces a neutral, low-Fe effluent, though the coagulation of the particles becomes more difficult with low initial Fe concentrations (Glover, 1975; Kuyucak, 2002). Lime may result in the scaling of equipment; the malfunctioning of the dosing equipment (leading to lower dosages being added to the AMD); the settlement of particles in pipelines and valves, which may cause inefficient metal removal (Maree *et al.*, 2004a) and the production of a large volume of water- and metal-rich sludge (Benner *et al.*, 1999; Kuyucak, 2002). The dewatering of the sludge is often difficult and expensive (Glover, 1975; Coulton *et al.*, 2003); methods to increase the sludge density include vacuum filtration, continuous pressure dewatering, frame- and plate-dewatering and centrifuge separation (Younger *et al.*, 2002) or by re-circulating the produced sludge, adding it to the mine water at the same time as the lime (Coulton *et al.*, 2003; Dey *et al.*, 2007).

Bacterial Sulphate Reduction

Bacteria can assist in the remediation of AMD (Johnson, 2003); the most important of these are sulphate reducing bacteria (SRB) which catalyse the reduction of Fe^{3+} and/or sulphate (Benner *et al.*, 1999; Johnson, 2003) and generate alkalinity. The SRB require a carbon source; an anoxic environment; $\geq 100 \text{ mg/L SO}_4^{2-}$; the absence of Fe^{3+} and Mn^{4+} (Gazea *et al.*, 1996; Batty and Younger, 2004) and are most efficient when the pH is >4 (Gazea *et al.*, 1996), though Prommer *et al.* (2000 cited in Woulds and Ngwenya, 2004) observed SRB at pH 3. In an anoxic environment, the sulphides react with metals to produce insoluble metal sulphides which precipitate out of solution (Gazea *et al.*, 1996; Batty and Younger, 2004; Johnson, 2003; Woulds and Ngwenya, 2004); representing an effective metal sink (Richards *et al.*, 1992 cited in Woulds and Ngwenya, 2004). The use of SRB to treat AMD has been limited because of the low degradability of the carbon source (Gibert *et al.*, 2005a) and the acidic drainage may consume the generated alkalinity decreasing the SRB's capacity to reduce SO_4^{2-} (Benner *et al.*, 1999).

Ferruginous mine drainage may continue for many decades after a mine has been abandoned and the cost, energy and maintenance involved with active remediation methods makes it impractical for most remote abandoned mine sites (Ziemkiewicz *et al.*, 2003) or where the AMD contains low metal concentrations. There is also a financial incentive to develop low-cost and low-maintenance remediation methods (Gazea *et al.*, 1996). The best available strategy is to develop a method where a single expenditure can achieve lasting results with limited additional costs and maintenance, until the treatment system has to be replaced, and this is most likely to be a passive method (Younger, 1997; Younger, 2000a; Nuttall and Younger, 2000).

8.2.3 Passive Remediation

Passive remediation uses natural energy sources (for example, gravity, microbial metabolic energy, photosynthesis) in a system which requires infrequent maintenance to keep the system operating efficiently (Gazea *et al.*, 1996; PIRAMID, 2003 cited in Batty and Younger, 2004). Passive methods are the remediation of choice when there is no problem of land availability (Younger, 2000b); though within the UK, the Coal Authority considers the lack of land as the greatest problem when constructing a passive system (Parker, 1997 cited in Younger, 2000b; Parker, 1999 cited in Jarvis and Younger, 2001). The processes

employed in passive remediation are often slow and require a longer reaction time than in active remediation therefore a larger area is needed to produce similar results. Passive remediation methods have mainly been used to treat net-alkaline coal mine drainage with a low metal concentration (where the main elements of concern are Fe and Mn); the use of passive methods to treat metal mine drainage is limited (Gazea *et al.*, 1996).

The most important passive remediation methods include aerobic and anaerobic wetlands; open limestone channels (OLCs); anoxic limestone drains (ALDs); and vertical flow wetlands (or RAPS - Rapid Alkalinity Producing Systems) (Ziemkiewicz *et al.*, 2003).

Aerobic wetland systems

Aerobic wetlands consist of a series of basins or channels with a fairly impermeable base, to prevent seepage, covered with <30 cm of soil, organic matter, clay or mine spoil onto which vegetation grows; and 10-50 cm deep water flows over the surface. An aerobic wetland is designed to treat net-alkaline mine drainage. Hellier *et al.* (1994 cited in Ziemkiewicz *et al.*, 2003) determined that aerobic wetlands were the most effective remediation method for mine drainage with a pH >5; the aerated drainage encourages Fe and Mn oxidation and hydrolysis causing metal oxyhydroxides to precipitate out of solution. The shallow water and vegetation regulates and reduces the flow of mine drainage through the wetland and the vegetation enhances bacterial activity, improves the settlement of Fe precipitates, inhibits the removal of precipitates and may translocate O₂ to the roots, which may promote oxidation within the substrate (Gazea *et al.*, 1996; Ziemkiewicz *et al.*, 2003; Wiseman and Edwards, 2004). The oxidation and hydrolysis reactions occur fast enough to make wetlands cost effective (Hedin *et al.*, 1994; Gazea *et al.*, 1996; Ziemkiewicz *et al.*, 2003).

Another remediation method for circum-neutral, Fe-rich waters is a series of sedimentation basins linked by a cascade (Glover, 1975), i.e. the mine drainage flows over steps which allows aeration and the Fe³⁺ to precipitate and settle out of solution in the basins (Burke and Banwart, 2002).

Anaerobic wetland systems

Anaerobic wetlands are designed to treat net-acidic mine drainage (Batty and Younger, 2004) which may contain high concentrations of dissolved O₂, Fe³⁺ and Al³⁺ (Gazea *et al.*,

1996); for successful remediation the mine drainage has to be neutralised. Anaerobic wetlands consist of deep (>30 cm) substrates of limestone-rich organic matter which are planted with vegetation (Ziemkiewicz *et al.*, 2003). The mine drainage mainly flows along the surface of the substrate, and the generated alkalinity raises the pH causing the precipitation of metal oxides, hydroxides, sulphides and/or carbonates (Batty and Younger, 2004). The organic-rich substrate also generates anoxic conditions which are required by SRB, detailed above (Gazea *et al.*, 1996).

Over time, wetlands decrease in efficiency with a reduction in surface area, retention time, organic substrate supply and alkalinity generation (Wieder, 1994; Woulds and Ngwenya, 2004). Infrequent maintenance is therefore required, including the occasional input of organic matter (Roane *et al.*, 1996), the cleansing of pipes and drainage channels, weeding and replacing the substrate every 20-25 years (Ransom, 1999). The problem of disposing of the substrate (consisting of contaminated biomass (plant and bacteria), substrate material and metal precipitates) is raised with the substrate requiring disposal as special or controlled landfill.

Wetlands require large areas of land (dependent on the flow rate and degree of contamination); for example, Garth Tonmawr in the Peleenna Valley, South Wales remediates coal mine drainage (average between 1991-2002 was flow: 22.1 L/second, total Fe concentration: 29.2 mg/L, Fe loading: 52.9 kg/day) and consists of five natural and constructed aerobic and anaerobic wetlands and covers an area of 6370 m² (Ransom, 1999; Wiseman and Edwards, 2004). Where large areas of land are unavailable, such remediation methods can not be used (Burke and Banwart, 2002), therefore present research is focussing on Fe removal methods that only require small areas of land (Younger, 2000b).

Limestone

There are many advantages to using limestone as a remediation material: it is relatively cheap and available; non-hazardous and easy to store; has a simple dosage control (no pH control is required as limestone dissolves at a pH <7); over-dosing the AMD is minimised (i.e. chemical wastage) and a denser sludge is produced (Glover, 1975; Maree *et al.*, 2004a).

The use of limestone as a remediation material is limited and has not been particularly successful as it has a lower solubility and dissolution rate compared to other alkaline chemicals and its effectiveness decreases if the AMD contains significant concentrations of Fe^{2+} and O_2 or $> \sim 5000 \text{ mg/L SO}_4$ (Glover, 1975; Gazea *et al.*, 1996; Cravotta and Trahan, 1999). As AMD is neutralised, Al- and Fe-oxyhydroxides precipitate out of solution coating the limestone, causing the dissolution rate and alkalinity production to decrease considerably (Gazea *et al.*, 1996; Drever, 1997). Cravotta and Trahan (1999), however, determined that even if the limestone was coated, it could still remediate AMD; their experiments showed that even in an oxic environment Fe and Al were reduced to $< 5 \%$ of the inlet concentrations, and the combination of oxyhydroxide precipitation and a $\text{pH} > 5$ promoted sorption and co-precipitation of dissolved metals (Mn, Cu, Co, Ni and Zn). To prevent the build-up of oxyhydroxides the limestone must either be very fine or mechanically scrubbed during the reaction (Glover, 1975). Limestone powder may be used as an alternative to lime powder as it is cheaper ($\sim 56 \%$), more easily stored, safer (only reacts in acidic environments) and reduces the need for a lime slaker (Maree *et al.*, 2004b).

Limestone may be contacted with the AMD by either limestone leach beds (LLBs) or open limestone channels (OLCs). LLBs are appealing because they are easy to construct and maintain (Ziemkiewicz *et al.*, 2003) and consist of a pond through which AMD flows (Black *et al.*, 1999 cited in Ziemkiewicz *et al.*, 2003). OLCs are open channels or ditches filled with limestone; they are most effective when the slope exceeds 12% so that the flow velocities help prevent the precipitation of oxyhydroxides; any formed precipitates are removed from the surface of the limestone and then transported through the channel or ditch (Cravotta and Trahan, 1999; Ziemkiewicz *et al.*, 2003). The limestone may be used as a stand-alone remediation method or in conjunction with other methods (Ziemkiewicz *et al.*, 2003). Steel slag fines (3-4 mm) may be used instead of limestone to treat AMD containing minimal Fe, Mn or Al (Simmons *et al.*, 2002 cited in Ziemkiewicz *et al.*, 2003).

Anoxic Limestone Drains

The coating of the limestone by Fe- and Al-oxyhydroxides (see above) may be avoided by using anoxic limestone drains (ALDs) as limited O_2 reduces the probability of Fe-oxyhydroxides precipitating. ALDs consists of high quality limestone ($> 90 \%$ CaCO_3) which is buried under several metres of clay and sealed to encourage the build-up of CO_2 .

For efficient operation, the AMD needs to contain <1 mg/L of dissolved O₂ and <2 mg/L Fe³⁺ or Al³⁺; AMD may first be directed through organic matter to decrease these concentrations (Gazea *et al.*, 1996; Cravotta and Trahan, 1999). Low O₂, Fe³⁺ and Al³⁺ are required because when anoxic AMD flows through the ALD, alkalinity is added and at a near neutral pH both Fe- and Al-hydroxides precipitate causing the ALD to fail (Gazea *et al.*, 1996; Ziemkiewicz *et al.*, 2003). The passage of AMD through the ALD should not change the concentration of Fe²⁺ and Mn (Gazea *et al.*, 1996) therefore an ALD commonly precedes a settlement pond or wetland where the aerobic environment promotes Fe²⁺ oxidation and Fe³⁺ and associated metals precipitate out of solution (Hedin *et al.*, 1994; Gazea *et al.*, 1996). ALDs are an efficient method of adding alkalinity to the AMD (Hedin *et al.*, 1994; Cravotta and Trahan, 1999; Burke and Banwart, 2002) and are more cost effective than compost wetlands (Gazea *et al.*, 1996).

ALDs may also be used to remediate Fe-poor, metal-rich net-alkaline waters. An ALD was used in field trials by Nuttall and Younger (2000) to remediate Zn-rich net-alkaline waters; the ALD (2 x 5 m bag containing 4 tonnes of limestone) raised the pH and caused smithsonite to precipitate out of solution reducing the Zn concentration by ~22 % (from an average influent of 7.3 mg/L to an average effluent of 5.8 mg/L). Eventually, the precipitated smithsonite would coat the limestone reducing its effectiveness (Younger, 2000b).

Vertical Flow Wetlands

Vertical flow wetlands (VFW) (or RAPS - Reducing and Alkalinity Producing Systems) incorporate both a wetland and ALD within one system, the water flows through a layer of organic matter and then through a bed of limestone (Ziemkiewicz *et al.*, 2003). Bacteria within the organic matter use available O₂ creating an anoxic environment which promotes the reduction of SO₄²⁻ and Fe³⁺ and metal sulphides may precipitate. Alkalinity may also be generated within the organic matter by the precipitation of elemental sulphur, Fe-sulphides and the degassing of H₂S (Batty and Younger, 2004; Ziemkiewicz *et al.*, 2003; Wiseman and Edwards, 2004). The anoxic mine drainage then flows into a settlement pond or wetland promoting Fe²⁺ oxidation and the precipitation of Fe³⁺ and associated metals (Batty and Younger, 2004; Ziemkiewicz *et al.*, 2003; Wiseman and Edwards, 2004). Batty and Younger (2004) found that VFWs are more efficient than compost wetlands in terms of metal removal and alkalinity production.

Surface Catalysed Oxidation Of Ferrous Iron

Surface Catalysed Oxidation Of Ferrous Iron (SCOOFI) is used to remediate ferruginous net-alkaline mine waters (Batty and Younger, 2004). SCOOFI occurs in two-steps: Fe^{2+} is adsorbed onto the surface of previously precipitated ochre by the formation of the surface complex XFeOFe^{2+} ; then once adsorbed the Fe^{2+} is oxidised *in situ* by dissolved O_2 with the ochre acting as a catalyst; adding further layers to the ochre. The surface precipitation conserves the adsorption sites (XFeOH) which further react to adsorb Fe^{2+} ions from solution and catalyse their oxidation to the ochre surface. This reaction is irreversible under oxic conditions and surface catalysed Fe^{2+} oxidation is more rapid than oxidation by O_2 in free solution (Younger, 2000b; Burke and Banwart, 2002). The adsorption of Fe^{2+} onto fresh ochre surfaces strongly depends on the pH of the solution, with adsorption rapidly decreasing in more acidic waters. If circum-neutral pH is maintained then this method can be efficient; if not a considerable increase in surface area (i.e. adsorption capacity) is required (Burke and Banwart, 2002). High surface area material onto which the ochre initially precipitates may include plastic trickle filter media, blast furnace slag (Burke and Banwart, 2002; Batty and Younger, 2004) and brushwood (Best and Aikman, 1983 cited in Burke and Banwart, 2002).

The rapid oxidation and efficient Fe removal mean that residence time can be very short (≥ 70 seconds), consequently remediation can occur without the presence of wetlands, therefore dramatically reducing the area of land required for remediation (Younger, 2000b). Younger *et al.* (2002) determined that SCOOFI reactors are much more efficient at removing Fe and Mn than aerobic wetlands (compared on a g/m^2 basis).

Permeable Reactive Barriers

Permeable Reactive Barriers (PRBs) have gained popularity in treating contaminated groundwater within the last decade (Blowes *et al.*, 2000). Vertical walls of reactive material are often contained within sand to help distribute the flow through the material and capped with clay to minimise infiltration from the surface and to promote anoxic conditions (Benner *et al.*, 1999). The reactive material is placed in the path of contaminated water (either groundwater or spoil tip discharge) promoting numerous biogeochemical reactions (including precipitation of metal sulphides, sorption, oxidation, SO_4^{2-} reduction, fixation and degradation) resulting in the removal of the contaminants

(Benner *et al.*, 1999; Blowes *et al.*, 2000; Burke and Banwart, 2002; Batty and Younger, 2004).

Reactive materials used include zero valent iron (Blowes *et al.*, 2000; 2003), bone-char pellets, amorphous ferric hydroxide, basic oxygen furnace slag (Blowes *et al.*, 2003) and mixtures containing organic carbon (Benner *et al.*, 1999; Batty and Younger, 2004; Gozzard *et al.*, 2005). Organic carbon mixtures are the most appropriate for treatment of mine drainage as it promotes SRB activity and SO_4^{2-} reduction (Benner *et al.*, 1999; Blowes *et al.*, 2003; Batty and Younger, 2004). The limiting factors are preferential flow through the material, preferential mass flux, the inhibition of the SRB by low temperatures, the loss of reactive surface area and permeability as metal sulphides precipitate; therefore a material must be chosen which maintains its permeability (Benner *et al.*, 1999; Blowes *et al.*, 2000). Preferential flow may be reduced by using a single reactive material (Gozzard *et al.*, 2005) though Amos and Younger (2003 cited in Gozzard *et al.*, 2005) determined that a mixture of reactive materials results in the greatest sulphate removal. After ≥ 15 years the reactive material will need to be replaced.

The reactive material may also be placed as an active barrier within the mine. Zoumis *et al.* (2000) investigated various materials including fly ash, red mud, tree bark, bentonite and zeolites and determined that fly ash and red mud showed the greatest removal of Zn, Cd, Ni and Mn by sorption and precipitation. Both these materials contain metal oxides with large surface areas and CaO which promotes an increase in pH and subsequent metal precipitation (Zoumis *et al.*, 2000).

Biosorption

Various organic materials have been shown to adsorb metals from waste waters (see Chapter 5.4), though their application for the remediation of AMD has been limited (Jeffers *et al.*, 1993). Jeffers *et al.* (1993) investigated the use of BIO-FIX beads (immobilised biomass in porous polysulfone beads) for the remediation of AMD from an abandoned Ag mine (pH 6.5 and Fe concentration between 20 and 60 mg/L) using 96 L of beads (16 bags of 6 L) placed in a trough 2.1 m long, 0.3 m wide and 0.3 m high which filtered out the precipitated Fe. The BIO-FIX beads were also tested at an abandoned Zn mine where 1 L/minute of AMD flowed through 88 L beads (16 bags of 5.5 L) in a trough, an average of 48-57 % of Fe, Cd, Cu, Pb and Zn was removed. This method was

determined to be most successful for treating low flows in remote areas (Jeffers *et al.*, 1993). Other biosorbents which have been used to remediate AMD in a laboratory environment include lignite (Mohan and Chander, 2006), grape stalks and cork powder (Santos *et al.*, 2004), microorganisms (Kuyucak, 2000), seaweed (Kratochvil and Volesky, 1998b), vegetal compost (Gibert *et al.*, 2005b) and activated sludge (Utigikar *et al.*, 2000).

8.3 Study site

8.3.1 Geology

The Libiola Fe-Cu sulphide mine is located 8 km north east of the village of Sestri Levante in the north-western Apennines, Italy (Figure 8.1). The mine is within the Gromolo drainage basin and is drained by the Rio di Boeno and the Rio Cattan (Cortecci *et al.*, 2001; Dinelli *et al.*, 2001), both tributaries of the Gromolo River. Sandstones and shales of the Gottero Sandstones, Val Lavagna Formation and ‘Palombini’ shales are exposed in the lower part of the Gromolo Basin, while a Mesozoic ophiolite suite dominates the upper Gromolo basin (Cortecci *et al.*, 2001; Dinelli *et al.*, 2001), see Figure 8.2.

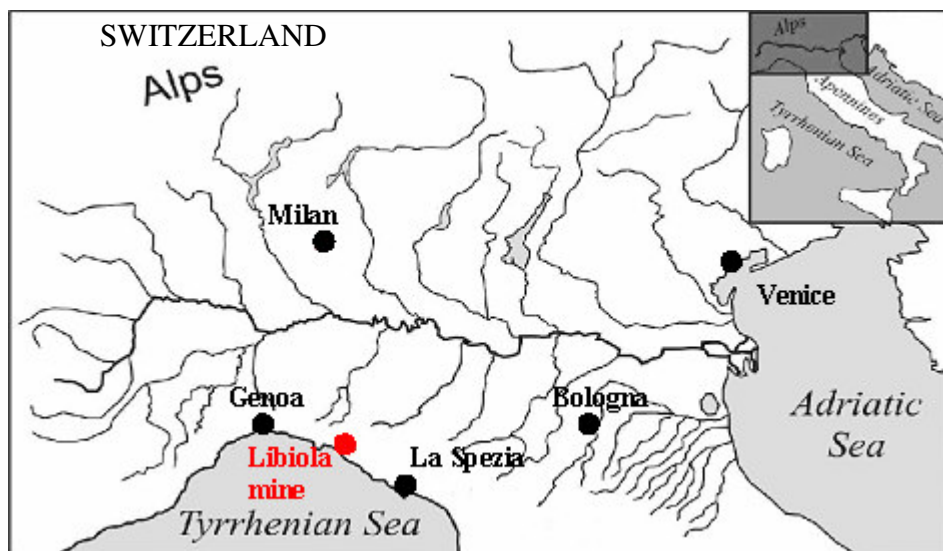


Figure 8.1. Location of the Libiola Fe-Cu mine, Italy (marked by the red dot).
Source: E. Dinelli

Mineralisation in the Libiola mine area is associated with the Mesozoic ophiolitic rocks of the Internal Ligurides outcropping in Eastern Liguria (Dinelli *et al.*, 2001; Dinelli and Tateo, 2002). The ophiolites consist of peridotites (variably affected by serpentinisation), gabbros and basaltic dykes (Accornero *et al.*, 2005) overlain by volcano-sedimentary cover

rocks of Jurassic-Upper Cretaceous age (Figure 8.2). These volcano-sedimentary rocks include tectonic and sedimentary breccias, massive and pillow lavas and pelagic sediments (cherts, micritic limestones and claystones) (Marini *et al.*, 2003; Carbone *et al.*, 2005). The Libiola ore deposits occur mainly within pillow and brecciated basalts (Bonatti *et al.*, 1976; Dinelli and Tateo, 2002; Carbone *et al.*, 2005) and rarely within the gabbro or peridotite units (Bonatti *et al.*, 1976). This sequence represents part of the Jurassic Ligurian-Piedmont oceanic crust, which separated the paleo-European and Adrai continental blocks (Carbone *et al.*, 2005); these continental blocks finally closed in Cretaceous or early Tertiary times (Bonatti *et al.*, 1976).

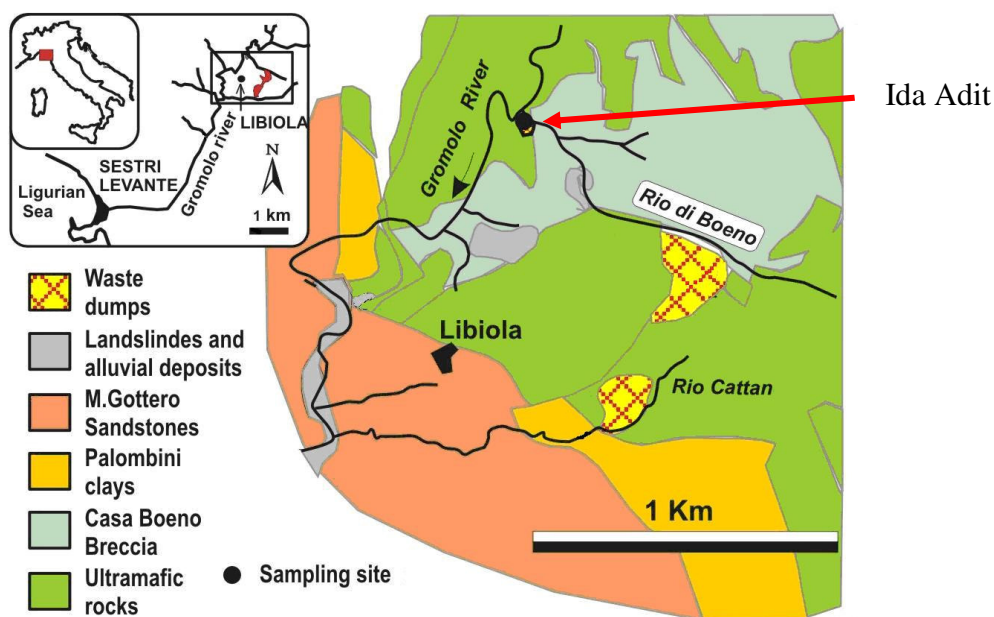


Figure 8.2. Geological map of the Libiola Fe-Cu mine, Italy.
After: Dinelli *et al.*, 2007

The Libiola sulphide deposit was originally generated through the liberation of metals from basalts by hydrothermal fluids, circulating through the basaltic-gabbroic crust at the mid-oceanic spreading centre. Upper mantle volatiles may also have provided metals to the thermal waters (Bonatti *et al.*, 1976). These deposits were then affected by submarine hydrothermal metamorphism and suffered intense tectonic deformation during the subsequent Apennine orogenesis (Dinelli *et al.*, 2001; Dinelli and Tateo, 2002; Accornero *et al.*, 2005; Marini *et al.*, 2003). The deposit comprised massive lenticular bodies and small pyrite and chalcopyrite aggregates, either filling vesicular cavities or concordant with the textures of pillows, subparallel to the surface of the pillow basalts and disseminated mineralisations. The overlying serpentinites also host stockwork-like veins, with pyrite,

chalcopyrite and quartz being the main components (Bonatti *et al.*, 1976; Marini *et al.*, 2003; Carbone *et al.*, 2005).

The Libiola sulphide ore deposit has an area $\sim 5.1 \text{ km}^2$ with a maximum thickness of $\sim 250 \text{ m}$ (Marini *et al.*, 2003) and is located between $\sim 335 \text{ m}$ and $\sim 230 \text{ m}$ above sea level (Cortecci *et al.*, 2001; Dinelli *et al.*, 2001). Libiola represents one of the most extensively exploited sulphide deposits in Italy, with the mine site extending over an area of $\sim 4 \text{ km}^2$ (Carbone *et al.*, 2005). The main ore minerals are pyrite and chalcopyrite with small amounts of sphalerite, pyrrhotite, marcasite, hematite, mackinawite, magnetite, cabanite and gold. The ore was extracted thorough both open cast and underground excavations, with seven open pits, more than thirty vertical shafts and 21 levels of tunnels (Dinelli *et al.*, 1998; Marini *et al.*, 2003; Accornero *et al.*, 2005; Carbone *et al.*, 2005).

The long history of mining at the Libiola Fe-Cu mine has left extensive areas covered by spoil tips. The mine waste was left in five major spoil tips, with numerous smaller deposits located close to the main mine adits and in total cover an area of $\sim 0.5 \text{ km}^2$ (Marini *et al.*, 2003; Accornero *et al.*, 2005; Carbone *et al.*, 2005). The mine spoil is reddish-yellow in colour, a result of Fe-rich precipitates and lack vegetation when compared to the surrounding wooded areas. The spoil is a poorly sorted mixture of mafic, ultramafic, basalt- and serpentinite-derived rock fragments and Fe-rich phases with relatively high concentrations of S (mean 0.3 %), Cu (mean 0.3 %) and Zn, As, Mo and Se (Dinelli *et al.*, 1998; 2001). High-angle stratification is a typical feature of the waste heaps due to an 'indurated' Fe-rich surface layer (Dinelli *et al.*, 2001; Marini *et al.*, 2003).

8.3.2 Mining history

Prehistoric artefacts, including wooden wedges, stone hammers and an oak pick handle, were discovered in a narrow man-made tunnel in the Libiola mine during the nineteenth century. Maggi and Pearce (2005) have radiocarbon dated the oak pick handle to between 3490 and 3120 cal B.C. in the early Copper Age i.e. at the beginning of the Bronze Age. In modern history the economic exploitation of the mine began in the seventeenth century and it was extensively exploited in the nineteenth and twentieth centuries, with maximum production attained at the beginning of the twentieth century, until mining activity ceased in the early 1960s (Dinelli and Lombini, 1996; Dinelli and Tateo, 2002; Accornero *et al.*,

2005). Between 1864 and 1962 over 1 million tonnes of Fe-Cu sulphide concentrates were produced, with an average grade of 7 to 14 Cu % (Carbone *et al.*, 2005). In addition, Cu was obtained from acid waters by treatment with Fe shavings (Marini *et al.*, 2003).

8.4 Libiola Mine Water Chemistry

Within the Libiola mine area there are three major mine water discharges, which flow continuously throughout the year. The drainage from the Ida adit was chosen for further study and as the location of the treatment plant trials because of its high metal concentrations; continuous discharge and its location (the mine adit is situated away from main roads, inaccessible by vehicles (access is down a rough, narrow path; descending ~90 m from the nearest place a vehicle can be parked to the mine adit). The mine drainage has an impact both on the aquatic environment and the aesthetic quality of the area, therefore the mine drainage requires remediation; and another advantage is that there is sufficient area and gradient for successful operation of the treatment plant. The remote nature of the mine fulfils the BIOMAN project's criteria of being remote and lessens the threat from thieves and vandals. The Ida adit is characterised by extensive precipitation of ochre (mainly schwertmannite and goethite), see Figures 8.3 and 8.4. Mine drainage samples were collected regularly every fortnight during 2004 and monthly during 2005 (data are presented in Appendix 12) by Dr. Enrico Dinelli and colleagues (Partner 2 of the BIOMAN project from the University of Bologna).

The main sulphide bearing minerals in the Libiola mining area are pyrite and chalcopyrite; the dissolution of these minerals and the lack of carbonates within the host rock and gangue minerals (to neutralise the produced acidity) leads to the release of an acidic and metal-rich mine drainage from the Ida adit. A summary of the element concentrations within the Ida mine drainage are presented in Table 8.1 (the full data set is shown in Appendix 12); during the survey period (between 2004 and 2005) the pH was more or less constant (at ~pH 2.6), the concentrations of elements analysed were much higher than those experienced in mid-Wales, with the exception of Zn which is similar to concentrations found within the Bwlch mine drainage. The Ida mine drainage waters are dominated by high concentrations of Al (~93 mg/L), Fe (~300 mg/L), Cu (~77 mg/L) and SO₄ (~4270 mg/L), therefore presenting a very challenging water to remediate.

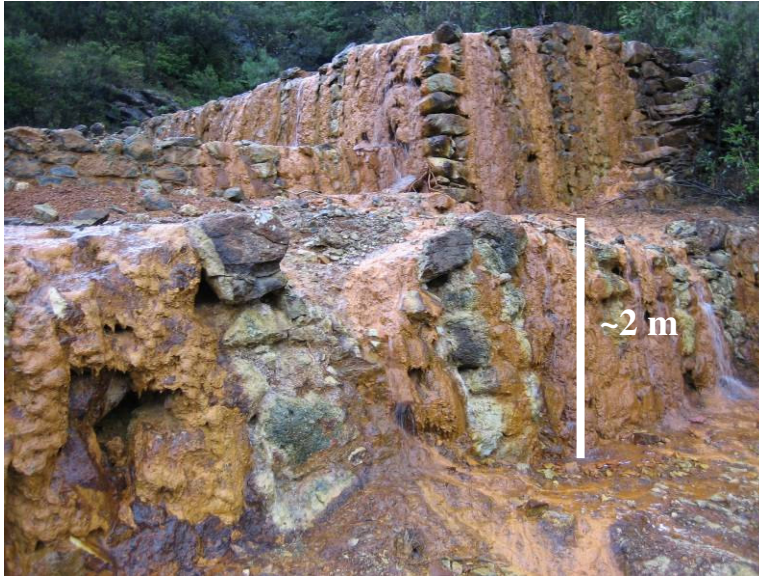


Figure 8.3. Intense ochre precipitation at the Ida mine site.



Figure 8.4. Ochre precipitation at the Ida mine site.
Note the brown ochreous sludge coating the river bed.

The chemical composition of the drainage waters is dependent on the flow regime and climatic conditions. The pH was relatively constant throughout the sampling period at pH

2.6. Generally, during months of higher rainfall (October, November and March) concentrations are diluted and during late spring and summer rainfall is at a minimum with increased concentrations (Figures 8.5 and 8.6). During warmer months intense evaporation occurs and efflorescent salts precipitate including epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), melanterite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and traces of chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), rozenite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$) and szmolnokite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot \text{H}_2\text{O}$) which occur as crusts and aggregates in water pools near the adit and as thin films along scours (Dinelli, pers. comm. 2007).

It is unlikely that a DS only treatment plant (such as was used in mid-Wales) would be suitable for remediation of the mine drainage without prior treatment to remove the majority of the Fe and reduce the acidity to circum-neutral. An Fe-free solution was required as previous results (see the Esgair Hir treatment plant, Chapter 7.3 and 7.4) show that even a small amount of Fe in solution (the Esgair Hir mine water contained <1 mg/L) can block the flow of the mine drainage through the DS bed; the Ida mine drainage contains ~240 mg/L Fe and without an Fe removal stage it is likely that the DS bed would be rapidly blocked, rendering the treatment plant effectively useless.

Table 8.1. Range and mean values of element concentrations in the Ida mine drainage.
The concentration range is shown in parentheses.

pH	Eh mV	Conductivity $\mu\text{S}/\text{cm}$	Temperature $^{\circ}\text{C}$	Cl mg/L	SO4 mg/L
2.6 (2.4 – 2.8)	585 (480 - 625)	5763 (4060 - 7250)	13.7 (10.2 - 17.2)	8.36 (5.5 - 17)	4273 (3150 - 5500)
Na mg/L	Mg mg/L	Al mg/L	K mg/L	Ca mg/L	Cr mg/L
29.7 (16.4 – 42)	479 (298 - 680)	93.3 (64 – 120)	1.1 (0.2 - 2.3)	304 (228 – 640)	0.37 (0.2 - 0.6)
Mn mg/L	Fe mg/L	Ni mg/L	Cu mg/L	Zn mg/L	
4.2 (2.9 – 6.0)	305 (210 - 421)	2.7 (1.8 - 3.7)	74.5 (46.2 - 99)	28.8 (20 - 45)	

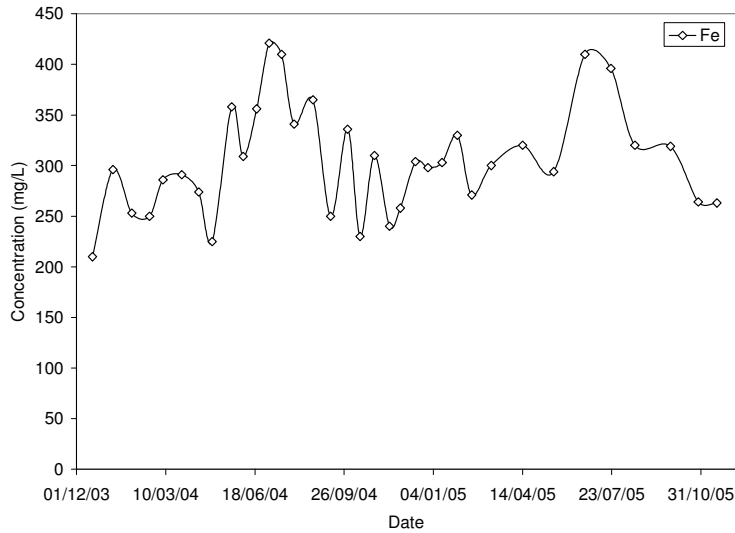


Figure 8.5. Fe concentration (mg/L) during 2004 and 2005 in the Ida mine drainage.

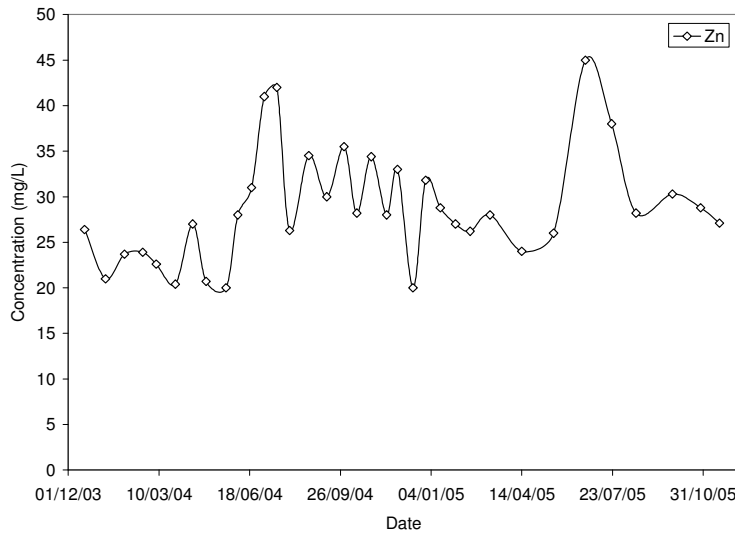


Figure 8.6. Zn concentration (mg/L) during 2004 and 2005 in the Ida mine drainage.

8.5 Ida Adit Treatment Plant

The Fe- and metal-rich mine drainage of the Ida adit required a different remediation method to the Fe-poor, circum-neutral mine drainage of mid-Wales. It was necessary to add three additional treatment stages, to allow the neutralisation of the mine drainage and for the Fe to be removed, before the mine water entered the DS treatment plant. The AMD was first treated to neutralise the mine drainage, the Fe was then removed and then the neutralised, Fe-poor mine water was introduced into the DS treatment plant (containing Algavi_(f) DS) as a final ‘polishing’ stage.

The field trials were limited because of time constraints imposed by the BIOMAN project and therefore the trial occurred only over two days. Although this time was not sufficient to fully characterise the physico-chemical characteristics of the remediation method, it did give an indication of the potential of the approach. The time constraints meant that a passive method of raising the pH and removing the Fe could not be used (see Section 8.4.3), therefore an active method of neutralising the acidic mine drainage and metal removal was used, with the addition to the mine drainage of alkaline chemicals.

The remediation of the Ida AMD occurred in several stages:

1) Flow regulation

The water first entered a 'header' tank to regulate the flow throughout the rest of the system. The water was regulated using the same inflow control pipe as used in the mid-Wales trials (Chapter 7.1.1) so that 1 L/minute was treated.

2) The addition of a neutralising agent

The addition of a neutralising agent to the acidic mine drainage was to raise the pH of the mine drainage from ~pH 2.4 to ~pH 6. In previous experiments (see Chapter 6.3.1) it was found that the pH of the solution (tested with a pH 3.3 and pH 6.6 synthetic mine drainage) did not greatly affect the adsorption capacity of the DS, but increasing the mine water to a pH of 6 would encourage the dissolved Fe to precipitate out of solution. Three different methods of neutralising the mine drainage were used: 1) a 1 M/L NaOH solution; 2) a 1 M/L Na₂CO₃ solution and 3) a 1/6 by weight slurry of the DS fines (see Chapter 5.8.4). The 1 M/L alkali solutions and the DS fines slurry were produced using 'clean' surface water which was found on-site; the chemical composition of the 'clean' water is presented in Appendix 13. This was considered to be a realistic scenario because a large scale treatment plant would have to use such a source given the remote position of the adit. The limited equipment available for use meant that the trial was conducted using basic equipment ('bucket chemistry'). The different neutralising agents were used to determine whether the agent used affected the amount of metals removed from the mine drainage.

NaOH and Na₂CO₃

Sodium hydroxide (Analytical Grade, Carlo Erba Reagents) tends to be used to treat mine waters with relatively low metal concentrations and despite its high cost; it is simple to add as a solution to the mine drainage (by a dosing pump); the NaOH reacts rapidly with the AMD and forms very fine ochre precipitates, which are difficult to remove from solution (Coulton *et al.*, 2003). Sodium carbonate (Analytical Grade, Carlo Erba Reagents) tends to raise the pH of the solution to ~pH 8.5 (compared to pH 10 when a hydroxide is used) and may not be suitable for the removal of metals which require a high pH (for example, Mn). Sodium carbonate has the advantage of being able to precipitate Fe³⁺, but its biggest disadvantage is that it is expensive when compared to other alkali chemicals (Coulton *et al.*, 2003). The NaOH trial operated overnight (~18 hours) and the Na₂CO₃ trial ran for four hours.

Using water from an onsite stream, 10 L of ~1 M/L NaOH and 10 L of ~1 M/L Na₂CO₃ were prepared. A simple experiment was conducted to determine the concentration of NaOH which was needed to be added to the AMD to neutralise the pH and for the Fe to begin to precipitate out of solution. 200 mL of AMD was placed in a plastic beaker and 1 mL aliquots of NaOH solution were added; after each addition the pH was measured, see Figure 8.7. After 10-15 minutes 11 mL of 1 M/L NaOH had been added to the AMD the solution pH was ~4.6 and the Fe was starting to precipitate out of solution; after 14 mL the solution pH was ~7.3. In the field system, alkali was added to the AMD via a battery powered dosing pump, which could be operated at varying voltages; the voltage chosen was 6 V which produced a flow of 38 mL/minute of NaOH to mix with 1 L/minute of mine drainage. The 1 M/L Na₂CO₃ alkali solution was also added to the mine drainage at this rate. The pH of the waters leaving the alkali addition tanks was ~6.7. The pH increase within the alkali addition tank, see Figure 8.8, caused the Fe to start to precipitate out of solution.

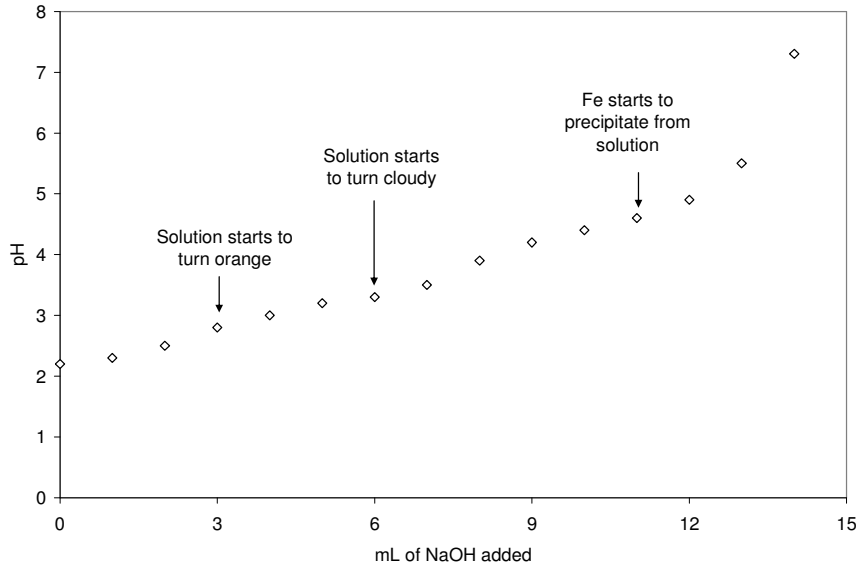


Figure 8.7. pH increase after the addition of 1M NaOH to the Ida adit mine drainage.



Figure 8.8. Alkali addition to the Ida mine drainage.

DS fines

The DS slurry experiment was started but could not be completed because of difficulties pumping the thick DS slurry into the mine drainage with the equipment available on site. The DS fines (<200 μm) were removed from the bulk Algavi DS before the larger particles were acid washed and dried (see Chapter 5.8.4). These were difficult to ‘wet’ and the fines resulted in a lumpy solution (see Figure 8.9) rather than one which is smooth and could be pumped using the dosing pumps. The DS fines are fine-grained and have a large surface area and potentially therefore have a large number of adsorption sites. A system which allowed a slurry of DS fines to be added to AMD has two possible advantages: firstly, the

alkaline reaction of this material would raise the pH (when the fines are mixed with MQ water a solution pH of ~12 is produced). Secondly, the large surface area of the material might adsorb some of the metals in the mine drainage. The neutralising and metal removal capability of the DS fines was previously tested in the laboratory (using AMD from Parys Mountain in North Wales, a Cu mine hosted in Kuroko-type deposits) and initial experiments showed a dramatic reduction in metal concentration, see Table 8.2. The experiment was conducted by contacting 400 mL Parys Mine Water with 5 g DS fines mixed in a small volume of water for 20 minutes and then filtering the solution through a 0.45 μm pore size Whatman[®] cellulose nitrate (WCN) membrane filter (see Chapter 3.2.2).



Figure 8.9. Lumpy solution of DS fines and water.

Table 8.2. The results of initial tests using DS fines to remove the metals from Parys Mountain acid mine drainage.

	Concentrations in Parys Mine drainage (mg/L)	Concentrations after treatment with DS <200 μm (mg/L)
Fe	285	1.4
Cu	14.9	1.4
Zn	40.6	1.6

Using the DS fines to remediate the AMD has a number of difficulties. The DS fines are not easily mixed with water therefore this problem needs to be solved before the fines can be used as a remediation tool. The small particles size of the DS fines means that it is

difficult to separate the DS fines from the AMD; therefore a method would be required to assist in this process, for example, using a flocculating agent, hydro-cyclone, vegetation to slow down the flow and settle out the fine particle or containing the fines in a filter bag (with a very small pore size). If these problems (mixing with water and settlement) could be solved then the DS fines would make an ideal neutralising agent to use.

3) Flocculation

A flocculating agent was added to the neutralised mine drainage to accelerate the settlement of the fine ochre precipitates formed when the AMD was neutralised (Figure 8.10). The flocculating agent (anionic polymer emulsion flocculant, Accepta product number 8012, batch 1106) was prepared to 0.1 % of the original solution (the supplier's recommendation) using the 'clean' water onsite and added to the AMD at ~3 % of the volume of the mine drainage. An initial test was conducted with the 1 % flocculating agent where 1 L mine drainage (now at ~pH 6.8) was collected in a 1 L plastic cylinder; the dosing pump was set to 3 V which produced a flow rate of ~30 mL/minute of flocculating agent. The Fe/ochre flocculated and settled out of solution, leaving 800 mL of clear solution after only a couple of minutes.

4) Settlement

After the addition of the flocculating agent the solution flowed into a 10 m length of MDPE blue water pipe (internal diameter of 25 mm, also known as alkathene pipe) to act as a mixing/reaction system to allow sufficient time for the flocculating agent to thoroughly mix with the neutralised mine drainage. The flocculated mine drainage was piped into a large (250 L) settlement tank to allow the flocculates to precipitate out of solution (Figure 8.11). The residence time of the solution in the settlement tank was about four hours.

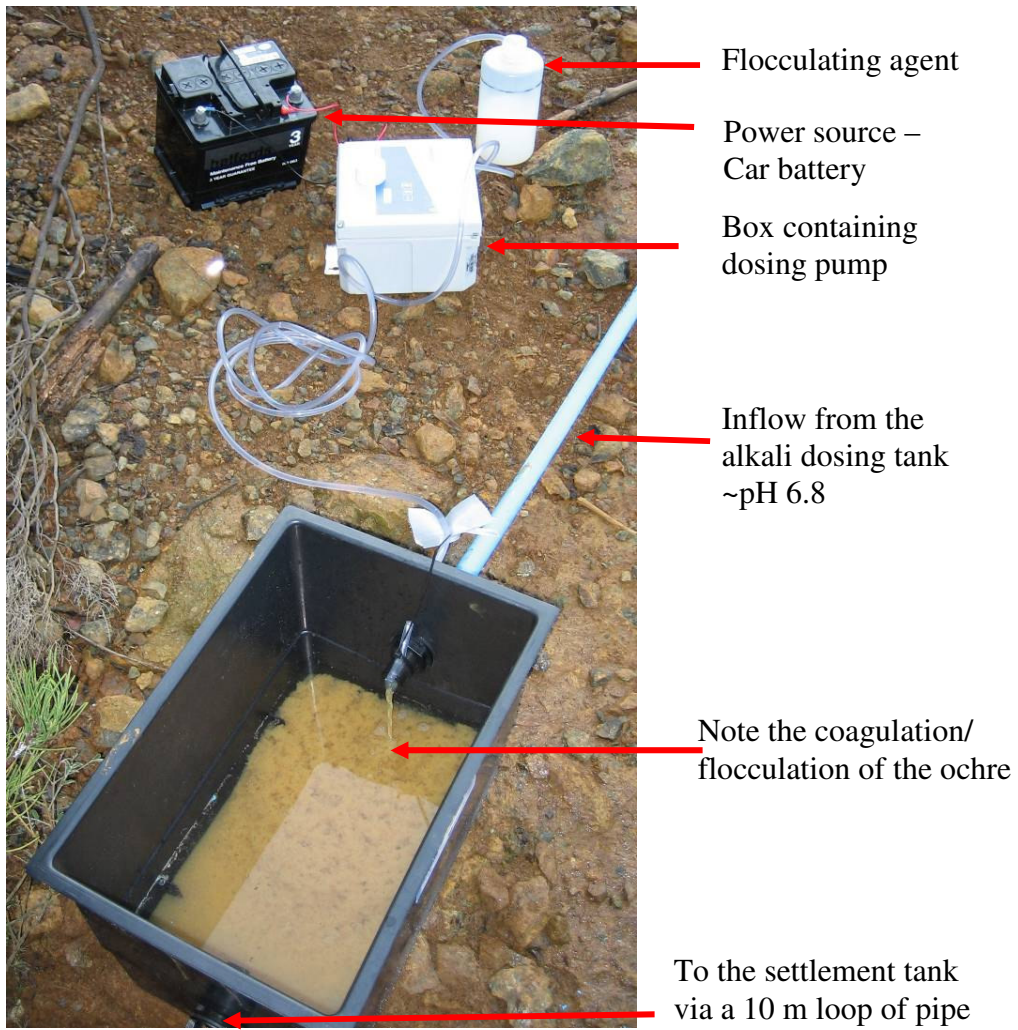


Figure 8.10. The addition of the flocculating agent to the neutralised mine drainage.



Figure 8.11. Settlement of the formed flocculates.

The main issue highlighted by this trial is the volume of flocculated ochre produced; when the NaOH trial was left overnight the settlement tank was full after ~16 hours. The settled, flocculated ochre would require removal and disposal, most likely as special/controlled landfill. The amount of ochre produced has implications for the operating cost and location of such a treatment plant. The produced ochre was gelatinous and would probably be very difficult to dewater, though there are methods (mainly associated with coal mine drainage) to do this. Methods may include a clarifier/thickener (or if the land was available, by lagoons), or via a filter press, vacuum filtration, continuous pressure dewatering, or centrifuge separation (Coulton *et al.*, 2003; Younger *et al.*, 2002). These removal methods, however, add to the cost, energy requirements and size of the required plant. The produced ochre could also be added to the beginning of the treatment system to help produce a denser sludge (Coulton *et al.*, 2003; Dey *et al.*, 2007), acting as a high surface media providing adsorption sites for the removal of metals from acidic and circum-neutral mine drainage (Bearcock, 2007) and phosphorous from waste water (Batty and Younger, 2004; Wiseman and Edwards, 2004). As the ochre would be free from organic matter and other materials, it could be used a pigment for a number of colouring applications (Hedin, 1999 cited in Wiseman and Edwards, 2004; Batty and Younger, 2004), though the ochre would still contain high concentrations of metals, for example, Cu, Al etc.

5) Dealginated seaweed treatment plant

Once the Fe precipitate had settled from the mine drainage, the Fe-poor, neutralised mine drainage was piped into the same DS treatment plant as used in mid-Wales (Chapter 7.1); Algavi_(f) DS was used. It was anticipated that the precipitation of the Fe would reduce the concentrations of other metals contained within the mine drainage by co-precipitation and thus, the DS treatment plant was predicted used as a final 'polishing' stage. The treatment system is shown in Figure 8.12 and 8.13.

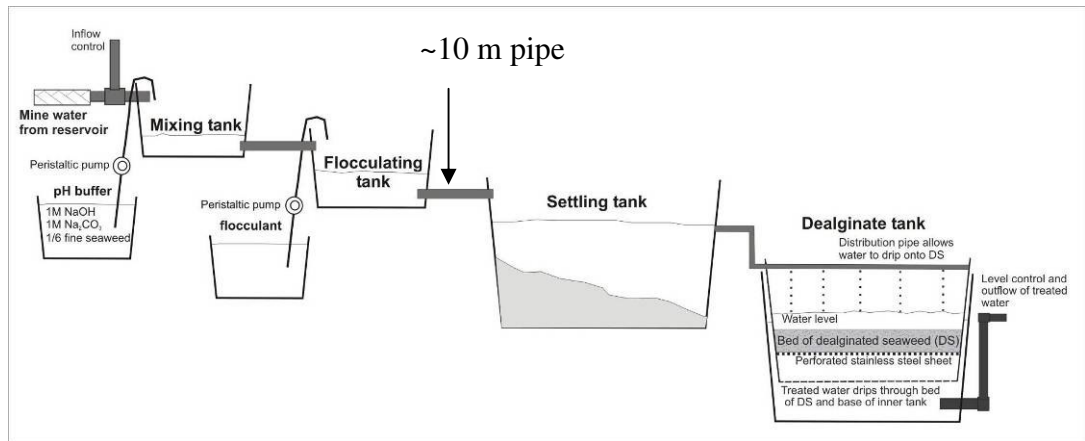


Figure 8.12. Schematic of the Ida adit pilot treatment plant.

From: Dinelli *et al.*, 2007

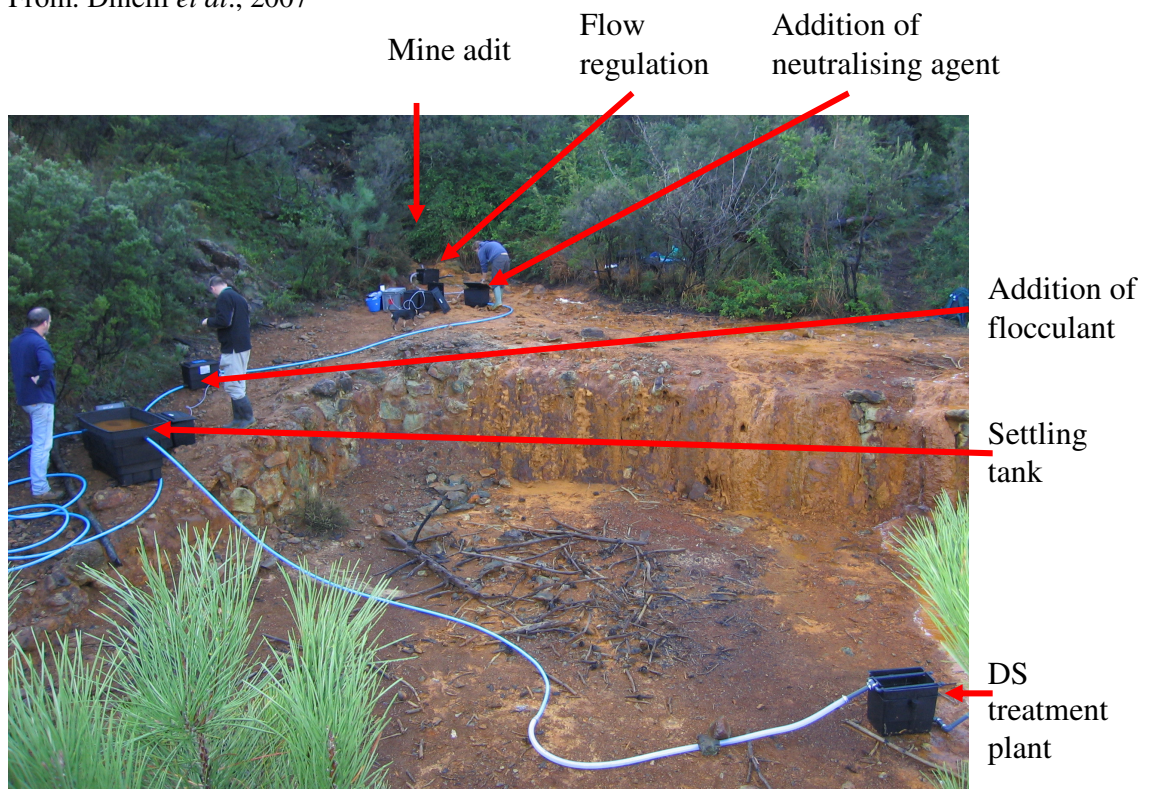


Figure 8.13. Photograph of the Ida adit pilot treatment plant system.

Samples were taken from each stage of the treatment system, filtered and acidified on site and then analysed at the end of the trial using the methods stated in Chapter 3. Temperature, pH and conductivity were measured directly in the field.

8.6 Results

The results of the field trials using the two different alkaline reagents are summarised in Table 8.3, and the full set of data is shown in Appendix 13. The results show that both

NaOH and Na₂CO₃ successfully neutralised the AMD and a large concentration of Fe and other metals was removed. The sharp decrease in pH that occurred during the NaOH trial was caused by the overnight failure of the alkali dosing pump, therefore untreated AMD was allowed to enter the DS treatment plant.

Table 8.3. Summary of the results from the Ida adit pilot treatment plant.

		Time	pH	Mn mg/L	Fe mg/L	Ni mg/L	Cu mg/L	Zn mg/L
NaOH								
26/11/2006	Inlet	1610	2.5	1.33	232	0.85	50.9	8.73
	Flocculant tank outflow	1650	5.5	0.12	0.28	0.12	0.11	0.06
	DS outlet	1720	6.4	0.16	0.64	0.03	0.10	n.d.
	DS outlet	1750	7.3	0.08	0.47	0.01	0.07	n.d.
27/11/2006	Inflow to DS tank	0950	2.5	1.65	210	0.90	50.6	8.47
	DS outlet	0950	6.1	0.99	6.69	0.76	79.6	7.72
Na₂CO₃								
	Inlet	1020	2.3	1.45	242	0.98	53.1	8.72
	Flocculant tank outflow	1230	7.4	0.99	0.15	0.67	0.67	3.18
	DS outlet	1230	6.3	0.76	0.61	0.86	1.64	7.49
	DS outlet	1300	6.7	1.06	0.20	0.54	1.05	4.76
	Inflow to DS – fresh DS	1415	7.8	0.10	0.23	0.21	0.33	0.43
	DS outlet - fresh DS	1415	7.2	0.02	0.56	0.01	0.04	0.01

n.d. = not detectable

NaOH trial

The addition of 1 M/L NaOH to the AMD increased the pH from 2.5 to 5.5 and facilitated the precipitation of Fe from solution. After the flocculating agent had been added and the flocculated ochre settled out of solution, the Fe concentration had been reduced from 232 mg/L to 0.3 mg/L, see Figure 8.14. The solution leaving the settlement tank also contained much lower metal concentrations because the metals had co-precipitated with the ochre, for example, the Cu concentration decreased from 51 mg/L to 0.1 mg/L and Zn from 8.7 mg/L to 0.06 mg/L. The water entering the DS tank was near neutral and contained low metal concentrations (with a chemical composition more similar to that found in the mine drainages of mid-Wales). After flowing through the DS treatment plant, the pH had risen to ~7 and the Ni and Zn concentrations had reduced further and the Cu, Mn and Fe concentrations were more or less the same. The waters leaving the DS treatment plant had low concentrations of Mn, Fe and Cu and virtually no Ni or Zn.

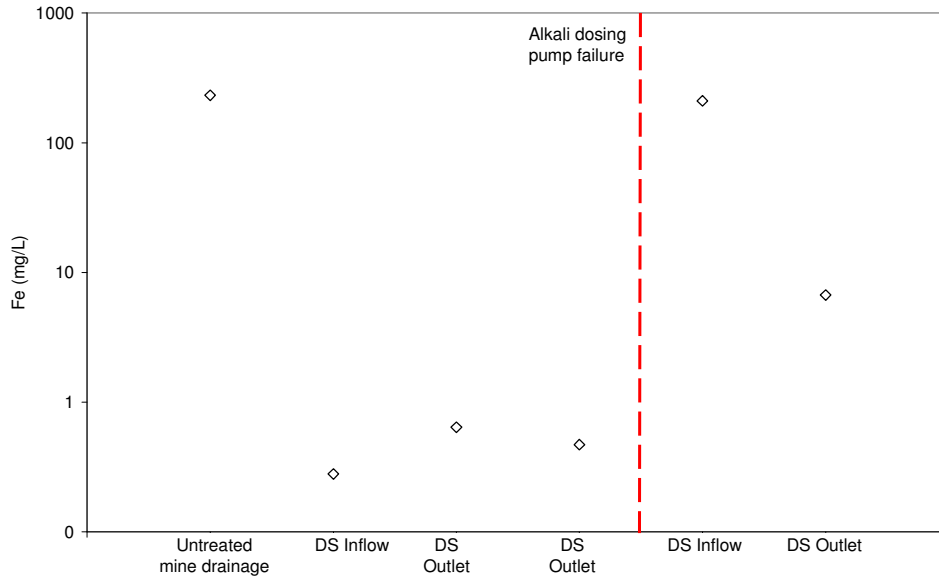


Figure 8.14. Fe concentration throughout the Ida pilot treatment system using NaOH as a neutralising agent.

Note logarithmic scale

The treatment system was left operating overnight (with no operator involvement); unfortunately, however, the dosing pump introducing the 1 M/L NaOH into the AMD failed, allowing acidic (pH 2.5) metal-rich mine drainage to flow straight into the DS treatment plant. Even though the dosing pump had failed the Fe concentration in solution was still slightly reduced (from 232 mg/L in the untreated mine drainage to 210 mg/L in the waters leaving the settlement tank), maybe caused by SCOOFI-type reactions within the settlement tank. Once the untreated mine drainage had passed through the bed of DS, the metal concentrations were reduced, especially Fe (from 210 mg/L to 6.7 mg/L). The concentration of Cu, however, had increased with the Cu being re-released back into solution, see Figure 8.15. This release of Cu may have been caused by the Cu exchanging for the Fe in the adsorption sites of the DS or by the acidic mine drainage causing the Cu to desorb/leach from the surface of the DS.

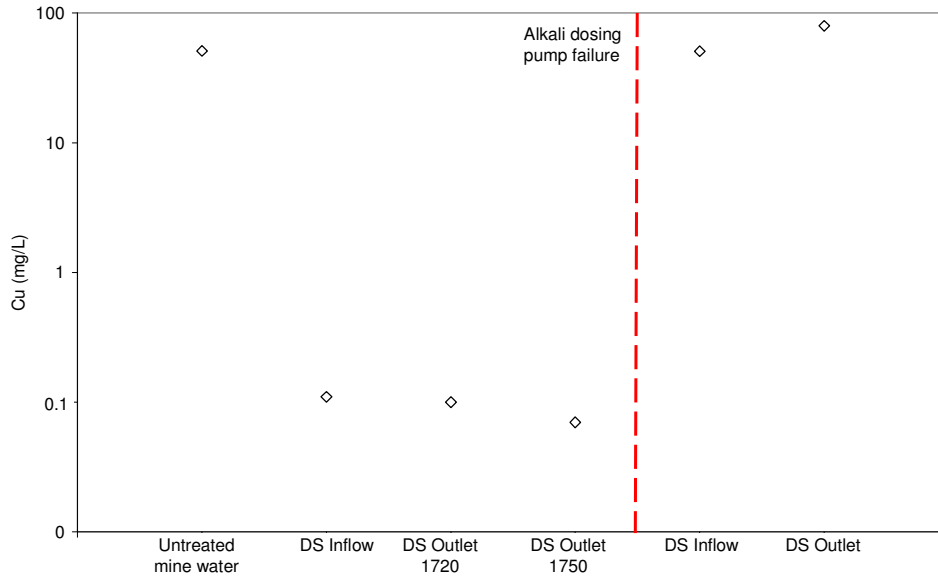


Figure 8.15. Cu concentration throughout the Ida pilot treatment system using NaOH as a neutralising agent.

Note the logarithmic scale.

Na₂CO₃ trial

Before the Na₂CO₃ trial was started the tanks and adjoining pipes were thoroughly rinsed to remove any traces of the NaOH used previously. The Na₂CO₃ trial was started using the same DS bed that had been used in the previous NaOH trial, though the plastic and stainless steel mesh covering the DS was rinsed to remove any precipitated ochre. The AMD was neutralised after the addition of 1 M/L Na₂CO₃, though it was noted that after the addition of the flocculating agent smaller flocs of the precipitated ochre were formed and therefore did not settle as fast. After the mine drainage had been neutralised and the ochre had settled out of solution, the pH had risen to ~7.4 (higher than at the same stage of the NaOH trial) and the metal concentrations were much reduced by co-precipitation/adsorption with the ochre. When compared to the results from the NaOH trial, the Na₂CO₃ removed a greater concentration of Fe and Cu and removed a lower concentration of Mn Ni and Zn. After neutralised, Fe- and metal-poor mine drainage had flowed through the DS treatment plant, the concentrations of Fe, Ni, Cu and Zn (see Figure 8.16) increased and the Mn concentration decreased by 0.2 mg/L, see Figure 8.17. The increase in metals in the outflow waters may suggest that the metals were being washed off the DS bed. After another 30 minutes the concentrations had decreased (except Mn), though concentrations were still greater than those leaving the settlement tank.

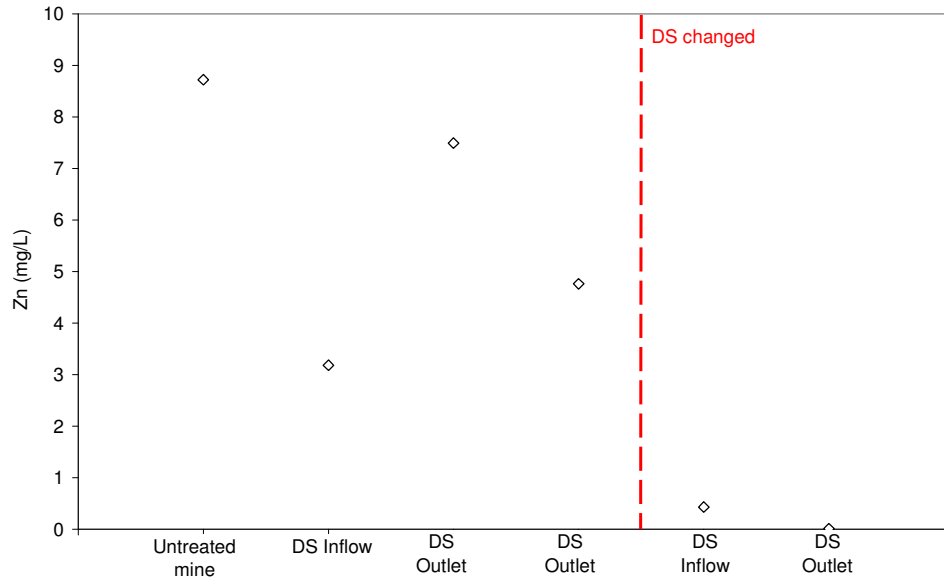


Figure 8.16. Zn concentration throughout the Ida pilot treatment system using Na_2CO_3 as a neutralising agent.

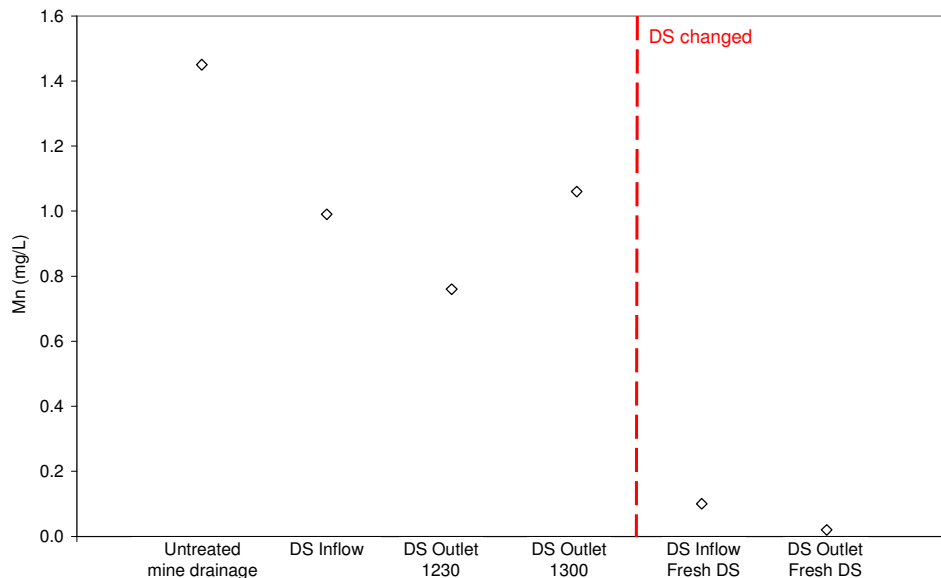


Figure 8.17. Mn concentration throughout the Ida pilot treatment system using Na_2CO_3 as a neutralising agent.

After the sample had been collected from the outflow of the DS treatment plant at 13.00, the DS bed was removed and a fresh bed of DS was placed into the treatment plant. The system was then allowed to settle for about an hour before a sample was taken. Once the Na_2CO_3 had been operating for several hours, the metal removal efficiency dramatically increased with very low concentrations of Mn, Fe, Ni, Cu and Zn. When compared to the flocculant tank outflow from the NaOH trial, the Na_2CO_3 trial is more efficient at removing Mn and Fe, but not as efficient at removing Ni, Cu and Zn. Once the settlement

tank effluent had flowed through the bed of fresh DS the metal concentrations were exceedingly low with concentrations of Mn, Ni, Cu and Zn all <0.05 mg/L and a Fe concentration <0.6 mg/L. When using Na₂CO₃ as a neutralising agent, the metal removal was greater than when using NaOH. This may be caused by the presence of carbonate ions in solution (from the Na₂CO₃ and from the carbonate particles within the DS bed) which cause metal carbonates to form and the subsequent filtering out of the metal carbonates onto the DS bed as well as the adsorption of the metals onto the DS itself.

Unfortunately the trial could not be continued for a longer period, but the metal removal could be predicted (using the mid-Wales treatment plant as an analogy) to occur for many weeks. Though eventually, as happened at Esgair Hir (Chapter 7.3 and 7.4), the low concentration of Fe in the mine drainage (0.2 mg/L at Esgair Hir and 0.6 mg/L in the mine drainage entering the DS plant in this Na₂CO₃ trial) would precipitate out of solution. This precipitate would block the distribution pipe holes and coat the nylon and stainless steel mesh on top of the DS bed; which would reduce and eventually stop the flow of mine drainage through the treatment plant.

The reduced metal concentrations attained after the solution had passed through the settlement tank indicate that metals were removed from solution by adsorption onto the Fe-oxyhydroxides. The adsorption and/or co-precipitation of metals is pH dependent; as the pH increases ≥ 6 the negatively charged surfaces of Fe-oxyhydroxides are able to adsorb cations from solution (Drever, 1997; Langmuir, 1997; Cravotta and Trahan, 1999). The addition of a neutralising agent to the Ida adit mine drainage increased the pH and this led to a decrease of metals within the mine drainage, first by adsorption onto Fe-oxyhydroxides and then because of the limited solubility of carbonates and oxyhydroxides (Drever, 1997). Cravotta and Trahan (1999) noted that below pH 7, Fe-, Al- and Mn-oxyhydroxides were generally not effective adsorbents; therefore the water leaving the settlement tank in the NaOH trial (pH 5.5 at 1650) should contain a greater concentration of metals than the Na₂CO₃ trial (pH 7.8 at 1415). However, this is not the case, as the NaOH trial removed more metals than the Na₂CO₃ trial (except Mn); this may be because the grain size of the NaOH-produced ochre may be smaller than that produced by the Na₂CO₃; White (2000) noted that adsorption increases with decreasing grain size because of the increase in surface area and therefore adsorption sites; however, this needs to be substantiated.

8.7 The next step

The results of the Ida adit trial only provide a brief snapshot of what could be achieved with a longer trial period. There are a number of additional aspects that could be considered to improve the data gained from the trials:

1) Increased trial period

Ideally, these trials would be operated for a number of weeks, or until the efficiency of the system decreased. A longer trial period would allow a greater understanding of the processes involved in the removal of metals.

2) An increased number of samples

Increasing the number of samples taken at each stage of the treatment system (for example, at the outflow of each tank) would provide a more detailed indication of the metal removal through the system i.e. how the pH or metal concentration changed after each treatment stage.

3) Alkalinity addition

This remediation method could be altered so that it requires less materials and operator involvement another way of neutralising the AMD would be needed. A cheaper and safer alternative to NaOH or Na₂CO₃ would be limestone powder (Maree *et al.*, 2004b) which could be introduced into the AMD via a gravity feed. Another method to neutralise the AMD would be the addition of DS fines (detailed in Chapter 8.5); or to allow the AMD to flow through an ALD (which would require the AMD to contain <1 mg/L dissolved oxygen and <2 mg/L Fe³⁺ and Al³⁺) or a VFW (both described in Chapter 8.2).

4) An alternative method of removing the Fe from solution

The precipitates produced in the above trials were very fine and formed a gelatinous and water-rich sludge. An alternative method which produces a more dense sludge would be desirable; possibilities include SCOOFI reactors and vertical flow reactors. SCOOFI reactors treat mine drainage which is nearly neutral, but Fe-rich and consist of a tank which is filled with high surface area media (for example, plastic trickle filter media, blast furnace slag or brushwood). The mine water is passed through the reactor and the ochre

precipitates onto the surface of the media within the reactor. The reactor can either be saturated (the mine water is aerated before entry into the plant) or unsaturated (aerated within the plant); the saturated reactor removes a greater concentration of Fe from solution, although mine waters containing >50 mg/L Fe^{2+} are unlikely to be treated using a single-step SCOOFI reactor (Younger *et al.*, 2002). Vertical flow reactors may consist of a tank with a sandstone/gravel bed suspended off the floor (similar to the layer of DS within the treatment plants used within this study). The ochre precipitates onto the gravel bed and Fe- and metal-poor water flows into the base of the tank under the baffle wall and up through a rise chamber, the water then flows over a weir before being discharged. This was used to treat 1 L/minute of circum-neutral coal mine drainage containing 8.4 mg/L Fe; the main problem encountered, relevant to this thesis, is that when the flow was increased, the Fe removal decreased (Sapsford *et al.*, 2007).

5) Alternative power supply

The power requirements for this trial were minimal, the small dosing pumps to add the alkali and flocculating reagent were operated using small car batteries. If the batteries were charged by solar panels, it would negate the access to the main power grid. Gravity fed dosing plants could also be investigated.

8.8 Summary

This Italian AMD field trial, although short, has demonstrated that, with additional stages, the DS treatment system can effectively remediate AMD. The Ida adit mine drainage is acidic (~pH 2.6) and contains high concentrations of metals, dominated by Al (~93 mg/L), Fe (~300 mg/L) and Cu (~77 mg/L). The mine drainage waters are difficult to remediate and, when compared to the mid-Wales treatment system, an additional three treatment stages are required. After the flow had been regulated to 1 L/minute, a neutralising agent was added to raise the pH and to encourage the precipitation of Fe (and subsequent co-precipitation of other metals); the fine precipitates were encouraged to flocculate and precipitate out of solution by the addition of a flocculating agent (added at ~3 % of the mine drainage volume). The solution then flowed through a ~10 m pipe to allow the complete mixing of the solution into a 250 L tank where the flocculates settled out of solution (residence time was about four hours). Once the Fe and other metals had

precipitated out of solution the mine drainage was piped into the DS treatment plant as a final 'polishing' stage.

Three neutralising agents were used: 1 M/L NaOH (trial operated overnight), 1 M/L Na₂CO₃ (operated for four hours) and 1/6 slurry by weight of DS fines (trial started but not completed). The DS fines trial was not completed owing to the difficulties of adding the lumpy solution to the AMD with the equipment available on site. Previous laboratory experiments, however, have shown that the DS fines are suitable for neutralising the AMD and because the DS fines have a large surface area and numerous functional groups the DS should simultaneously adsorb metals from solution. A method of mixing the DS with water to make a smooth, pumpable mixture and a method of separating the fines from the remediated mine drainage are required before this material can be successfully used.

This trial has shown that both 1 M/L NaOH and 1 M/L NaCO₃ successfully neutralised the Ida adit mine drainage and removed large concentrations of metals. The addition of 1 M/L NaOH raised the pH to ~5.5 causing the Fe to precipitate out of solution (the concentration decreased from 242 mg/L in the adit drainage to 0.3 mg/L after the settlement tank); co-precipitation of other metals also occurred, for example, Cu concentration decreased from 51 mg/L to 0.1 mg/L and Zn from 8.7 mg/L to 0.06 mg/L. The concentrations of Ni, Cu and Zn further decreased after the mine drainage had flowed through the DS bed; Fe and Mn concentrations, however, slightly increased. Unfortunately, overnight the dosing pump adding the NaOH to the AMD failed, allowing acidic Fe- and metal-rich mine drainage to flow directly into the DS bed. Although the AMD had not been neutralised, the Fe concentration decreased from 232 mg/L in the adit drainage to 210 mg/L in the settlement tank effluent. The metal concentration was lowered after passage through the DS bed, though Cu was released back into solution, possibly exchanging with the Fe at the adsorption sites or the acidic mine drainage, caused the desorption of the Cu from the DS surface.

The Na₂CO₃ trial was then started, using the same DS bed as in the NaOH trial. After the addition of 1 M/L Na₂CO₃ and the ochre had settled out of solution, the pH had increased to ~pH 7.4. The Fe and Mn concentrations were lower and the Ni, Cu and Zn concentrations were slightly higher than at the same stage in the NaOH trial. After the Fe- and metal-poor mine drainage had flowed through the DS bed, the concentration of Fe, Ni,

Cu and Zn all increased probably caused by the metals washing off the DS bed, and the Mn concentration slightly increased. After another 30 minutes the concentrations of Fe, Ni, Cu and Zn decreased and Mn slightly increased; the DS bed was then removed and replaced by fresh DS. The removal of Fe and other metals increased, once the ochre had settled out of solution, after the treatment system had been operating for several hours. After the settlement tank effluent had flowed through the fresh DS bed, the metal concentrations were very low with Mn, Ni, Cu and Zn concentrations all <0.05 mg/L and Fe < 0.6 mg/L. Metal removal using Na₂CO₃ as a neutralising agent and fresh DS was greater than when using NaOH. This improved removal maybe caused by the increased concentration of CO₃ ions present in solution, causing the precipitation of metal carbonates which filter out on passage through the DS bed, the additional carbonate particles within the DS bed and the adsorption of the metals onto the DS itself.

The main problem highlighted by these trials is the production of a large quantity of Fe-oxyhydroxide precipitates. This very gelatinous and water-rich sludge would be very difficult and expensive to dewater before disposal. Methods are available, however, which were pioneered in coal mine drainage remediation, which include a clarifier/thickener (or if the land was available, a lagoon), or via a filter press, vacuum filtration, continuous pressure dewatering, or centrifuge separation. This additional equipment would increase the cost, energy requirements and size of the required plant. Because the produced ochre is free from organic matter or debris, alternative uses could be made instead of it being disposed of as special or controlled landfill. The ochre could be used as a pigment or it could be re-circulated into the treatment system to produce a more dense sludge possibly reducing the amount of alkali and flocculating reagents which would need to be added to the system.

CHAPTER 9:

Conclusions

The main focus of this thesis was to develop and demonstrate an innovative method for the biosorption of metals from waters draining abandoned metal mines. Dealginated seaweed (DS), a waste product from the alginate industry, was used as a biosorbent. The overall aim was to improve the quality of the mine drainage water and reduce its impact on its receiving water course, which would then comply with EQS set by the EU and local regulatory agencies. Two areas of Europe were selected for further study: mid-Wales (15 mine drainages and two receiving water courses) and Italy (the Libiola mine). The sites have different geologies, climates and they discharge contrasting mine waters; the drainage from the mid-Wales mines are mostly circum neutral, Fe-poor and metal-rich, whereas the Libiola mine drainage is acidic, Fe- and metal-rich.

The work reported in this thesis expands that which was conducted as part of a three-year (between 2003 and 2006) EU-LIFE Environment project (LIFE03 ENV/UK/000605) called “BIOsorption of Metals from Abandoned miNes” (or BIOMAN). The project was a collaboration between members of the Institute of Geography and Earth Science, Aberystwyth University; the Department of Chemical and Process Engineering, University of Sheffield (who designed and built the treatment plant) and the School of Earth and Geoenvironmental Sciences, University of Bologna (who monitored the composition of the Libiola mine drainage and assisted in the operation of the field trial at the Libiola mine).

The compositional variation of the mine drainage water, from a number of sites, in relation to the seasons and rainfall was determined; these data were then used to select sites for treatment. The physico-chemical and adsorption characteristics of DS were determined. Using the mine drainage and DS data, a treatment plant was designed and then deployed and monitored at several mine sites (three in mid-Wales and one in Italy). The treatment plant was designed to be practical, low-cost, low-technology and to require low levels of maintenance and operator involvement, which would offer potential as a best available technique not entailing excessive cost.

9.1 Summary of Key Findings

9.1.1 Mid-Wales mine drainage composition

- Metalliferous ores have been worked, to a greater or lesser extent, in every county in Wales, though the oldest and one of the most productive was Ceredigion, which included the heart of the mid-Wales orefield. Even though the mines in the mid-Wales orefield have been abandoned for over 100 years, there is still a legacy of metal-rich spoil tips and contaminated drainage waters.
- Fifteen mine drainage waters and two receiving water courses are circum-neutral and Fe-poor (<1 mg/L) caused by limited pyrite and/or marcasite in the orebody. The mine drainage waters, however, contain high concentrations of metals especially Cu, Zn, Cd and Pb, which cause the receiving waters to fail current water quality standards set by the EC and local regulatory agencies.
- The most severely contaminated mine drainages are Bwlch, Frongoch and Wemyss with concentrations of Cu ≤ 99 $\mu\text{g/L}$, Zn ≤ 42 mg/L, Cd ≤ 99 $\mu\text{g/L}$ and Pb ≤ 2.8 mg/L.
- Two of the mine drainages sampled contained Fe: Cwm Rheidol is acidic (average pH 3.4) and contains ≤ 21 mg/L Fe and Cwmystwyth is circum-neutral and has an ochre-stained drainage adit. These mine drainages are also highly contaminated with concentrations ≤ 25 $\mu\text{g/L}$ Cu, ≤ 33 mg/L Zn, ≤ 72 $\mu\text{g/L}$ Cd and ≤ 1.4 mg/L.
- The composition of sampled waters varied throughout the year, but did not necessarily show a clear seasonal variation.
- The majority of those elements that do show seasonal variation increase to a summer maximum caused by limited dilution, increased oxidation of the host rock and ore minerals in the warmer, drier conditions and an increased water-rock interaction time. Zinc, Cd and Pb, however, tend to increase in winter and this may be related to the increased oxidation in the summer creating easily soluble sulphate salts, which are mobilised by the increasing precipitation in the autumn or the increased precipitation encouraging the dissolution of the minerals.
- The mine water composition does not dramatically change over a 24 hour period at Cwm Rheidol and Cwmystwyth. Iron showed a minor change, slightly increasing during the night time at Cwm Rheidol. At Cwm Rheidol, a decrease in the concentration of Fe^{3+} and a simultaneous increase in Fe^{2+} concentration occurred at around 0500 and 2100. These variations occur at dawn and dusk and may be caused by

the photochemical reduction of hydrous ferric oxides or the bacterially mediated reduction of Fe^{3+} . The bacteria may be stimulated by the low light levels and the temperature of the water.

- Determining the season or month when the minimum and maximum metal concentrations occur within the mine drainage is very important, especially if a treatment plant is deployed at that site. For example, when maximum concentrations occur in the mine drainage, the treatment plant effluent needs to be closely monitored to ensure that the DS has not saturated with metals.

9.1.2 Biosorption - Laboratory experiments

- Two different types of DS were used during these experiments: Algavi and Girvan. The Algavi DS was further divided into that which contained CaCO_3 (Algavi_(c)), and that which was CaCO_3 free (Algavi_(f)). Algavi DS is obtained from the processing of solely *Laminaria digitata*; whereas Girvan DS is obtained from the treatment of predominantly *Ascophyllum nodosum* with minor amounts of *Macrocystis pyrifera*, *Lessonia flavicans*, *Durvillea potatorum*, and *Laminaria hyperborea*.
- Algavi_(f) DS had a greater adsorption capacity than Algavi_(c) DS; when 0.5 g DS was reacted with 50 mL Bwlch mine water for 180 minutes, Algavi_(f) removed 24.2 mg/L Zn (94.9 %) and Algavi_(c) removed 29.1 mg/L Zn (82.7 %); initial concentrations were 25.5 mg/L and 35.2 mg/L respectively.
- The greater adsorption capacity of Algavi_(f) DS (than Algavi_(c) DS) was not caused by different preparation methods (both were prepared in the same way), nor did the Algavi_(f) have a larger surface area. The greater adsorption capacity of the Algavi_(f) DS may have been caused by a more thorough acidification (because the CaCO_3 within the Algavi_(c) neutralised a significant portion of the acid) which removed a greater concentration of Ca and Na from the surface of the DS, exposing a larger number of binding sites for the metal ions to adsorb to.
- The thorough acid washing had a positive effect on the adsorption capacity of the Algavi DS, therefore Girvan DS was also subjected to acid washing. Contrary to the Algavi results, acid washing had a negative effect on the adsorption capacity of Girvan DS. After 180 minutes, 0.5 g acid washed Girvan DS (Girvan_(a)) removed 29.8 mg/L Zn (84.7 %) from 50 mL Bwlch mine water and the raw Girvan DS (Girvan_(r)) i.e.

which had not been acid washed) removed 36.6 mg/L Zn (97.9 %); initial concentrations were Girvan_(a) 35.2 mg/L and Girvan_(f) 37.4 mg/L

- Girvan_(f) DS was used as received and the additional acidification and drying may have negatively affected the adsorption of Girvan_(a) DS. The surface area, number and availability of binding sites may have been reduced in the Girvan_(a) DS.
- Girvan_(f) DS had a greater adsorption capacity than Algavi_(f) DS. After 180 minutes, 0.5g Girvan DS had removed 730 µg/L Pb (98.2 %) from 50 mL Bwlch mine water and Algavi_(f) removed 723 µg/L (97.3 %); initial Pb concentration was 743 µg/L. The Girvan DS had a smaller surface area than the Algavi DS and this therefore was not a controlling factor. The greater adsorption capacity of the Girvan DS may be because the parent seaweed (from which the DS was derived from) contained different types, numbers and availability of binding sites. Girvan DS was used as received, but the Algavi DS was sieved (only particles >0.18 mm were used) and subjected to additional acidification and drying which may have adversely affected the adsorption capacity.
- During the experiments the pH of the filtrate did not remain below pH 7, therefore metal removal by biosorption alone was not measured, some metal removal by precipitation and subsequent filtration from solution may also have occurred. This pH increase is advantageous from an application perspective as it may enhance metal immobilisation and removal, and increase the apparent overall metal removal from solution.
- Algavi_(f) DS was chosen for further detailed study; even though Girvan DS had a greater adsorption capacity, supply problems prevented the acquisition of large quantities of this material.
- Over 80 % Zn, Cd and Pb were removed after 15 minutes contact between 0.5 g Algavi_(f) and 50 mL Bwlch mine water (initial concentrations: Zn 25.5 mg/L, Cd 68.5 µg/L and Pb 744 µg/L); after this rapid uptake, the removal rate slowed down and >90 % was removed after 30 minutes. After ~60 minutes the removal rate for Cd was reasonably stable and after 180 minutes the removal rate for Zn and Pb was more or less stable. The removal rate slows down after the surface binding sites are saturated and the metal ions diffuse into the interior of the DS particle.
- Comparisons were made between Bwlch mine water (containing a whole suite of elements) and a synthetic Bwlch mine water (containing no Mg, K and Ca and reduced Na concentrations) to determine whether the presence of major cations affected the

adsorption capacity of the DS. Insignificant differences in metal uptake were observed suggesting that the major cations contained within the mine drainage did not affect the amount of adsorption which occurred.

- Whether the pH of the solution affected the uptake capacity was also tested by reacting synthetic mine water with similar chemical compositions at pH 3.3 and 6.6. The pH did not make a significant difference to the amount of metals removed from solution which is consistent with the findings of Romero-Gonzalez *et al.* (2000) and Wilson and Edyvean (1993a) who found that DS adsorbed metals over a wide pH range (between 2 and 7).
- The removal of Zn and Pb increased with an increase in DS weight until 0.5 g, after which no significant further increase in adsorption occurs. For example, 15 mg/L Zn was removed using 0.1 g DS; 24 mg/L was removed by 0.5 g and 25 mg/L was removed by 1 g DS. The removal of Cd, however, increased until 0.5 g, where the Cd had completely been removed from solution i.e. no further adsorption could occur. The low weight of DS for maximum removal is advantageous as it means that a smaller treatment plant is required, reducing the space required and the overall cost.
- The metal adsorption by 0.5 g DS was compared between single metal solutions between 1-100 mg/L and mixed metal solutions between 1-100 mg/L, e.g. the 1 mg/L solution contained 1 mg/L each of Zn, Cd and Pb (total metal concentration of 3 mg/L). The presence of additional metals in solution did not affect the adsorption capacity of the DS; though there was a slight reduction in Zn adsorption (above 25 mg/L) in the presence of Cd and Pb.
- Ion exchange has been determined as the main mechanism for metal removal by the DS; therefore as the metal in question is adsorbed then another ion should be released. In the single metal experiments, the concentration of Ca in the filtrate was measured and was found to increase as the amount of metal adsorbed increased. It has to be noted that when 0.5 g DS is reacted with MilliQ water ~35 mg/L Ca is released; therefore, Ca is released even when no metals are present in solution. It is known that during the production of alginate, the DS undergoes a Ca-dewatering process. The correlation between the amount of metal ion adsorbed and Ca released shows a more or less straight line relationship when compared on a moles/L basis (Ca and Zn: $r = 0.96$, Ca and Cd: $r = 0.92$ and Ca and Pb: $r = 0.84$); if the relationship is not 1:1 then

other metal removal mechanisms (including complexation, physical adsorption or micro-precipitation) maybe involved.

- The experiments using Algavi_(c), Algavi_(f) and Girvan DS have shown that the metal ions are not adsorbed at the same rate or in the same concentration, with DS showing a greater tendency to adsorb Pb > Cd > Zn with increasing concentrations. When 1 L Bwlch mine water was reacted with 0.5 g DS for 30 minutes 53 % of Pb, 30 % of Cd and 16 % Zn was removed (initial concentrations: Pb 667 µg/L, Cd 77 µg/L and Zn 27.9 mg/L). The affinity of a metal to the DS may be controlled by the element's atomic weight, atomic number, ionic radius, electro-negativity, hydraulic radius and its co-ordination number (Kuyucak and Volesky, 1988b; Volesky and Holan, 1995; Figueira *et al.*, 2000; Jeon *et al.*, 2002).

9.1.3 Biosorption - Mid-Wales field trials

- The mid-Wales field trials show that DS can be successfully used to remediate circum neutral mine drainage waters.
- The maximum metal adsorption occurs within the first hour of operation; for example, at the Bwlch 1L/minute treatment plant (containing ~3 kg Algavi_(c)) 98 % of Zn, Cd and Pb being removed from the mine drainage, after which the removal decreases.
- During the first hour of operation a significant amount of Na, K, Mg and Ca were released; in the outflow of the 2 L/minute Algavi_(f) treatment plant at Alltycrib, 201 mg/L Na and 214 mg/L Ca were released (washed off) from the DS. No further Na was released (i.e. inlet and outlet concentrations were the same) after about eleven days and Ca after about twelve days.
- The DS has an adsorption capacity for Pb > Cd > Zn.
- The first metal to saturate the DS bed is Zn. The 3kg Algavi_(c) 1 L/minute treatment plant at Bwlch saturated with Zn after five days (average initial concentration was 25 mg/L) after which it desorbed from the DS and was released back into solution. When the treatment plant was deployed at a site with lower metal concentrations the DS adsorbed metals for longer before saturating; at Alltycrib, saturation of 2 kg Algavi_(f) DS saturated after about nine days (average inlet concentration was ~1 mg/L Zn).
- Cadmium is the next metal to saturate the DS. At the 1 L/minute treatment plant at Bwlch, 3 kg Algavi_(c) DS saturated with Cd after about eleven days (average inlet concentration was 64 µg/L); at Alltycrib, Cd did not saturate the 2 kg Algavi_(f) DS,

although the concentrations in the inlet and outlet waters were nearing the detection limit of the ICP-MS and therefore large errors may be involved.

- The DS has a high capacity for Pb. During the operation of the Bwlch 1 L/minute treatment plant, >90 % Pb was removed by Algavi_(c) DS, >95 % by Girvan DS and >80 % Algavi_(f) DS (average initial concentrations were ~696 µg/L, ~886 µg/L and ~886 µg/L respectively). When the treatment plant was removed from Alltycrib (average initial concentration was 125 µg/L) after 21 days between 6 and 22 % Pb was still being removed, though the removal could not have continued for much longer. The DS bed did not saturate with Pb except at Esgair Hir where Algavi_(c) DS saturated after ~65 days and the carbonate sand bed saturated after ~13 days. The high capacity of DS for Pb was also shown when the Algavi_(c) DS bed was digested and the Pb was shown to be concentrated in the top 20 mm of the bed. Only ~25 % of the bed was saturated with Pb, implying that the bed could continue to remove Pb for another 60 days or so (until a total of ~100,000 L of Bwlch mine water had flowed through the treatment plant).
- Once the DS has saturated with Zn and Cd; Pb exchanged with these metals, which may explain the high capacity of the DS for Pb. The amount of Zn and Cd was relatively constant through the bed, though slightly higher amounts occurred in the lower 10 mm. In the top 20 mm, Pb and Zn had a 1:1 relationship and in the lower 80 mm Pb and Cd had a 1:1 relationship.
- The capacity of the DS to adsorb Cd > Zn was also shown in the core digestions. Within the Bwlch Algavi_(c) and Esgair Hir carbonate sand beds the relationship of Zn: Cd was ~300:1 and within the mine water the relationship was ~400:1 and ~430:1 (respectively) which confirms the preference of the DS for Cd rather than Zn.
- Deploying the treatment plant at Alltycrib showed that the treatment plant can be successfully scaled up in size (to treat 2 L/minute). The DS bed saturated with Zn after nine days (average inlet concentration ~1 mg/L) but neither Cd nor Pb saturated the DS bed after 21 days.
- The mine drainage at Esgair Hir contains minor amounts of Fe (average concentration was 0.2 mg/L), the Fe precipitates out of solution and additional metals simultaneously co-precipitate out of solution. To determine whether the main removal mechanism is the biosorption of metals and not the filtration of the formed precipitates onto the DS bed. A treatment plant containing 2 kg Algavi_(c) DS was deployed for 66 days, after

which a plant containing 9.2 kg carbonate sand for 14 days. Over a 14 day period, the Algavi_(c) removed >80 % of the Zn and the carbonate sand removed between 20 % and -20 % (average inlet concentration was ~0.24 mg/L Zn). When the total amount of metal removed by the bed of material is compared, the Algavi_(c) DS removed 3.6 mg whereas the carbonate sand only removed 0.37 mg; therefore the main metal removal mechanism is biosorption onto the DS, rather than the precipitation and filtrations of metals.

- The adsorption capacity of the DS is Girvan > Algavi_(c) > Algavi_(f); the capacity of the DS was tested by deploying three 1 L/minute treatment plants at Bwlch; 2 kg Girvan removed 40.3 g Zn, 3 kg Algavi_(c) removed 50.6 g Zn and 2 kg Algavi_(f) removed 18 g Zn. Although the Algavi_(c) looks to have removed a greater amount of Zn; if the amount of metal removed is regarded as a percentage of the dry weight of DS then the adsorption capacity is shown much more clearly: 2.02 % of the Girvan DS is Zn, 1.7 % of the Algavi_(c) is Zn and 0.9 % of the Algavi_(f) DS is Zn.
- Contrary to the laboratory experiments, Algavi_(c) DS has a greater adsorption capacity than Algavi_(f). Both DS release Ca, although a greater concentration initially released from the Algavi_(c) DS. No further Ca is released from the Algavi_(f) DS after ~4 hours, whereas after ~72 hours ~5 mg/L is still being released from the Algavi_(c) DS. The presence of the carbonate particles within the Algavi_(c) DS increases the concentration of carbonate within the mine drainage, facilitating the precipitation of metal carbonates which would filter out within the DS bed and remove a greater concentration of metals. The Algavi_(c) DS also has a larger surface area than the Algavi_(f) DS (2.79 m²/g compared to 1.23 m²/g); which allows a greater number of binding sites to be exposed for adsorbing the metals. The Algavi_(f) DS was subjected to a more thorough rinsing with water and acidification, which removed a greater amount of Na, K, Mg and Ca, making the cations unavailable for ion exchange.
- There are a number of problems which need to be remedied before the successful use of the DS treatment plant as a remediation tool: 1) Organic matter needs to be removed from the drainage. At Alltycrib, the connecting pipes and distribution pipe holes were blocked with leaves and other organic matter reducing the flow of mine drainage through the treatment plant. 2) The concentration of Fe within the mine drainage needs to be reduced. At Esgair Hir, the mine drainage contained minor amounts of Fe (~0.2 mg/L) and this had a major effect on the operation of the treatment plant. The Fe precipitated out of solution and blocked the distribution pipe holes and coated the

upper plastic and stainless steel mesh. The precipitated Fe reduced the flow of mine drainage through the treatment plant (the flow through the carbonate sand bed reduced from 1 L/minute to 0.5 L/minute in two days) and impeded the metal adsorption onto the DS. After 15 days of operation, the Algavi_(c) DS bed had to be stirred to remove the Fe coating and to reinstate the flow; this initially caused a large release of metals, then the removal increase to about the same as it was before the bed was stirred. The metal removal and flow steadily decreased as the Fe again precipitated out of solution until the bed had to be stirred again after 29 days. Therefore, for the treatment plant to operate reliably, the Fe has to be removed from solution before entry into the plant.

- The successful operation of the treatment plant requires that DS is added to the plant dry and granulated and that the treatment plant is robust. The 10 L/minute treatment plant deployed at Bwlch was not successful at removing large quantities of metals from the mine drainage. To save time, the DS was added to the treatment plant wet (i.e. not drier and granulated); small channels developed around the edge of the DS bed allowing mine drainage and some DS to flow directly into the base of the treatment plant, with minimal contact between the DS and the mine drainage. The channels may have been created by the 10 L/minute treatment plant having a greater flow of water through the bed, a greater head of water above the bed or the design characteristics of the treatment plant. Also, when the DS is added to the treatment plant dry and is contacted with the mine drainage the DS swells and ‘seals’ the treatment plant allowing intimate contact with the mine drainage and the DS. The design of the 10 L/minute treatment plant is different to the smaller 1 L/minute treatment plant; the stainless steel and plastic mesh below the DS bed is elevated from the base of the treatment plant by sporadic stainless steel supports. The stainless steel mesh may have buckled under the weight of the DS therefore a tight seal between the tank and the mesh was not formed allowing channels to develop and the DS to be lost into the base of the tank. A design more similar to the 1 L/minute treatment plants (i.e. an inner and outer tank) may be more suitable.

9.1.4 Acid Mine drainage remediation

- The drainage from the Ida adit at Libiola, Italy, is acidic (pH 2.5) and contains high metal concentrations, dominated by Al (~93 mg/L), Fe (~300 mg/L) and Cu (~77 mg/L).

- Three additional treatment stages are required compared to the mid-Wales treatment plant: 1) the addition of an alkali to raise the pH to ~6; 2) the addition of a flocculating agent to facilitate the removal of Fe and 3) a settlement tank (retention time ~4 hours) to allow the flocculated ochre to settle out of solution.
- The alkali used to neutralise the AMD affects the amount of metal removed from solution.
- 1 M/L NaOH – the addition of 1 M/L NaOH (at 38 mL/minute) increased the pH of the AMD (to ~5.5) and the Fe began to precipitate, the effluent of the settlement tank showed a Fe decrease of ~232 mg/L Fe; metals also co-precipitated with the ochre, the concentration of Cu decreased from 51 mg/L in the untreated mine drainage to 0.1 mg/L after the settlement tank and Zn decreased from 8.7 mg/L to 0.06 mg/L. Once the Fe- and metal-poor water had flowed through the Algavi_(f) DS bed, the pH increased to ~7 and the drainage contained low metals concentration and virtually no Ni and Zn. Overnight, however, the alkali dosing pump failed allowing acidic metal-rich drainage to flow straight into the DS treatment plant. The effluent from the treatment plant contained lower concentrations of Fe (from 232 mg/L in the untreated mine drainage to 6.7 mg/L); Cu was released from the DS bed, either through the exchange of the Cu for the Fe or the acidic drainage desorbing the Cu from the surface of the DS.
- 1 M/L Na₂CO₃ – The trial started using the same DS bed as used in the NaOH trial. When the AMD was neutralised and the ochre settled out of solution, the pH had increased to ~7.4. The Fe and Mn concentrations were lower and the Ni, Cu, Zn concentrations were higher than at the same stage of the NaOH trial. The concentrations of Fe, Ni, Cu and Zn increased after passage through the DS bed, probably caused by the wash off of the metals from the DS. The DS bed was then replaced by fresh DS after the treatment system had been operating for several hours the removal efficiency increased and Fe concentrations decreased from 232 mg/L in the untreated mine water to 0.23 mg/L in the treatment plant inlet and Cu decreased from 53 mg/L to 0.33 mg/L. After passage through the fresh DS, the metal concentrations were very low; Mn, Ni, Cu and Zn concentrations were all <0.05 mg/L and the Fe concentration was <0.6 mg/L. Increased removal may have been caused by the increased concentration of CO₃ ions within the system, facilitating the formation of

metal carbonates which would precipitate and filter out of solution within the settlement tank or the DS bed.

- 1/6 by weight slurry of DS fines – DS fines (<0.2 mm) were removed in the preparation of the DS. When mixed with water a pH 12 solution is produced, unfortunately the produced slurry is not smooth and not easily added to the AMD. Laboratory experiments showed that when 5 g of DS fines are made into a slurry with a small amount of water and then added to 400 mL of metal-rich acid mine drainage, the pH was neutralised and the metals were removed from solution, for example, Fe was reduced from 285 mg/L to 1.4 mg/L in 20 minutes. If a method of mixing the DS fines with water and separating the DS fines after the AMD had been treated can be found, then this represents a sustainable tool to remediate the AMD.
- The precipitation of large quantities of gelatinous and water-rich sludge was the main problem. A method of de-watering the sludge or producing a denser sludge is required, for example a clarifier/thickener, a filter press, vacuum filtration, continuous pressure dewatering, or centrifuge separation. This additional equipment would increase the cost, energy requirements and size of the required plant. Instead of the sludge being disposed of as special or controlled landfill, the ochre could be used as a pigment (because it is free from organic matter and other debris, though it will contain high concentrations of metals) or it could be re-circulated into the treatment system to produce a more dense sludge possibly reducing the amount of alkali and flocculating reagents that would need to be added to the system.

9.2 Overall conclusions

- The main conclusion to be gained from this thesis is that DS can be used to remediate circum-neutral mine drainage through biosorption and filtration of formed metal carbonates. Girvan DS has the highest metal adsorption capacity followed by Algavi_(c) DS, then Algavi_(f) DS. This bioremediation process could also remediate other waste waters such as effluent from electroplating industries. The DS may also be used to remediate AMD, with the addition treatment stages of alkali and flocculant addition and the settlement of the formed flocs.
- The DS has been proven to be stable (i.e. it is not affected by algal growth and it does not degrade over time) and the process does not require constant operator involvement.

- DS fulfils the criteria required for it to be a competitive remediation material: low cost, readily available in large quantities, is effective over a wide concentration range and in solutions containing multiple elements, the rate of metal removal is rapid, no additional chemicals are required, no sludge is produced and the metals can be desorbed and the DS re-used.
- The low cost of the Algavi DS (~£660 per tonne, including delivery) means that it can be used where other remediation methods are too expensive (for example, the use of specifically grown algae and fungi which costs between £2000 - £10000 per tonne [Wang and Chen, 2009]; ion exchange; or evaporation). A more cost-efficient source of DS may be to purchase wet Girvan DS before it is discharged into the sea and then dry and granulate it on a large scale.
- The low capital and operating cost of the dealginated seaweed treatment plant, therefore, allows the remediation to occur where there are limited revenue streams available to pay for it, for example, waters discharging from abandoned mines and in developing countries. Money may be generated by reclaiming the metals from the eluant (the solution used to desorb the metals) by electrochemical methods.

9.3 Recommendations for further study

There are a number of further studies which could be conducted to expand the results presented within this thesis, these include:

- Investigate the variation in mine water composition more thoroughly and determine the source of the elements within the mine drainage, detailed in Chapter 4.7. This would enable a more thorough remediation strategy to be prepared.
- Desorption of metals from the metal-saturated DS needs to be investigated to enable the metals to be removed from the DS and the DS re-used, which increases its cost-effectiveness. Within this thesis only a very basic desorption test was undertaken which showed that the Zn can be removed from Algavi_(c) DS by 0.1 M HCl. Detailed experiments are required that compare the metal removal using various acids (HCl, HNO₃, H₂SO₄ and acetic acid), various strengths of acid, varying contact times and various contact methods (for example, column or batch experiments).
- During field trials a greater number of samples need to be taken and analysed to provide a better indication of the metal removal rate and characteristics, especially

within the first 24 hours of operation (frequent samples of the inlet and outlet waters were only taken at the Bwlch Dual 1 L/minute trial).

- The field trials would need to be increased to permit treatment of 10 and 100 L/minute. This would determine whether the smaller treatment plants could be successfully scaled-up and whether the full discharge from most mines could be treated.
- Redesign of the treatment plant: At Alltycrib, organic matter blocked the connecting pipes and the holes of the distribution pipe, therefore in future treatment plants a screen is required to prevent the organic matter from entering any part of the plant. The 10 L/minute treatment plant also requires redesigning. Instead of sporadic stainless steel supports elevating the stainless steel, plastic mesh and DS bed off the base of the treatment plant either more frequent supports are required or the inner and outer tank design of the 1 L/minute treatment plants could be used.
- Investigate the impact of the treatment plant on the receiving water courses, i.e. whether the treatment plant remove sufficient metal concentrations so that the water courses comply with environmental quality standards.
- Examine the wider potential use of a DS treatment plant for treating other types of waste waters, including industrial and urban, which may have higher metal concentrations, a different combination of elements, or a different pH.
- Different treatment plant set-ups could be explored, instead of using two tanks one within the other. Jeffers (1993) used porous bags of biosorbent placed in a trough through which the water flowed, or by passing mine water up through a series of tanks. Once saturated, the first bag within the trough or tank (i.e. the most metal-rich) is removed and the next bag moved up to take its place, moving the bags up the trough or tank system. A fresh un-saturated bag can then be placed at the end of the treatment system; this procedure is then repeated as required.
- Improved acid mine drainage trials, as detailed in Chapter 8.7.

9.4 A final note

It has to be remembered that any remediation method can only transfer or contain the pollution, a waste product will nearly always be produced; as Wilson and Edyvean (1993a) state “there are no easily found panaceas!”

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