



*Reflections on acid mine drainage (Fanny Creek settling pond)*

# **Characterization of Drainage Chemistry in Fanny Creek Catchment and Optimal Passive AMD Treatment Options for Fanny Creek**

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A thesis submitted in partial fulfilment of the requirements

for the degree of

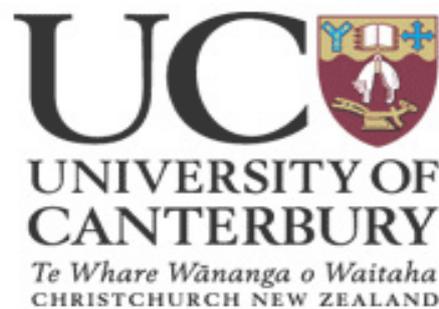
Master of Science in Geology

in the University of Canterbury

by

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## Abstract

Fanny Creek drains from Island Block opencast coal mine, near Reefton on the West Coast of the South Island of New Zealand, and is impacted by acid mine drainage (AMD). The objectives of this study were to characterise drainage chemistry in Fanny Creek catchment, and to determine optimal passive treatment strategies for Fanny Creek AMD for future pilot or full-scale application. This was undertaken by monthly monitoring in Fanny Creek catchment between February 2008 and January 2009 to collect drainage chemistry and flow data. Laboratory trials of suitable passive AMD treatment systems were conducted and their treatment performance assessed to select and design optimal passive treatment strategies for Fanny Creek AMD.

Oxidation of pyrite in Brunner Coal Measure sediments at Island Block mine generates AMD. Fanny Creek originates from a number of AMD seeps on the eastern waste rock slope of Island Block mine. Seeps have low pH (<3.23) and a single detailed metal analysis indicates drainage is enriched with aluminium and iron, and contains elevated concentrations of manganese, copper, nickel, zinc and cadmium relative to applicable water quality criteria such as ANZECC guidelines. Acidity and metal loadings of drainage in the catchment indicates AMD from the northern waste rock slope contributes most of the acidity (~70%) and metal (60%) in Fanny Creek, and acts to re-dissolve additional metals upon mixing with drainage from other slopes.

The most suitable location for a passive AMD treatment system in Fanny Creek catchment is on the Waitahu Valley floor, near monitoring site R12, because this allows for sediment removal prior to a treatment system. Fanny Creek AMD at site R12 was characterized in detail because this data assists with selection and design of passive AMD treatment systems. Fanny Creek at site R12 contains on average 6.0 mg/L aluminium, 1.3 mg/L iron, 3.1 mg/L manganese, 0.49 mg/L zinc, 0.14 mg/L nickel, 0.0071 mg/L copper and 0.00048 mg/L cadmium. Average pH at site R12 was 3.95, calculated acidity averaged 42.7 mg CaCO<sub>3</sub>/L, and flow rate ranged from 1.5 L/s to about 30 L/s. Acidity and metal generation from Island Block mine increases linearly with flow in the catchment, and therefore Fanny Creek drainage chemistry is not significantly affected by rainfall dilution. Natural attenuation of AMD occurs by addition of un-impacted alkaline drainage from Greenland Group basement rocks, wetland ecosystem processes, and geochemical reactions along Fanny Creek that decrease acidity and

metal concentrations before AMD discharges into the Waitahu River. During low flow conditions (summer months), surface flow of AMD into the Waitahu River does not occur because of subsurface flow loss.

Three suitable passive AMD treatment options for Fanny Creek AMD were selected and trialed at 'bench top' scale in a laboratory. These included a sulfate reducing bioreactor (SRBR), a limestone leaching bed (LLB), and an open limestone channel (OLC). The potential to mix Waitahu River water with Fanny Creek to neutralize AMD was also investigated. Fanny Creek AMD was employed for laboratory trials, and influent flow rates into SRBR, LLB and OLC systems were regulated to assess performance at different hydraulic retention times (HRT). Optimal HRTs for future treatment system designs were determined from effective AMD treatment thresholds, and include 51 hours, 5 hours and 15 hours for SRBR, LLB and OLC systems, respectively.

To determine optimal treatment options for Fanny Creek AMD the effectiveness of each trial option was compared to applicable water quality criteria, and scale up implications of treatment options was assessed. The SRBR system had most effective AMD treatment, with water quality criteria achieved for metals, greatest alkalinity generation, and highest pH increase. However, a full scale SRBR system has significant size requirements, and long term treatment performance may be limited. The LLB system decreased metals to below, or just slightly above criteria for all metals, and has significantly smaller size requirements compared to a SRBR system. The OLC system was least effective, with effluent above water quality criteria for all metals except iron, and with lowest alkalinity generation. The Waitahu River is capable of neutralizing AMD because it is slightly alkaline. The flow volume of river water required for neutralization is between 65 L/s and 140L/s, which can be gravity fed to mix with Fanny Creek. These results indicate that either a LLB treatment system or the Waitahu River Mixing option are the optimal passive treatment strategies for Fanny Creek AMD. On site pilot scale testing of SRBR and LLB systems, and the Waitahu River Mixing option is recommended because of AMD treatment uncertainty, and to more accurately select and design full scale passive treatment strategies.

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# CHAPTER ONE

## Introduction

### 1.1 Background

Coal mining on the West Coast of the South Island of New Zealand is an important economic activity and has an extensive history. Island Block opencast coal mine, in the Garvey Creek Coalfield near Reefton, is owned by Solid Energy New Zealand Limited (Solid Energy) and is currently inactive. Historic mining at Island Block has caused acid mine drainage (AMD) in Fanny Creek catchment below the mine site.

Solid Energy is considering resuming mining operations at Island Block, which will involve disposal of 3 million m<sup>3</sup> of waste rock into Fanny Creek catchment. Solid Energy requires environmental work to examine ways to mitigate the impacts of AMD in this catchment.

Passive treatment systems, such as constructed wetlands, effectively treat AMD when designed and implemented appropriately (Younger et al., 2002). Passive treatment of AMD is in the developmental stage in New Zealand and is an area of ongoing research. Solid Energy is currently implementing AMD treatment systems, trialing innovative treatment options and collecting necessary water quality and flow data from selected sites to assist with future rehabilitation work. A high priority rehabilitation and treatment area for Solid Energy is the Garvey Creek Coal field, which has limited geochemical and environmental data available.

The objective of this research is to collect data to characterize and examine the current AMD issue in Fanny Creek catchment, to identify suitable passive AMD treatment systems and conduct laboratory trials for determination of optimal passive rehabilitation strategies for Fanny Creek AMD.

## **1.2 Objectives**

The main objectives of this study are:

- To characterise drainage chemistry in Fanny Creek catchment.
- To relate drainage chemistry to geology in the catchment.
- To identify suitable passive AMD treatment options for Fanny Creek and to trial these at laboratory scale.
- To interpret and evaluate the effectiveness of laboratory scale passive AMD treatment systems.
- To determine optimal passive treatment options for remediation of Fanny Creek AMD for future pilot or full scale application.

## **1.3 Investigation methodology**

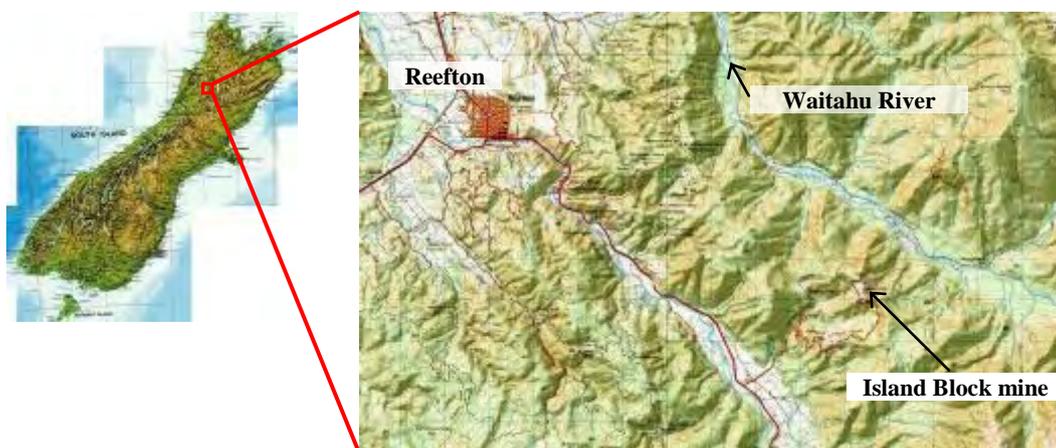
Drainage chemistry in Fanny Creek catchment was characterized by monthly site visits to monitor drainage and flow rates in the catchment. Initial data were used to identify suitable passive AMD treatment options for Fanny Creek based on water chemistry and catchment characteristics. Using previous experience of small scale passive AMD treatment systems, laboratory trials were initiated of selected systems and data collected to assess performance of each system at a range of flow rates. Interpretation and analysis of data collected from laboratory trial investigations enabled treatment processes and effectiveness to be evaluated.

Results of trial passive AMD treatment systems were used to determine optimal treatment operating conditions and develop specific design criteria for each system, which are then used as a basis for comparison between the different treatment options for Fanny Creek. Evaluation of AMD treatment effectiveness at optimal operating conditions and implications for full scale application of trial systems determined optimal passive treatment strategies for Fanny Creek AMD. This study also identifies future research requirements for Island Block mine.

## **1.4 Location of Study Area**

Island Block mine lies within the Victoria Range foothills, on the top of the hillside between the Waitahu and Inangahua valleys (Figure 1.1). Island Block is visible from the Lewis Pass

highway, and is 10 km south-west of the Reefton township. Island Block is situated in the Garvey Creek Coalfield and mined coal from several shallow dipping coal seams. Fanny Creek catchment is situated below the mine on the opposite side of hill from the highway, and drains north-east into the Waitahu River.



**Figure 1.1: Location of Island Block opencast coal mine near Reefton (Topo Map, 2010).**

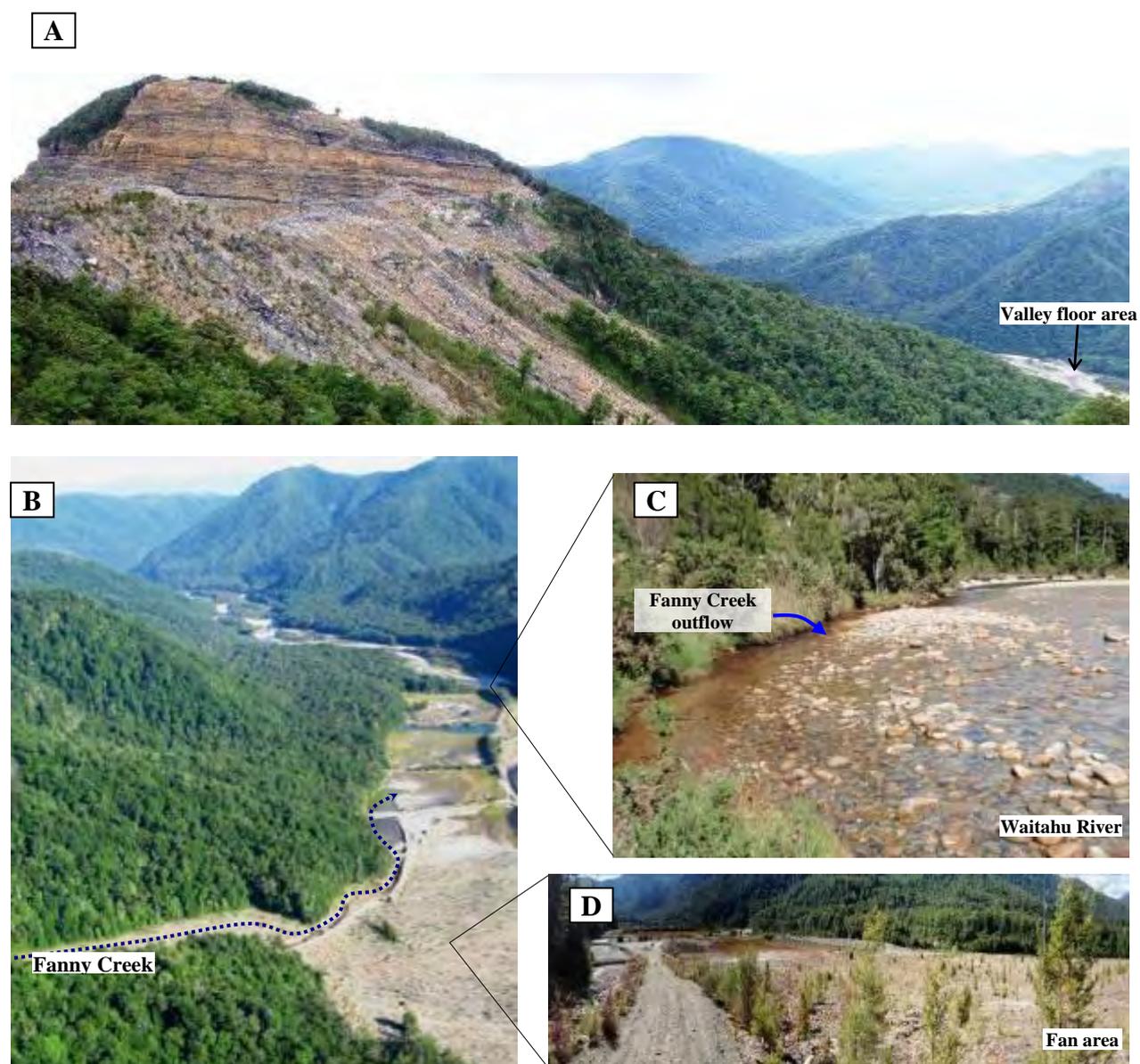
## 1.5 Site description

A steeply cut highwall curves around the hillside at Island Block mine, exposing gently dipping ( $10^\circ$ ) coal measure strata (Figure 1.2). The highwall ranges in height from about 80 - 110 m, with coal previously mined at the base from the main 'A' seam in the Brunner Coal Measure sequence. The remainder of the coal mine at the hill top is relatively flat, containing waste rock and remnant coal stock piles. Slopes adjacent to Island Block drop steeply away ( $\sim 50^\circ$ ), and consist of sparsely vegetated waste rock slopes. The western waste rock slope forms the headwaters of Garvey Creek, while the eastern slopes comprise the upper areas of Fanny Creek catchment. Island block is accessed by a metal road via an active coal mine, Echo mine, and a 4WD track leads down to Fanny Creek in the Waitahu Valley.

Fanny Creek drains from the eastern waste rock slopes of Island Block, and is impacted by acid mine drainage (AMD) (Raj, 2002). Midway downhill drainage combines to form a moderately steep, constricted main channel. On the valley floor there is a wide flat sediment fan with mature beech seedlings planted by Solid Energy for re-vegetation. Fanny Creek runs northwards beside the hill along the edge of fan, through a series of settling basins to remove

sediment, and then discharges into the large Waitahu River which drains from the Victoria Range foothills (Figure 1.2).

The surrounding catchment areas that are not affected by mining operations are densely vegetated by native bush. Climate is typical of the West Coast of the South Island, with an average annual rainfall in Reefton of ~2000 mm, and mean maximum temperatures between 10 – 23 °C (Niwa, 2010). During winter snow often falls at the mine site.



**Figure 1.2: Island Block mine eastern highwall and waste rock slopes (A). B) Lower catchment area. C) Discharge to the Waitahu River. D) Valley floor fan area. All photos look north.**

### **1.5.1 Mining History**

Mining in Garvey Creek started in 1947, but coal mining at Island Block began in 1962, by a previous state owned company. Overburden was disposed of in Fanny Creek catchment until 1985, after which Solid Energy took over operation and disposed overburden on the hilltop, although some was placed on the southern most waste rock slope as recently as 1996 (J Foster, pers comm., 2010). During operation, Solid Energy removed 20 – 30 000 tpa of bituminous coal, with low ash and sulfur. Mining operations at Island Block ceased in 2002, but Solid Energy plan to access the remaining coal resource and dispose approximately 3 million m<sup>3</sup> of overburden in Fanny Creek catchment (P Weber, pers comm., 2010).

### **1.5.2 Regional Geology**

Island Block mine is located in the Eocene Brunner Coal Measures (45 – 40 Ma). Basement rocks that coal measures unconformably overlie are Cambrian to Ordovician Greenland Group meta-sediments (Nathan et al., 2002). Overlying Brunner Coal Measures are shallow marine sediments of the Kiata Formation (Suggate, 1957).

### **1.5.3 Local Geology**

#### **1.5.3.1 Greenland Group**

At Island Block mine the Brunner Coal Measures lie unconformably on Ordovician Greenland Group meta-sediments, the oldest rocks in the Reefton area (495 ± 11 Ma) (Adams, 1975). Greenland group rocks consist of unfossiliferous indurated sandstone and mudstones deposited along a passive continental margin sequence, and have undergone low-grade metamorphism (Nathan et al., 1986). Carbonate minerals are found disseminated in Greenland Group sediments because of hydrothermal alteration (Christie & Brathwaite, 2003).

#### **1.5.3.2 Brunner Coal Measures**

Tectonism during the mid to late Eocene caused marine transgression and localised basin formation resulting in the deposition of the Brunner Coal Measures (45 – 40 Ma) (Nathan et al., 1986), in a fluvial to estuarine environment (Flores & Sykes, 1996).

Brunner Coal measures are spread throughout North Westland and Buller, including the Garvey Creek Coalfield and Island Block mine. The Garvey Creek Coalfield is nearly 8 square kilometers in area, on the hilltops between the Inangahua and Waitahu valleys (Suggate, 1957). Coal is mostly mined from a basal 'A' seam, which ranges in thickness from 8 – 15 m within the coal field. The maximum thickness of the coal measure sequence is 320 m, while the thickness of overburden at Island Block is about 100 m (Lucus, 2002). Coal measure sediments are rich in quartz (Newman, 1988) and feldspar (Titheridge, 1992) derived from basement rock. Sediments typically consist of a localized basal conglomerate, quartzose grit and sandstones, siltstones, mudstone, carbonaceous mudstone and coal, and overall the sequence fines upwards (Suggate, 1957). Post depositional processes deposited pyrite either disseminated, framboidal (Weisener & Weber, In press) or as cement (Newman, 1988).

### **1.5.3.3 Kaiata Formation**

The Kaiata Formation conformably overlies, and laterally interfingers with the Brunner Coal Measures. The Kaiata Formation predominantly consists of massive, dark grey/brown carbonaceous mudstone, with inclusions of thin sandstone layers. The Kaiata Formation formed during marine transgression and was deposited in a shallow marine environment (Nathan, 1986).

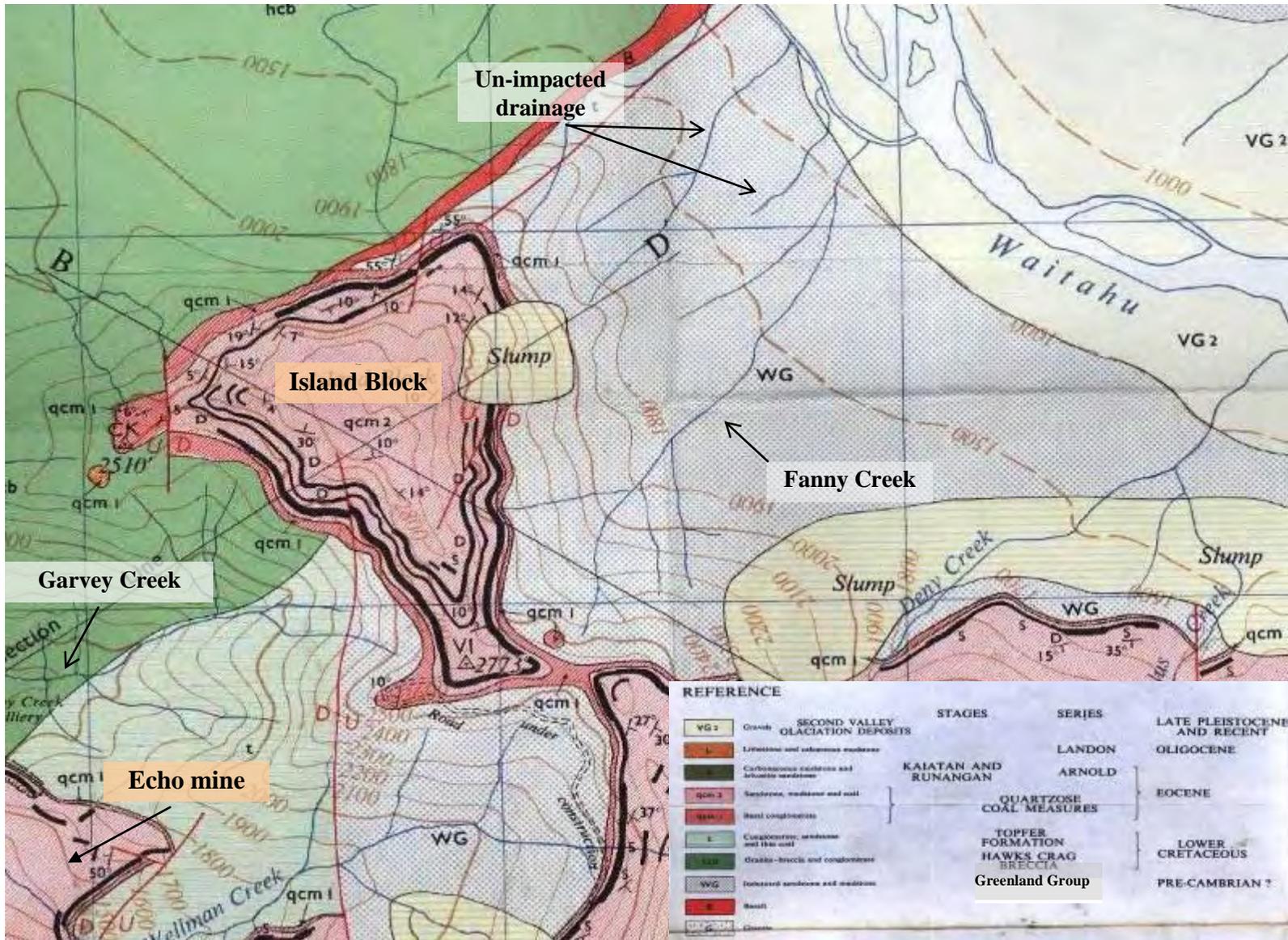


Figure 1.3: Geology of the Island Block mine area (modified from Suggate, 1957).

## 1.6 Thesis format

This thesis is organised into six chapters. The current chapter sets the scene and describes field site location and geology of the Island Block area which is relevant to drainage chemistry in the catchment.

Chapter Two reviews acid mine drainage water chemistry and presents the limitations of environmental data in Garvey Creek Coalfield. Characterization of catchment drainage chemistry from monthly monitoring are presented and discussed, and the issue of Fanny Creek AMD described.

Chapter Three gives a brief overview of passive AMD treatment systems relevant to this study and serves as an introduction to the following chapter. The reader is referred to Appendix II for a detailed review of the principles of passive AMD treatment systems and how they remediate AMD. Appendix II (E) includes a detailed review of relevant passive AMD treatment systems described in the chapter.

Chapter Four presents the methodology and results of laboratory trials of selected passive AMD treatment systems.

Chapter Five discusses the results of passive AMD treatment system laboratory trials. The discussion includes a description of AMD treatment effectiveness, interpretation of remediation processes, and optimal operating treatment conditions for the different trial systems. The effectiveness of trial treatment systems is compared to determine optimal passive remediation strategies for Fanny Creek AMD and future investigation requirements are outlined.

Chapter Six is a synthesis of drainage chemistry in Fanny Creek catchment and of laboratory trials of passive AMD treatment systems. Future work required to more accurately characterise AMD and determine optimal passive treatment solutions for Fanny Creek AMD is summarized.

## CHAPTER TWO

# Characterization of Drainage Chemistry in Fanny Creek Catchment

### 2.1 Introduction

This chapter characterizes drainage chemistry in Fanny Creek catchment. Initially, AMD drainage chemistry and previous environmental studies in Garvey Creek Coal field and Island Block Mine are reviewed. The limitations of current data are outlined in relation to selection and design of passive AMD treatment systems for Fanny Creek AMD.

The specific objectives of Fanny Creek catchment drainage chemistry characterization are:

- To characterise catchment drainage pattern and environs
- To monitor and sample drainage chemistry in the catchment
- Identify sources of AMD and their relative contributions to Fanny Creek
- Identify changes in drainage chemistry along Fanny Creek
- To relate drainage chemistry to geology
- To characterise streams not affected by AMD

These objectives were achieved by collection of monthly water sampling data, which involved:

- Analysis of metal concentrations
- Measurements of acidity and alkalinity concentrations
- Measurements of water quality parameters such as pH, conductivity, dissolved oxygen
- Measurement of flow rates

Characterization of drainage is essential to select and design the most effective passive treatment system for remediation of AMD (Watzlaf et al., 2003).

A single detailed metal analysis for samples collected in March characterized drainage chemistry and identified elevated metals in the catchment relative to applicable water quality criteria. Elevated metals are the focus of subsequent data analysis.

To determine contributions of AMD from different sites, metal and acidity loadings of elevated metals are quantified for AMD seeps and other sites in the catchment.

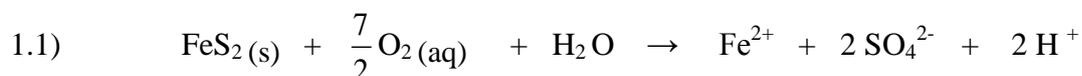
The drainage chemistry of Fanny Creek catchment is presented from its source at Island Block, to the outflow of Fanny Creek in the Waitahu River. Various sites are focused on along Fanny Creek to describe primary AMD characteristics, changes in chemistry, and sites relevant to passive AMD treatment selection and design.

## 2.2 Review of Acid Mine Drainage Water Chemistry

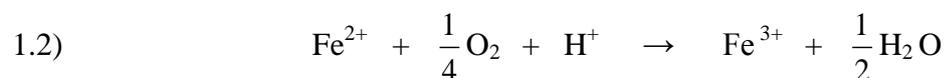
Acid mine drainage (AMD) is the most significant environmental problem facing the mining industry (Brown et al., 2002). Historic mining on the West Coast of the South Island releases AMD into drainage catchments. The aqueous chemistry of mine water drainage has been thoroughly researched (Younger et al., 2002; Brown et al., 2002), however, the geology and geochemistry of mine drainage in New Zealand is currently being investigated (Pope et al., In press, a b; Weisener & Weber, In press; Rait et al., In press; Trumm, In press; McCauley et al., In press; Trumm & Watts, In press).

### 2.2.1 AMD Generation

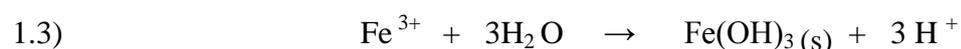
AMD forms when sulfide minerals, such as pyrite ( $\text{FeS}_2$ ) contained within ore, coal or waste rock are exposed to oxygen and water (Brown et al., 2002). Oxidation of these minerals generates acid and is often accompanied by elevated concentrations of dissolved metals and sulfate (Watzlaf et al., 2003). This occurs by natural weathering processes, however, it is accelerated by mining activities that can disturb vast quantities of sulfide bearing rock. Stumm and Morgan (1996) summarize AMD formation. Pyrite oxidation releases dissolved ferrous iron ( $\text{Fe}^{2+}$ ), sulfate ( $\text{SO}_4^{2-}$ ) and acidity ( $\text{H}^+$ ) into solution (1.1).



In the presence of sufficient dissolved oxygen, ferrous iron oxidises to ferric iron ( $\text{Fe}^{3+}$ ), consuming acidity in the process (1.2).



However, at pH above 3.5, ferric iron is not soluble and precipitates as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ), which releases acid that can lower pH (1.3) (Brown et al., 2002).



At low pH (<3.5) ferric iron is soluble and can replace oxygen as an oxidizing agent, releasing more acidity (1.4). This process is self-perpetuating because the ferrous iron produced can re-oxidize to ferric iron which re-initiates reactions (1.2 – 1.4) (Younger et al., 2002).



Although both dissolved oxygen and ferric iron oxidize pyrite, the rate at which ferric iron oxidizes pyrite is generally faster than oxygen. Therefore, the rate determining step in the pyrite weathering process is oxidation of ferrous to ferric iron (1.2), which creates a ready supply of ferric iron to react with pyrite (Singer & Stumm, 1970).

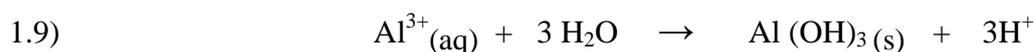
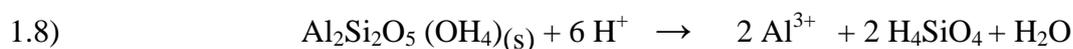
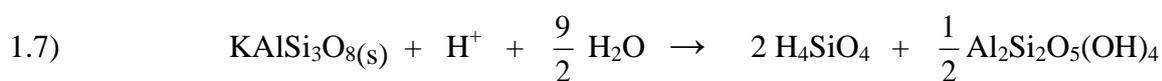
Ferrous iron oxidation can occur either by abiotic (purely chemical) and/or by microbial processes. At near neutral pH, oxidation is mostly abiotic. However, microbial processes predominate at pH 2 - 4 (Brown et al., 2002), with bacteria such as *Thiobacillus ferrooxidans* catalyzing reaction 1.2. Bacterial catalysis can accelerate the ferrous iron oxidation rate by a factor larger than  $10^6$  (Singer & Stumm, 1970). Therefore, generation of acidity is more rapid at lower pH (Brown et al., 2002; Younger et al., 2002).

Weathering of metal sulfides other than pyrite, for example sphalerite ( $\text{ZnS}$ ) and galena ( $\text{PbS}$ ), will not produce acidity (1.5, 1.6), but can release other metal ions into solution (Younger et al., 2002).





Metals are generally more soluble at lower pH, thus, acidity generated by pyrite oxidation can leach trace metals from surrounding rock material, such as arsenic, copper, nickel, zinc, manganese. Dissolution of aluminosilicates (feldspars and micas) can also release aluminium ions (1.7, 1.8), which then generate further acidity upon hydrolysis and precipitation (1.9) (Watzlaf et al., 2003). However the overall dissolution of aluminium from aluminosilicate minerals and its subsequent precipitation as an aluminium hydroxide is neutral in regards to the acid balance (1.8 and 1.9)



### 2.2.2 Acidity

There are four types of acidity which contribute to low pH (Stumm and Morgan, 1996);

- organic acidity (dissolved organic carbon)
- carbon dioxide acidity (dissolved carbon dioxide and carbonic acid)
- proton acidity (free hydrogen ions)
- mineral acidity (dissolved metals), or Lewis acidity

Acidity in coal mine drainage is primarily associated with proton acidity ( $\text{H}^+$ ) and mineral acidity from dissolved metal ions ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ). These dissolved metals are considered acidic because they can hydrolyse and generate protons (1.3, 1.9). The following formula uses pH and dissolved metal concentrations (in mg/L, represented by  $C_{\text{Al}}$ ,  $C_{\text{Fe}^{2+}}$ ,  $C_{\text{Fe}^{3+}}$ ,  $C_{\text{Zn}}$ ) to accurately calculate total acidity and quantify its components (modified from Watzlaf et al., 2003):

$$50.045 ((3 C_{\text{Al}} / 26.98) + (2 C_{\text{Fe}^{2+}} / 55.85) + (2 C_{\text{Fe}^{3+}} / 55.85) + (2 C_{\text{Zn}} / 65.38) \dots + 1000(10^{-\text{pH}}))$$

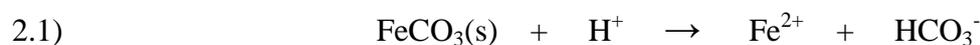
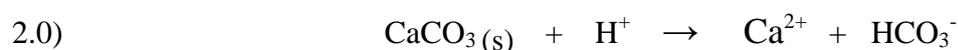
Calculated acidity is reported in mg/L as calcium carbonate equivalent (mg  $\text{CaCO}_3/\text{L}$ ) because this material (limestone) is commonly used in AMD treatment (Brown et al., 2002).

### 2.2.3 AMD Flushing

Under saturated conditions, pyrite oxidation products are transported by water from the weathering zone. However, these products can accumulate as soluble compounds in unsaturated void spaces that are exposed to the atmosphere within waste rock material, or highwalls. If void spaces subsequently become saturated, stored acidity and soluble compounds can enter solution and cause a temporary, more concentrated flush of AMD (Younger et al., 2002).

### 2.2.4 Acid Neutralisation

Weathering of carbonates and silicates can neutralize acidity generated by pyrite oxidation and naturally buffer pH. Common carbonate minerals include calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), magnesite ( $\text{MgCO}_3$ ) and rhodochrosite ( $\text{MnCO}_3$ ), and during dissolution consume proton acidity and release bicarbonate alkalinity (2.0). Weathering of siderite ( $\text{FeCO}_3$ ), however (2.1), has no net neutralizing effect because the ferrous iron released can oxidize and generate acidity as demonstrated by equations 1.2 and 1.3 (Younger et al., 2002).



In addition, metals can be attenuated within receiving environs, particularly by wetland processes that occur in substrates, water, and vegetation (Sheoran and Sheoran, 2006). Processes include settling, sedimentation, sorption, oxidation, hydrolysis, precipitation, co-precipitation, cation exchange, photodegradation, phytoaccumulation, biodegradation, microbial activity and plant uptake. However, complex combinations of these processes are involved, and removal of metals from the aquatic environment may not be long term.

### 2.2.5 Ecological Effects

Mine drainage can impact ecological systems of fresh water resources (Harding & Boothryd, 2004). Studies in New Zealand document significantly reduced invertebrate taxonomy in AMD impacted streams (Winterbourn et al. 2000), and either death or impaired health for fish species exposed to AMD (Harding and Boothryd, 2004). Causes of impacts are attributed to

low pH, and increased metal concentrations, suspended solids, and smothering of streambeds with sediment or precipitates (Harding & Boothryd, 2004).

### **2.2.6 AMD on the West Coast**

Certain coal mining operations on the West Coast of the South Island has adversely affected downstream aquatic ecosystems. Coal mines hosted within the Brunner Coal Measures are more likely to produce acidic, metal enriched mine drainage (Pope et al., In press, a, b) and a number of studies document its characteristics and effects (Lindsay et al., 2003; de Joux, 2003; Harding & Boothryd, 2004; de Joux & Moore, 2005; Black et al., 2005; Trumm 2006, 2008). Drainage typically has low pH (2.5 – 4), high iron and aluminium concentrations (variable ratio Al:Fe), and can have elevated concentrations of trace elements (Lindsay et al., 2003; Black et al., 2005; Pope et al., In press, a; Weisener & Weber, In press; Trumm & Watts, In press).

AMD occurs from oxidation of pyrite within Brunner Coal Measures (Weber et al., 2006; Pope et al., In press). Pyrite formed in coal measure sediments by diagenetic processes after deposition of overlying marine Kaiata mudstones and associated sea water ingress (sulfur source) (Suggate, 1957). Mudstones are reported to have greater acidity generating potential than other lithologies, such as sandstones (Weber et al, 2006; Pope et al., in press, b), attributed to high pyrite content, as well as finer grain size which is more reactive (Weber & Weisener, In press). Mudstone and coal lithologies also produce elevated nickel concentrations (Alicorn Leon & Anstiss, 2002; de Joux & Moore, 2005) and Weber et al. (2006) demonstrate pyrite is the source mineral. High aluminium concentrations are due to leaching of minerals such as feldspars, micas, or clays, which are abundant in coal measure sediments (McCauley et al., 2009).

In addition, stream quality and AMD data from the west coast region have recently been collated into a database (DAME), and variation in drainage chemistry is primarily attributed to regional geology, mine type, hydrogeology, and local rock types (Pope et al., in press, a). This information has been combined with geochemical, ecological and remediation data to create a framework for predicting and managing water quality impacts of mining on streams (Cavanagh et al., 2010).

### **2.2.7 Garvey Creek Coal Field and Island Block Mine**

Although general geochemical and environmental data is available for Brunner Coal Measures, data specific to the Garvey Creek Coalfield is limited. Herrmann and Baumgartner (1992) identify a trend in the coal field of increasing sulfur content (1 – 7 wt. %) related to either a lacustrine or estuarine depositional environment, respectively. Stratigraphic interpretation of the sequence at Island Block has separated overburden into five different lithologies, typical of coal measure sediments for geotechnical investigation (Lucus, 2002).

Rock samples collected at Echo and Island Block coal mines have established acid neutralizing and acid producing characteristics of sediments disturbed by mining (CRL Energy Ltd unpublished data; Raj, 2002). Carbonaceous mudstone – siltstone, and coal lithologies had greatest short and long term acid producing potential (Raj, 2002). This agrees with CRL Energy data, and other regional Brunner Coal Measure observations (Pope et al., In press, b; Weber et al., 2006). Leach column tests using typical Island Block overburden have also been performed on-site.

Studies of AMD within the Garvey Creek coal field are mostly from Island Block and Echo mines drainage, and include Wellman, Garvey, and Fanny Creeks (CRL Energy Ltd unpublished data; Raj, 2002; Barnden & Harding, 2005; Solid Energy unpublished data). Sites with low pH and elevated concentrations of aluminium and iron are identified, and trace metals such as manganese, copper, nickel, zinc and arsenic are present (CRL Energy Ltd unpublished data; Harding, 2005; Barnden & Harding, 2005; Raj, 2002; Pope et al., In press a).

Solid Energy has monitored water quality at sites in Fanny Creek catchment since August 1995 (Appendix I, A). Raj (2002) report data from these sites between January and July 2002, and completed metal analysis on two occasions. On one occasion, Fanny Creek prior to discharge contained 4.89 mg/L aluminium, 1.59 mg/L iron, 1.53 mg/L manganese. Most AMD from Island Block drains east into Fanny Creek, with minimal contribution to Garvey Creek to the west (pH >4.8), however, Fanny Creek AMD still has no detectable impact on the downstream water quality of the Waitahu River (Raj, 2002).

Detailed information on Fanny Creek drainage chemistry and accurate flow rate information were absent prior to this study. Further data was required both in the wider catchment area of Fanny Creek and of seasonal drainage chemistry and flow rate variation.

### **2.2.8 Summary**

The primary control on mine drainage chemistry is the mineralogical composition of rocks disturbed by mining (Pope et al., In press, b). This in turn affects pH, an important variable for the mobility and bioavailability of metal ions (Younger et al., 2002). Other secondary factors for drainage chemistry include, microbial activity, oxygen concentration (Younger et al., 2002), grain size, minerals reactivity (Weisener & Weber, In press), climate, mining methods and AMD mitigation techniques (Pope et al., In press, a).

Therefore, AMD chemistry is highly site specific, and requires field investigation to characterize drainage chemistry. At Island Block mine, and within Fanny Creek catchment, detailed information on drainage chemistry is lacking and this data is essential for effective management of AMD. The remainder of this chapter focuses on characterization of drainage chemistry in Fanny Creek catchment, and information that will assist design of passive treatment systems to remediate AMD.

## **2.3 Methodology of Fanny Creek Catchment Drainage Chemistry Characterization**

### **2.3.1 Rationale**

Sampling and measurement of physiochemical properties was completed on a monthly basis for almost a year, from 2 February 2008 to 13 January 2009. This monitoring duration identified seasonal fluctuations in chemistry and variations in flow.

Fieldwork enabled collection of other parameters relevant for design of passive AMD treatment systems, such as site topography, available land area, accessibility, and presence of suspended sediment.

### **2.3.2 Site Selection**

Monitoring sites within the catchment include as near to the source of AMD as possible (AMD seeps), confluences along Fanny Creek, un-impacted tributaries to Fanny Creek, prominent hydrological features (ponds, rivers), as well as previous monitoring sites (Figure 2.1). An oblique schematic map shows monitoring sites and the layout of drainage in the catchment (Figure 2.2). Sites incorporate those previously monitored by Solid Energy, labeled 'R' (for Reefton), and by Raj (2002) (IB5). Samples from AMD seeps are labeled 'S' (S1 – S9), sites along Fanny Creek are labeled 'IB' (IB6 - IB12), and drainage not impacted by AMD labeled 'U' (U1 – U6). At confluences, sampling sites are distinguished by suffixes; either 'a' 'b' or 'c'. To allow sufficient mixing of drainage, the downstream sample site was at least five times the width of the main channel downstream of the confluence (J Pope, pers comm., 2008). The area around site R12 is the preferred location in the catchment for a passive AMD treatment system (P Weber, pers comm., 2008), and site R5 represents Fanny Creek discharge to the receiving environment (Figure 2.3). Certain monitoring sites in the catchment are displayed in Appendix I, B.

### **2.3.3 Monitoring Frequency**

Monitoring at sites within the upper catchment (S1 – S9, and confluences IB10, IB11) was conducted during February, March, April, 2008 due to time and budget constraints. Other sites (downstream of IB5) were sampled on a monthly basis. However, due to variables such as flow and access, a complete record was not always possible at all sites on all sample occasions.

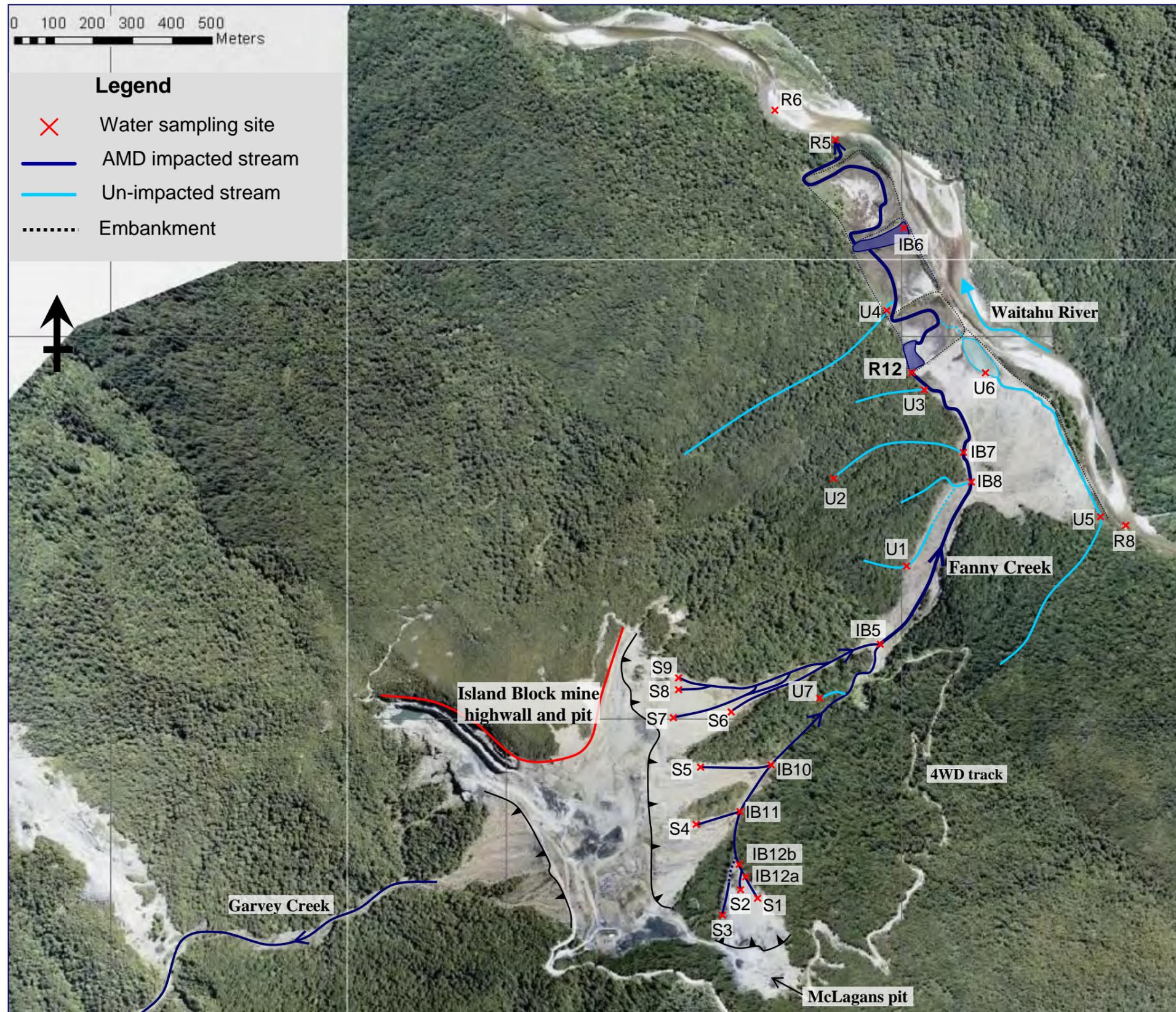


Figure 2.1: Aerial photo map of Fanny Creek catchment drainage and water monitoring sites. Only the primary label is shown for confluence sampling sites to avoid clutter (instead of all three sample sites at confluences)

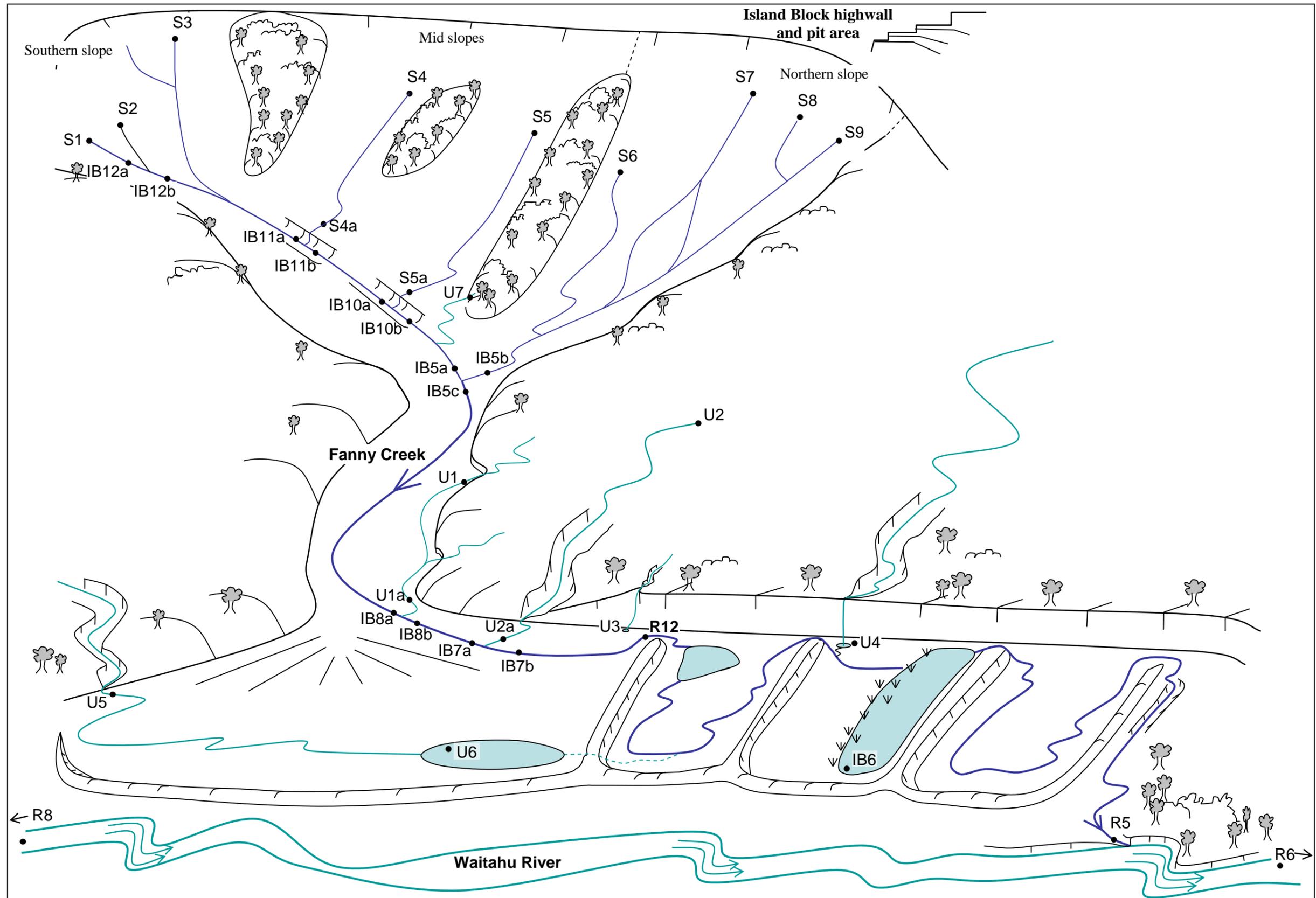


Figure 2.2: Schematic oblique map of Fanny Creek catchment drainage and water monitoring sites, looking south-west. The different areas of Island Block mine waste rock slopes indicated (southern, mid and northern).



**Figure 2.3: Fanny Creek monitoring sites R12 (top) and R5 (bottom). The area around site R12 is the preferred location for a passive AMD treatment system in the catchment, and site R5 is immediately before Fanny Creek enters the Waitahu River (river seen in background of inset picture).**

### **2.3.4 Water Sampling**

Monitoring of sites involved measurement of water quality parameters pH, electrical conductivity (EC) and dissolved oxygen concentration (DO). Samples were collected for alkalinity, acidity, metal and sulfate analysis.

Monitoring was conducted by sampling in an upstream direction, beginning at site R6. Water quality parameters were measured at the time of sampling, using calibrated portable instruments. Electrical conductivity and pH were measured using a Eutech Cyberscan meter, and a dissolved oxygen meter measured DO. Water chemistry samples were collected with no head space free in HDPE bottles. Samples for acidity and alkalinity analysis were

unpreserved, whereas, metal and sulfur samples were preserved with nitric acid (pH <2) to keep metals in solution. Samples for dissolved metal analysis were passed through a 0.45 µm filter into bottles (removing particulate), while samples for total metals were unfiltered. Care was taken not to disturb the sampling site. Samples were stored in a chilly-bin whilst in the field, and then refrigerated until analysed.

Acidity (to pH 3.5, 5, 7) and alkalinity (to pH 3.7) concentrations were determined by titration methods (Lewis & McConchie, 1994). Samples were titrated on the evening of collection. Metal concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS), and sulfur was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) at R.J Hill Laboratories Ltd.

#### **2.3.4.1 Metal Analysis**

A single detailed assessment of dissolved metals was obtained for selected sites sampled on March 7, 12, and 13. This included extended metal analysis (32 metals) for AMD seep sites IB12b, S5, S7, and at site R12. Sites S2, IB11a, S4, S6, S8 (AMD seeps or near), confluences IB5, IB7, and Fanny Creek outflow (R5) were also analysed for samples collected in March; however, only 12 metals were analysed due to budget constraints (Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Zn). Metal analysis at confluence IB7 also included total metal analysis (particulate fraction) and included un-impacted drainage at sites U2a and U2 (IB7 sites also analysed in May and July). All sites included dissolved sulfur analysis, which was then converted to sulfate concentrations (mg/L).

Detailed metal analysis of samples collected in March were compared to relevant water quality criteria, such as ANZECC guideline ‘trigger’ values (80% protection of aquatic species in freshwater) and recent, probably more applicable resource consent conditions for the proposed Cypress opencast coal mine (Appendix I, C), owned by Solid Energy NZ near Westport (Table 2.1). Metals that were elevated include aluminium, iron, manganese, copper, nickel, zinc and cadmium. These metals were analysed on a monthly basis at sites R12 (dissolved and total metals) and R5 (dissolved metals). Dissolved calcium and sulfur were also measured at these sites.

### 2.3.4.2 Water Quality Criteria

Table 2.1: Relevant water quality criteria for Fanny Creek AMD.

Parameter	Cypress Mine consent conditions			ANZECC trigger values
	30-day median	90th percentile limit	Maximum limit (mg/L)	80% species protection
Total sus. solids		20 mg/L	100	-
pH	≥ 4.5	≥ 4.0	-	-
Acid soluble aluminium	-	-	3.0*	-
Acid soluble iron	-	-	5.0	-
Dissolved manganese	-	-	-	3.6
Dissolve copper	-	-	-	0.0025
Dissolved nickel	-	-	0.05 - 0.15	0.017
Dissolved zinc	-	-	0.15	0.031
Dissolved cadmium	-	-	0.00018 - 0.003	0.0008
Dissolved arsenic <sup>(5+)</sup>	-	-	-	0.36

\*Acid soluble aluminium concentration likely adjusted to ~1 mg/L (P Lindsay, pers comm., 2009). There are no ANZECC guideline values for iron, and aluminium (pH<6.5).

### 2.3.4.3 Flow Rate

Flow rate measurements are used to calculate fluxes of acidity and metal, and to determine the size of a passive treatment system (PIRAMID Consortium, 2003). Wherever possible, flow rate was determined by a V-notch weir (Appendix I, B), with flow computed by measurement of water depth over the notch (Berkman, 1995). Smaller flows were measured using a bucket or 500 ml jug and timer, with flow calculated by the time taken to collect a known volume of water. At least three measurements were taken at each site and averaged to calculate flow. Flow rate was estimated when circumstances such as precluded either method, such as dispersed flow, or flow larger than ~15 L/s.

### 2.3.5 Data Analysis

Measured acidity and alkalinity concentrations were calculated from titrations, and reported in mg/L as calcium carbonate equivalent (mg CaCO<sub>3</sub>/L). Calculated acidity concentrations of samples were calculated using the equation described in Section 2.2.2 (Watzlaf et al. 2003). Dissolved aluminium and iron concentrations, and pH were incorporated, because associated acidity is applicable to acidity titrations and passive treatment. Acidity associated with other metal cations, such as Mn, Cu, Ni, Zn was not included because of their high solubility at pH achieved in titrations (J Pope, pers. comm., 2008). Calculations assume all dissolve iron is

ferric ( $\text{Fe}^{3+}$ ) because no iron species analysis was taken during sampling (thus acidity represents maximum values).

Acidity and metal loading loadings throughout the catchment were also computed because they show the flux of components a treatment system would be required to remove. In addition, loadings have implications for design, maintenance, and longevity of treatment systems (Watzlaf et al., 2003).

Acidity and metal loadings were calculated by multiplying corresponding concentration and flow rate data (Appendix I, B). Acidity loading is reported in units of calcium carbonate required per day for neutralization ( $\text{kg CaCO}_3/\text{day}$ ). Metal loading is in units of mass of metal per day (i.e.  $\text{kg/day}$ ), and as moles of metal per day (moles metal/day). Contributions of individual components to acidity and metal loadings were calculated on a percentage basis, by dividing individual component loading by the total loading at the site.

## **2.4 Results of Monitoring Fanny Creek Catchment Drainage**

Table 2.2 summarizes data from sites monitored in Fanny Creek catchment between February 2008 and January 2009. Lowest average pH was at AMD seep site S8 (pH 2.91), while highest average pH was at site U2 (pH 6.49). Average electrical conductivity for AMD ranged from  $207 \mu\text{S/cm}$  (S1) to  $3653 \mu\text{S/cm}$  (S7). In the upper catchment, highest average flow rate occurred at site S6 ( $0.49 \text{ L/s}$ ), and lowest at S5 ( $0.017 \text{ L/s}$ ). Fanny Creek outflow (R5) had the highest flow rate overall. Average measured acidity (pH 7) was highest for site S7 ( $318.3 \text{ mg CaCO}_3/\text{L}$ ). Average alkalinity (pH 3.7) was highest at un-impacted drainage site U2 ( $80.0 \text{ mg CaCO}_3/\text{L}$ ). Results of all water quality, chemistry and flow rate measurements are provided in Appendix I, C.

**Table 2.2: Data summary table of Fanny Creek catchment water monitoring sites. Data includes average pH, average electrical conductivity (EC), flow rate, average dissolved oxygen (DO), and average measured acidity (pH 7) and alkalinity (pH 3.7) as mg CaCO<sub>3</sub>/L. ‘N’ indicates the number samples collected between February 2008 - January 2009.**

	Sample Site	pH	EC uS/cm	Flow rate (L/s)			DO (mg/L)	Acidity (pH7)	Alkalinity (pH 3.7)	n
				Av.	Max.	Min.				
Upper Catchment (AMD Seeps)	S1	4.02	272	0.038	0.049	0.027	6.8	30.0	20 <sup>(n=1)</sup>	3
	IB12a	4.06	469	0.042	0.049	0.035	9.4	-	-	3
	S2	3.90	725	0.20	0.26	0.14	6.9	25.0	10 <sup>(n=1)</sup>	3
	IB12b	3.90	739	0.30	0.39	0.22	8.2	20.0	-	3
	S3	3.62	173	0.055	0.074	0.018	9.5	22.5	-	3
	S4	3.07	1412	0.040	0.062	0.021	7.9	82.5	-	3
	S5	3.13	2019	0.017	0.021	0.015	7.1	135.0	-	3
	S6	3.03	2060	0.49	0.49	0.49	8.6	155.0	-	3
	S7	2.97	3653	0.15	0.22	0.088	7.2	318.3	-	3
	S8	2.91	3028	0.10	0.12	0.089	9.0	292.5	-	2
S9	3.2	1465	0.15	0.18	0.12	9.2	156.7	-	3	
Mid Catchment	IB11a	4.88	492	0.53	0.78	0.28	8.3	12.5	-	3
	IB11b	3.42	718	1.1	1.9	0.52	7.9	52.5	-	3
	S4a	3.19	856	0.38	0.43	0.33	8.0	85.8	-	3
	IB10a	3.43	751	1.7	2.2	1.2	9.3	49.2	-	3
	IB10b	3.59	809	2.1	2.6	1.6	8.2	51.7	-	3
	S5a	3.64	1113	0.27	0.43	0.18	7.8	65.0	-	3
	U7	6.24	-	-	-	-	-	-	35.0	1
	IB5a	3.54	661	4.6	10	1.6	9.8	31.0	-	5
	IB5b	3.18	2042	2.1	4.5	0.92	9.2	144.0	-	5
IB5c	3.42	1400	6.7	14.5	2.5	9.3	90.1	-	9	
Lower Catchment	IB8a	3.62	972	-	-	-	8.6	-	-	4
	IB8b	3.68	908	-	-	-	-	-	-	4
	U1a	5.81	207	1.3	3.0	0.030	10.6	-	32.5	2
	U1	6.38	446	-	-	-	13.5	-	48.8	4
	IB7a	3.59	871	11.3	26	1.2	9.0	65.8	-	9
	IB7b	3.96	750	12.5	30	1.5	8.9	45.8	-	9
	U2a	6.48	190	1.2	3.97	0.30	11.0	-	69.4	9
	U2	6.49	236	0.36	0.42	0.31	11.1	-	80.0	3
	U3	6.05	99	0.061	0.079	0.044	-	-	28.3	3
	R12	<b>3.95</b>	<b>755</b>	<b>12.5</b>	<b>30</b>	<b>1.5</b>	<b>7.98</b>	<b>44.7</b>	-	<b>9</b>
	U5	6.22	79	2.8	6.0	1.0	-	-	22.5	6
	U6	6.14	79	N/A	-	-	-	-	21.4	7
	U4	5.84	265	6.7	20	0.50	10.5	-	28.9	9
	IB6	4.25	508	N/A	-	-	8.7	28.6	10 <sup>(n=2)</sup>	7
	R5	4.33	462	17.5	50	0.0	7.8	21.7	10.6 <sup>(n=4)</sup>	8
R8	5.60	60	-	-	-	9.9	-	22.8	8	
R6	5.31	110	-	-	-	10.8	-	22.5	5	

Detailed metal analysis of samples collected in March (Table 2.3) display only metal analytes that were measured at all sites, as well as sulfate and calculated acidity (most metals in extended metal analysis are therefore omitted). All metal analysis completed on samples is provided in Appendix I, C. Monthly data for R5 are in Appendix I, D.

Highest metals and sulfate concentrations occurred at AMD seep site S7, and include 55.0 mg/L aluminium, 3.3 mg/L iron, 13 mg/L manganese, 3.0 mg/L zinc and 1400 mg/L sulfate (Table 2.3). Overall, lowest concentrations were measured at site IB11a (drainage from southern waste rock slope). Similarly, calculated acidity was highest at site S7 (359.5 mg CaCO<sub>3</sub>/L) and lowest at IB11a (4.0 mg CaCO<sub>3</sub>/L).

**Table 2.3: Dissolved metal analysis (mg/L) and calculated acidity (mg CaCO<sub>3</sub>/L) at water monitoring sites in Fanny Creek catchment. Samples collected on 7<sup>th</sup>, 12<sup>th</sup>, and 13<sup>th</sup> of March, 2008.**

Dissolved metals (mg/L)	Sample sites									
	S2	IB12b	IB11a	S4	S5	S6	S7	S8	R12	R5
Aluminium	1.1	1.2	0.22	8	17	19	55	38	7.8	3.5
Iron	1.9	1.6	0.93	2.1	0.66	0.97	3.3	1.7	1.7	0.15
Manganese	5.9	5	3.7	1.5	5.2	8.8	13	13	3.5	1.9
Copper	0.0037	0.0038	0.0023	0.0047	0.012	0.023	0.033	0.024	0.0084	0.0046
Nickel	0.11	0.092	0.058	0.078	0.3	0.41	0.79	0.73	0.17	0.092
Zinc	0.31	0.26	0.15	0.25	1.3	1.6	3.0	2.9	0.59	0.32
Cadmium	0.00022	0.00024	0.000089	0.00014	0.0011	0.0014	0.0035	0.0029	0.00065	0.00032
Chromium	<0.0005	<0.0005	<0.0005	0.0012	0.0015	0.0026	0.0048	0.0039	<0.0005	<0.0005
Cobalt	0.07	0.061	0.037	0.037	0.17	0.22	0.38	0.37	0.081	0.044
Lead	0.00035	0.00053	0.00012	0.00039	0.0012	0.00084	0.0053	0.0031	0.0011	0.0003
Magnesium	33	33	20	18	75	93	180	150	50	25
Arsenic	-	<0.001	-	-	<0.001	-	<0.001	-	<0.001	-
Calcium	26	22	16	15	59	88	140	140	39	25
Sulphate	234	210	135	210	590	779	1400	1348	350	183
Calc. acidity (mg CaCO <sub>3</sub> /L)	23.0	21.7	4.0	120.9	147.6	150.9	359.5	257.7	54.6	21.5

At confluence IB5 (Table 2.4), dissolved metal and sulfate concentrations are higher at site IB5b compared to IB5a, indicated by calculated acidity concentrations of 149.0 mg CaCO<sub>3</sub>/L and 37.0 mg CaCO<sub>3</sub>/L, respectively. At confluence IB7, dissolved metals in March are slightly higher at IB7a, compared to downstream at IB7b, while in May aluminium and iron concentrations almost halve between IB7a and IB7b.

**Table 2.4: Dissolved metal concentrations (mg/L) at confluences IB5 and IB7 along Fanny Creek. Detailed metal analysis collected on 7 March 2008, and for selected metals at IB7 confluence on May 31/05/2008.**

Dissolved metals (mg/L)	Confluence sample sites (March)							
	IB5a	IB5b	IB5c		IB7a	IB7b	U2a	U2
Aluminium	3.2	20	12		8.1	7.1	0.048	0.024
Iron	1.1	2.0	1.7		1.7	1.5	<0.02	<0.02
Manganese	2.2	8.5	5.4		3.7	3.7	0.011	0.00089
Copper	0.0032	0.020	0.012		0.0088	0.0082	-	<0.0005
Nickel	0.081	0.44	0.27		0.19	0.17	0.00058	<0.0005
Zinc	0.23	1.6	0.95		0.65	0.60	0.0014	0.0014
Cadmium	0.00019	0.0015	0.00082		0.00061	0.00059	<0.00005	<0.00005
Chromium	<0.0005	0.0018	0.00099		0.00053	<0.0005	<0.0005	<0.0005
Cobalt	0.04	0.21	0.13		0.094	0.084	0.00024	<0.0002
Lead	0.00053	0.0024	0.0016		0.0012	0.0012	<0.0001	0.0004
Magnesium	24	98	62		49	45	13	13
Arsenic	-	-	-		-	-	<0.001	-
Calcium	22	90	58		42	40	11	12
Sulfate	189	809	509		390	330	12	-
Calc. acidity (mg CaCO <sub>3</sub> /L)	37.0	149.0	90.8		58.5	46.8	0.32	0.20
					<b>May (31/05/2008)</b>			
				<b>Aluminium</b>	1.5	0.64	0.024	-
				<b>Iron</b>	7.5	4.5	0.023	-
				<b>Calcium</b>	55	43	12	-

#### 2.4.1 R12 monitoring site

Drainage chemistry at site R12 between February 2008 and January 2009 shows little variation, although flow rate varied considerably (Figure 2.3). Average flow rate from bucket and timer measurements was 12.5 L/s, with a maximum of 30 L/s estimated, and minimum of 1.5 L/s was measured. pH ranged between 3.58 and 4.51, with a average of 3.95. Electrical conductivity averaged 755  $\mu\text{S}/\text{cm}$  (460 - 1550  $\mu\text{S}/\text{cm}$ ) and dissolved oxygen averaged 7.98 mg/L (4.96 - 8.93 mg/L) (Table 2.2). Measured acidity (pH 7) averaged 44.7 mg CaCO<sub>3</sub>/L (40.0 - 60.0 mg CaCO<sub>3</sub>/L), and average calculated acidity was similar, with 42.7 mg CaCO<sub>3</sub>/L (32.8 - 54.6 mg CaCO<sub>3</sub>/L).

Average dissolved metal concentrations (highest to lowest) were 34 mg/L (24 - 42 mg/L) for calcium, 6.0 mg/L for aluminium (4.9 - 7.8 mg/L), 3.1 mg/L for manganese (2.0 - 4.1 mg/L) and 1.3 mg/L for iron (0.64 - 2.5 mg/L). Average zinc and nickel concentrations are an order of magnitude lower, with 0.49 mg/L for zinc (0.41 - 0.59 mg/L), and 0.14 mg/L for nickel (0.11 - 0.17 mg/L), while average concentrations are lowest for copper, 0.0071 mg/L (0.0042

- 0.0084 mg/L), and cadmium, 0.00048 mg/L (0.00034 - 0.00059). Sulfate concentrations averaged 298 mg/L (225 - 360 mg/L).

Average total metal concentrations measured 6.6 mg/L for aluminium (5.5 – 8.3 mg/L), 1.8 mg/L for iron (1.1 – 2.7 mg/L), 3.4 mg/L for manganese (2.2 – 4.5 mg/L), 0.0079 mg/L for copper (0.0044 - 0.011 mg/L), 0.16 mg/L for nickel (0.12 - 0.20 mg/L), 0.53 mg/L for zinc (0.44 - 0.65mg/L), and 0.00053 mg/L for cadmium (0.00035 - 0.00066 mg/L).

A slight downward trend for aluminium, iron and manganese concentrations is apparent. Aluminium to iron ratio averaged 4.8 (2.4 - 6.7) and was far less varied compared to AMD seeps. Total and dissolved metal concentrations are comparable, which indicates minimal suspended metal particulate in the water column. On all occasions pH at R12 exceeds ferric iron solubility (pH 3.5) therefore dissolved iron measured is ferrous iron.

Metals that require removal are included in Figure 2.4 (calcium data are found in Appendix I, D). A high iron measurements in May (~8.0 mg/L) depart from expected trends and is likely due to analytical error, therefore, iron concentration at R12 in May is taken from analysis ~200 m upstream at site IB5b (0.64 mg/L). Analysis of cadmium was ceased after September due to low concentrations relative to ANZECC guidelines (in hindsight measurement should have continued because concentrations were elevated compared to Cypress water quality criteria). A single analysis of arsenic in March measured below detection limits (<0.001 mg/L).

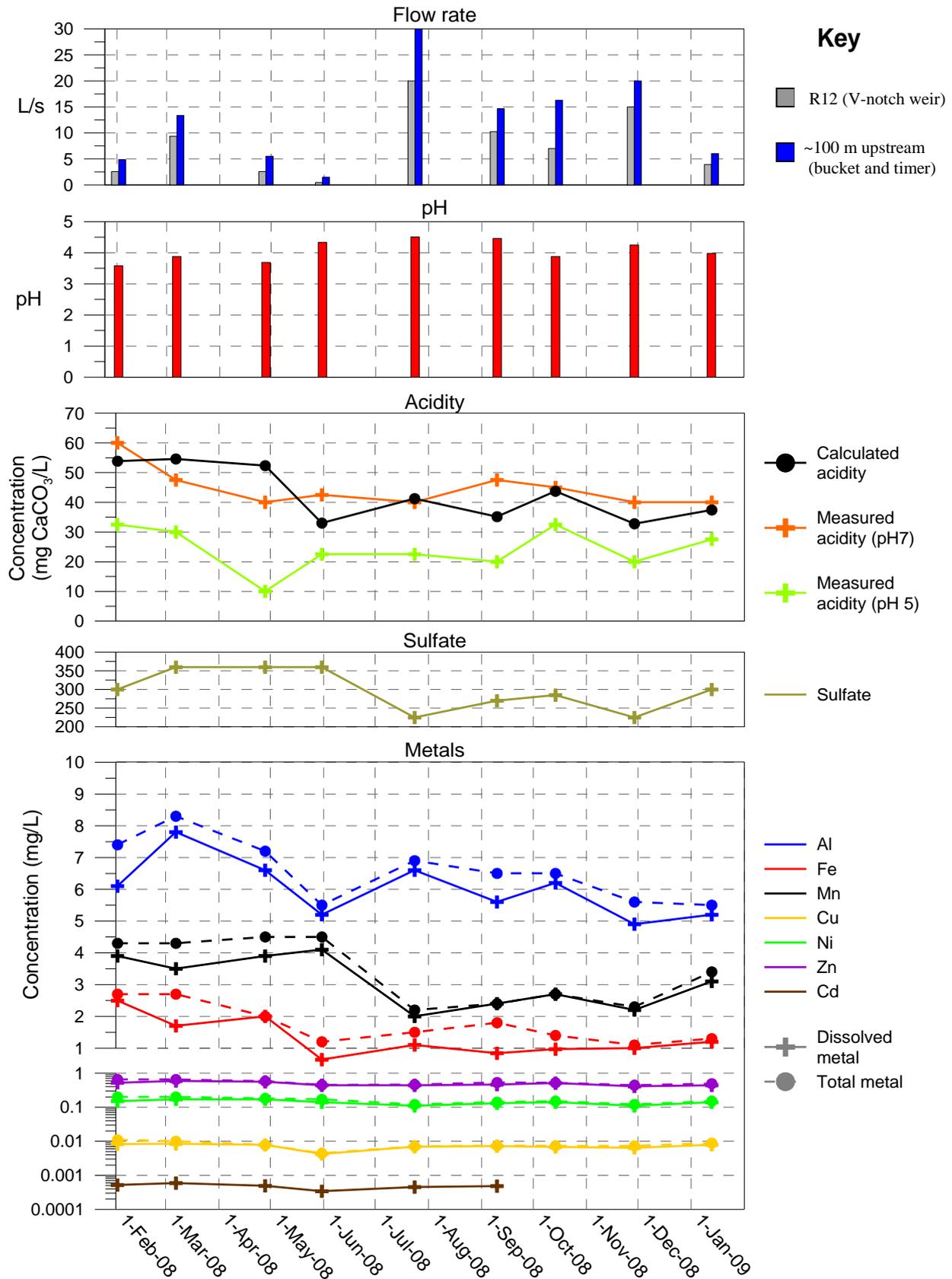


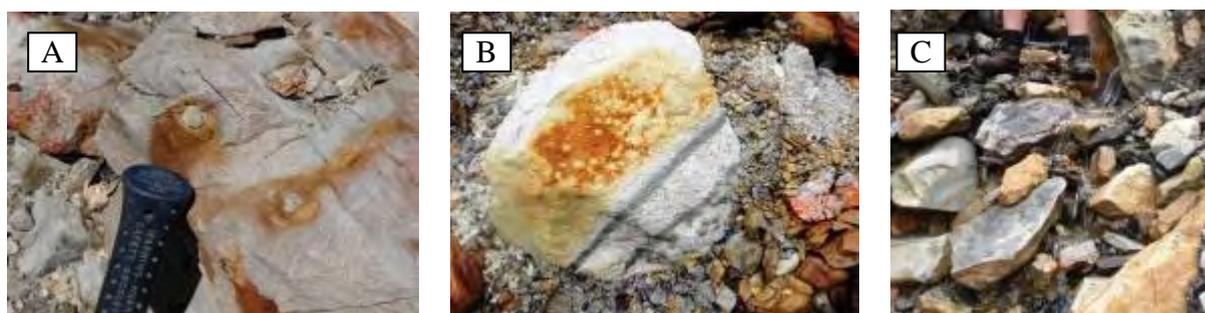
Figure 2.4: Monthly flow rate, pH, acidity, sulfate and metal concentration data at site R12 (prior to settling ponds) between 2 February 2008 and 13 January 2009.

## 2.5 Discussion of Fanny Creek Catchment Drainage Chemistry

### 2.5.1 Catchment Drainage Pattern

Most runoff from Island Block reports into Fanny Creek (Raj, 2002), likely due to the northwards dip of coal measure strata which directs drainage towards the Waitahu Valley into Fanny Creek.

Fanny Creek originates from a number of AMD impacted seeps on the steep eastern waste rock slopes of Island Block mine (Figure 1.2). Waste rock is typical of Brunner Coal Measure lithologies, and consists of course – fine sandstones, and carbonaceous siltstones and mudstones. Large (>20 mm) grey pyrite nodules and cement are common in sandstone lithologies (Figure 2.5).



**Figure 2.5: Brunner Coal Measure waste rock from Island Block mine (A, B, C) and AMD seep (C). Grey nodules and bands in left and centre images are likely pyrite ( $\text{FeS}_2$ ). Orange iron staining indicates pyrite weathering.**

AMD drainage sites in the catchment can be distinguished by their location, either on southern, mid, or northern waste rock slopes (Figure 2.2). Mid and northern slopes are adjacent to the main Island Block highwall and pit (~600 m across), while the southern slope (~150 m across) is below McLagans pit to the south-west of the main Island Block pit (Figure 2.1). Each slope drains AMD into Fanny Creek. Drainage from southern and mid waste rock slopes combines to form a southern tributary, and drainage from the northern slope forms a northern tributary. Tributaries coalesce midway down the hillside to form the main Fanny Creek channel. The larger catchment area of the southern tributary (IB5a) had on average more than twice the flow of the northern tributary (IB5b), with 4.6 L/s (1.6 - 10.0 L/s) compared to 2.1 L/s (0.92 - 4.5 L/s). Streams not affected by AMD, or un-impacted, drain

from surrounding bush covered hillsides and also contribute to Fanny Creek (particularly in lower catchment areas).

Sediment within the first settling pond on the valley floor indicates waste rock fines travel down slope during high flow conditions (Appendix I, B). Suspended sediment should be removed prior to passive AMD treatment systems, in order to avoid clogging of the system. Therefore, a future treatment system must be located on the valley floor, where the relatively flat gradient enables sediment removal in settling ponds. On the valley floor, the large fan provides an appropriate space for a large-scale passive AMD treatment system (1000 m across by 150 m wide). For this reason, characterization of AMD focuses on site R12 (prior to existing settling basins) because water parameters and chemistry at this site likely reflect AMD that a passive treatment system would receive.

After site R12, Fanny Creek enters the series of settling basins, and forms a winding channel system, with a large pond in the second basin. Wetland vegetation is well established.

## **2.5.2 Upper Catchment: Source AMD**

### **2.5.2.1 Water parameters and drainage chemistry**

The drainage chemistry of source AMD, or seeps, (S1 - S9) was monitored between February and April 2008. The chemistry of AMD seeps includes the most concentrated AMD in Fanny Creek catchment (Tables 2.2 and 2.3).

Average AMD seep flow rate is relatively low, ranging from 0.017 L/s (S5) to 0.49 L/s (S6) (Table 2.2). Flow rate was influenced by rainfall prior to sampling. Additional seeps and higher flows occurred after heavy rainfall (March), although, some seeps recorded very consistent flows (i.e. 0.49 L/s at site S6 in March and April).

Average pH of most AMD seeps was  $\leq 3.62$  (pH 2.91 – 4.06). The pH of seeps on the southern waste rock slope was higher, with average pH between 3.62 (S3) and 4.06 (IB12a). The pH of seeps on mid and northern slopes was lower, with average pH between 2.91 (S8) and 3.20 (S9). In addition, average measured acidity (pH 7) concentrations was lowest for southern most seeps ( $\leq 30$  mg CaCO<sub>3</sub>/L), and highest for northern most seeps (155 - 318.2 mg CaCO<sub>3</sub>/L).

Average dissolved oxygen concentrations ranged between 6.8 (S1) and 9.5 (S3) mg/L. This indicates mine drainage is oxygenated and dissolved iron is likely to be ferric. Detailed metal analysis of selected sites in March characterized source drainage chemistry and highlighted elevated metals in the catchment (Table 2.3). Concentrations of dissolved constituents varied, despite sample sites being only a few hundred meters of each another. Metal concentrations ranged from 1.1 – 55.0 mg/L for aluminium, 0.66 – 3.3 mg/L for iron, 1.5 – 13.0 mg/L for manganese, 0.0037 – 0.033 for copper, 0.078 – 0.79 mg/L for nickel, 0.25 – 3.0 mg/L for zinc, and 0.00014 – 0.0035 for cadmium. Sulfate concentrations ranged between 210 and 1400 mg/L.

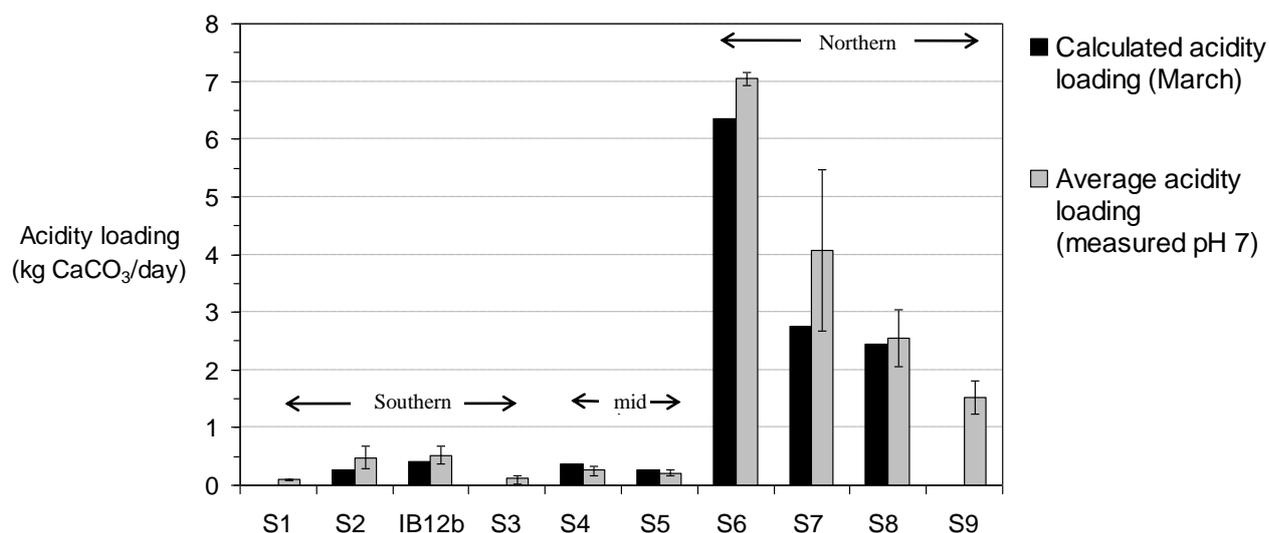
Overall, AMD from Island Block waste rock is typical of drainage from opencast coal mines in Brunner Coal Measure sediments. Drainage is enriched with aluminium and iron, and contains elevated concentrations of trace metals such as manganese, copper, nickel and zinc (Lindsay et al., 2003; de Joux, 2003; de Joux & Moore, 2005; Black et al., 2005; Trumm 2006, 2008; Pope et al., In press, a). Aluminium to iron ratio is highly variable (0.58 – 25.8), caused principally by aluminium which varied greatly. Manganese is the most elevated trace metal, followed by zinc. Correlated with pH and acidity, metals concentrations are lowest for seeps on the southern waste rock slope (higher pH), and highest for seeps on the northern slope (lowest pH).

#### **2.5.2.2 Source of AMD in Fanny Creek**

AMD in Fanny Creek is derived from pyrite in overburden disposed on the hill top, eastern waste rock slopes and to a lesser extent the highwall. Sources are likely similar to those reported for Brunner Coal Measures (de Joux, 2003; de Joux and Moore, 2005; Black et al., 2005; Weber et al., 2006; McCauley et al., 2009; Pope et al., In press, a, b). Metal solubility increases as pH decreases, and aluminium is mobilized from feldspars and micas which are abundant in coal measure sediments (Lindsay et al., 2003; Black et al., 2005). Other trace metals such as copper, nickel and zinc easily dissolve under acidified conditions (Black and Craw, 2001; Brown et al., 2002) and could be sourced from either pyrite (Weber et al., 2006), other metal sulfides (chalcopyrite, sphalerite) or from surrounding sediment matrix (Black & Craw, 2001). Elevated arsenic concentrations do not occur in Fanny Creek as reported elsewhere (Black & Craw, 2001) which indicates pyrite is not enriched with arsenic, or it cannot mobilize in the low pH conditions. The occurrence of manganese could be related to

diagenetic ankerite nodules which have been found in the coal field (Newman, 1988) or possibly sourced from carbonates in Greenland Group basement that could contain manganese.

### 2.5.2.3 Acidity and Metal Loadings



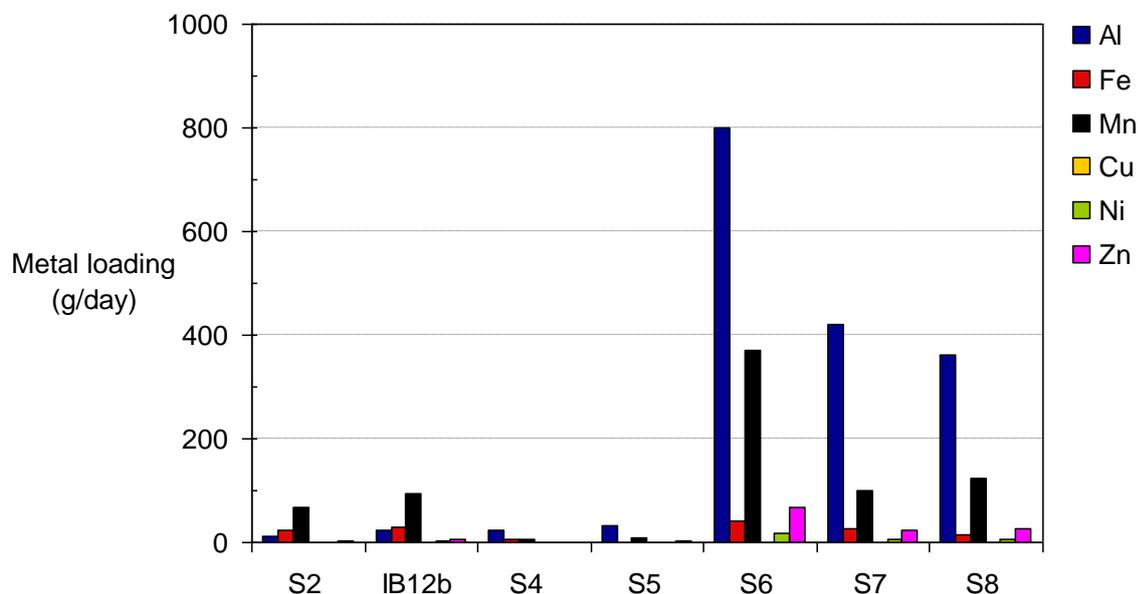
**Figure 2.6: Acidity loadings at or near AMD seeps in Fanny Creek catchment (kg CaCO<sub>3</sub> per day). Bars indicate maximum and minimum loadings.**

Calculated acidity (kg CaCO<sub>3</sub>/day) and metal loadings (g/day, and moles of metal/day) of AMD seeps are calculated from data collected on 12<sup>th</sup> and 13<sup>th</sup> March, 2008 (Figures 2.6 and 2.7). Comparison between sites is possible because no rain fell overnight. Average acidity loadings are also calculated from measured acidity of samples collected during February, March and April, 2008.

Overall, calculated acidity loadings from the single detailed metal analysis in March are similar to measured acidity loadings (pH 7) averaged from the initial months seeps were sampled (with the possible exception of site S7) (Figure 2.6). This indicates metal concentrations of source drainage measured in March (and other parameters such as flow rate and pH) are largely representative of longer term AMD characteristics at those sites.

Acidity loadings differ considerably between seep sites. Calculated acidity loadings range from 0.27 kg CaCO<sub>3</sub>/day (S2, S5) to 6.36 kg CaCO<sub>3</sub>/day (S6), and average measured acidity loading ranges between 0.095 kg CaCO<sub>3</sub>/day (S1) and 7.04 kg CaCO<sub>3</sub>/day (S6). On average,

seeps located on the northern waste rock slope have highest acidity loading (1.53 - 7.04 kg  $\text{CaCO}_3/\text{day}$ ) in the Fanny Creek catchment, compared to seeps on mid and southern slopes ( $\leq 0.51$  kg  $\text{CaCO}_3/\text{day}$ ).



**Figure 2.7: Metal loadings at or near AMD seeps in Fanny Creek catchment (grams of metal per day). Samples collected on 12th and 13th March, 2008.**

Loadings of important metals also differ significantly between seeps (Figure 2.7). Loadings range from 12.8 - 800.8 g/day for aluminium, 1.2 - 40.9 g/day for iron, 4.6 - 370.9 g/day for manganese, 0.014 - 0.97 g/day for copper, 0.24 - 17.3 g/day for nickel, and 0.77 - 67.4 g/day for zinc. AMD seep S6 is responsible for all maximum loadings, while seep S4 is responsible for most minimum loadings.

Metal loadings are correlated to acidity loadings. Seeps on the northern slope release more dissolved metal than other seeps. This is noticeable for aluminium, with loadings greater than 360.6 g/day (S8), while on mid and southern slopes loading is no greater than 31.0 g/day (S5). Higher loadings on the northern waste rock slope are due to higher metal concentrations in northern seeps compared to others (Table 2.3), as well as larger flow volumes from these areas (0.088 – 0.49 L/s in March). Loadings are dependant on concentration and flow rate, so, loadings from seep S6 are greatest, although metal concentrations are highest for seep S7 (flow rate at S6 ~5 times greater than S7 in March). Similarly, despite more concentrated AMD on mid waste rock slopes (S4, S5), loadings from southern seeps (S2, IB12b) are

greater due to higher (0.22 L/s at IB12b compared to 0.021 L/s at S5). However, despite the trend, iron and manganese loadings of southern seep drainage is comparable to loadings of northern seeps, which are greatly more acidic. This is partly because iron concentration does not vary between sites to the same degree as other metals (i.e. aluminium), and drainage from southern seeps contains relatively elevated manganese concentrations (up to 5.9 mg/L).

Similarly molar loadings show AMD seep S6 discharges most metal (38.7 moles metal/day), more than twice that of the next highest (S7), while seeps S4 and S5 discharge least metals ( $\leq 1.4$  moles metal/day) (Table 2.5). Correlated with acidity and metal loadings (g/day), seeps on the northern slope (S6, S7, S8) have much higher molar metal loading compared to seeps on mid and southern waste rock slopes.

**Table 2.5: Molar metal loading at or near AMD seeps within Fanny Creek catchment. The contribution (%) of each metal to molar loading is shown in the lower table. Samples collected on 12th and 13th March, 2008.**

Slope	Molar metal loading (moles of metal/day)						
	Southern		Mid		Northern		
AMD seep	S2	IB12b	S4	S5	S6	S7	S8
Moles of metal /day	2.2	3.2	1.1	1.4	38.7	18.4	16.5
Contribution to loading (%)							
Aluminium	21.5	26.0	80.7	82.4	76.8	84.9	81.0
Iron	17.9	16.8	10.2	1.5	1.9	2.5	1.8
Manganese	56.5	53.3	7.4	12.4	17.5	9.9	13.6
Copper	0.031	0.035	0.020	0.025	0.039	0.022	0.022
Nickel	1.0	0.9	0.4	0.7	0.8	0.6	0.7
Zinc	2.5	2.3	1.0	2.6	2.7	1.9	2.6

On average, aluminium makes up almost two thirds (64.8%) of metals drained in the seeps, followed by manganese (24.4%), iron (7.5%), zinc (2.2%), while nickel and copper contribute <1% to metal load. However, there is a distinct difference in drainage composition between seeps on the southern slope and those on mid and northern slopes. On average, for seeps on the southern slope, manganese contributes the majority of metal loading (54.9%), followed by aluminium (23.7%) and iron (17.3%). Conversely, at other seeps, aluminium contributes to the majority of metal loading (81.2%), with lower contributions of manganese (12.1%) and iron (3.6%).

#### **2.5.2.4 Summary of Source AMD in Fanny Creek Catchment**

- Fanny Creek is sourced from a number of AMD impacted seeps that drain from the eastern waste rock slopes of Island Block mine.
- Most AMD seeps have low pH (average  $\leq 3.62$ ), and variable chemistry typical of opencast coal mines hosted in Brunner Coal Measures. AMD is enriched with aluminium and iron, and contains elevated concentrations of trace metals, especially manganese, but also copper, nickel, zinc and cadmium.
- AMD seeps on mid and northern waste rock slopes have lower pH, and higher acidity and metal concentrations compared to seeps on the southern waste rock slope.
- Acidity and metal loadings are greatest for seeps on the northern most slope.
- Acidity and metal loadings are higher for seeps on the southern waste rock slope, compared to more concentrated seeps on mid waste rock slopes, due to relatively higher flow volumes.
- The composition of source drainage chemistry differs between waste rock slopes. Source drainage from mid and northern slopes contains primarily aluminium, whereas, manganese is the dominant metal in seep drainage on the southern waste rock slope.

#### **2.5.2.5 Variation in AMD source chemistry**

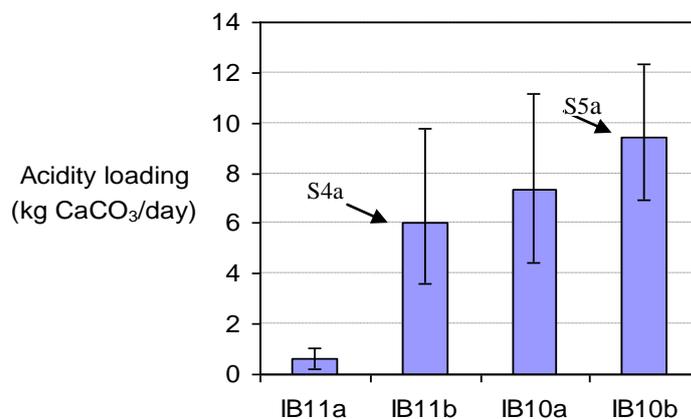
The difference in source drainage chemistry from waste rock slopes is likely due to the age and source of waste rock materials. Although no waste rock has been placed on mid and northern slopes since 1985 (Fanny Creek sidecast), the hillside immediately above (Island Block pit area) was the site of most recent overburden disposal (1985 - 2002). Most recent waste rock disposal in McLagans pit and sidecast (southern slope) was in 1996. Therefore, water infiltrating and percolating through relatively younger, more reactive waste rock on the hillside above the mid and northern slopes could be the reason why AMD seeps are on these slopes are more acidic and metal rich.

In addition, drainage could be influenced by source and associated mineralogy of waste rock material. Waste rock on the southern slope and adjacent area above comes from McLagans pit, rather than from Island Block, and there could be compositional variations in waste rock between these pits (e.g. greater pyrite in waste rock from Island Block pit). It is also possible

that greater dissolution of carbonate minerals either from underlying Greenland Group basement or within coal measure sediments, such as rhodochrosite ( $\text{MnCO}_3$ ) or ankerite ( $\text{Fe/Mg/MnCO}_3$ ) (Newman, 1988), occurs on the southern slope compared to mid and northern slopes. This is supported by elevated pH at certain sites on the southern slope (S1, IB12a). A localized abundance of ankerite could also explain the higher concentration of manganese in source drainage from the southern waste rock slope.

### 2.5.3 Southern Fanny Creek Tributary

The southern tributary of Fanny Creek comprises drainage from southern and mid waste rock slopes. The contribution of the southern slope to AMD in the southern tributary is characterized by site IB11a, immediately upstream of where drainage from the mid waste rock slope initially enters the tributary. Average pH at IB11a is relatively high with pH 4.88, and metal concentrations are low (0.22 mg/L aluminium, 0.93 mg/L iron, 3.7 mg/L manganese) which results in minimal acidity loading at this site (0.6 kg  $\text{CaCO}_3$ /day) (Figure 2.8). Acidity that drains from the southern slope is probably buffered to some extent by carbonate mineral dissolution because prior to site IB11a Fanny Creek incises into Greenland Group basement rock. After drainage from the mid waste rock slope enters the southern tributary (sites S4a and S5a) the average pH (site IB10b) drops to 3.59 downstream of these tributaries (Table 2.2), and acidity loading is increased more than ten fold (9.4 kg  $\text{CaCO}_3$ /day). Therefore, acidity and metal in Fanny Creek's southern tributary is principally sourced from AMD seeps on the mid waste rock slope.

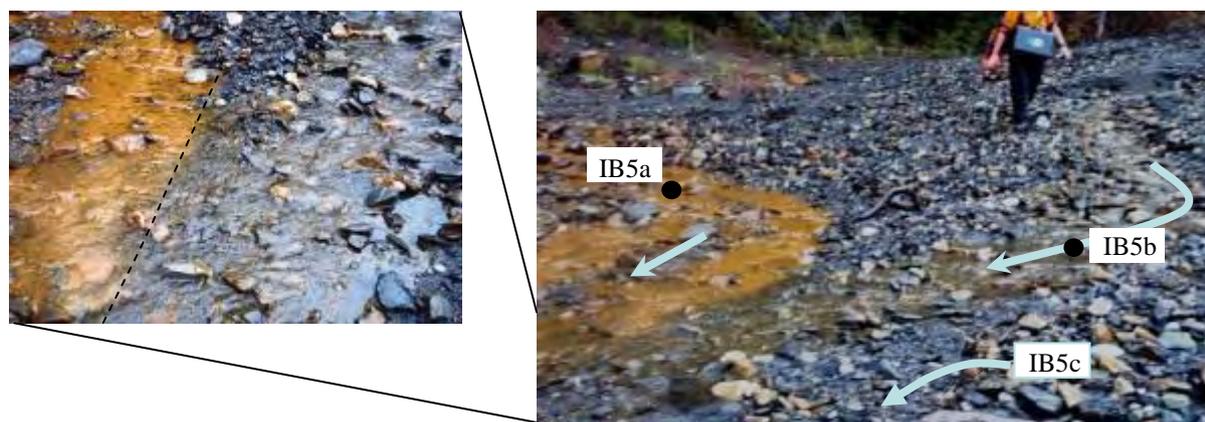


**Figure 2.8: Average measured (pH 7) acidity loading along the southern Fanny Creek tributary. Bars indicate maximum and minimums. Arrows indicate where AMD enters from mid waste rock slopes.**

### 2.5.4 Mid Catchment: Southern and Northern Tributary Confluence

IB5 confluence is located midway down the catchment (Figure 2.2) where southern (IB5a) and northern (IB5b) Fanny Creek tributaries combine. Monitoring site IB5c is 30 m downstream of the confluence. Sampling occurred from February to July, 2008, and dissolved metal analysis was completed on samples collected on 7<sup>th</sup> March (Table 2.4).

Drainage from the northern tributary (IB5b) has higher acidity and metal concentrations, and lower pH, than the southern (IB5a) tributary (Table 2.2 and 2.4). The average pH of the northern tributary was 3.18 (3.08 – 3.36) compared an average pH of 3.54 (3.44 – 3.68) for the southern tributary. Average measured acidity for the northern tributary was almost five times more than the southern tributary, with 144 mg CaCO<sub>3</sub>/L compared to 31 mg CaCO<sub>3</sub>/L. Metal analysis in March showed the northern tributary was more metal rich, containing 20 mg/L aluminium, 2.0 mg/L iron, and 8.5 mg/L manganese, whereas the southern tributary contained 3.2 mg/L aluminium, 1.1 mg/L iron and 2.2 mg/L manganese. The difference in water chemistry affects the appearance of either tributary. The streambed of the southern tributary is orange/brown with iron oxyhydroxide precipitates because the solubility of ferric iron is exceeded, while the northern tributary is relatively free of metal precipitate because pH is <3.5 and ferric iron is soluble (Figure 2.9).

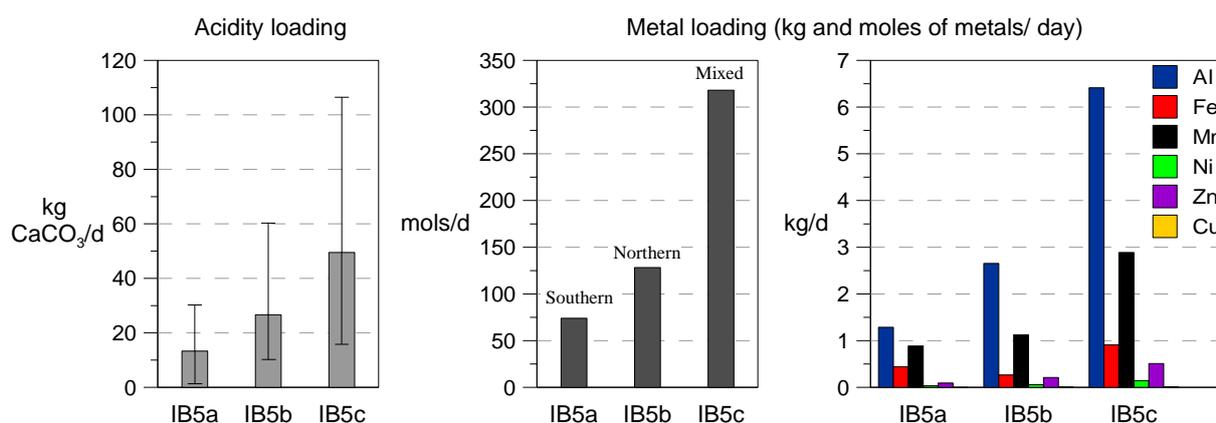


**Figure 2.9: Photo of IB5 confluence with Fanny Creek southern (IB5a) and northern (IB5b) tributaries. The photo illustrates orange iron hydroxide precipitate on the stream bed of the southern tributary, and the mixing interface of streams.**

Downstream of the southern and northern Fanny Creek tributary confluence (site IB5c), acidity and metal concentrations increase and pH decreases, compared to drainage from the

southern tributary. The pH at site IB5c averaged 3.42 (3.2 – 3.49), acidity measured on average 90.1 mg CaCO<sub>3</sub>/L, and metal analysis in March showed drainage contained 12 mg/L aluminium, 1.7 mg/L iron and 5.4 mg/L manganese.

Average measured (pH 7) acidity loadings (kg CaCO<sub>3</sub>/day) for IB5 confluence are calculated between February and July, along with metal loadings in March (moles of metal/day and kg/day for individual metals) (Figure 2.10).



**Figure 2.10: IB5 confluence acidity and metal loadings. Average acidity loadings are calculated from measured acidity (pH 7) of samples collected between February and July, 2008, bars indicate minimum and maximums. Metal loadings are calculated from samples collected on 7<sup>th</sup> March 2008.**

The northern tributary contributes more acidity and metal to Fanny Creek than the southern tributary, despite having on average less than half as much flow. Average acidity loading of the northern tributary (IB5b) was more than double that of the southern, with 27.5 kg CaCO<sub>3</sub>/day compared to 12.6 kg CaCO<sub>3</sub>/day. Similarly, the northern tributary drains nearly twice as much metal than the southern, with 128.3 compared to 73.9 moles metals/day. Individual metal loadings reflect this, with northern tributary loadings greater for all metals (except iron) which includes 2.7 kg/day aluminium, 1.13 kg/day manganese, 0.27 kg/day iron and 0.21 kg/day zinc. Downstream of the confluence, measured acidity loadings averages 48.3 kg CaCO<sub>3</sub>/day, molar metal loading was 318.0 moles of metal/day and individual metal loadings include 6.4 kg/day aluminium, 2.89 kg/day manganese, 0.91 kg/day iron and 0.51 kg/day zinc.

This confluence is important because the contribution of each tributary to Fanny Creek AMD, and thus waste rock slopes above, can be characterized (Table 2.6). Acidity and metal contributions (percentage basis) are calculated from loadings of each tributary relative to the combined loading initially drained into the confluence by both tributaries (i.e. IB5a / (IB5a + IB5b)). On average, the northern tributary (IB5b) contributes 70.8% of acidity, and 63.4% of all dissolved metal ions drained into the confluence. On the occasion in March, the northern tributary contributes 67.3% of all aluminium, 56.0% of all manganese and more than 64% of all copper, nickel and zinc. However, the southern tributary (IB5a) contributes more dissolved iron (62.5%) than the northern tributary (Table 2.6).

**Table 2.6: Average acidity loading (Feb - July) and metal loading (March) contributions of southern (IB5a) and northern (IB5b) Fanny Creek tributaries calculated from samples collected at confluence IB5. Increases in acidity and metal loadings downstream at IB5c are also given.**

	Contribution to loading (%)		Downstream loading increase (%)
	IB5a	IB5b	IB5c
<b>Average measured acidity (pH 7) kg CaCO<sub>3</sub>/day</b>	29.2	70.8	24.0
<b>Molar metal loading (moles of metals per day)</b>	36.6	63.4	57.3
<b>Metal loading (kg /day)</b>	<b>IB5a</b>	<b>IB5b</b>	<b>IB5a</b>
<b>Aluminium</b>	32.7	67.3	62.9
<b>Iron</b>	62.5	37.5	28.5
<b>Manganese</b>	44.0	56.0	43.5
<b>Copper</b>	32.7	67.3	62.9
<b>Nickel</b>	35.8	64.2	58.8
<b>Zinc</b>	30.3	69.7	66.7

Downstream at site IB5c, acidity and metal loadings are greater than combined loadings at IB5a and IB5b (Table 2.6). On average, acidity loading increases by 24.0%, and metal loadings increased by 57.3 % (moles metals/day), with an average increase of 53.9% for each metal (kg/day) compared to the sum of the loading in tributaries. The most feasible explanation for this increase is that when acidic, low pH drainage in the northern tributary mixes with the southern tributary, iron precipitate either in suspension or from the streambed in southern tributary dissolves in the lower pH conditions created. Dissolution of iron also releases other metals that had adsorbed to iron particulate, explaining the increase for other

metals. This can almost be observed by a thinning of iron precipitate at the mixing interface (Figure 2.9).

Therefore, drainage from the northern Island Block waste rock slope (northern Fanny Creek tributary) contributes the majority of Fanny Creek AMD, because it drains more acidity (~70%) and metal (~60%) than the southern tributary, and also dissolves additional metal upon mixing. Overall, AMD in Fanny Creek derives from mid and northern waste rock slopes, because the contribution of AMD from the southern waste rock slope is relatively minor.

## **2.5.5 Lower Catchment**

### **2.5.5.1 IB7 confluence**

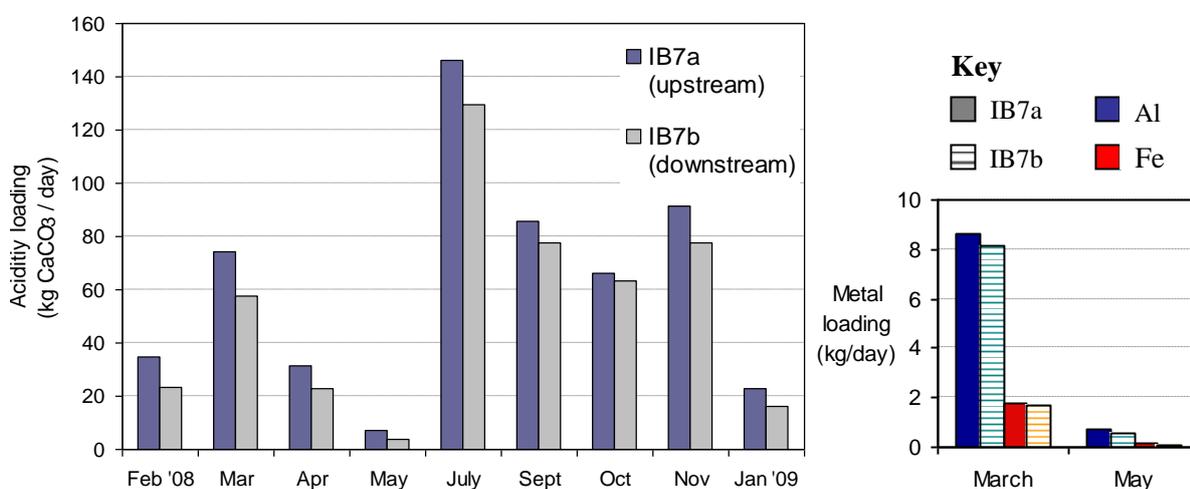
Confluence IB7 is situated along Fanny Creek, about 200 m upstream of site R12 and the settling ponds (Figure 2.1). At this site, un-impacted alkaline drainage from the adjacent hillside enters Fanny Creek. Monthly samples were collected at upstream (IB7a) and downstream (IB7b) sites along Fanny Creek, and of alkaline drainage before entering Fanny Creek (U2a). Alkaline drainage (U2a) had average pH of 6.48 (5.85 – 7.8 pH) and average alkalinity concentrations of 69.4 mg CaCO<sub>3</sub>/L (50 – 82.5 mg CaCO<sub>3</sub>/L) (Table 2.2). Concentrations of dissolved metals are very low (0.048 mg/L aluminium, <0.02 mg/L iron, and <0.001 mg/L arsenic). Flow rate at U2a averaged 1.19 L/s (0.30 – 3.97 L/s).

Christie & Brathwaite (2003) found carbonates such as dolomite, ankerite, and ferroan magnesite in Greenland Group meta-sediments near Reefton. Therefore, alkalinity in un-impacted drainage is probably derived from weathering of these minerals as drainage flows over Greenland Group basement that comprise the majority of the hillside below Island Block mine (Suggate, 1957) (Figure 1.3). Inspection of bedrock near the source of the alkaline tributary (site U2) verified that Greenland Group sediments were present.

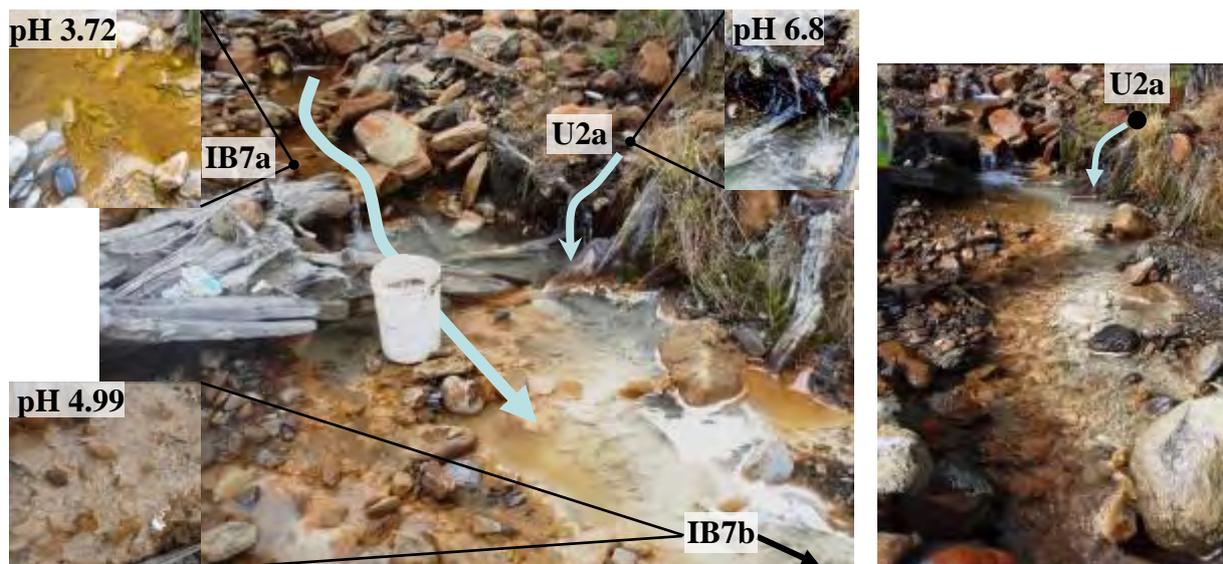
This confluence is significant because it demonstrates mixing of drainage chemistry from different lithologies in Fanny Creek catchment. In addition to dilution, mixing of alkaline drainage results in partial neutralization of AMD, as indicated by a decrease in acidity and dissolved metal loading between upstream (IB7a) and downstream (IB7b) sites (Figure 2.11). On average, downstream measured acidity loadings (IB7b) decrease by 22.2%, and ranges

between 46.3% (May) and 4.6% (October). Reduction in aluminium loading ranged from 5.1% (March) to 24.8% (May), and iron decreased by between 4.5% (March) and 46.5% (May). The pH of Fanny Creek increased immediately downstream, with average pH of 3.96 at site IB7b compared to 3.59 upstream at site IB7a.

The drop in acidity loading downstream is caused by neutralization of proton acidity ( $H^+$ ) in Fanny Creek by reaction with bicarbonate alkalinity. As a result, pH increases, which causes aluminium and iron removal by hydrolysis and precipitation of hydroxides and oxyhydroxides. Iron removal (mainly ferrous as  $pH > 3.5$  for most months) is likely caused by adsorption to aluminium hydroxide, which catalyzes ferrous iron oxidation and subsequent precipitation (Younger et al., 2002). Aluminium hydroxide is observed by an accumulation of a white precipitate in the streambed downstream of the confluence. However, removal of iron is not as obvious because ferric iron precipitate is already present in the streambed (Figure 2.12). However, on most occasions, insufficient alkalinity was contributed by site U2a to counteract acidity generated by iron and aluminium hydrolysis. This resulted in a drop in pH downstream at R12, displayed further on in Figure 2.17.



**Figure 2.11: Upstream (IB7a) and downstream (IB7b) measured acidity (pH 7) and metal loadings of Fanny Creek at IB7 confluence monitoring site. Acidity loadings (kg CaCO<sub>3</sub>/day) are calculated from data collected between February 2008 and January 2009. Metal loadings for aluminium and iron (kg/day) are calculated from samples collected in March and May, 2008.**



**Figure 2.12: Fanny Creek upstream (IB5a) and downstream (IB5b) of un-impacted alkaline drainage (U2a). Left image displays Fanny Creek sampled on 31 May, 2008, with insets of iron (upper) and aluminium (lower) precipitation on the stream bed. Right image shows Fanny Creek on 7 March, 2008, illustrating downstream mixing zone and white aluminium precipitate.**

### 2.5.5.2 Other Un-impacted Alkaline Drainage

In addition to drainage from site U2, other un-impacted alkaline streams drain from adjacent hillsides, sites U1 - U5 (Appendix I, B). These drain from Greenland Group basement rock, and neutralize Fanny Creek AMD. The drainage chemistry of these streams is similar to U2a, with average pH between 5.84 (U4) and 6.49 (U2), and average alkalinity concentrations between 22.5 (U5) and 48.8 (U1) mg CaCO<sub>3</sub>/L (Table 2.2). Flow rates vary, with largest and most persistent flow at U4 and U5, with 6.7 L/s (0.5 - 20L/s) and 2.8 L/s (1 - 6 L/s), respectively (Figure 2.13 and Table 2.2). Sites U3 and U1a have lower, more intermittent flow that averages 0.061 L/s and 1.3 L/s, respectively. The extent of alkalinity loading in alkaline streams is controlled primarily by flow volume; thus, drainage from site U4 inputs most alkalinity of all alkaline streams (0.864 - 60.5 kg CaCO<sub>3</sub>/day) (Appendix I, D). Input of alkalinity into Fanny Creek from site U5 is limited, because drainage ponds behind the first settling basin (site U6 in Appendix I, B) and does not usually mix with AMD. During high flow conditions however, the alkaline drainage in the pond overflows the embankment and enters Fanny Creek.

Un-impacted alkaline drainages are an important mechanism that attenuates acidity in Fanny Creek. Any future passive treatment designs should incorporate alkaline drainages to optimize natural conditions.



**Figure 2.13: Un-impacted alkaline drainage from site U4 mixing with Fanny Creek AMD in the second settling basin. White aluminium precipitates indicates mixing zone with increased pH.**

### 2.5.5.3 R12

Monitoring site R12 is situated along Fanny Creek immediately before the settling basins on the Waitahu Valley floor (Figure 1.2 and 2.3). The R12 site is the preferred locality in the catchment for AMD treatment because the surrounding large, flat area provides a suitable space for a full scale passive AMD treatment system (section 2.5.1). Monthly monitoring at this site allowed detailed characterization of AMD, and this is valuable for selection and design of effective passive treatment.

#### 2.5.5.3.1 Flow rate

Flow rate at R12 is given from bucket and timer measurements ~100 m upstream (Appendix I, B), because the V-notch weir at R12 gave lower values due to sub-surface flow of AMD in sediment. Flow rate varied considerably, as a consequence of seasonal variation and weather on the West Coast. An average of 12.5 L/s was recorded, with higher flows in winter and spring (14.7 – ~30 L/s) and lower flow in summer months (1.5 – 5.5 L/s), although 13.3 L/s was measured in March (recent rainfall). Flow data is considered approximate, especially above ~15 L/s, as these flows are estimated. In addition, subsurface runoff is not quantified and therefore flow measurements represent minimum AMD flow values.

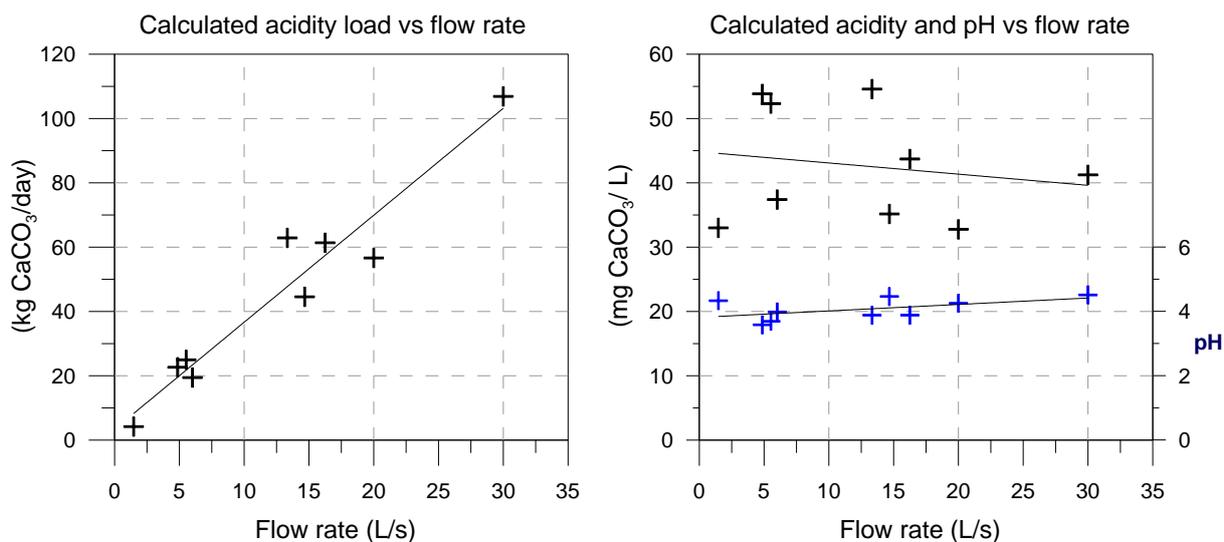
### 2.5.5.3.2 Drainage Chemistry

Concentrations of dissolved metals at R12 are lower than at most AMD sources (seeps). Average dissolved concentrations of elevated metals measured 6.0 mg/L for aluminium, 1.3 mg/L for iron, 3.1 mg/L for manganese, 0.49 mg/L for zinc, 0.14 mg/L for nickel, 0.0071 mg/L for copper and 0.00048 mg/L for cadmium. This is due to natural attenuation processes along Fanny Creek, such as dilution with surface and ground waters, neutralization with alkaline run-off, oxidation and precipitation (particularly iron and aluminium), and sorption reactions that remove metals from solution (Black et al., 2005; Webster-Brown, 2005).

Average dissolved oxygen concentrations at R12 (7.98 mg/L) indicate AMD is oxygenated, caused by the steep channel gradient which aerates drainage and oxidizes ferrous iron (shown by the abundance of ferric iron precipitate on Fanny Creek streambed) (Table 2.2). Although, some ferrous iron is still present as shown by that measured in samples (iron must be ferrous as pH is  $>3.58$  at R12 on all occasions).

Drainage chemistry at R12 is relatively consistent during the sample period (Figure 2.4). Measured acidity concentrations only vary between 40.0 and 60.0 mg CaCO<sub>3</sub>/L. Only minor variation occurs for concentrations of elevated metals, aluminium, iron and manganese. Iron differs by an order of magnitude (2.5 mg/L - 0.64 mg/L) and manganese differed by about half (4.1 - 2.0 mg/L). Concentrations of trace metals copper, nickel and zinc were very steady.

The minor extent of drainage chemistry variation occurs despite a considerable difference in flow rate in Fanny Creek during sample occasions (1.5 L/s - ~ 30 L/s). Metal and acidity concentrations are expected to decrease as drainage is diluted by rainwater runoff. Overall this is not the case, reflected by July which records highest flow (~30 L/s) yet concentrations of calculated acidity (41.2 mg CaCO<sub>3</sub>/L) and metal (6.6 mg/L aluminium, 1.1 mg/L iron) that are close to average. Therefore, drainage chemistry at site R12 is largely independent of flow rate, and not affected greatly by rainfall dilution. Consequently, acidity loading increases in a linear fashion as flow rate increases at R12 (Figure 2.14).



**Figure 2.14: Calculated acidity loading (kg CaCO<sub>3</sub>/day), and calculated acidity concentration (mg CaCO<sub>3</sub>/L) and pH at site R12 vs Fanny Creek flow rate (L/s).**

This suggests drainage chemistry in Fanny Creek is primarily geochemically controlled, with release of acidity and metal in equilibrium with the amount of flow in the catchment. In other words, the rate at which acidity and metals are generated from Island Block mine and waste rock is proportionate to drainage (almost 1:1), with more dissolved constituents with greater flow in Fanny Creek. It is likely the additional AMD is derived from weathering products of pyrite such as hydroxides, hydroxyl-sulfates and sulfates that are stored within waste rock, instead of pyrite oxidation directly (given rate limitations). Dissolution of secondary acidic minerals is rapid, and the associated flushed acidity offsets the effects of rainfall. However, given a long enough rainfall duration, acidity loading would likely decline as secondary minerals are used up, and as the extent of dilution would overcome dissolution of acidic salts.

Such flushing is supported by results at R12 in March, which records maximums in calculated acidity (54.6 mg CaCO<sub>3</sub>/L) and aluminium (7.8 mg/L) concentrations, even though flow was moderately high (13.3 L/s). Heavy rainfall occurred a week before sampling in March, which would have released acidity and metals from secondary acidic minerals stored within waste rock, or possibly stream bed sediments as water levels rose. Data also support the short term nature of this process as flushing is overcome by dilution, indicated by the downward trend in acidity concentration with flow rate at R12 (Figure 2.14). This trend shows flushing does not dramatically increase concentrations of dissolved AMD constituents in Fanny Creek, although this could be due to lack of sampling immediately after a rainfall event (initial flush).

Accordingly, data suggest dilution does have a slight affect on drainage chemistry, with minor variations that relate to rainfall run-off.

Although a very weak trend, acidity concentrations at site R12 are higher during low flow conditions and slightly lower in high flow conditions (Figure 2.14). This is by demonstrated by low pH in February (pH 3.58) and April (pH 3.69) at low flow (~5 L/s), while during winter and spring pH is marginally higher (pH 3.88 – 4.51) (Figure 2.3). In addition, maximum pH occurs at the highest flow recorded (~30L/s). Less acidic AMD during higher flows is most likely from increased dilution by rainfall runoff and input from alkaline streams. Similarly, the slight downward trend for aluminium, iron and manganese concentrations is probably related to seasonal dilution, with concentrations increasing again during drier months (suggested by January data).

On the other hand, very low flow conditions accentuate geochemical reactions in Fanny Creek, which has a slight affect on drainage chemistry at site R12. Sampling at the end of May illustrates this, when flow at R12 measured 1.5 L/s. At these conditions, calculated acidity (33.0 mg CaCO<sub>3</sub>/L) and metal concentrations (aluminium 5.2 mg/L) at R12 are lowered, and pH is elevated to 4.33 (Figure 2.4). This is caused by an enhanced affect of alkaline drainage upstream (U2a). Because flow is less varied at U2a compared to Fanny Creek, a greater proportion of alkalinity is entered at U2a compared to acidity in Fanny Creek, enabling greater acidity neutralization, and thus more metals removal. Variations of the extent of neutralization and metal precipitation at different flows are in Appendix I (B).

### **Summary of drainage chemistry at R12 with flow rate:**

Drainage chemistry of Fanny Creek at R12 is primarily geochemically controlled and not significantly affected by rainfall dilution. This is shown by minimal variation in acidity and metal concentrations at the range of flow rates recorded (1.5 – 30 L/s) .

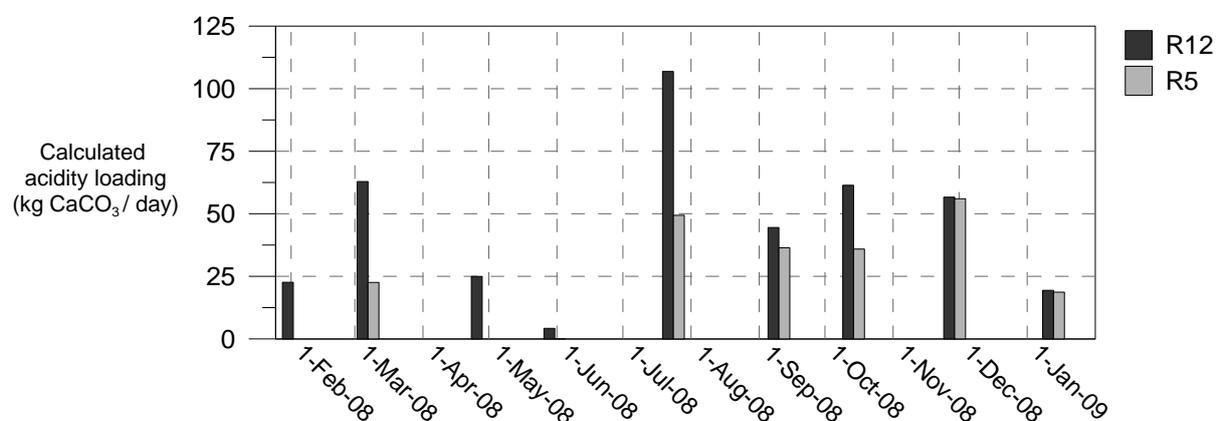
- Acidity loading at R12 increases linearly with flow rate. The rate at which acidity and metals are generated from Island Block mine and waste rock is proportionate to drainage, with more solutes with increased flow in Fanny Creek.
- Acidity and metals in Fanny Creek are likely sourced from secondary minerals of pyrite oxidation stored within waste rock, which undergo rapid dissolution during increased flow conditions.

Minor variations in drainage chemistry at R12 occur at different flow conditions, related to the affects of rainfall dilution, and geochemical processes.

- Very low flow (~2 L/s): drainage at R12 is less acidic with higher pH, due to an enhanced geochemical neutralization affect by upstream mixing of un-impacted alkaline drainage
- Low flow (~5 L/s): drainage is slightly more acidic, with lowest pH recorded (Feb, April).
- Low - Moderate flow (5 – 15 L/s): drainage becomes less acidic, and has higher pH due to dilution from surface runoff (and alkaline drainage). However, within this range flushing of dissolved metals could result in more acidic drainage.
- High flow (> ~20 L/s): Fanny Creek is least acidic, with highest pH due to dilution with surface runoff and input of un-impacted alkaline drainage.

### 2.5.5.3.3 Acidity and Metal Loading

Acidity and metal loadings at site R12 (Figures 2.15 and 2.16) illustrate the extent of acidity and metal removal required by a passive treatment to remediate AMD (loadings at site R5 are included because these are discussed further on).

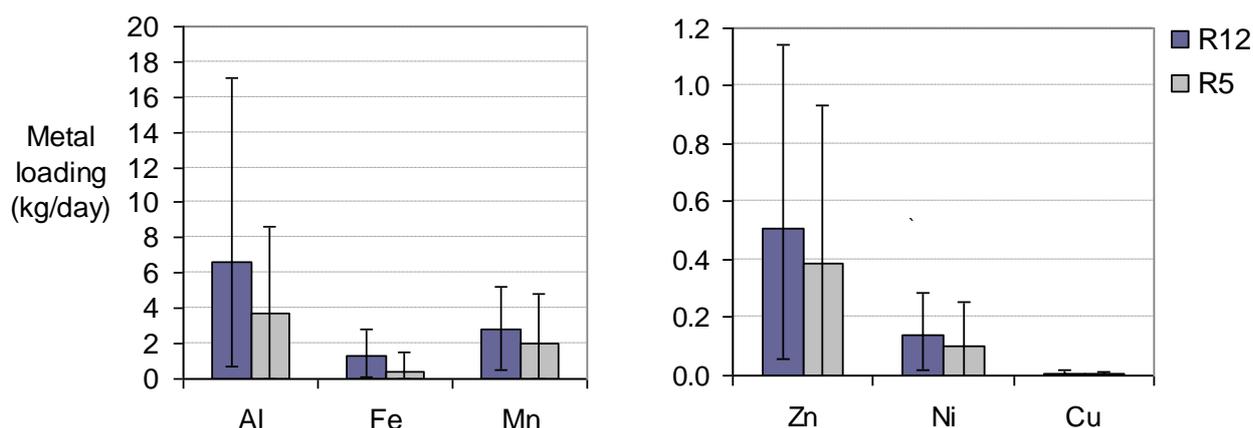


**Figure 2.15: Calculated acidity loading (kg CaCO<sub>3</sub>/day) at sampling sites R12 and R5 computed from monthly monitoring data (Feb 2008 – Jan 2009). Acidity loading is given in terms of kg as CaCO<sub>3</sub> per day.**

Calculated acidity loading at sampling site R12 averaged 44.8 kg CaCO<sub>3</sub>/day (Figure 2.15), and ranged between 4.2 and 106.9 kg CaCO<sub>3</sub>/day. Loading is controlled primarily by flow rate, with greatest loading during July (maximum recorded flow) and minimum loading during May (lowest flow). Acidity associated with aluminium hydrolysis contributed to the majority of acidity loading on all occasions. On average, aluminium contributes 79.7 % (63.1

– 89.1 %), iron 8.1 % (5.2% – 12.5%), while proton acidity ( $H^+$ ) accounted for 12.2% (3.8 – 24.5%) of calculated acidity at R12.

Dissolved loadings of elevated metals at R12 (Figure 2.16) averaged 6.6 kg/day for aluminium (0.66 - 17.1 kg/day), 1.3 kg/day for iron (0.082 - 2.9 kg/day), 2.8 kg/day for manganese (0.52 – 5.2 kg/day), 0.51 kg/day for zinc (0.056 - 1.14 kg/day), 0.14 kg/day for nickel (0.018 – 0.29 kg/day), and 0.0077 kg/day for copper (0.00053 – 0.018 kg/day). Similarly, metal loading is controlled by flow rate, with more dissolved metals during higher flows. On a molar basis, aluminium contributed to the majority of metal loading, with on average 71.4 % (64.1 – 79.1%), followed by 18.0% for manganese (11.8 – 25.9%), 7.4% for iron (4.0 – 12.7%), and 2.4% for zinc (2.2 – 2.6%). Other metals (Cu, Ni, Cd) contributed <1% to molar metal loading at R12.



**Figure 2.16: Average dissolved metal loading (kg/day) at R12 and R5 sampling sites computed from monthly monitoring data (Feb 2008 – Jan 2009). Maximum and minimum loadings shown as error bars. Note different scales used for graphs.**

Maximum acidity and metal loadings at R12 are approximate, as values could be greater due to the limitations of the methods flow rate measurement. Additionally, it is likely that larger flows occurred and thus greater acidity and metal loadings between sampling occasions.

#### 2.5.5.4 R5 (Fanny Creek Outflow)

Monitoring site R5 is located after the series of settling basins, where Fanny Creek enters the Waitahu River and (Figure 1.2 and 2.3). Water chemistry at R5 represents discharge to the receiving environment.

#### 2.5.5.4.1 Water Parameters and Chemistry

The drainage pattern between site R12 and R5 within the series of settling basin is complex. On certain occasions, flow measurements and observations show loss of flow to the subsurface occurs, while at other times flow is increased by addition of un-impacted drainage that enters at the second settling basin (Appendix I, D).

On all occasions, flow rate at site R5 after the valley floor settling basins differs compared to that measured beforehand at site R12 (Table 2.2). Flow at R5 is either lower, caused by subsurface flow loss within settling basins, or higher, due to input of flow from un-impacted alkaline drainage at site U4 (Figure 2.13). The relative affect of either depended mainly on the flow conditions. During low flow conditions (February, April and May) subsurface flow within settling basins resulted in no surface flow at site R5 (despite flow at R12). This is also reported by previous monitoring (Raj, 2002, Solid Energy NZ unpublished data). However, during higher flow conditions, flow occurs in the channel at R5 and AMD discharges to the Waitahu River. During these occasions, the flow volume of Fanny Creek is increased by un-impacted alkaline drainage (U4).

The pH of AMD at site R5 is higher than upstream at site R12, with average pH of 4.33 (3.91 – 5.6 pH) compared to pH 3.95 (R12). When flow at R5 occurs, calculated acidity concentrations average 18.1 mg CaCO<sub>3</sub>/L, which is half of the average at R12 during the same occasions (40.8 mg CaCO<sub>3</sub>/L). Concentrations of metals are also roughly half at R5. AMD contains on average 2.68 mg/L aluminium, 0.25 mg/L iron (erroneous measurement in May excluded), 1.47 mg/L manganese, 0.0039 mg/L copper, 0.076 mg/L nickel, 0.27 mg/L zinc, and 0.00026 mg/L cadmium. Relative to ANZECC guidelines, metals that exceed trigger values (parenthesis) include copper (0.0025 mg/L), nickel (0.017 mg/L) and zinc (0.031 mg/L). Relative to resource consent conditions for Cypress mine, limits (parenthesis) are exceeded for aluminium (~1 mg/L) and zinc (0.15 mg/L), and lower limits are exceeded for nickel (0.05 - 0.15mg/L) and only just for cadmium (0.00018 – 0.0030 mg/L). In addition, pH is only marginally above the required median criteria value (pH 4.5).

Results of this study are comparable to previous monitoring of Fanny Creek (Raj, 2002; Solid Energy unpublished data) (Appendix I, A). Raj (2002) does however report slightly more acidic, metal rich AMD on the two occasions sampled.

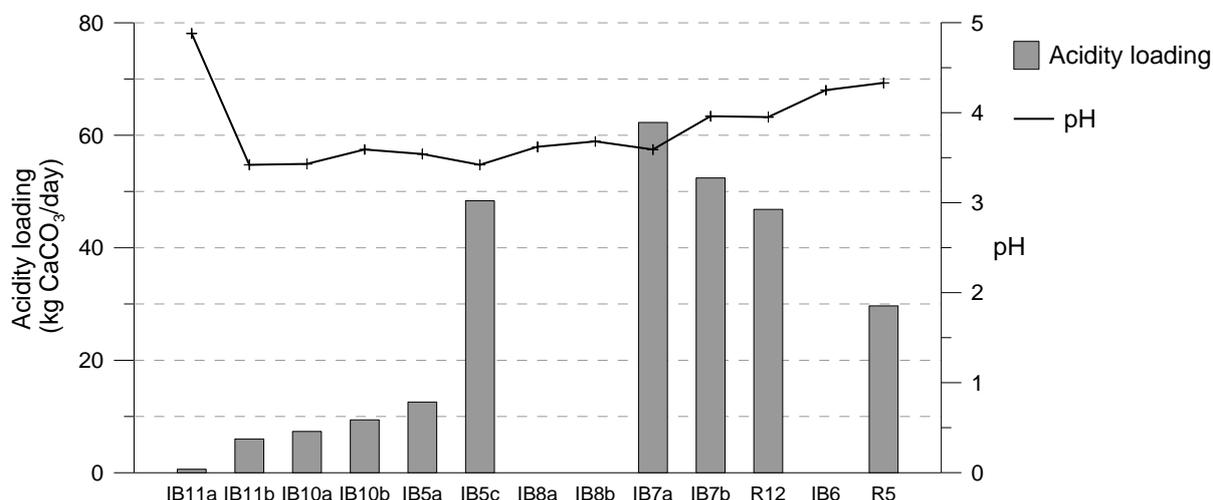
The primary cause of lower acidity and metal concentrations at site R5 is probably due to mixing with alkaline drainage from site U4. Alkaline drainage has substantial flow (up to ~20 L/s) and thus contributes considerable alkalinity (Appendix I, D), supported by a trace of alkalinity in drainage at R5 (~10 mg CaCO<sub>3</sub>/L). Consequently, acidity is neutralized and metals are removed from solution (increased pH), which is clearly visible by white aluminium precipitate as soon as drainage from U4 enters Fanny Creek (Figure 2.13). The average decrease of acidity and metal loadings between R12 and R5 (Figures 2.12 and 2.13) by almost a third also indicates acidity and metals are removed within settling basins, but a portion of this is also likely caused by subsurface flow loss. Attenuation of AMD likely occurs as Fanny Creek flows through the wetland system of channels, ponds and vegetation established within the settling basins. Processes such as oxidation and precipitation reactions, adsorption to mineral surfaces (particularly iron hydroxides) and organic matter, and uptake by biota (Webster-Brown, 2005; Black et al., 2005; Sheoran & Sheoran, 2006) most certainly contribute to water quality improvement between R12 and R5 (Appendix I, B).

Acid mine drainage discharged at R5 has no detectable impact on the high flow (~15 – 20 cumecs), net alkaline (15 – 30 mg CaCO<sub>3</sub>/L) Waitahu River. There is no decline in pH or alkalinity downstream of Island Block mine (R8 and R6, Table 2.2) in the Waitahu River. AMD impacts visually however by staining the river bed adjacent to settling basins dark orange ferric iron precipitate (which verifies subsurface flow from settling basins).

The settling basin area is likely to be compatible with future passive treatment strategies. The area could be utilized for sediment removal prior to a treatment system, such as in the first settling basin. Alkaline drainage and established wetland can be used and optimized for post treatment of effluent from a passive system, to retain metal precipitate and provide final ‘polishing’ before Fanny Creek discharges to the receiving environment.

## 2.6 Summary

Average measured acidity loading (kg CaCO<sub>3</sub>/day) and average pH along Fanny Creek illustrate the overall picture of drainage chemistry in Fanny Creek catchment (Figure 2.17).



**Figure 2.17: Average measured acidity loading (kg CaCO<sub>3</sub>/day) and average pH at sites along the southern tributary and main channel of Fanny Creek (waste rock slopes to outflow).**

Acidity from the southern waste rock slope is negligible (IB11a); however, drainage from mid waste rock slopes contributes AMD and lowers pH in the southern tributary to 3.54 (IB5a) and increases acidity loading to 12.6 kg CaCO<sub>3</sub>/day (IB5a) (Figure 2.17). AMD from the northern tributary greatly contributes to acidity in Fanny Creek, increasing acidity loading to 48.4 kg CaCO<sub>3</sub>/day (site IB5c), with a decrease of pH to 3.42. Downstream in the main channel Fanny Creek gains acidity (62.3 kg CaCO<sub>3</sub>/day at IB7a), either by addition of subsurface AMD flow or by dissolution of previously accumulated metal precipitates in the streambed. Input of un-impacted alkaline drainage from surrounding hillsides act to dilute and neutralize acidity in Fanny Creek, and remove dissolved metals, as indicated by an increase of pH to 3.96 at site IB7b, and a decrease in acidity loading to 52.4 kg CaCO<sub>3</sub>/day. Water quality further improves as Fanny Creek flows through the settling basins on the valley floor, caused by input of more alkaline drainage and natural wetland AMD attenuation processes. Loss of flow in Fanny Creek also occurs in the settling ponds due to subsurface flow. As a result, acidity and metal in Fanny Creek are removed before AMD discharges into the Waitahu River, indicated by a decrease in acidity loading at site R5 by about a third (29.7 kg CaCO<sub>3</sub>/day) compared to beforehand at site R12, and a pH increase to 4.33.

## 2.7 Future Work

Drainage chemistry of Fanny Creek catchment is characterized in detail by this study. Continued monitoring and further investigation is required:

- Compile accurate flow data for passive treatment system design. More precise flow rate measurements are required at site R12 during high flow conditions (> 15 L/s). This may require construction of a rectangular weir or an automated flow monitoring system.
- This study did not characterise drainage chemistry during and immediately after heavy rainfall. Sampling should occur on a number of occasions, particularly after drier months, to determine initial flush AMD concentrations, and its duration and frequency. Impacts of flushing on the wider catchment should also be assessed. It is possible flush chemistry would not impact on the Waitahu River significantly.
- Changes in Fanny Creek AMD through time should be identified. Long term drainage chemistry should be characterized and accounted for in any future passive treatment designs.

Aspects that require investigation for future mining operations:

- As mining resumes, more frequent monitoring of Fanny Creek is required (monthly basis). This will determine any changes in drainage chemistry, which may influence options for passive AMD treatment. Sediment flux from Island Block mine should be monitored to appropriately design or maintain settling ponds prior to a passive treatment system (to avoid clogging).
- Analysis of data from leach column tests by Solid Energy to provide information on acidity and metal leaching behavior of waste rock over time. Using hydrological data (flow and rainfall), results can be scaled up to model and predict acidity generation of additional overburden disposed in Fanny Creek catchment.
- Detailed geochemical analysis (acid-base accounting) of *in situ* overburden to characterise acid producing potential of lithologic units and predict drainage chemistry (data provided in Appendix I, E). These results have implications for waste rock management and AMD mitigation. Additional sampling of McLagans pit lithologies may identify mineralogical differences that are responsible for the contrast in drainage chemistry compared to Island Block pit waste rock.

## CHAPTER THREE

### Literature Review: Passive Treatment of Acid Mine Drainage

#### 3.1 Introduction

This chapter briefly reviews three suitable passive AMD treatment systems for Fanny Creek AMD. The treatment systems reviewed are:

- Sulfate reducing bioreactor (SRBR)
- Limestone leaching bed (LLB)
- Open limestone channel (OLC)

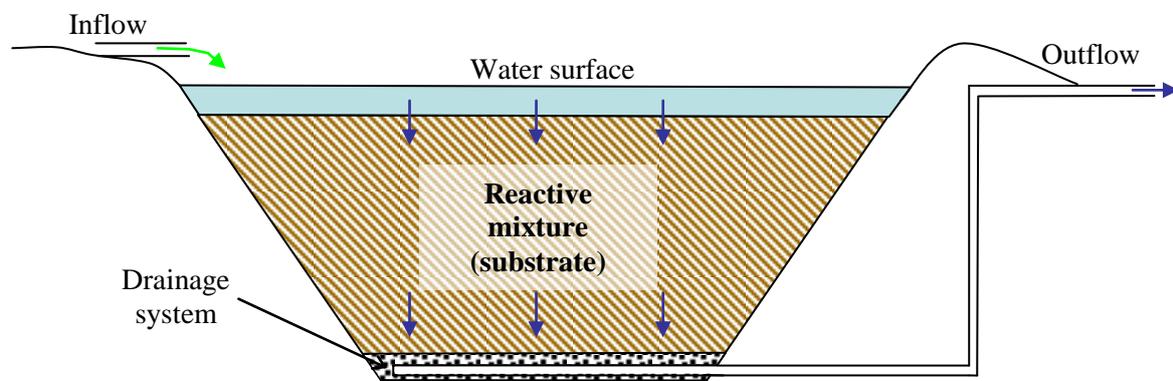
These passive AMD systems are introduced, and an overview is given of their AMD remediation processes, factors that can influence treatment performance, and design criteria for field application at mine sites. To avoid repetition the review combines limestone leaching bed and open limestone channel treatment systems because these have similar remediation processes.

Passive remediation of acid mine drainage (AMD) is reviewed in detail in Appendix II. This includes a description of the principles of passive AMD treatment, and a review of metal and acid neutralization processes that operate within these systems. In addition, the various aspects of SRBR, LLB and OLC passive treatment systems mentioned in this chapter are reviewed in depth in Appendix II, E.

## 3.2 Review of Selected Passive AMD Treatment Systems

### 3.2.1 Sulfate Reducing Bioreactor

Sulfate reducing bioreactors for treatment of AMD are a relatively recent development (McCauley et al., 2008). AMD is passed through an inorganic and/or organic reactive mixture, termed ‘substrate’ (Gusek, 2002; Neculita et al., 2007). Flow is typically vertical (Figure 3.1), although horizontal flow designs are reported (Zaluski et al. 2003; McCauley et al., 2008; 2009). SRBRs can be used to treat highly acidic mine drainage that contains a wide range of dissolved metals (Figure 3.2) (Gusek, 2002; Gusek & Wildeman, 2002).



**Figure 3.1: Schematic design of a sulfate reducing bioreactor passive treatment system (adapted from Gusek, 2002).**



**Figure 3.2: A sulfate reducing bioreactor operating at a mine site (Gusek, 2002).**

### **3.2.1.1 Remediation Processes**

SRBR treatment systems remediate AMD by complex chemical and biological processes associated with microbial sulfate reduction. (Doshi 2006; McCauley et al., 2008). This process is can immobilize metals and generate alkalinity (Gusek, 2002; Gilbert et al., 2004; Doshi, 2006; Neculita et al., 2007) (Appendix II, B, C). Sulfate reduction can transform dissolved metals such as iron, copper, nickel, zinc, into minerals such as sulfides, sulfates, and carbonates (Doshi, 2006; Neculita et al., 2007), and aluminum is also precipitated, though its removal is less well understood (Gusek & Wildeman, 2002)

Other important metal removal mechanisms include adsorption, bio-adsorption, co-precipitation, and metal precipitation on the surface of substrate materials and bacteria (Neculita et al., 2007; McCauley et al., 2008; 2009).

### **3.2.1.2 Factors that Influence Performance**

A variety of factors can influence SRBR treatment performance, which relate primarily to the extent of bacterial activity (Doshi, 2006; Neculita et al. 2007). The most crucial factor is the availability of carbon from a suitable organic source to sustain bacterial metabolic processes (Gazea et al., 1996; Gusek, 2002; McCauley et al., 2008). Secondary factors that influence bacterial activity and performance include:

- Redox conditions
- pH
- Water chemistry
- Temperature
- Reactive substrate material mixture
- System configuration and hydraulic properties

(Watzlaf et al., 2003; Gilbert et al., 2004; Tsukamoto et al., 2004; Doshi, 2006; Zagury et al. 2006; Neculita et al., 2007; McCauley et al., 2008; 2009).

### **3.2.1.3 Design Criteria**

Three main types of design criteria are recommended for sizing SRBR treatment systems:

- Metal molar volumetric loading

- Acidity areal loading
- Hydraulic retention time

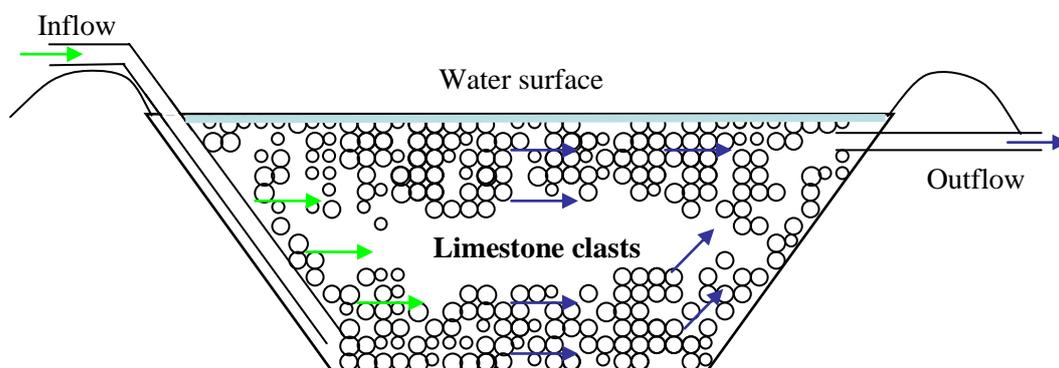
(Younger et al., 2002; Rose & Dietz, 2002; Thomas and Romanek, 2002; Watzlaf et al., 2003; Ziemkiewicz et al., 2003; Skousen & Ziemkiewicz, 2005; Wildeman et al., 2006; Kuyucak et al., 2006; McCauley et al., 2008; 2009)

However, criteria represent conservative values because of the recent development of SRBR systems and limited field validation of criteria (Younger et al., 2002; McCauley et al., 2009).

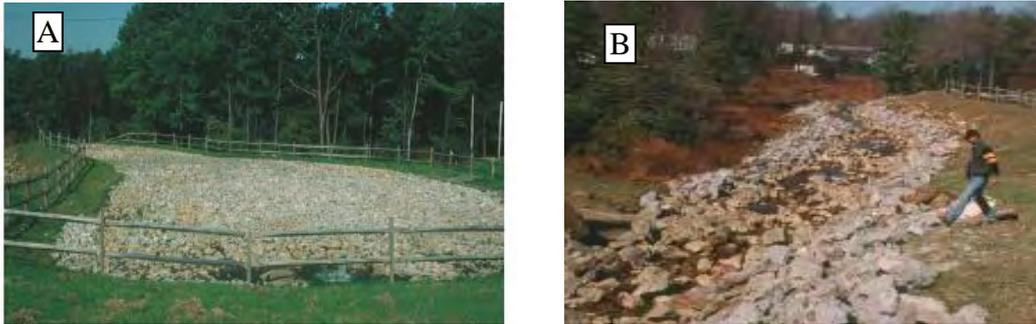
### 3.2.2 Limestone Leaching Bed and Open Limestone Channel

Passive treatment of AMD can occur by using limestone to neutralize acidity and generate alkalinity (Younger et al., 2002). These systems are commonly used limestone is inexpensive, widely available, and it is relatively cheap to construct and maintain treatment systems (Sasowsky et al., 2000).

Limestone leaching beds (LLBs) consist of an open, rectangular bed of limestone clasts (10 – 100 mm) which allows horizontal flow of AMD through pore spaces (Figure 3.3 and 3.4) (Cravotta III & Ward; 2008; Denholm et al., 2003). Open limestone channels (OLCs) transmit water along a channel or ditch lined with large limestone clasts (Ziemkiewicz et al., 1994; O’Sullivan, 2005) (Figure 3.3). AMD is directed into the channel, and is aerated as it travels downhill (Cravotta III et al., 2004).



**Figure 3.3: Schematic design of a limestone leaching bed passive treatment system. Adapted from Skousen (1997).**



**Figure 3.4: Limestone leaching bed (A) and open limestone channel (B) passive treatment systems operating to treat AMD (Skousen & Ziemkiewicz, 2005).**

### 3.2.2.1 Remediation Processes

Limestone leaching beds and open limestone channels are aerobic passive treatment systems (Ziemkiewicz et al. 1997; Younger et al., 2002; Trumm, 2007). The primary mechanism that removes dissolved metals are oxidation and hydrolysis reactions (Cravotta III & Trahan, 1999) (Appendix II, B).

The systems use dissolution of calcite in limestone to neutralize acidity and generate alkalinity (Appendix II, C). This increases pH which removes dissolved metals such as ferric iron and aluminium because solubility of these metals decreases with increasing pH (Younger et al., 2002; Cravotta III & Trahan, 1999). Trace metals can also be removed by adsorption and co-precipitation with iron and aluminium precipitates (Younger et al., 2002; Cravotta III & Trahan, 1999; Cravotta III, 2008).

### 3.2.2.2 Factors that Influence Performance

Precipitation of metal is a major factor influencing performance of LLB and OLC treatment systems (Cravotta III & Trahan, 1999; Younger et al., 2002; Watzlaf et al., 2003). Limestone can become encrusted by iron and/or aluminium precipitates ('armour'), which can reduce calcite dissolution (Cravotta III & Trahan, 1999; Santomartino & Webb, 2007).

In addition, metal precipitates can accumulate within systems causing clogging which reduces porosity and permeability and can led to channelization of AMD (short circuiting). Channelization ultimately causes failure of treatment systems due to reduced AMD contact time with limestone for neutralization of AMD (Ziemkiewicz et al., 1994; Cravotta III & Ward, 2008). Authors recommend drainage pipes (especially for LLBs) to allow flushing of

accumulated precipitates (Cravotta III & Trahan, 1999), however, there is no consensus on whether flushing maintains long term performance (Cravotta III et al., 2008). The rate of limestone dissolution also can be influenced by:

- Temperature
- pH
- Reactive surface area (limestone clasts size)
- Microbial activity
- Limestone quality

(Ziemkiewicz et al., 1994; Cravotta III & Trahan, 1999; Jage et al., 2001; Younger et al., 2002; Watzlaf et al., 2003; Rose, 2004; Cravotta III & Ward, 2008)

### **3.2.2.3 Design Criteria**

Design guidelines for LLB and OLC treatment systems are tentative due to the variable rate of limestone dissolution (Cravotta III et al., 2008). Design criteria for LLB and OLC treatment systems are based on:

- Influent AMD concentrations
- Hydraulic retention time
- Limestone clast size
- Flow velocity
- Gradient (OLC)

(Cravotta III & Trahan, 1999; Ziemkiewicz et al., 1997; Black et al., 1999; Younger et al., 2002; PIRAMID Consortium, 2003; Watzlaf et al., 2003; Skousen & Ziemkiewicz, 2005; Santomartino & Webb, 2007).

Design Criteria for LLB and OLC treatment system aim to minimize accumulation of metal precipitates (Ziemkiewicz et al., 1996). However, criteria are still provisional and relatively poorly defined (Younger et al., 2002; Skousen & Ziemkiewicz, 2005)

### **3.3 Summary**

Much research overseas has focused on passive AMD treatment systems over the last two decades. These systems are considered a proven treatment technology by many authors, as long as they are appropriately selected and designed (Younger et al, 2002).

Despite a number of studies of AMD in New Zealand, little research has focussed on remediation (Trumm et al. 2005, 2006, 2008; Trumm, 2007; McCauley et al. 2008, 2009). Specific passive treatment methods are yet to be proven to treat mine drainage specific to New Zealand and its unique environment (rainfall and topography). The implementation of passive treatment systems and evaluation of their performance will enable validation and design improvements for different passive technologies (McCauley et al., 2006).

## **CHAPTER FOUR**

### **Laboratory Trials of Passive AMD Treatment Systems: Methodology and Results**

#### **4.1 Introduction**

Chapter Four describes the methodology of laboratory trials of passive AMD treatment systems and displays the results of measurements, analysis and observations of trial systems.

Passive AMD treatment requires a phased approach for the design and implementation of passive systems (Gusek, 2002; Watzlaf et al., 2003; PIRAMID Consortium 2003; Trumm, 2007). This involves laboratory based trials and on-site pilot scale testing performed with AMD that requires treatment, prior to construction of a full-scale treatment system (Gusek, 2001, 2004; Trumm, 2007). This approach allows for the evaluation and verification of selected treatment options, reducing the financial risk of rehabilitation failure (Doshi, 2006; Trumm, 2007). The phased approach is used in the current study, and is the rationale for laboratory trials of passive AMD treatment systems for Fanny Creek AMD.

Four treatment options for Fanny Creek AMD were trialed at laboratory scale. A selection process was employed using Fanny Creek catchment water chemistry and site characteristics to narrow down suitable passive treatment options to trial at laboratory scale. Their effectiveness to treat Fanny Creek AMD was documented by measurements and analysis of water quality and chemistry, and by observations.

Metal analysis was completed for three of the four options. The fourth option was conceived in the latter stages of the project and budget and time constraints precluded detailed metal analysis. Metals identified as elevated in Fanny Creek catchment are the focus of metal analysis for the other trial options.

## **4.2 Selection Methodology of Suitable Passive Treatment Systems for Fanny Creek AMD**

A flow chart developed by Trumm (2007) specific to AMD sites in New Zealand was used to select potentially suitable passive treatment options for Fanny Creek AMD (Appendix III, A). The flow chart identified the following passive treatment options:

- **Oxidising Systems:**
  - Limestone leaching bed
  - Slag leaching bed
  - Open limestone channel
  - Oxic limestone drain
  - Limestone sand dosing
  
- **Reducing Systems:**
  - Vertical flow wetland
  - Anaerobic wetlands

Of those suggested, a limestone leaching bed (LLB), open limestone channel (OLC), and a reducing treatment system were selected for subsequent laboratory trials, as they were considered most appropriate for Fanny Creek and available resources (D Trumm, pers comm., 2008). The reducing treatment option was a sulfate reducing bioreactor (SRBR) system because this treatment technology has recently been investigated in New Zealand (McCauley et al., 2008, 2009).

Additionally, an alternative site specific forth passive treatment option was trialed at laboratory scale. This involved investigation of the neutralizing capacity of the Waitahu River and the potential to mix Fanny Creek AMD with buffered river water.

## **4.3 Methodology of Laboratory Trials**

Laboratory trials of selected passive treatment options were conducted. The SRBR, LLB and OLC treatment systems were 'bench top scale' and trialled in a laboratory at CRL Energy Ltd, in Christchurch. The Waitahu River Mixing option was tested in a laboratory in Reefton. Trials were conducted to assess treatment performance, identify optimal passive treatment

strategies for Fanny Creek AMD, and obtain data to size and configure future pilot or full scale passive treatment systems.

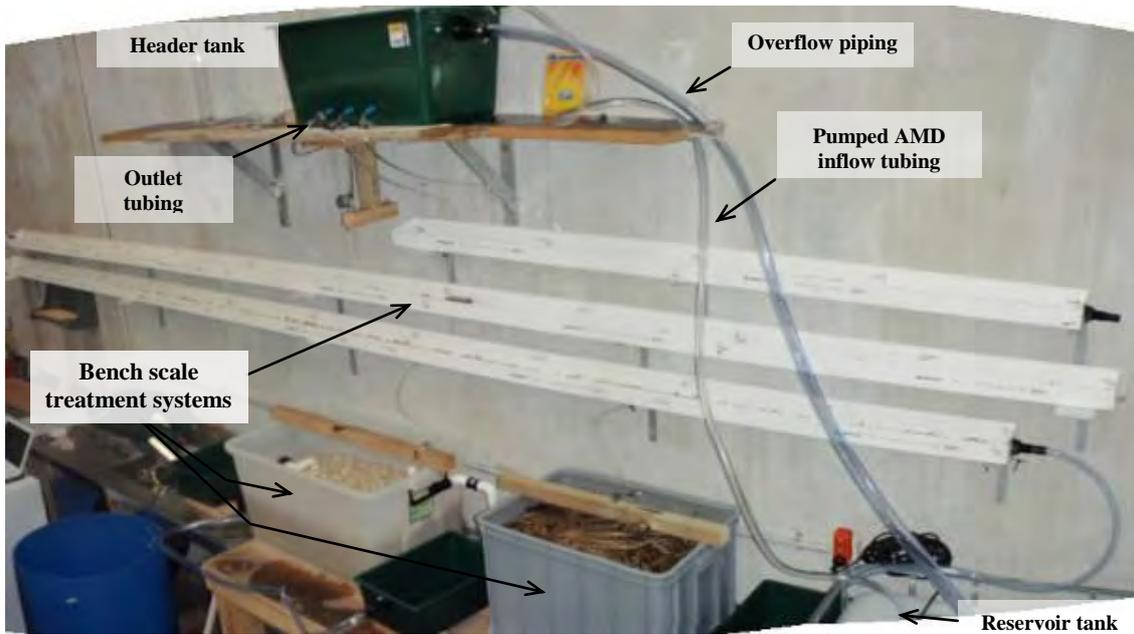
### **4.3.1 SRBR, LLB and OLC Treatment Systems**

#### **4.3.1.1 Collection of Fanny Creek AMD**

The AMD used for bench scale passive treatment system trials was sourced from Fanny Creek, at IB5c. This location was chosen because the trial designed to simulate treatment of worst likely AMD at R12. A pump was used to extract AMD from Fanny Creek and fill 1000 L high-density polyethylene (HDPE) tanks (Appendix III, C). AMD was transported to the laboratory in Christchurch where it was stored and left undisturbed until used for bench scale treatment systems trials.

#### **4.3.1.2 Laboratory AMD Supply**

AMD was supplied to bench scale treatment systems from an adjacent 1000 L ‘reservoir tank’ that had a submersible pump which transferred AMD up to a 56 L capacity plastic container, or ‘header tank’, sitting on a shelf, 2.4 m off the ground (Figure 4.1). The header tank provided a constant head in order to maintain uniform water pressure for influent AMD flow rates into treatment systems. This was achieved by installing a 32 mm diameter overflow pipe on the header tank that ran back to the reservoir tank below. Three outlet holes in the header tank fed AMD under gravity down to each treatment system via 4 mm internal diameter plastic tubing. Metal clamps (60 mm in length) at the ends of plastic tubing were used to regulate influent flow rate (Appendix III, C).



**Figure 4.1: Laboratory trial AMD supply for bench scale passive treatment systems.**

### 4.3.1.3 Experimental Design Methodology

#### 4.3.1.3.1 Hydraulic Retention Time

The experimental design of bench scale passive treatment systems was based on hydraulic retention time (HRT) within treatment systems (Table 4.1). HRT is a measure of the average length of time AMD is in contact with reactive treatment materials within passive systems. In relation to bench scale trials, HRT in the SRBR provides an estimate of how long it takes AMD to percolate down through the reactive substrate mixture. Similarly, HRT for the LLB and OLC indicates the approximate time taken for AMD to travel from the inflow to outflow. HRT (in hours) is calculated by the following equation:

$$(Eq\ 4.1) \quad \text{Hydraulic Retention Time (hours)} = \frac{\text{AMD Volume (m}^3\text{)}}{\text{Flow rate (m}^3\text{/ hr)}}$$

Where:

- i) AMD Volume is the amount of AMD (m<sup>3</sup>) in contact with solid reactive materials within passive treatment systems and directly reflects the porosity of the system.
- ii) Flow rate is the amount of AMD (m<sup>3</sup>) that passes through the passive treatment system per hour.

Throughout the experiment the HRT in bench scale treatment systems was systematically decreased, with a proportionate increase in flow rate and acidity and metal loadings. Initial HRTs were based on conservative design criteria established for respective passive treatment systems (D Trumm, pers com., 2008). The experiment tested whether these criteria could be refined to determine optimal designs for sizing larger passive treatment systems. Optimal HRTs, operating ranges, and failure thresholds were identified by analysis of effluent water quality.

The SRBR treatment system was designed to have an initial HRT of 60 hours, while the LLB and OLC treatment systems were started with a HRT of 15 hours. The HRT was reduced as the trial proceeded to a minimum of 5 hours for all treatment systems. The HRT for the LLB and OLC systems was reduced in one hour intervals, and the HRT for the SRBR system was reduced in larger intervals (between 12 and 1 hours). The HRTs for the SRBR, LLB and OLC during the latter half of the trial were designed to match and allow comparison between systems. Initial HRTs were used as a control and repeated mid way through and at the end of the trial to identify changes in treatment performance over time (from the accumulation of metal precipitates for instance). Each HRT operated for a prescribed time period (HRT period), and the duration of HRT periods were shortened as the trial progressed from 12 days, to one week, to three days, because the supply of AMD was limited. The duration of each HRT trial period was at least three times that of the operating HRT, and sampling was not conducted until effluent water quality was considered representative of treatment afforded by the operating HRT.

**Table 4.1: Experimental design parameters for bench scale SRBR, LLB and OLC passive treatment systems. The table displays designed hydraulic retention times (HRT), associated influent AMD flow rates, the duration of each HRT period, and the total trial duration for each treatment system.**

<b>SRBR</b>	HRT (hours)	60	48	24	18	60	12	10	9	8	7	6	5	60
	Flow rate (L/day)	11	14	28	37	11	55	66	73	83	94	110	132	11
	HRT period (days)	12	12	12	12	12	12	7	7	7	3	3	3	12
	Trial duration	1 month			2 months			3 months			~ 4 months			
<b>LLB</b>	HRT (hrs)	15	14	13	12	15	11	10	9	8	7	6	5	15
	Flow rate (L/day)	39	42	45	49	39	53	59	65	74	84	98	118	39
	HRT period (days)	12	12	12	9	7	9	7	7	7	3	3	3	7
	Trial duration	1 month			2 months			3 ¼ months						
<b>OLC</b>	HRT (hrs)	15	14	13	12	15	11	10	9	8	7	6	5	15
	Flow rate (L/day)	30	32	34	37	30	40	45	49	56	64	74	89	30
	HRT period (days)	12	12	12	9	7	9	7	7	7	3	3	3	7
	Trial duration	1 month			2 months			3 ¼ months						

#### 4.3.1.3.2 Flow Rates and Sizing

To calculate flow rates that satisfy designed HRTs for the trial, equation 5.1 was rearranged:

$$(Eq. 4.2) \quad \text{AMD flow rate (m}^3/\text{hr)} = \frac{\text{AMD Volume (m}^3\text{)}}{\text{Hydraulic Retention Time (hours)}}$$

Calculating AMD flow rate (equation 4.2) required the designed HRTs and AMD Volumes of bench scale treatment systems. Appropriate treatment system sizes were selected (Table 4.2) (Appendix III, B). Porosity was measured to determine AMD Volumes and used to calculate flow rates for HRTs (Appendix III, B).

**Table 4.2: Selected SRBR, LLB and OLC bench scale treatment system sizes, volumes and amount of AMD required for the trial duration for each system.**

	<b>Reactive material volume (L)</b>	<b>Measured AMD Volume (L)</b>	<b>Measured porosities (%)</b>	<b>Amounts of AMD required (L)</b>
<b>SRBR</b>	50	27.5	55	4553
<b>LLB</b>	50	24.5	49	5270
<b>OLC</b>	21.6	18.5	N/A	3992
<b>Total amount of AMD required to supply all three systems:</b>				13 815

#### **4.3.1.4 Operation**

The SRBR treatment system operated for 116 days, and the LLB and OLC treatment systems operated for 112 days. The durations of HRT periods in some cases were lengthened to accommodate flow rate adjustments. Assessment of metal removal (metal analysis) was not completed for the OLC treatment system after 87 days (8 hours HRT) because of poor performance. The 6 hour HRT period for treatment systems was excluded due to the need to conserve AMD for subsequent HRTs. At day 87 the LLB and OLC systems did not receive AMD for 7 days, and the SRBR was reduced to the initial HRT (lowest flow rate) as AMD supply was low.

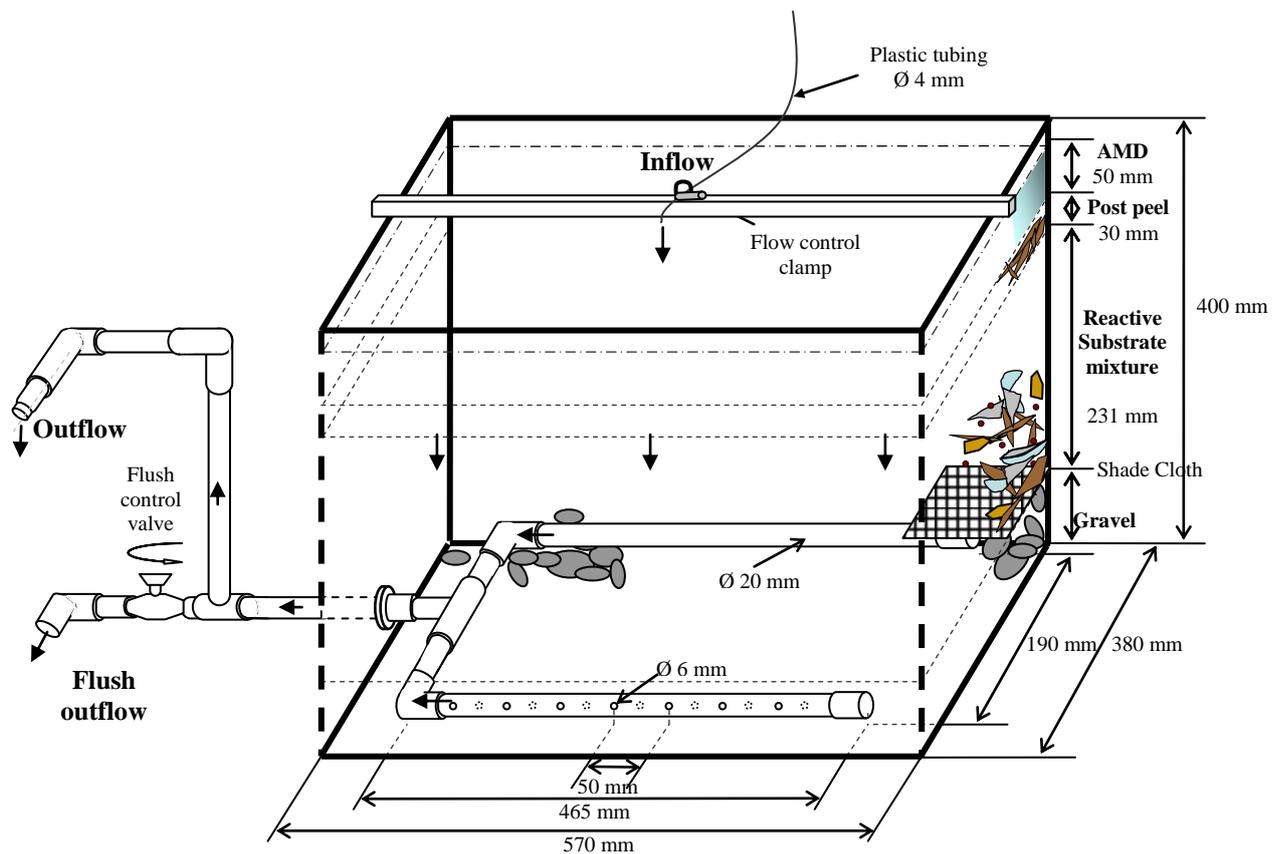
At the end of the trial (after the final control HRT period) the SRBR and LLB bench scale treatment systems were flushed, rapidly draining AMD from treatment systems. Observations and measurements were taken to assess the effectiveness of flushing to remove accumulated metal precipitates.

#### **4.3.1.5 Design Configurations, Construction and Materials**

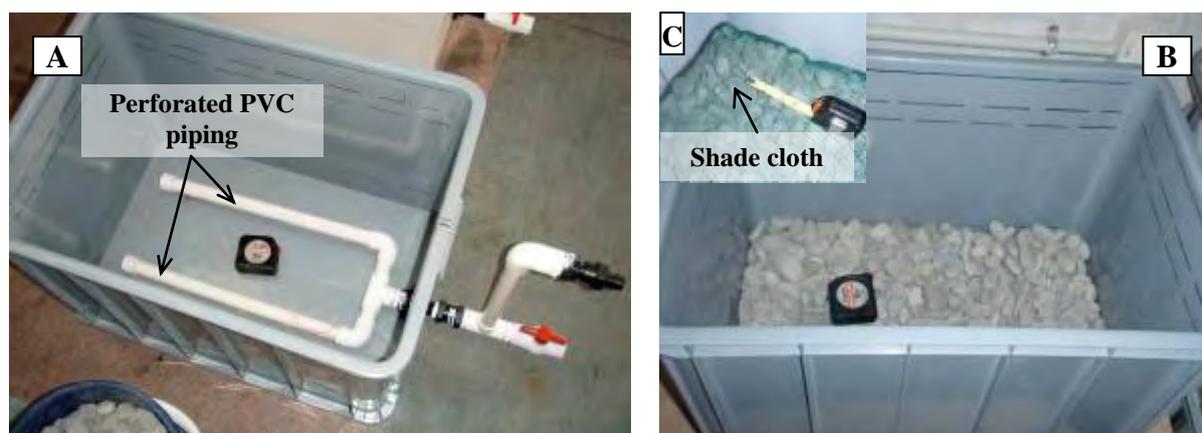
##### **4.3.1.5.1 Sulfate Reducing Bioreactor**

The bench scale SRBR treatment system was based on designs of McCauley et al. (2008, 2009) and employed a vertical down-flow configuration, in a 90 L capacity plastic storage container (Figure 4.2).

The SRBR system comprised three layers. Material volumes were measured using graduated buckets, and weighed before placement in the SRBR. The lower layer consisted of greywacke gravel (20 – 40 mm diameter), with an average calcium weight percentage of 0.241 (McCauley et al., 2008). The gravel layer was 70 mm thick, and had a volume of 15 L (weighing 26.1 kg). This layer also contained perforated polyvinyl chloride (PVC) piping (20 mm internal diameter) to drain effluent from the system (Figure 4.3). Drainage piping consisted of two length-wise parallel pipes, on either side of the long axis of the container and had alternating inlet holes on outward facing sides. Pipes were joined using connector elbows (fixed together using PVC cement glue) and threaded plumbing fittings. Shade cloth was placed over the gravel layer to filter substrate particles that could clog drainage pipe inlets (inset in Figure 4.3).



**Figure 4.2: Schematic drawing of the bench scale SRBR treatment system.**



**Figure 4.3: Drainage layer of the bench scale SRBR treatment system. A) internal and external piping structures. B) lower gravel bed covering drainage piping. C) Shade cloth placed over gravel.**

The reactive substrate mixture (AMD treatment material) overlaid the gravel drainage layer. Substrate had a volume of 50 L, and a thickness of 231 mm. Substrate composition included mussel shells (30%), post peel (35%), *Pinus radiata* bark (20%), compost (10%), and previously used SRBR substrate (5%) from McCauley (2008) (Figure 5.5 and Table 5.3). Mussel shells were sourced from mussel farm waste, and included to generate alkalinity. Shells were received fragmented (20 mm – 70 mm) with waste flesh attached. Post peel (a by-product of fence post manufacture) consisted of timber shards 10 mm wide and 60 – 130 mm long. Bark chips measured approximately 30 mm in diameter. Compost was coarse and friable and purchased from Bunnings Warehouse. Previously used SRBR substrate was included to stimulate bacterial colonization. Substrate material was weighed and mixed evenly and placed on top of the gravel layer (and shade cloth).



**Figure 4.4: Materials used for the SRBR reactive substrate mixture. A) Materials individually clockwise from upper left: post peel, mussel shells, compost and bark chips. B) Materials once mixed and formed into substrate.**

**Table 4.3: Materials used in the reactive substrate mixture for the bench scale SRBR treatment system.**

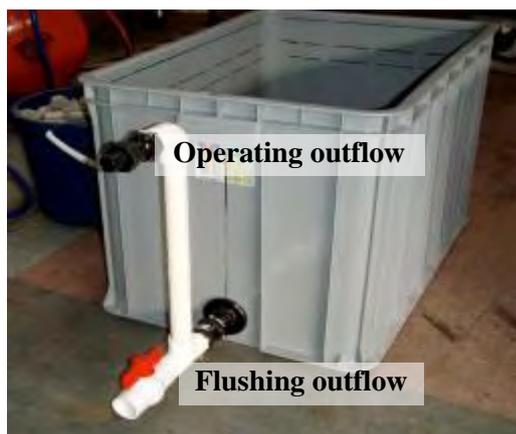
SRBR reactive substrate material	Proportion (%)	Volume (L)	Weight (kg)
Mussel shells	30	15	10.51
Post peel	35	17.5	5.0
Bark	20	10	2.95
Compost	10	5	3.69
Used SRBR substrate	5	2.5	1.39
Total	100	50	23.54

A 30 mm thick layer of post peel was placed over the reactive substrate mixture (Figure 4.5), to promote uniform flow by distributing AMD evenly across the substrate surface. The SRBR was filled from the bottom to avoid air pocket and a layer of water 50 mm deep was maintained over the post peel layer to promote anaerobic conditions. The surface level of water was controlled by the height of the external outflow piping.



**Figure 4.5: Placement of SRBR materials into the container. A) reactive substrate mixture prior to being overlain by the post peel layer (B).**

The SRBR was configured so that influent AMD entered from the centre of the upper surface (dropping 40 mm to the water layer), and percolated down through materials. Drainage piping within the gravel layer conveyed effluent to external piping adjacent to the container (Figure 5.7). During normal operation, effluent traveled up external piping and discharged from the outflow, falling 265 mm to a subsequent settling pond. Rapid draining or ‘flushing’ is used to remove accumulated metal precipitates from pore spaces of vertical flow treatment systems (Kepler and McCleary, 1997; Watzlaf et al., 2003). To enable flushing, a valve was incorporated onto adjacent piping that could divert effluent to the ‘flush outflow’ (Figure 5.7, 5.8).



**Figure 4.7: External outflow piping for the SRBR treatment system showing normal operation outflow, and during flushing.**



**Figure 4.8: Bench scale SRBR treatment system fully constructed and operating to treat AMD. AMD flow path indicated.**

#### **4.3.1.5.2 Limestone Leaching Bed**

The bench scale LLB treatment system was housed in a 100 L capacity, slightly trapezoidal plastic storage container (Figure 4.8). The reactive treatment material was entirely limestone clasts, sourced from Karamea on the West Coast and composed of 100% calcite (XRD analysis, Appendix III, C). Limestone was crushed using a hydraulic press to obtain suitable sized clasts, approximately 10 - 30 mm in length (Figure 4.9). The volume of limestone material within the LLB system was 50 L, which made a 190 mm thick limestone bed, weighing 72.3 kg. Prior to placement in the container limestone clasts were washed in tap water to remove clay and soil from clast surfaces so that this did not influence results.

AMD traveled horizontally through the limestone bed to maximize contact time with limestone clasts. Vertically orientated perforated PVC piping (20 mm internal diameter) conveyed AMD into and out of the system (Figure 4.10). To achieve even flow distribution, inflow and outflow drainage piping resembled upside-down 'U' shapes, with alternating holes, orientated 90° to flow direction. Influent AMD dropped 190 mm into inflow piping, and was directed evenly into the system. Effluent entered outflow piping and was conveyed upwards to be discharged to a subsequent settling pond. Water level was maintained at 10 mm above limestone clasts by the level of the outflow piping (Appendix III, C).

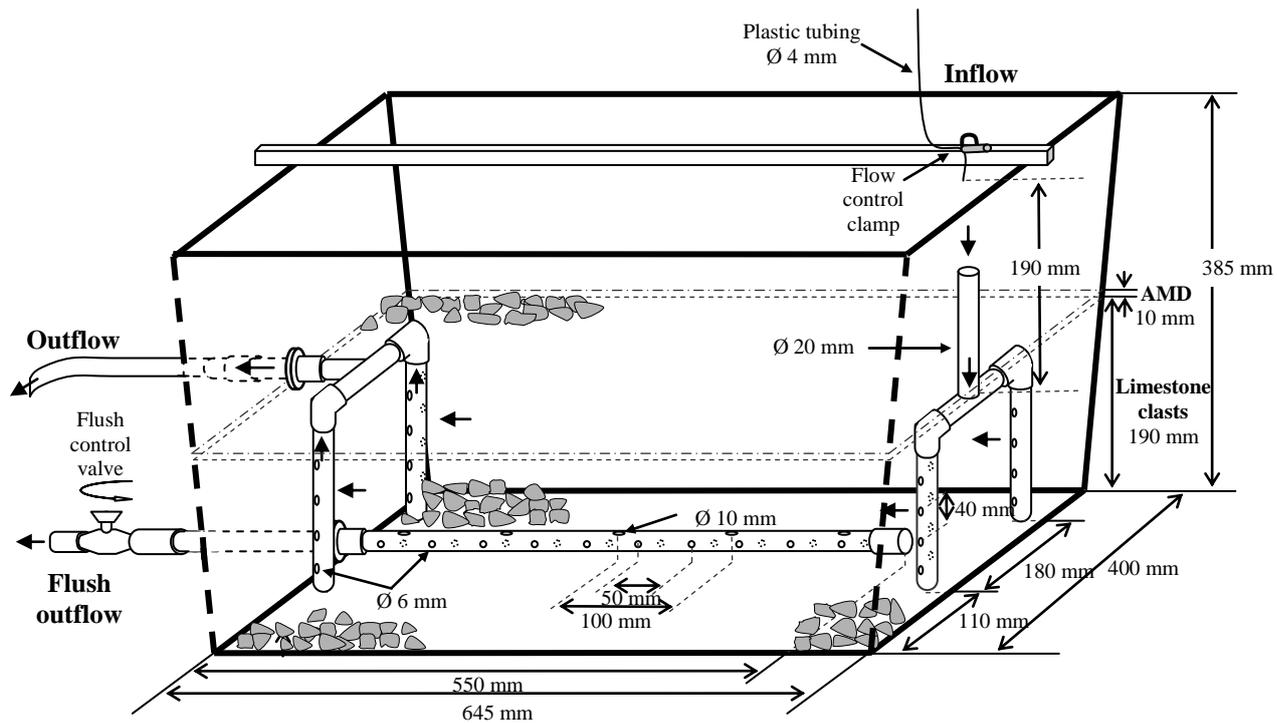


Figure 4.8: Schematic drawing of the bench scale LLB treatment system.

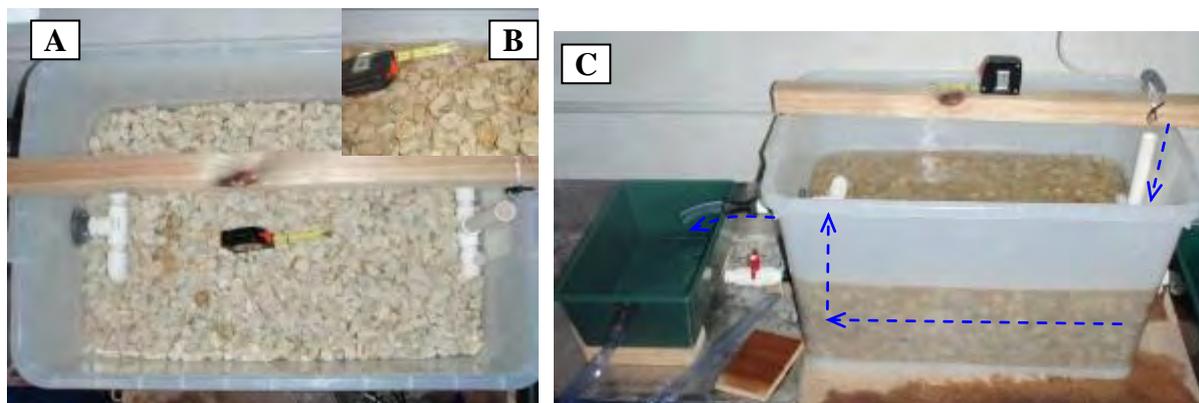


Figure 4.9: Limestone clasts used in the bench scale LLB treatment system.



**Figure 4.10: Bench scale LLB treatment system drainage pipe structures. A) Internal inflow and outflow pipe structures, and the flush pipe with a single layer of limestone clasts. B) External outflow piping, under normal operating conditions (upper pipe), and during system flushing (lower red tap).**

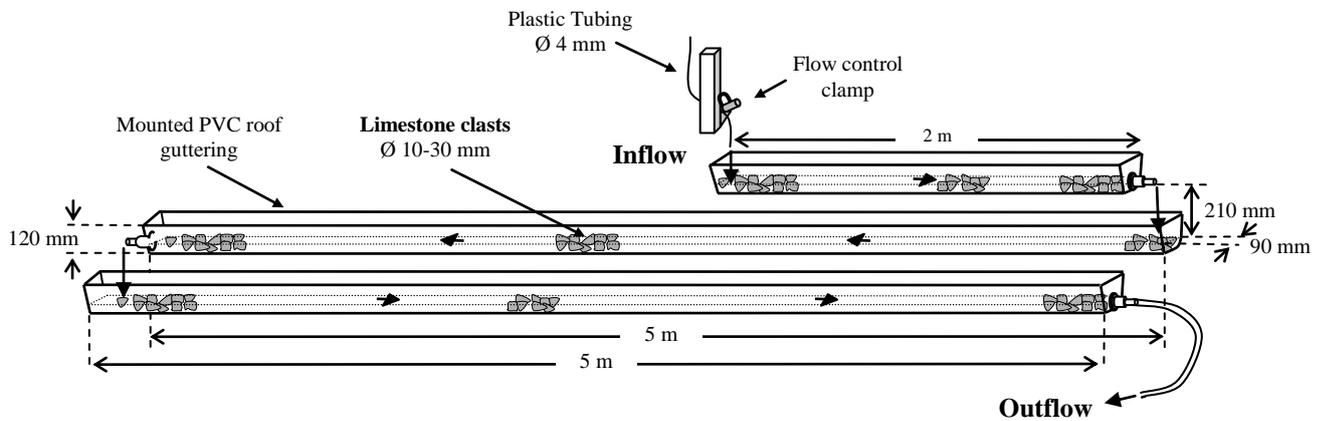
Most LLB treatment systems are constructed with a flushing system to remove accumulated metal precipitates and mitigate limestone armouring and system clogging (Cravotta III, 2008). Therefore, a separate perforated flush pipe was incorporated at the base of the limestone bed (Figure 4.10), 550 mm long with alternating inlet holes on outer (6 mm  $\phi$ ) and upper (10 mm  $\phi$ ) facing sides. Upper facing holes were larger to enable better transmissivity of flow out of the system during flushing, increasing the potential to dislodge precipitates. Once pipe structures had been installed limestone clasts were placed in the container, completing construction of the system (Figure 4.11).



**Figure 4.11: Bench scale LLB treatment system fully constructed. A) Plan view of limestone clasts with inset (B) of surface once filled with AMD. C) AMD flow path through the LLB system (picture taken before settling pond reached full capacity).**

#### 4.3.1.5.3 Open Limestone Channel

In order to achieve target HRT, the OLC system was constructed sub-horizontal with  $<1\%$  gradient, instead of sloping 10 – 20% as recommended by authors (Ziemkiewicz et al., 1994; Skousen & Ziemkiewicz, 2005).



**Figure 4.12: Schematic drawing of the bench scale OLC treatment system.**

A channel was formed from PVC roof guttering and AMD flowed from one end to the other. Guttering was mounted horizontally onto the laboratory wall using steel frames. A slight gradient was created by placing thin (5 mm) plastic sheets between the gutter and metal frames. The limestone used was sourced and prepared in the same way as described for the LLB treatment system. The channel was filled with limestone clasts placed one deep (Figure 4.13), with a total limestone volume of 21.6 L and weight of 18.9 kg.



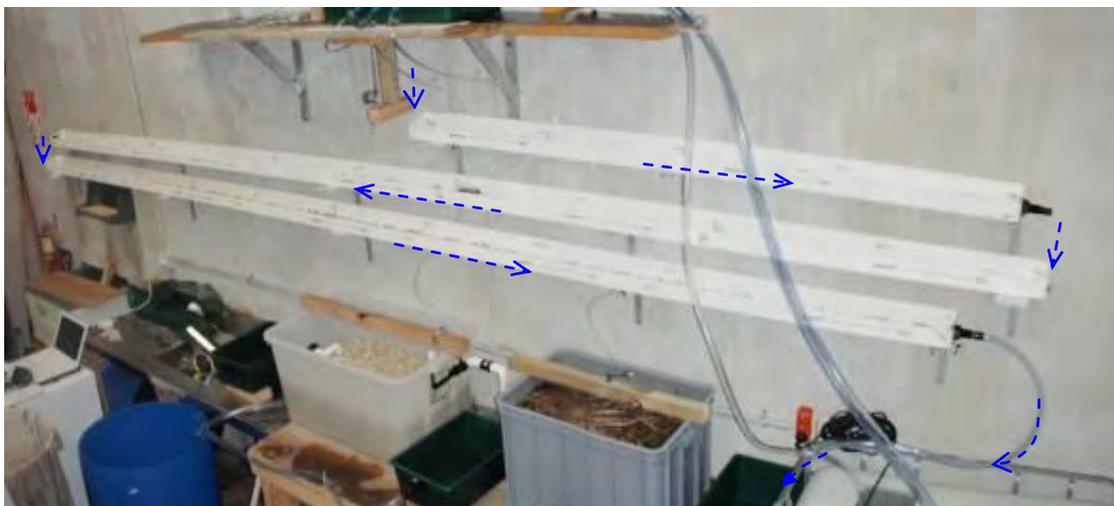
**Figure 4.13: Bench scale OLC treatment system after placement of limestone clasts in the channel.**

The channel measured 12 m long and was divided into three tiers (2 m, 5 m, 5 m) to accommodate the length within the laboratory space. Guttering was 90 mm wide, with sides 120 mm high. space. The gutter ends were blocked off, creating a water level to simulate a natural stream channel. A tube transmitted flow between tiers with AMD falling 210 mm to the channel below. Limestone clasts were exposed 5 mm at upstream channel ends and submerged by approximately 20 mm at downstream ends (Figure 4.14).



**Figure 4.14: Channel end design and water level within the bench scale OLC treatment system. A) Flow transfer between channel tiers. B) shows exposed limestone clasts upstream, and (C) submerged clasts at downstream channel ends.**

AMD entered at the beginning of the upper tier, and flowed down gradient through the system. AMD dropped from one tier to the next, and was discharged at the end of the lower tier via 20 mm diameter plastic tubing to a subsequent settling pond on the laboratory bench. The OLC was not fitted with a flushing mechanism. The bench scale OLC treatment system fully constructed is displayed in Figure 4.15.



**Figure 4.15: Bench scale OLC treatment system fully constructed. Flow path indicated.**

#### **4.3.1.5.4 Settling Ponds**

Each bench scale treatment system discharged into a separate 12 liter capacity plastic container, 350 mm long, 200 mm wide and 180 mm high (green containers in Figure 4.1). Effluent from treatment systems discharged at the opposite end to where it entered the container, forming a 140 mm deep 'pond' after each system to simulate a final settling pond commonly used in full scale passive treatment systems. The pond outlet incorporated a threaded bung that allowed water sampling of pond effluent (Appendix III, C). Water quality of settling pond effluent was regarded as the maximum treatment efficacy afforded by bench scale treatment systems due to possible secondary treatment processes occurring in the ponds (e.g. settling of particulate). Treated effluent was then transported by tubing to a waste drum and disposed of appropriately.

#### **4.3.1.6 Data Collection, Measurement and Methods**

##### **4.3.1.6.1 Influent Flow Rates**

Flow rates were controlled by adjusting metal clamps on plastic tubing that conveyed AMD from the header tank into treatment systems. Appropriate flow rates were achieved by using 10 ml and 25 ml graduated cylinders and electronic timers. Following this, 2000 ml beakers (and then small buckets during greater flow rates) were used over a period of approximately one hour, for more accurate measurement of influent AMD flow rate (Appendix III, C). Collected AMD was weighed to determine the exact volume discharged over the recorded time period. Influent AMD flow rates were typically measured daily and adjusted when necessary.

##### **4.3.1.6.2 Water Sampling**

Water sampling was carried out to assess performance of bench scale treatment systems and this involved the measurement of water quality parameters as well as collection of water samples for water chemistry analysis. Sampling was conducted at the end of each HRT period for each treatment system, prior to increasing flow rate to the following HRT. Water quality parameters measured were pH, electrical conductivity (EC) and dissolved oxygen (DO), using portable instruments at the time of sampling. Water chemistry analysed included acidity, alkalinity, and concentrations of iron, aluminium, copper, nickel, zinc, manganese, calcium, and sulfur. Water sampling focused on influent AMD and effluent discharged both directly

from treatment systems (before subsequent settling ponds), and effluent discharged from treatment system settling ponds. Settling pond effluent represented final treatment performance, therefore, metal analysis was completed after every HRT period. Conversely, metal analysis for effluent discharged directly from treatment systems (before settling pond) was completed approximately every second HRT period. Water sampling was also conducted on surface water, particularly for OLC and SRBR systems, settling ponds, and during flushing of SRBR and LLB treatment systems. Observations and photographs were taken throughout the trial.

Water sampling involved collection of treatment system effluent in a glass beaker to obtain samples for water chemistry analysis, and then measurements of water quality parameters (pH, EC, DO) were taken. Sampling directly from the SRBR treatment system involved placing the glass beaker so that effluent trickled into the beaker (instead of dripping), so that dissolved oxygen concentration measurements were not greatly affected by aeration. Samples for acidity and alkalinity analysis were collected in unpreserved HDPE bottles, while samples for metals and sulfur analysis were collected in nitric acid preserved HDPE bottles (pH <2.0).

Metal analysis of water samples from bench scale treatment systems involved measurement of dissolved and particulate (total) metal fractions. Dissolved and total metal analysis was completed for influent AMD for the initial three HRT periods, however following this acid soluble metal analysis was completed because influent contained minimal metal particulate. Influent AMD metal concentrations at each HRT period for all three bench scale treatment systems were taken from the LLB system inflow. Dissolved and total metal analysis was completed for effluent from bench scale treatment systems (before and after settling ponds). Samples for dissolved metal analysis were filtered with a 0.45 µm filter, whereas samples for total and acid soluble metal analysis were unfiltered. Water samples were refrigerated until analysed.

#### **4.3.1.6.3 Analysis Methods**

Water samples were analysed by R.J. Hill Laboratories Ltd. Metals concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) and sulfur was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) (then converted to mg/L sulfate). Total iron and ferrous iron concentrations were measured using a

Hach Spectrophotometer, and ferric iron was calculated by subtracting ferrous iron from total iron.

Portable instruments were calibrated prior to taking measurements. pH and EC were measured with a Eutech Cyberscan pH and EC meter, calibrated with pH 4.01 and 7.00 standards and to a 0.01 M (1413  $\mu\text{S}/\text{cm}$  at 25°C) and 0.1 M (12,890  $\mu\text{S}/\text{cm}$  at 25°C) KCl solution. DO was measured with a meter, calibrated in the instrument's chamber which maintains 100% water-saturated air. Influent acidity (to pH 7) and effluent alkalinity (to pH 3.7) were determined by titration methods (Lewis & McConchie, 1994) a few hours after sample collection, using titrants of 0.1N HCl and 0.1 N NaOH, respectively.

#### **4.3.1.7 Autopsy of Trial Treatment Systems**

An 'autopsy' of bench scale SRBR, LLB and OLC treatment systems was completed after the conclusion of the trial. This involved laboratory analytical techniques to investigate the nature and extent of metal precipitates within treatment systems. Information was gathered on metal mineralogy, qualitative and quantitative elemental compositional data, and high resolution images were obtained. This information is useful because it provides an insight into the stability of metal precipitates, and allows system longevity to be predicted with more certainty.

##### **4.3.1.7.1 Data Collection**

Autopsy samples were collected from solid reactive treatment materials within bench scale treatment systems. SRBR treatment system samples were collected prior to flushing to avoid exposure and potential oxidation of metal sulfides present. Conversely, collection of LLB treatment system samples occurred immediately after flushing to avoid disturbing limestone clasts during flushing. Samples from the OLC were collected whilst it operated. SRBR and LLB samples were collected from the upper, mid and lower sections of the reactive substrate mixture and limestone clast bed, respectively. OLC samples were gathered from at selected distances along the channel. SRBR samples were obtained by inserting a zip lock bag to selected depths to take substrate material (included water to saturate samples), and then sealing the bag while still submerged. LLB and OLC samples were obtained by carefully

removing limestone clasts and placed into zip lock bags (also saturated). Solid reactive treatment materials were immediately placed in the freezer until analysed.

Following sample collection, an ‘autopsy’ was conducted on the SRBR and LLB treatment systems. This involved the systematic extraction and removal of materials within treatment systems to enable observations of metal precipitation and any features (such as preferential flow) within the interior of treatment systems.

Samples were taken of metal precipitates accumulated in the bottom of settling ponds (sludge), and of flushed metal precipitates. Sludge was drawn into a syringe and transferred to HDPE bottles along with pond water (head space free) and refrigerated until analysed.

#### **4.3.1.7.2 Autopsy Analysis**

Solid reactive treatment materials and sludge samples were analysed by scanning electron microscopy (SEM) at Canterbury University. Sample preparation involved dehydration by passing each through a graded bath series (30 – 60 minutes) of initially ethanol and then ethanol-amyl acetate (10%, 25%, 50%, 75% and 100%). Samples were then transferred to a carbon dioxide bomb for critical point drying, and then put on a SEM mount and gold coated for conductivity. Quantitative elemental composition analysis was conducted using the SEM instrument by energy dispersive spectrometry (EDS) at various locations on samples, and high magnification images were taken to document surface morphology and textures.

AMD sludge samples were also analysed by X-ray diffraction (XRD) and X-ray fluorescence methods at Canterbury University. Samples were dried prior to this at 50° C for two days to remove all water. XRD provided information on sludge mineralogy and XRF provided quantitative elemental composition.

### **4.3.2 The Waitahu River Mixing Option**

#### **4.3.2.1 Experimental Design and Methodology**

The design for the Waitahu River Mixing experiment was based on the principle that Waitahu River water could be used neutralize Fanny Creek AMD. Therefore, the potential for mixing Waitahu River water with Fanny Creek AMD to achieve effective treatment was assessed.

The Waitahu River Mixing option was assessed by compilation of monthly acidity and flow rate data from monitoring sites R12 and IB5c, along with alkalinity data from the Waitahu River upstream of Island Block (site R8). Evaluation of this option also accounted for likely worst AMD which is why drainage at site IB5c was included.

Acidity and alkalinity data were used to calculate a ratio of river water required to neutralize AMD to pH 5 for each month sampled (equation 4.3). Neutralization to pH 5 removes ferric iron and aluminium, and associated acidity. The ratio was combined with Fanny Creek flow data (at R12) to calculate the flow rate (L/s) of Waitahu River water required to neutralize Fanny Creek AMD for each sampling event (equation 4.4).

(Eq. 4.3) Acidity and alkalinity ratio calculated by:

$$= \frac{\text{Fanny Creek acidity (mg/L CaCO}_3 \text{ to pH 5)}}{\text{Waitahu River alkalinity (mg/L CaCO}_3 \text{ to pH 3.7)}}$$

(Eq. 4.4) Waitahu River flow rate (L/s) required to neutralize AMD to pH 5 calculated by:

$$= \text{Ratio} * \text{Fanny Creek flow rate (L/s)}$$

Worst case projections were determined by using maximum Fanny Creek acidity and flow rate data and minimum Waitahu River alkalinity data. This predicted the maximum flow volume of alkaline water needed to neutralize Fanny Creek AMD during worst likely AMD conditions.

To verify the calculated Waitahu River flow rate to neutralize Fanny Creek, Waitahu River water was mixed (titrated) with Fanny Creek AMD while the pH was measured. The titrant was Waitahu River water and was added in known amounts to 50 ml of AMD collected from R12. The pH was continuously measured with a calibrated pH meter, and addition of river water was ceased when pH 5 was reached. The amount of Waitahu River water added was then compared to the calculated ratio from acidity and alkalinity data. This was conducted in a laboratory on the same day as water samples were collected from the field site.

In addition, a method for transferring river water to the AMD treatment area (site R12) was investigated. A desktop study (Google Earth) along with field observations was completed to

assess the elevation of the Waitahu River compared to the AMD treatment area, because this affected how water could be transferred from the Waitahu River.

## 4.4 Results of Laboratory Trials

### 4.4.1 Bench Scale SRBR, LLB and OLC Treatment Systems

#### 4.4.1.1 Experimental Design Parameters

Measured experimental parameters for bench scale SRBR, LLB and OLC passive AMD treatment systems differ slightly from design values (Table 4.4). On certain occasions influent flow rates were inaccurate from design HRTs, shown by equivalent measured HRTs for the LLB system initially. To account for such flow variation, an average HRT was calculated from flow rates measured on days prior to water sampling (Appendix III, D). Average measured HRTs are presented rounded to the nearest hour, because this gives a better indication of the HRT accuracy achieved for the trial. The SRBR treatment system was shortened from 56 to 5 hours HRT, the LLB system from 14 to 5 hours HRT, and the OLC system from 15 to 5 hours HRT. Control HRTs are very similar, therefore comparison of performance through time is possible.

**Table 4.4: Measured experimental parameters for bench scale SRBR, LLB and OLC treatment systems. The table shows measured hydraulic retention times (hours), influent AMD flow rates (L/day), and the duration of each HRT period (days).**

<b>Sulfate reducing bioreactor (SRBR)</b>												
<b>Measured HRT (hrs)</b>	56	51	24	18	57	14	10	9	8	7	5	58
<b>Measured flow rate (L/d)</b>	11.9	13.1	27.7	36.9	11.7	49.0	65.7	71.4	81.0	95.0	124.5	11.4
<b>HRT duration (days)</b>	10	13	12	14	7	11	7	8	3	5	4	8
<b>Limestone leaching bed (LLB)</b>												
<b>Measured HRT (hrs)</b>	14	14	13	12	15	11	10	9	8	7	5	15
<b>Measured flow rate (L/d)</b>	41.4	42.5	45.3	48.8	40.5	52.6	56.7	66.2	72.5	83.0	115.8	39.1
<b>HRT duration (days)</b>	10	13	12	9	8	14	7	7	3	5	4	4
<b>Open limestone channel (OLC)</b>												
<b>Measured HRT (hrs)</b>	15	14	13	12	17	11	10	9	8	8	5	16
<b>Measured flow rate (L/d)</b>	30.3	31.7	34.2	37.0	26.1	39.0	45.2	50.3	56.5	59.2	84.3	28.6
<b>HRT duration (days)</b>	10	13	12	9	8	14	7	7	3	5	4	4

Influent and effluent water parameters and chemistry data are presented at the end of each HRT period, for each HRT tested. Therefore, results are in chronological order and show changes in treatment performance with increasing influent AMD flow rate and decreasing HRT.

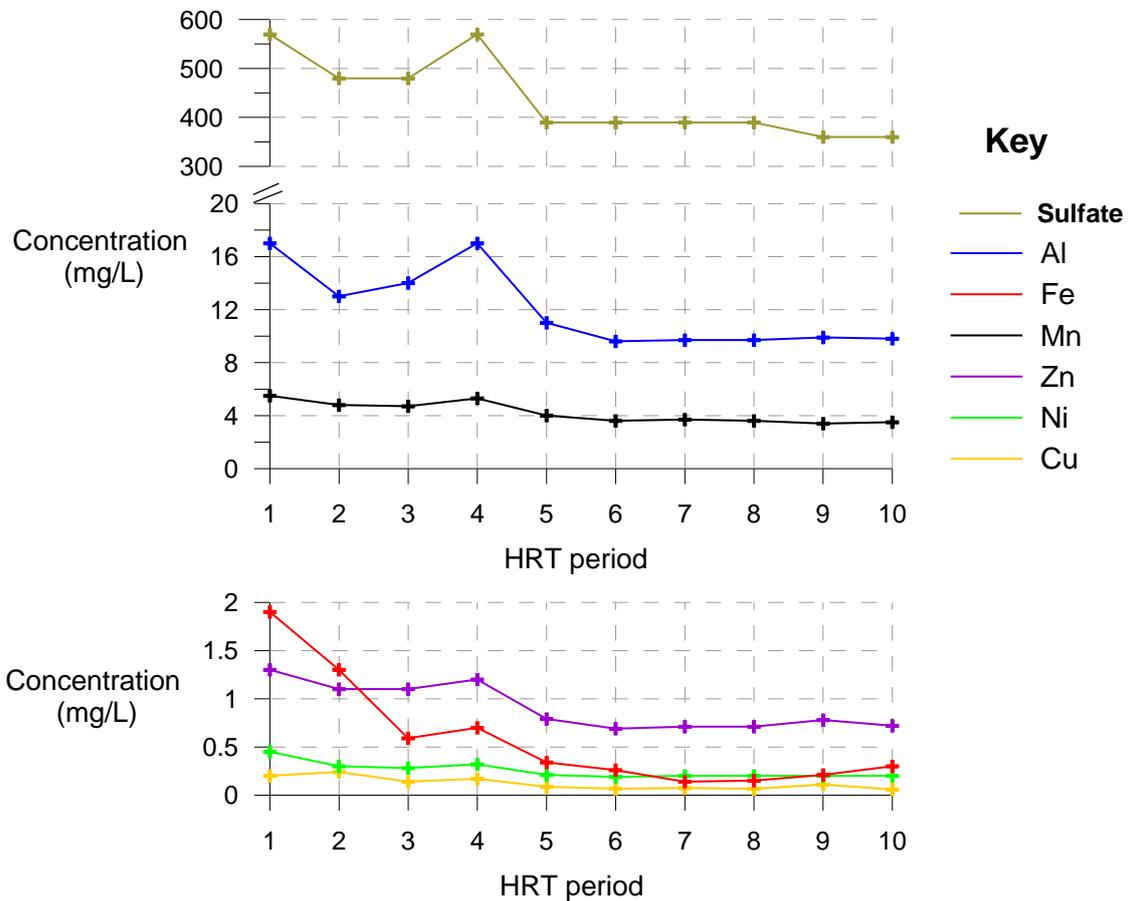
#### 4.4.1.2 Influent AMD

Influent AMD chemistry varied during laboratory trials of bench scale treatment systems (Table 4.5 and Figure 4.16). The pH of influent ranged between 3.92 and 3.23, and calculated acidity ranged between 72.3 and 128.5 mg/L CaCO<sub>3</sub>. Average influent metal concentrations were 11.3 mg/L for aluminium (9.6 – 17 mg/L), 0.57 mg/L for iron (0.14 – 1.9 mg/L), 3.9 mg/L for manganese (3.2 – 5.5 mg/L), 0.11 mg/L for copper (0.059 – 0.24 mg/L), 0.24 for nickel (0.19 – 0.45 mg/L), 0.87 mg/L for zinc (0.69 – 1.3 mg/L) and 44 mg/L for calcium (38 – 58 mg/L). Influent sulfate concentrations averaged 407 mg/L (360 – 569 mg/L). Appendix III (D) includes influent AMD water quality and chemistry data collected over the trial duration.

**Table 4.5: Summary of influent AMD water quality parameters and chemistry during laboratory trials of bench scale treatment systems. Units are mg/L unless otherwise specified. Acidity units are in mg/L as CaCO<sub>3</sub>. N is equal to 10.**

	Mean	Average	Min	Max
pH	-	3.46	3.23	3.92
Electrical conductivity (µS/cm)	824	793	727	1021
Dissolved oxygen	6.48	6.49	3.89	9.06
Calculated acidity	84.5	78.5	72.3	128.5
Measured acidity (pH 7)	91.2	96.7	85	125
Acid soluble aluminium	11.5	10.5	9.6	17
Acid soluble iron	0.59	0.32	0.14	1.9
Fraction ferric (Fe <sup>3+</sup> )	0.47	0.26	0.11	1.52
Acid soluble manganese	4.0	3.7	3.3	5.5
Acid soluble copper	0.12	0.099	0.059	0.24
Acid soluble nickel	0.24	0.2	0.19	0.45
Acid soluble zinc	0.87	0.77	0.69	1.3
Acid soluble calcium	45	41	39	58
Dissolved sulfate	416	390	360	569

Influent AMD metal concentrations for trial treatment systems were highest during initial HRTs periods (1 – 4) (Figure 4.16). After the fourth HRT period, however, influent metal concentrations decreased, and were less varied.



**Figure 4.16: Influent AMD acid soluble metal and sulfate (mg/L) concentrations for bench scale treatment systems after each hydraulic retention time (HRT) period.**

#### 4.4.1.3 Metal Analysis of Bench Scale Treatment System Settling Pond Effluent

Settling pond effluent represents final AMD treatment for bench scale SRBR, LLB and OLC systems, therefore, metal analysis at the end of each HRT period is presented for each system (Figure 4.17). Metal analysis of effluent directly from treatment systems (before settling ponds) is in Appendix, III (E).

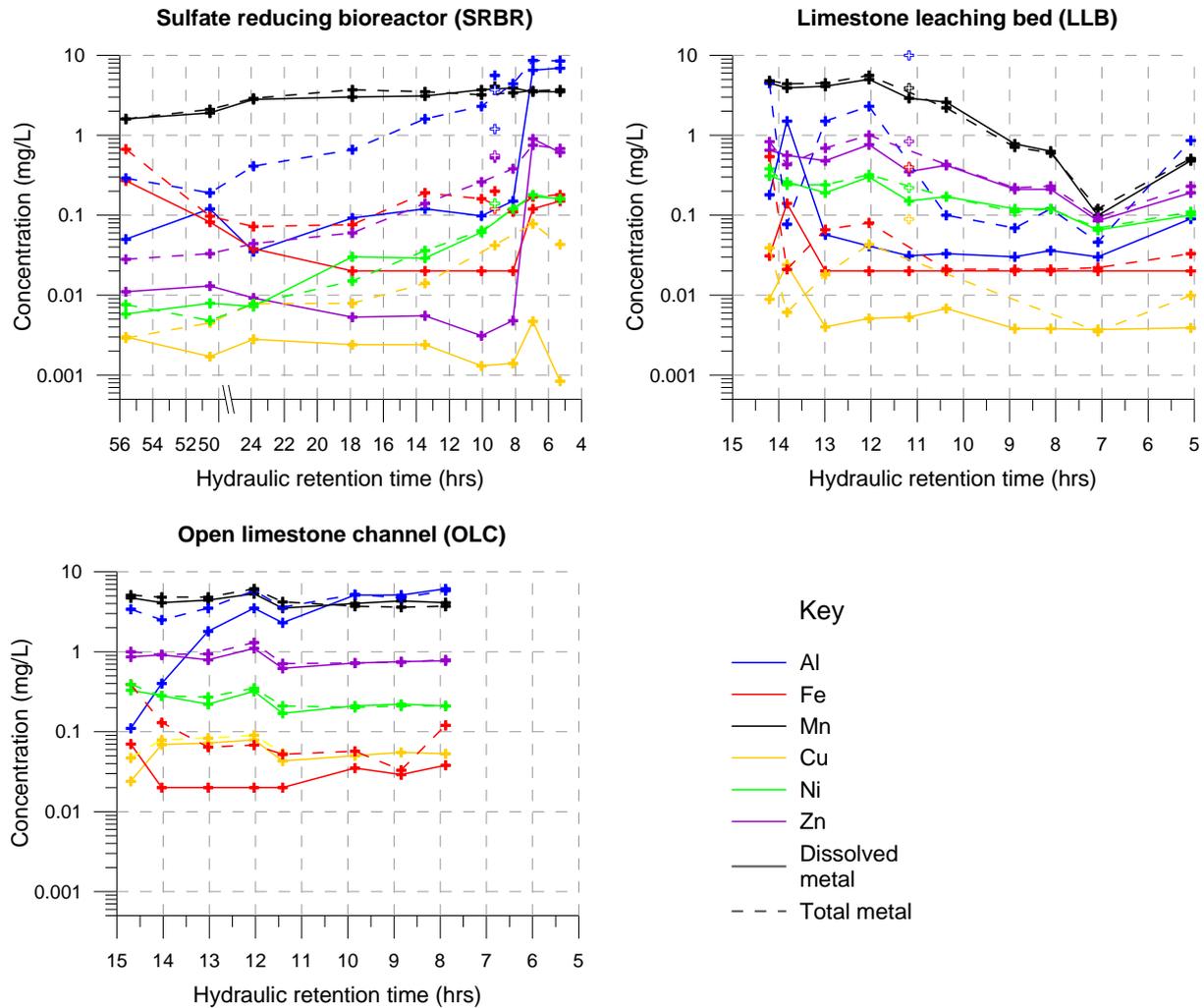
Metal concentrations in settling pond effluent differ for each treatment system (Figure 4.17). In general, metal concentrations increase as flow rates increase and HRT decreases, although for the LLB system metal concentrations The effectiveness of treatment at different HRTs for each system is indicated by minimum and maximum effluent metal concentrations.

Minimum dissolved and total (parentheses) metal concentrations in SRBR settling pond effluent were 0.035 mg/L (0.19 mg/L) for aluminium, <0.020 mg/L (0.072) for iron, 1.6 mg/L (1.6 mg/L) for manganese, 0.00084 mg/L (0.0029 mg/L) for copper, 0.0058 mg/L (0.0048 mg/L) for nickel, and 0.0031 mg/L (0.028) for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 6.9 mg/L (8.6 mg/L) for aluminium, 0.27 mg/L (0.67 mg/L) for iron, 4.1 mg/L (3.7 mg/L) for manganese, 0.042 mg/L (0.078 mg/L) for copper, 0.17 mg/L (0.18 mg/L) for nickel, and 0.90 mg/L (0.75 mg/L) for zinc.

Settling pond effluent for the LLB system had minimum dissolved and total (parentheses) metal concentrations of 0.030 mg/L (0.046 mg/L) for aluminium, <0.020 mg/L (<0.021 mg/L) for iron, 0.099 mg/L (0.12 mg/L) for manganese, 0.0037 mg/L (0.0035 mg/L) for copper, 0.065 mg/L (0.069 mg/L) for nickel, and 0.085 mg/L (0.094 mg/L) for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 1.5 mg/L (10 mg/L) for aluminium, 0.14 mg/L (0.54 mg/L) for iron, 5.0 mg/L (5.6 mg/L) for manganese, 0.024 mg/L (0.089 mg/L) for copper, 0.31 mg/L (0.38 mg/L) for nickel, and 0.76 mg/L (1.0 mg/L) for zinc.

Minimum dissolved and total (parentheses) metal concentrations in OLC settling pond effluent were 0.11 mg/L (2.5 mg/L) for aluminium, <0.020 mg/L (0.033 mg/L) for iron, 3.5 mg/L (3.6 mg/L) for manganese, 0.024 mg/L (0.047) for copper, 0.17 mg/L (0.20 mg/L) for nickel, and 0.62 mg/L (0.71 mg/L) for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 6.1 mg/L (5.8 mg/L) for aluminium, 0.070 mg/L (0.39 mg/L) for

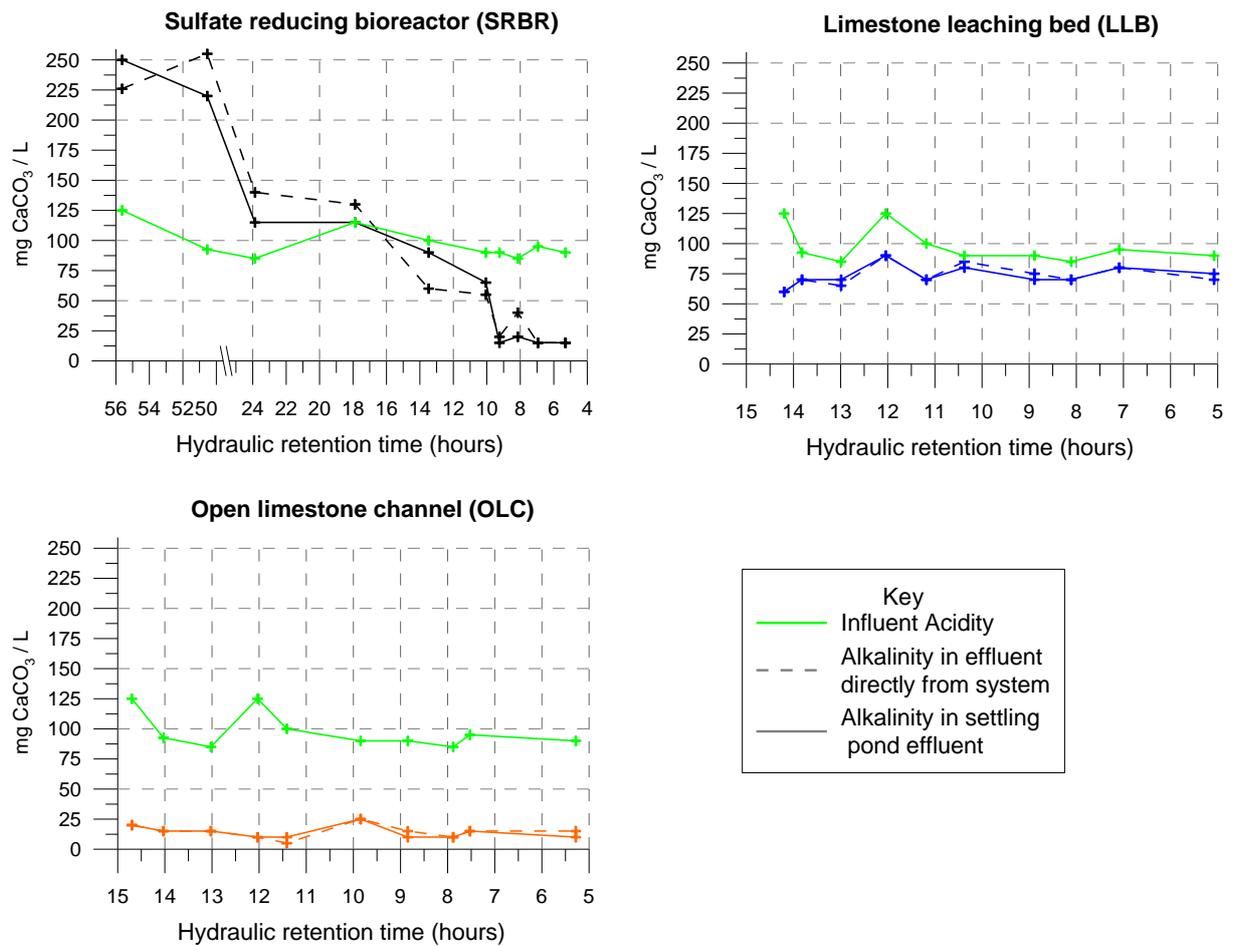
iron, 5.3 mg/L (6.1 mg/L) for manganese, 0.079 mg/L (0.090 mg/L) for copper, 0.33 mg/L (0.39 mg/L) for nickel, and 1.1 mg/L (1.3 mg/L) for zinc.



**Figure 4.17: Dissolved and total metal analysis (mg/L) of settling pond effluent for SRBR, LLB and OLC systems at different hydraulic retention times (hours).**

#### 4.4.1.4 Acidity and Alkalinity

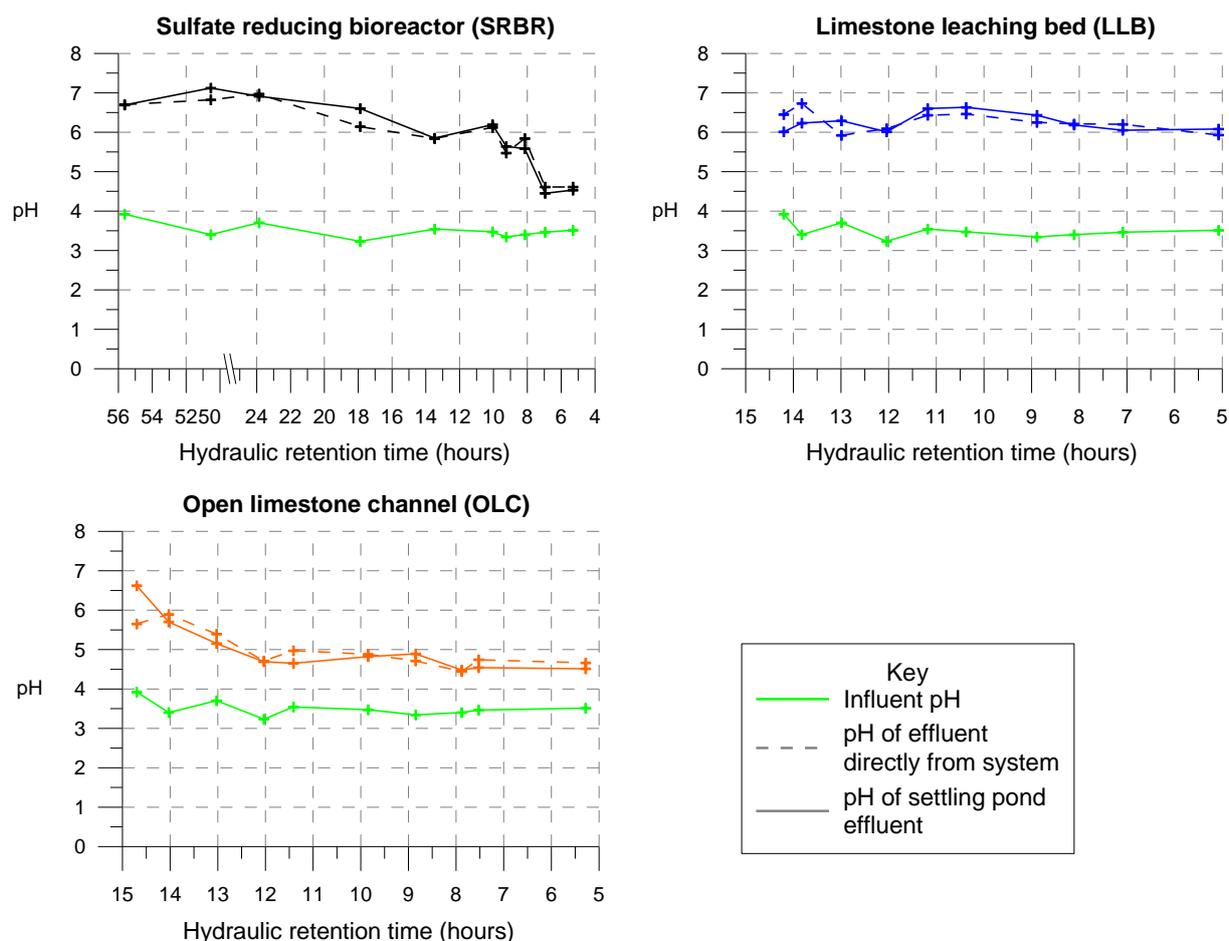
Influent AMD measured acidity (Figure 4.18) ranged between 85 and 125 mg CaCO<sub>3</sub>/L during bench scale treatment system trials. Alkalinity generation was greatest for the SRBR system (Figure 4.18), with effluent directly from the system containing 255 mg CaCO<sub>3</sub>/L at 51 hrs HRT. However, at HRTs <8 hours effluent alkalinity decreases to 15 mg CaCO<sub>3</sub>/L. Alkalinity generation is steady for the LLB system over the range of HRTs tested, averaging 74 mg/L CaCO<sub>3</sub> (60 - 90 mg CaCO<sub>3</sub>/L). Alkalinity concentrations were lowest in effluent from the OLC system, with values ≤25 mg CaCO<sub>3</sub>/L at every HRT tested.



**Figure 4.18: Measured influent acidity and effluent alkalinity (mg CaCO<sub>3</sub>/L) for SRBR, LLB and OLC systems at different hydraulic retention times (hours). Effluent includes discharge directly from treatment systems and discharge from settling ponds.**

#### 4.4.1.5 pH

The pH of influent AMD ranged from 3.23 to 3.92 during laboratory trials (Figure 4.19). The SRBR system produced the greatest increase (Figure 4.19), with a pH of 7.12 in settling pond effluent at 51 hours HRT. However, at HRTs <8 hours, pH decreases to a minimum of 4.45 in SRBR settling pond effluent. The pH of effluent from the LLB settling pond is most constant, and ranged between 6.01 and 6.63. Maximum pH for effluent from the OLC system was 6.62 (15 hours HRT), however, pH decreases to <5 at HRTs <13 hours.



**Figure 4.19: pH of influent and effluent for SRBR, LLB and OLC systems at different hydraulic retention times (hours). Effluent includes discharge directly from treatment systems and discharge from settling ponds.**

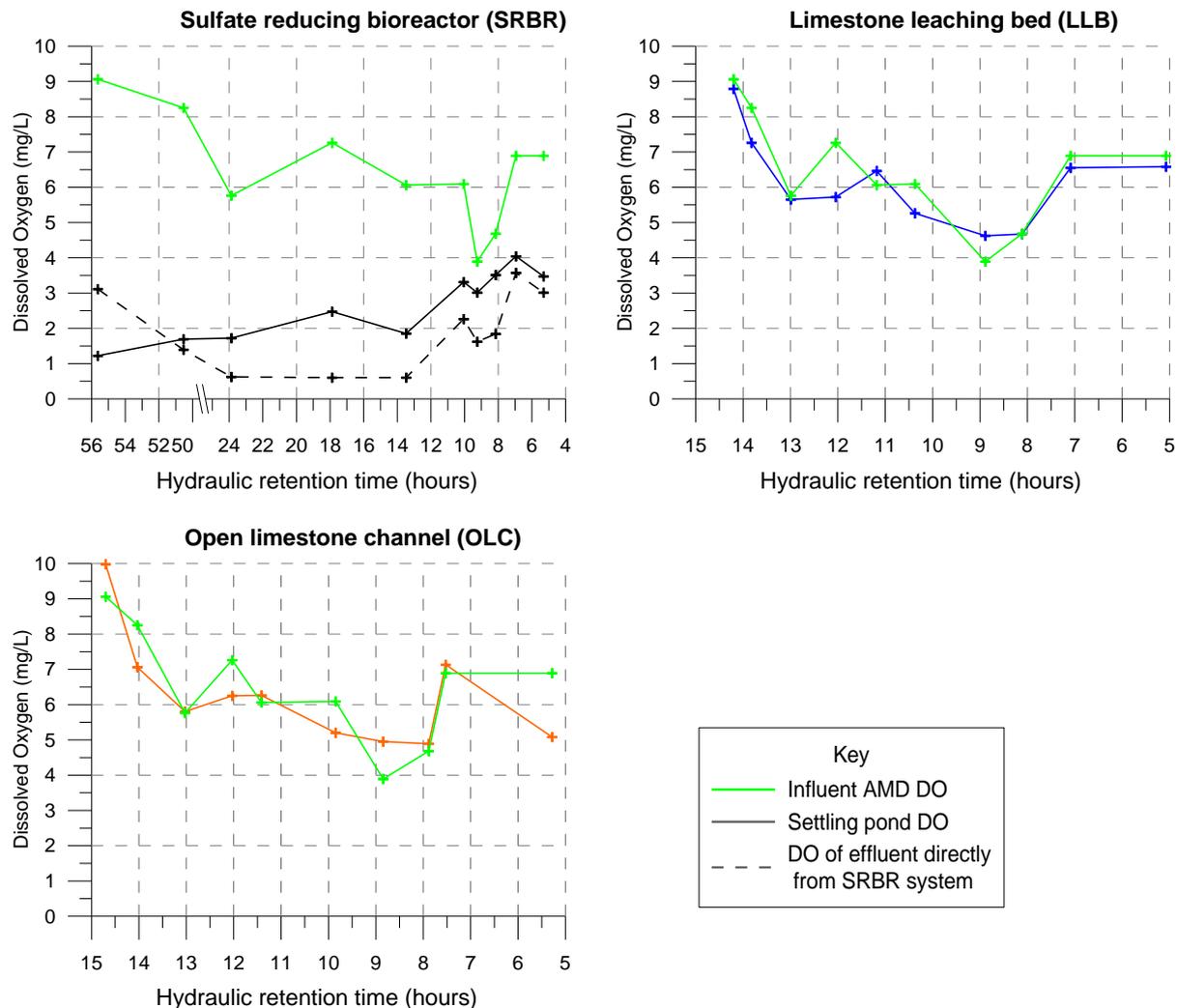
#### 4.4.1.6 Electrical Conductivity

Electrical conductivity ( $\mu\text{S}/\text{cm}$ ) measurements are very similar for influent AMD and effluent from treatment system settling ponds (Appendix III, E). Influent conductivity averaged  $824 \mu\text{S}/\text{cm}$  ( $727 - 1021 \mu\text{S}/\text{cm}$ ). The SRBR system had highest effluent conductivity, with  $1259 \mu\text{S}/\text{cm}$ , however, conductivity declines to  $672 \mu\text{S}/\text{cm}$  at 5 hours HRT. Conductivity of effluent from LLB and OLC treatment systems is similar to influent AMD.

#### 4.4.1.7 Dissolved Oxygen

Influent AMD dissolved oxygen (DO) concentrations averaged  $6.48 \text{ mg}/\text{L}$  ( $3.89 - 9.06 \text{ mg}/\text{L}$ ) (Figure 4.20). The SRBR settling pond had lowest settling pond DO concentrations ( $1.22 \text{ mg}/\text{L}$ ) and concentrations in effluent directly from the SRBR system between 24 and 14 hours

HRT were very low (0.6 mg/L). Influent and effluent DO concentrations for LLB and OLC settling ponds were similar to influent AMD, with average concentrations of 6.16 and 6.26 mg/L, respectively.

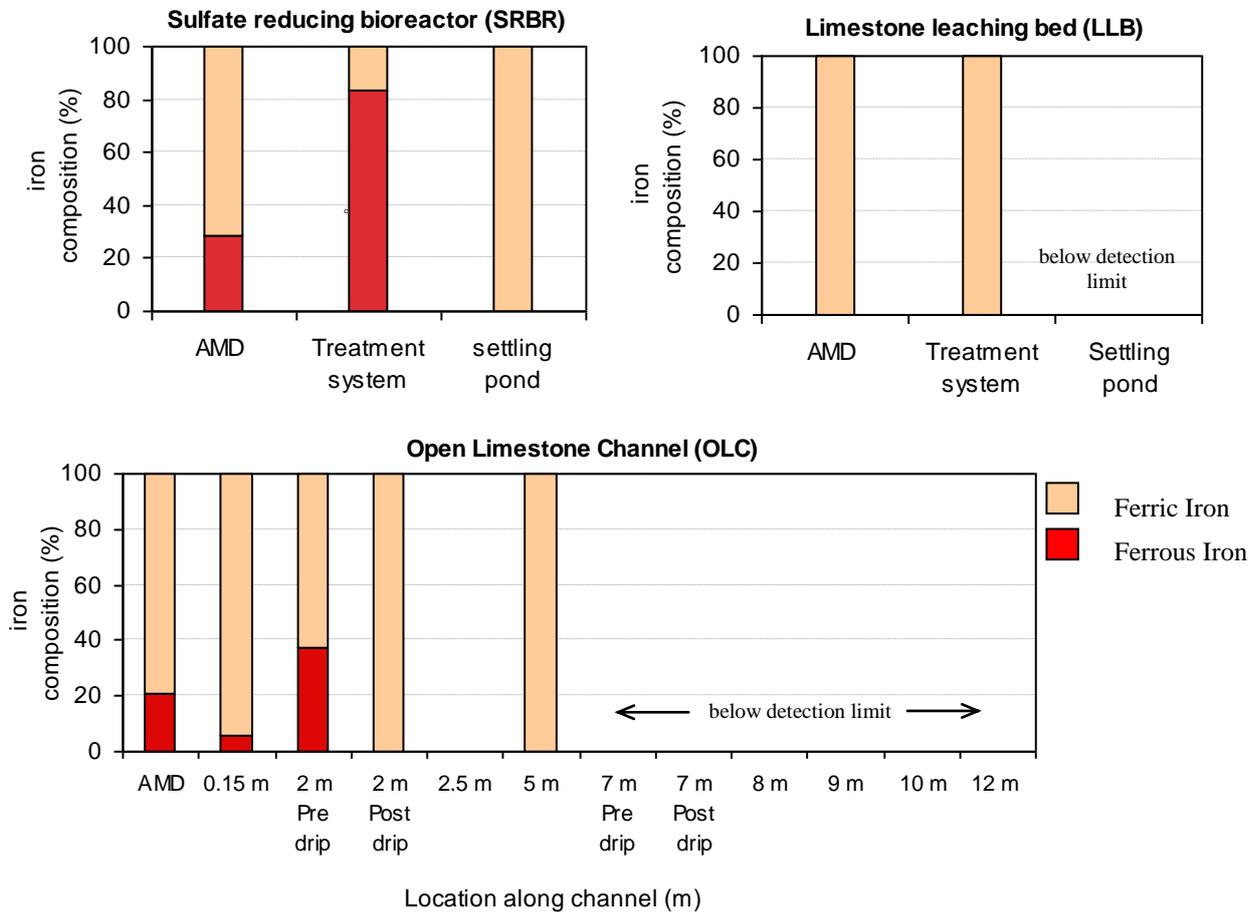


**Figure 4.20: Dissolved oxygen concentrations (mg/L) of influent AMD, treatment system settling ponds, and of effluent directly from the SRBR system at different hydraulic retention times (hours).**

#### 4.4.1.8 Influent and Effluent Iron Species Composition

The SRBR system displays the most change in iron speciation on the occasion sampled (Figure 4.21). The proportion of ferrous iron increases from 29% in influent AMD, to 83% in effluent discharged directly from the SRBR system, however, iron in settling pond effluent is then 100% ferric. Influent and effluent iron is 100% ferric for the LLB treatment system, and

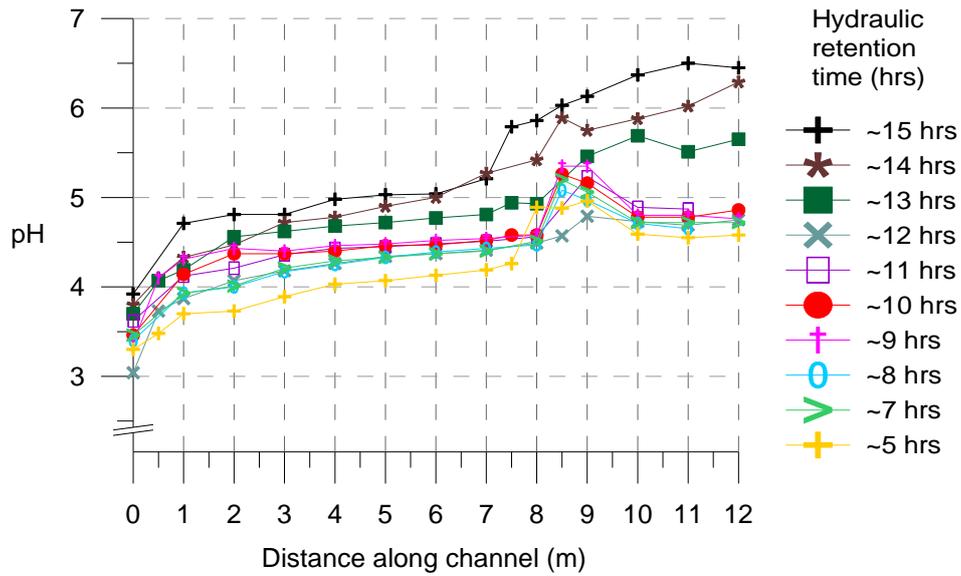
for the OLC system the proportion of ferrous iron decreases at post drip sampling points, at distances of 0.15 m and 2 m along the channel. Metal concentration data measured by the spectrophotometer are provided in Appendix III (D).



**Figure 4.21: Iron species composition (% ferrous or ferric) of influent and effluent for bench scale SRBR, LLB, and OLC treatment systems. Measurements obtained at 58 hrs HRT for the SRBR system, and 5 hrs for LLB and OLC systems. No iron composition data indicates concentrations below spectrophotometer detection limits.**

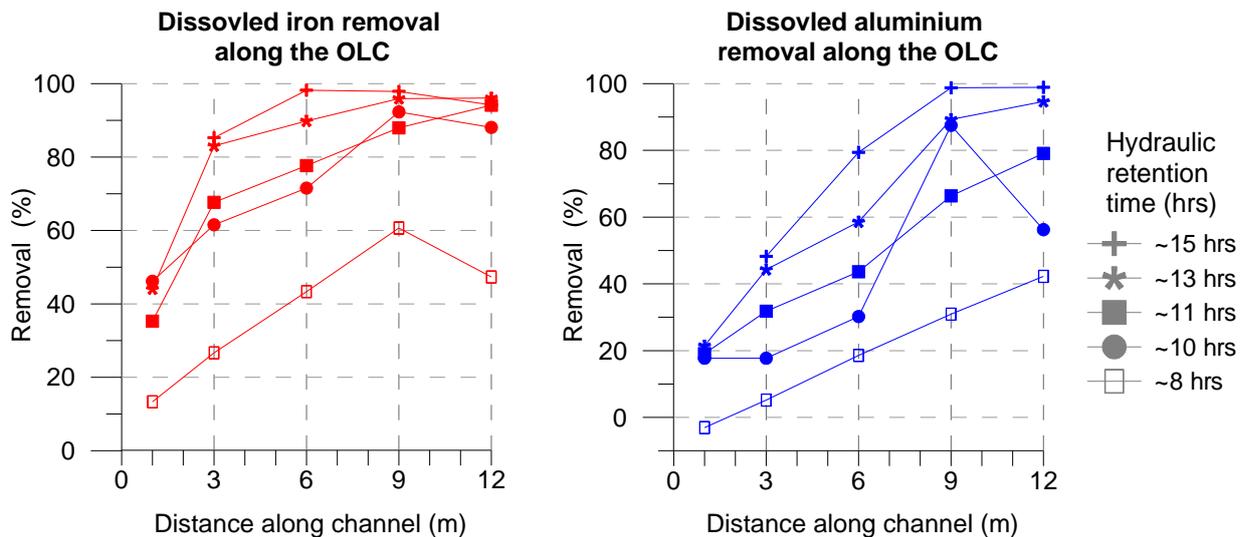
#### 4.4.1.9 pH, and dissolved iron and aluminium along the OLC treatment system.

The pH increases along the OLC system shown at approximately one meter intervals for each HRT tested (Figure 4.22). Overall, pH at measured distances decreases as HRT is shortened, with a maximum pH of effluent discharged from the system (at 12 m) of 6.45 at 15 hrs HRT, and a minimum of pH 4.58 at 5 hrs HRT. At all HRTs tested there is a spike in pH to about pH 5 between 7 m and 9 m along the channel.



**Figure 4.22: pH variation with distance along the OLC treatment system for each hydraulic retention time (hours).**

Removal of iron and aluminium is greatest at the longest HRT (15 hrs) in the OLC system (Figure 4.23). Maximum removal occurs at 6 m (98.2%) for iron, and at 12 m (98.8 %) for aluminium. Removal of iron and aluminium is lowest at the shortest HRT tested (8 hrs), with only 60.7% (Fe) and 42.3% (Al) removal.



**Figure 4.23: Dissolved iron and aluminium removal efficiency (%) along the OLC treatment system for different hydraulic retention times (hrs).**

#### **4.4.1.10 Observations**

##### **4.4.1.10.1 Sulfate Reducing Bioreactor**

The appearance of the SRBR treatment system differed over the trial duration (Figure 4.24). Ochre precipitate soon appeared on the SRBR underneath the AMD influent drip, along with ochre flocculent on the water surface. Ochre precipitate adhered to post peel at the SRBR surface and accumulated over time. Where mussel shells were emergent amongst the upper post peel layer, a white (and sometimes ochre) precipitate was present on the inside surface of the shell. Algae appeared on surface materials after ~80 days, and became more abundant as the trial progressed. An area that was mostly algae free was present corresponding to a shaded zone. At times during the trial areas of ochre precipitate on post peel at the surface changed to a black color for short periods of time (several hours), and bubbles and white flocculent on the water surface also appeared (i.e. day 30). Ochre precipitate appeared in the settling pond after 2 days, however, this turned light grey/brown and accumulated as this color until the end of the trial.

An odour of hydrogen sulfide was present about mid way through the second HRT period of 51 hours (19 days after operation began). The odour increased in strength to a point where a mask was required when water sampling was conducted. At day 80, mid way through the 9 hour HRT, the odour of hydrogen sulfide was noticeably weaker, and by day 108 (5 hours HRT) was very weak to absent.

Day 2 (56 hrs HRT)



Day 25 (51 hrs HRT)



Day 30 (24 hrs HRT)



Day 87 (8 hrs HRT)



Day 116 (58 hrs HRT)



**Figure 4.24: Photos of the SRBR treatment system showing changes over the trial duration.**

#### 4.4.1.10.2 Limestone leaching bed

White and ochre precipitate accumulated on the surface of the LLB system, and around limestone chips in the bed as the trial progressed, and white precipitate accumulated in the settling pond (Figure 4.25). By day 69, precipitates covered most limestone clasts and pore spaces on the surface of the LLB system. Between days 76 and 80 limestone chips within the bed darkened (black color), coinciding with a dark grey precipitate in the settling pond (day 87), and a black precipitate around the edge of the pond where effluent entered. As the trial progressed, the color within the within the limestone bed continued to darken, and grey precipitate continued to settle in the pond.

**Day 14 (14 hrs HRT)****Day 30 (13 hrs HRT)****Day 69 (11 hrs HRT)****Day 87 (8 hrs HRT)****Day 112 (15 hrs HRT)****Figure 4.25: Photos of the LLB treatment system showing changes over the trial duration.**

#### **4.4.1.10.3 Open limestone channel**

Soon after operation of the OLC treatment system (11 days) an ochre precipitate formed in the OLC treatment system and adhered to limestone clasts at the inflow (0 m) (Figure 4.26). However, ochre precipitate diminished with distance along the channel and was only minor at 1.0 m. At the start of the middle tier (2.0 m below drip from upper tier) another accumulation of ochre precipitate was present, and also diminished with distance. As the trial continued, ochre precipitate increasingly accumulated on limestone clasts in the channel (especially at 0 m and 2.0 m), and was gradually present further down the OLC system. However, ochre was not observed downstream of 5 m distance, except for a slight orange tinge at 7.0 m, and between 8.25 and 9 m).

White precipitate was present at 0.25 m, and gradually accumulated on limestone clasts and within the channel as the trial progressed. Between 7.0 m and 8.25 m (lower tier) the amount of white precipitate in the channel increased, developing into a thick white sludge within the channel. During initial HRTs (<13 hours HRT) white precipitate was not present on limestone chips downstream of 8.5 m. As the trial continued, white precipitate accumulated and a sludge zone completely filled the channel and covered limestone clasts between 8.25 m and 8.75 m. The sludge zone increased in length with time, to about 9.75 m, but after this distance precipitate density decreased, though remained present in smaller quantities until the outflow of the OLC system (12 m distance). The sludge zone varied in color with the upstream section a creamy orange (8.25 – 9.0 m), while between 9.0 – 9.75 sludge was whiter.

White precipitate in the settling pond accumulated soon after operation began and accumulated throughout the trial.

## Day 47 (12 hrs HRT)



## Day 108 (5 hrs HRT)



Figure 4.26: Photos along the OLC treatment system showing changes over the trial duration, and with increasing distance along the OLC system. Arrows at distances of 2 m and 7 m along the channel indicates which tier of the channel the photo relates to. An upwards arrow indicates the upper channel tier, and a downwards arrow indicates the lower channel tier (at an equivalent distance).

#### 4.4.1.11 Flushing Bench Scale Treatment Systems

Flushed water from the SRBR system is initially black/brown during the first 8 L flushed, but becomes increasingly clear and colorless after 15 L flushed, and a strong odor of hydrogen sulfide was present. Water flushed from the LLB treatment system was light grey in color for the duration of flushing (Figure 4.27) (Appendix III).

The surface of the SRBR treatment system was disturbed prior to flushing by collection of samples for autopsy analysis, therefore, observations relating to the affect of removing accumulated precipitates was not possible. The surface of the LLB treatment system after flushing (pre-autopsy) shows ochre and white precipitate remained on limestone clasts (Figure 4.27). During flushing, precipitate within the pore spaces of upper limestone clasts were dislodged and in motion, although, little vertical transport of precipitate downwards was observed.



**Figure 4.27: Flushing SBRB and LLB treatment systems. Treatment systems after flushing are shown on the right.**

The metal concentrations of flushed water from the LLB treatment system are highest for all analytes except calcium (Table 4.6).

**Table 4.6: Total metal analysis of water drained from the SRBR and LLB treatment systems during flushing (mg/L).**

<b>Total metals</b>	<b>SRBR</b>	<b>LLB</b>
<b>Aluminium</b>	69	510
<b>Calcium</b>	120	110
<b>Copper</b>	0.39	3.3
<b>Iron</b>	5.8	27
<b>Manganese</b>	3.9	30
<b>Nickel</b>	0.39	2.3
<b>Sulphur</b>	130	160
<b>Zinc</b>	3.7	24
<b>Sulphide</b>	8.2	-

## 4.4.2 Treatment System Autopsy

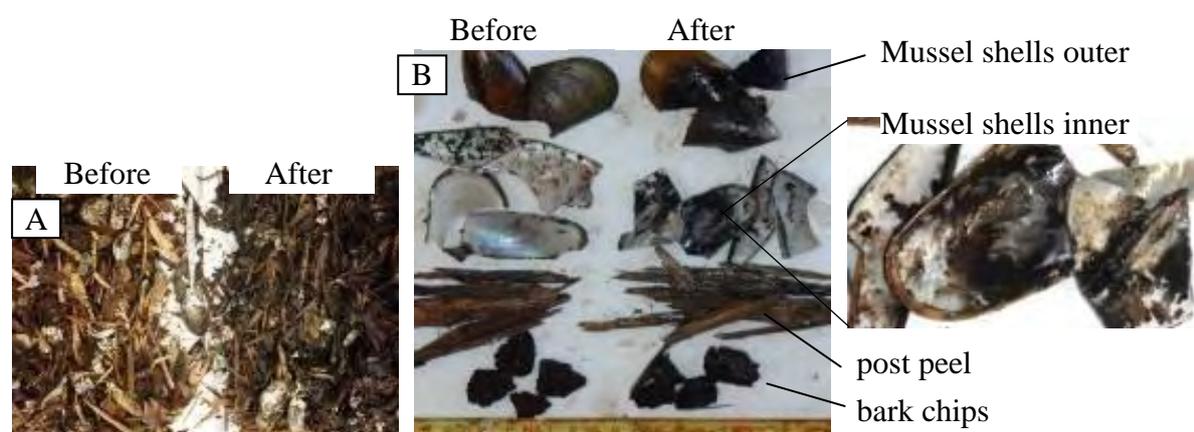
### 4.4.2.1 Sulfate Reducing Bioreactor

Autopsy of the SRBR system after 116 days of operation revealed a black-brown and light grey precipitate and sludge amongst the organic substrate mixture (Figure 4.28). No evidence of preferential flow paths was observed.



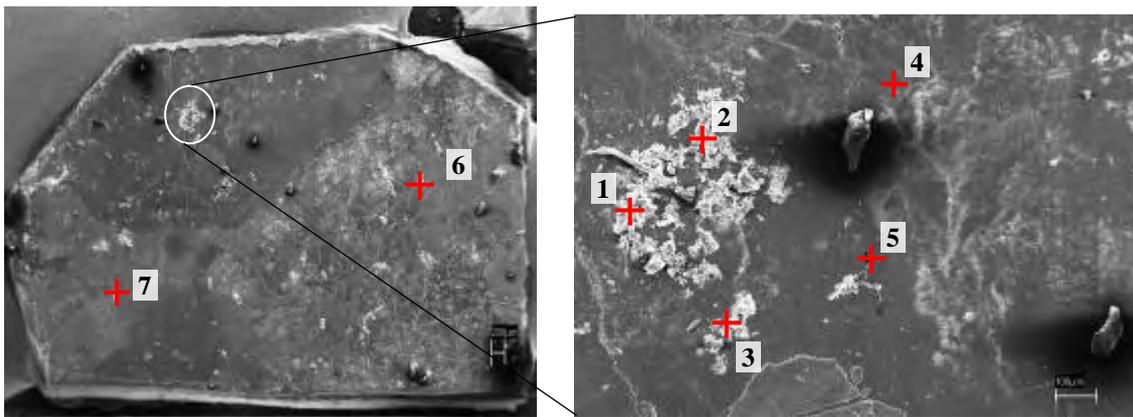
**Figure 4.28: Internal appearance of the SRBR treatment system reactive substrate mixture after AMD treatment. The upper post peel layer has been removed and the green shade cloth is seen at the bottom (spoon for scale).**

After autopsy the reactive substrate mixture of the SRBR system is darker in color and includes dark black-brown sludge material (Figure 4.29). A black precipitate is present adhering loosely to the inside surfaces of mussel shell samples after AMD treatment.

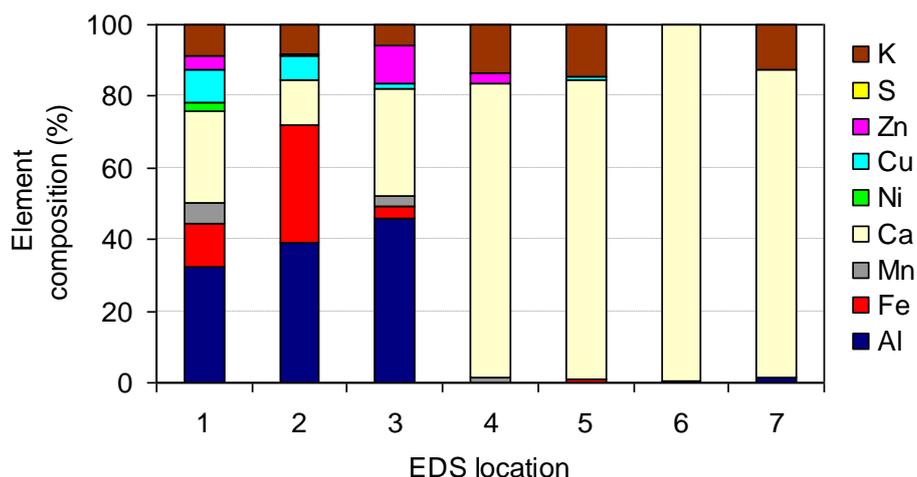


**Figure 4.29: SRBR system substrate materials before and after AMD treatment. A) Substrate mixture. B) Individual materials.**

Scanning electron microscopy (SEM) images of the inside surface a mussel shell sample after AMD treatment indicate irregular areas of metal accumulation are present (Figure 4.30). Energy dispersive spectrometry analysis (EDS) indicates the elemental composition of the mussel shell surface is mainly calcium (locations 4 - 7) (Figure 4.31). However, the irregular areas have high concentrations of metals, containing aluminium (45.7%), iron (32.7%), zinc (10.7%), copper (9.2%), manganese (5.7%) and nickel (2.3%) (locations 1 to 3).



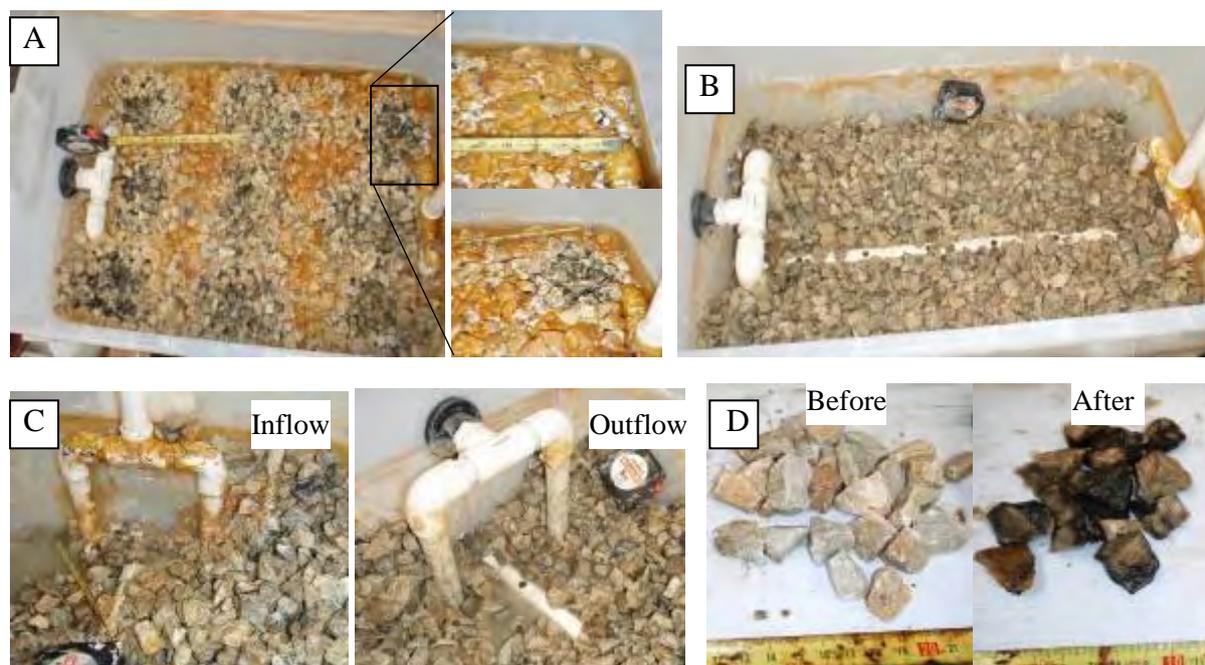
**Figure 4.30: SEM image of the inside surface of a mussel shell sample from the SRBR system after AMD treatment. Sample obtained from the centre of the lower section of the reactive substrate mixture. Numbers 1 - 7 indicate locations of EDS analysis.**



**Figure 4.31: Quantitative elemental composition analysis at EDS locations 1 – 7 on a mussel shell sample from the SRBR system after AMD treatment.**

#### 4.4.2.2 Limestone Leaching Bed

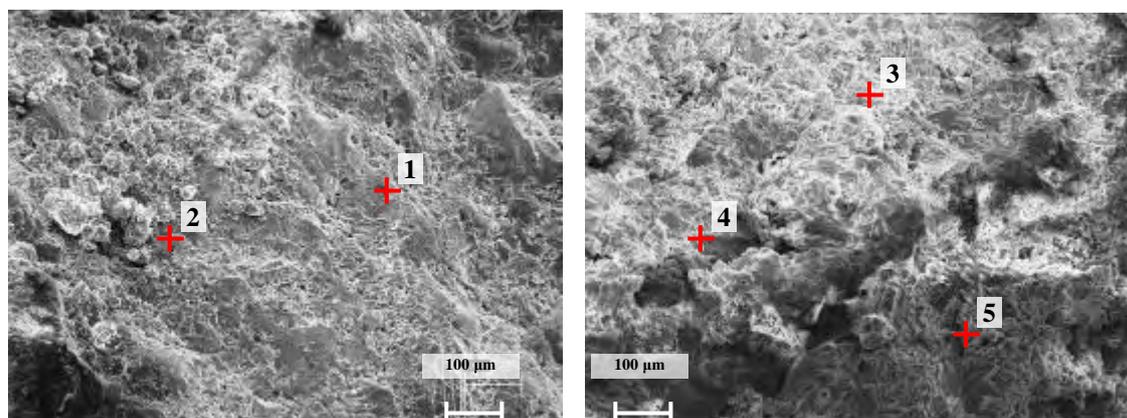
Autopsy of the LLB treatment system after 112 days of operation showed accumulations of ochre and white precipitate on limestone clasts at the surface, and within pore spaces in the limestone bed, especially near inflow piping (Figure 4.32). White precipitate was mostly present in pore spaces below the surface of the LLB system, decreasing with distance from the inflow and with depth into the bed. Most limestone clasts had a black precipitate adhering to clast surfaces.



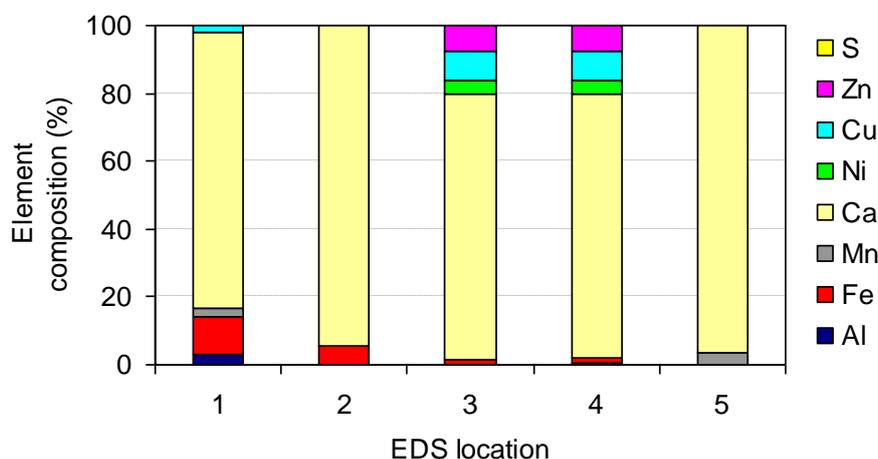
**Figure 4.32: Internal appearance of the LLB system during system autopsy. A) Surface of the limestone bed. B) Near the flush pipe at the bottom of the bed. C) Inflow and outflow. D) Limestone clasts before and after AMD treatment.**

Scanning electron microscopy images and elemental composition analysis (EDS) of two limestone clasts samples from the LLB treatment system after AMD treatment give differing results (Figures 4.33 - 4.36). The surface of a limestone clast from near the inflow end has an irregular, sugary texture (Figure 4.33), and is composed primarily of calcium with concentrations  $\geq 77.9\%$ . Maximum concentrations for other metals are 11.5% for iron, 8.3% for copper, 7.8% for zinc, 4.1% for nickel, 3.6% for manganese, and 2.8% for aluminium (Figure 4.34). However, another limestone clast sample obtained near the outflow of the LLB system displays metal precipitate, and nodules ranging from about 5 – 40  $\mu\text{m}$  in diameter on the limestone surface (Figure 4.35). Elemental composition analysis of surficial metal

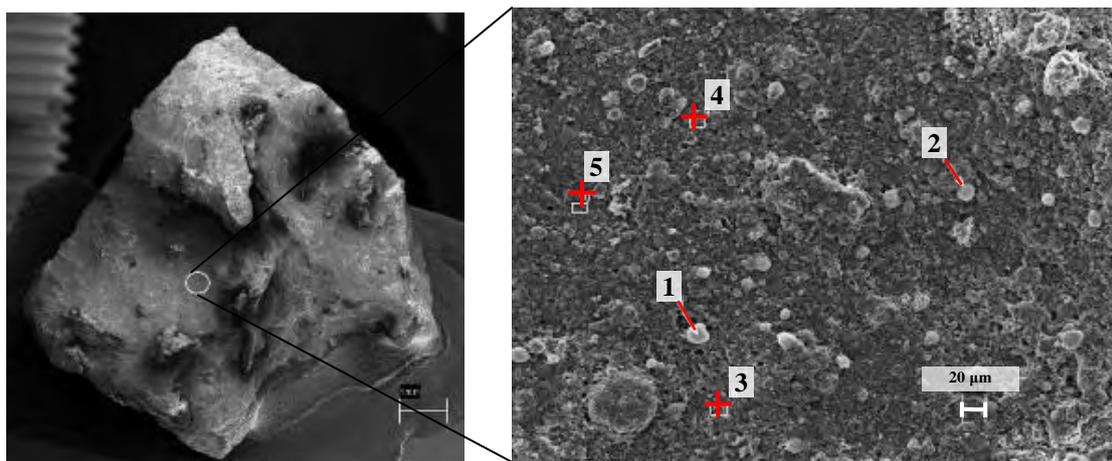
precipitate (EDS locations 3 - 5) indicate that it is iron rich (>78.0%), with aluminium in minor concentrations ( $\leq 14.3\%$ ) (Figure 4.36). Analysis at locations 1 and 2 indicate nodules are composed mainly of manganese (up to 52.4 %), and also contain iron ( $\leq 26.1\%$ ), zinc ( $\leq 9.6\%$ ), aluminium ( $\leq 5.8\%$ ), copper ( $\leq 1.9\%$ ) and nickel ( $\leq 1.0\%$ ).



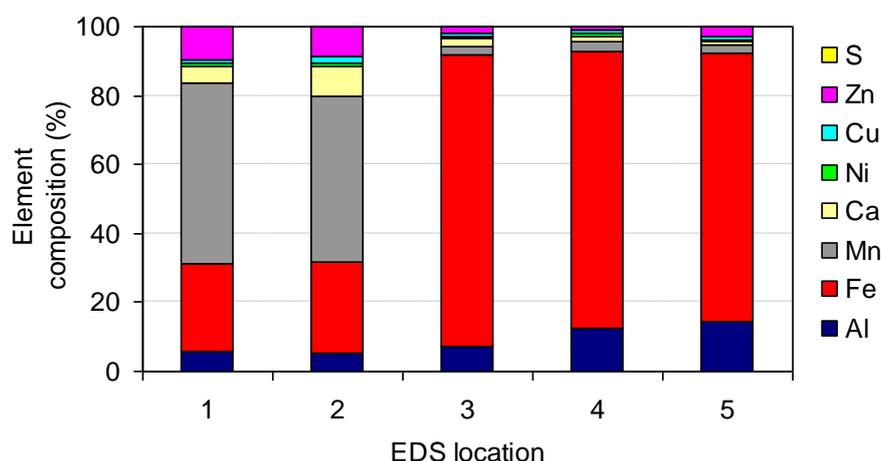
**Figure 4.33: SEM image of the surface of a limestone clast from the LLB system after AMD treatment. Sample obtained from the lower-mid section near the inflow. Numbers 1 - 5 indicate locations of EDS analysis.**



**Figure 4.34: Quantitative elemental composition analysis at EDS locations 1 – 5 of a limestone clast sample from the LLB system after AMD treatment.**



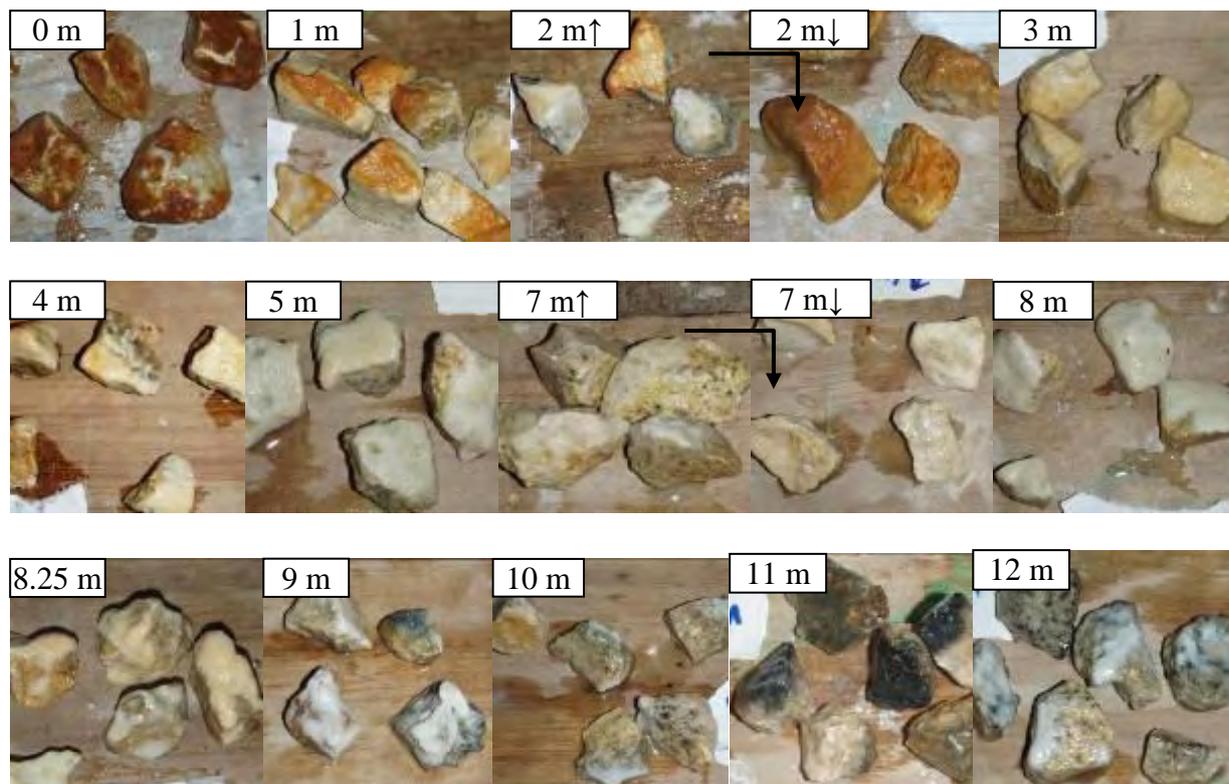
**Figure 4.35: SEM images of a limestone clast from the LLB system after AMD treatment. Sample obtained from the lower-mid section near the outflow. Numbers indicate locations of EDS analysis.**



**Figure 4.36: Quantitative elemental composition analysis at EDS locations 1 – 5 on a limestone clast sample from the LLB system after AMD treatment.**

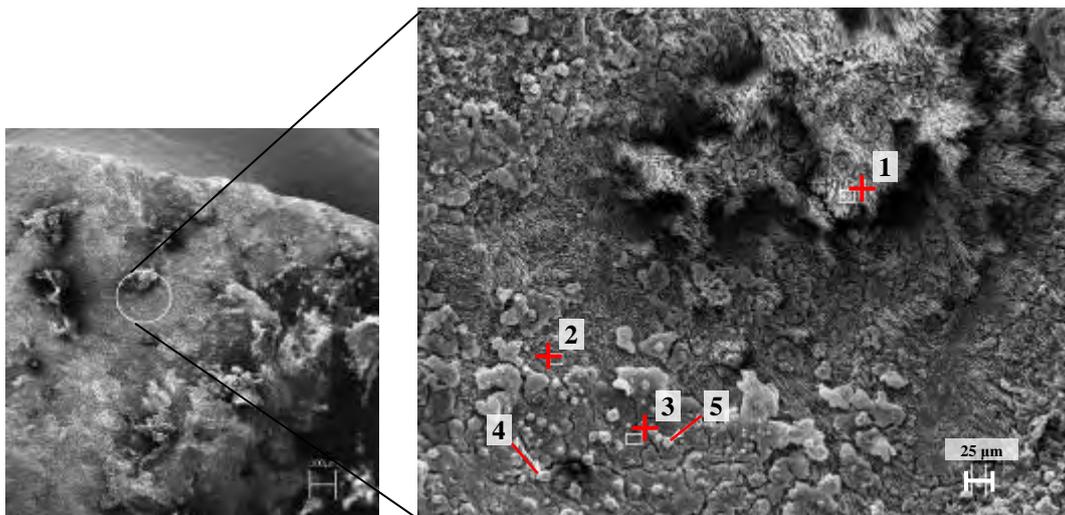
#### 4.4.2.3 Open limestone channel

Limestone clasts in the OLC treatment system have more ochre precipitate at 0 m, 1 and 2 m distance (below influent AMD drip and at the beginning of the middle tier) but precipitate diminishes with distance along channel (Figure 4.37). Ochre precipitate forms an encrusting over clasts indicative of iron armouring, especially clasts at the inflow. White precipitate is present on clasts from about 1 m distance to the OLC system outflow at 12 m distance. Black precipitate that had a spotty appearance is present on limestone clasts at 2 m distance, and increases in abundance along the channel, becoming particularly prominent on clasts downstream of 8.5 m.

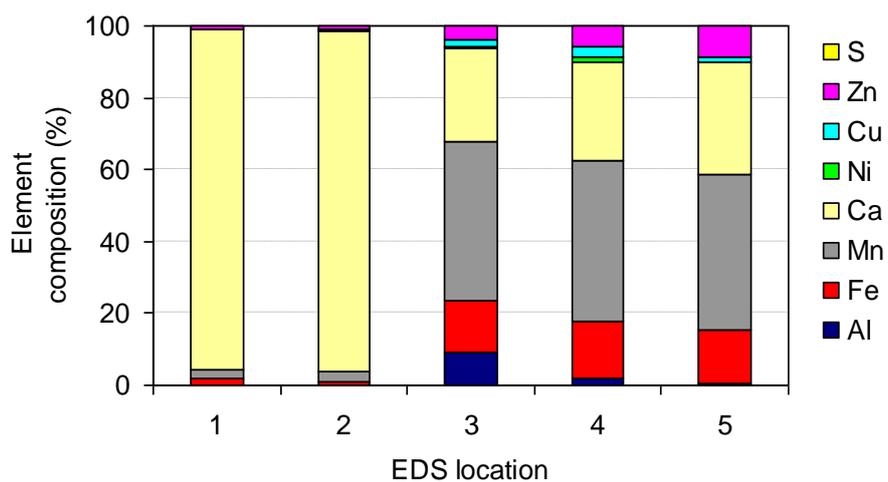


**Figure 4.37: Limestone clasts showing metal precipitation with distance along the OLC system. Black arrows at 2 m and 7 m locations indicate drip points where AMD is transferred to the channel tier below.**

A limestone clast from 12 m distance along the OLC treatment system after operation has a surface texture with sharp elongated crystal-like structures, overlain by a thin, relatively smooth platy layer (Figure 4.38). Rounded nodules are approximately 5 – 20  $\mu\text{m}$  across and are present amongst the overlying smooth layer. Elemental composition analysis (Figure 4.39) indicates sharp elongated structures (locations 1 and 2) are composed mostly of calcium ( $\leq 94.7\%$ ), while the overlying layer and nodules (locations 3, 4, 5) comprise mainly manganese ( $\leq 44.4\%$ ), with smaller proportions of iron ( $\leq 16.0\%$ ), aluminium ( $\leq 9.1\%$ ) and zinc ( $\leq 8.5\%$ ).



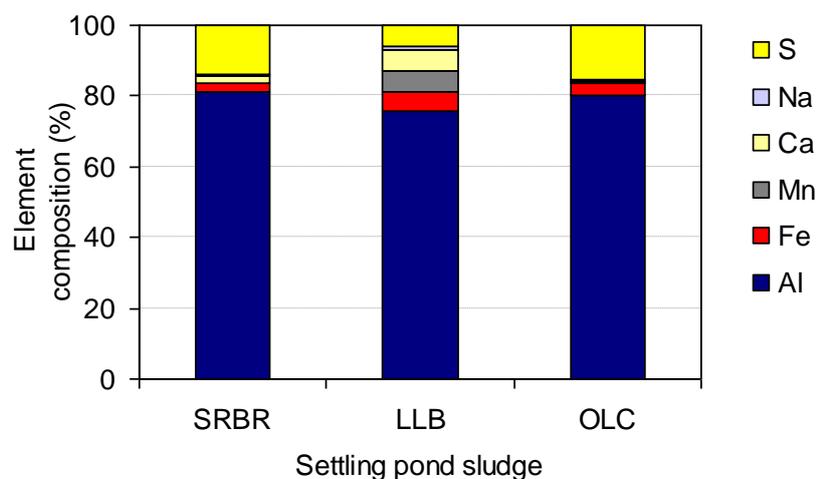
**Figure 4.38:** SEM image of a limestone clast from the OLC system after AMD treatment. Sample obtained from the outflow (12 m distance along the OLC). Numbers 1 – 5 indicate locations of EDS analysis.



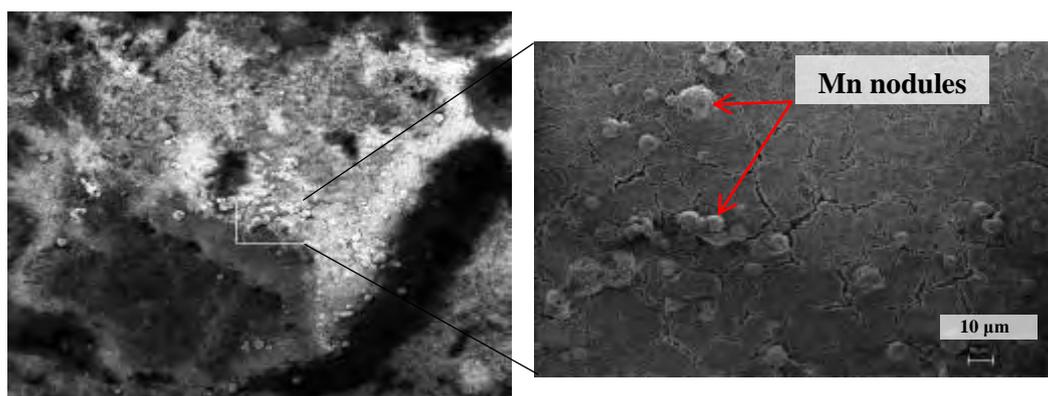
**Figure 4.39:** Quantitative elemental composition analysis at EDS locations 1 – 5 on a limestone clast from the OLC system after AMD treatment.

#### 4.4.2.4 Settling pond sludge

X-ray fluorescence analysis of settling pond sludge from each treatment system indicates sludge is composed mainly of aluminium ( $\geq 76.0\%$ ) (Figure 4.40). Sludge from the LLB system contains higher proportions of manganese (6.1%), calcium (5.6%) and iron (5.2%) than sludge from SRBR or OLC systems. XRF analysis is similar to the composition determined from SEM analysis (Appendix III, E). A SEM image of LLB settling pond sludge shows nodules are present (Figure 4.41), which have similar composition to those present on limestone clast surfaces from the treatment system (Appendix III, D).

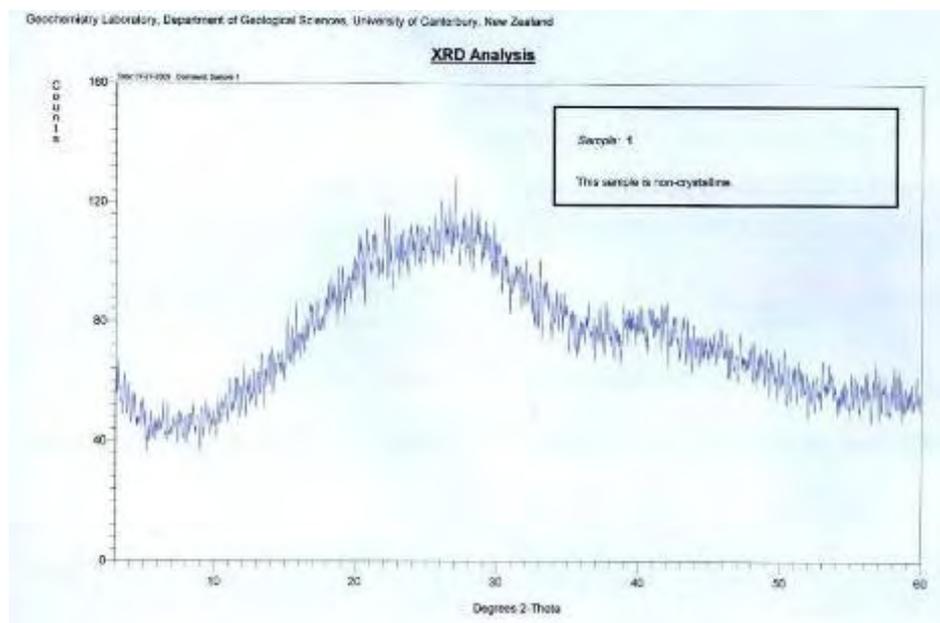


**Figure 4.40: Bulk elemental composition of SRBR, LLB and OLC settling pond sludge determined by X-ray fluorescence analysis.**



**Figure 4.41: SEM image of LLB settling pond sludge showing rounded manganese nodules and sludge in the background.**

X-ray powder diffraction analysis of SRBR, LLB and OLC settling pond sludge returned rounded diffraction patterns with no distinct peaks, indicating sludge samples were non-crystalline (Figure 4.42) (Appendix III, E).

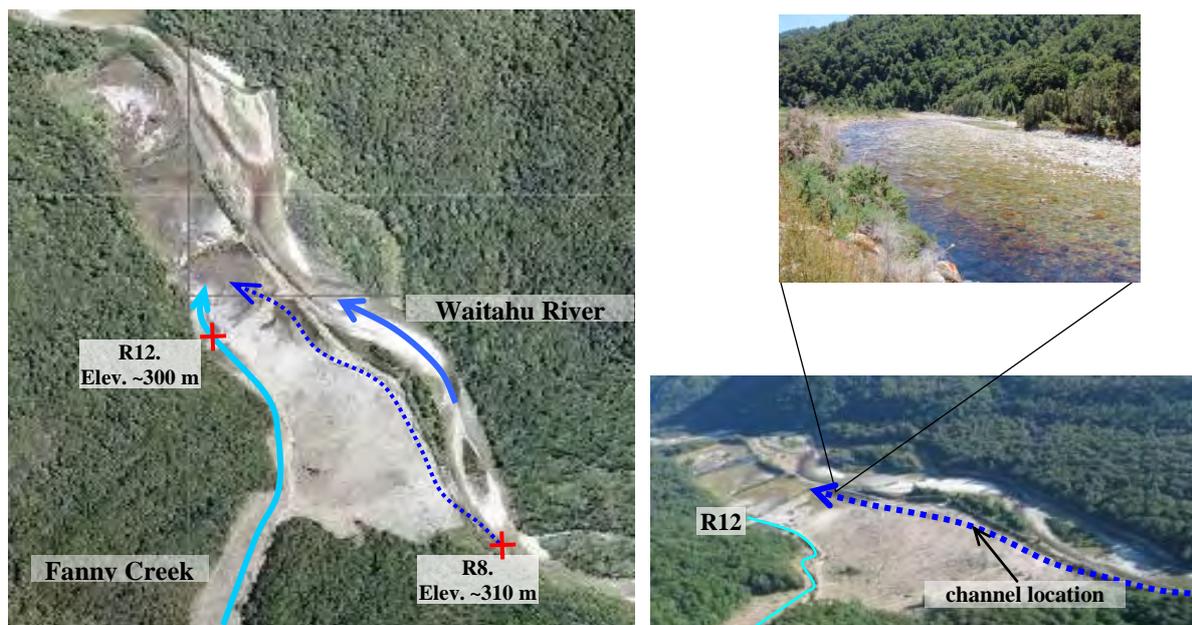


**Figure 4.42: X-ray power diffraction pattern of sludge from the SRBR system settling pond.**

#### **4.4.3 The Waitahu River Mixing Option**

Field observations indicate the elevation of the proposed Fanny Creek AMD treatment area (site R12) is above the adjacent level of the Waitahu River by about 3 – 4 m (Figure 4.43). However, further up valley at monitoring site R8 the Waitahu River is closer to the level of the sediment fan, although the river bed is still about 2 m lower than the fan surface. Desktop investigation of topography confirms an elevation drop from site R8 to R12, from about ~310 m to ~300 m (Google Earth, 2010). Therefore, river water could be transferred under gravity for mixing with Fanny Creek AMD.

A passive technology for lifting water was also investigated to determine if such a system could be more economic than gravity flow with its associated channel construction costs. The Hydraulic Ram Pump System was identified, which operates without electricity and uses the ‘water hammer’ effect to transfer water from a lower to higher elevation (Jennings, 1996, WOT, 2010) (Appendix III, E).



**Figure 4.43: Potential channel location to transfer water from the Waitahu River (site R8) to the proposed AMD treatment area (site R12).**

Monthly monitoring show the Waitahu River is slightly alkaline, with an average concentration of 23 mg CaCO<sub>3</sub>/L (15 – 30 mg CaCO<sub>3</sub>/L) (Table 4.7). The calculated ratio of Waitahu River water required to neutralize Fanny Creek AMD at site R12 averaged 1.1 (1.1 part river water to 1 part AMD). However, an average ratio of 2.7 is required to neutralize more acidic AMD from site IB5c. Worst case conditions give calculated ratios of 2.2 and 4.7 for neutralization of AMD at sites R12 and IB5c, respectively.

Ratios calculated from monthly acidity and alkalinity data indicate that about 16 L/s (1.1 – 45 L/s) of Waitahu River water needed to neutralize Fanny Creek AMD at site R12, while roughly 39 L/s (2.5 – 120 L/s) is required for neutralization of AMD at IB5c (Table 4.7). However, assuming worst case conditions, a much greater volume of river water is required, with 65 L/s needed for neutralization of AMD at R12, and 140 L/s needed for AMD at site IB5c.

**Table 4.7: Summary of monthly monitoring data used to calculate the flow volume of Waitahu River water (L/s) required to neutralize Fanny Creek AMD to pH 5. Parameters include measured Fanny Creek acidity at sites R12 and IB5c (mg CaCO<sub>3</sub>/L), Waitahu River alkalinity at site R8 (mg CaCO<sub>3</sub>/L), calculated ratio required for neutralization of AMD, and flow rate (L/s) at R12.**

Month	Fanny Ck acidity (pH 5)		Waitahu Alkalinity (pH 3.7)	Calculated ratio to neutralise AMD to pH 5		Fanny Ck flow rate (L/s)	Waitahu River flow rate (L/s) needed for AMD neutralization	
	R12	IB5c	R8	R12	IB5c	R12	R12	IB5c
Feb	32.5	65	25	1.3	2.6	4.9	6.3	12.6
Mar	30	47.5	25	1.2	1.9	13.3	16.0	25.3
April	10	55	25	0.4	2.2	5.5	2.2	12.1
May	22.5	50	30	0.75	1.7	1.5	1.1	2.5
July	22.5	60	15	1.5	4.0	30	45.0	120
Sept	20	70	-	-	-	-	-	-
Oct	32.5	60	17.5	1.9	3.4	16.3	30.2	55.7
Nov	20	70	20	1.0	3.5	20	20.0	70.0
Jan	27.5	55	25	1.1	2.2	6.0	6.8	13.2
<b>Average</b>	24.2	59.2	23	1.1	2.7	12.2	15.9	38.9
<b>Worst case conditions</b>	32.5	70	15	2.2	4.7	30	65	140

Addition of Waitahu River water to Fanny Creek AMD from the R12 monitoring site was completed to verify the river water volumes (L/s) calculated from monthly acidity and alkalinity data (Table 4.8). Mixing of water samples collected from the months of October, November and January give actual ratios of 1.8, 1.52 and 1.0, respectively. Calculated ratios from measured acidity and alkalinity monitoring data for corresponding months are 1.86, 1.0, and 1.1, respectively.

**Table 4.8: Mixing of Waitahu River water with Fanny Creek AMD (R12) to verify calculated volume (L/s) of river water for neutralization of AMD to pH 5.**

Month	Fanny Creek vol. (ml)	Waitahu vol. (ml) added to neutralise to pH 5	Actual ratio to neutralize to pH 5	Calculated ratio to neutralize to pH 5
Oct	50	90	1.80	1.86
Nov	50	76	1.52	1.0
Jan	50	50	1.00	1.1

## CHAPTER FIVE

### Discussion of Passive AMD Treatment System

#### Laboratory Trials

##### 5.1 Introduction

This chapter discusses the results of laboratory trials of bench scale passive AMD treatment system, and their success with regard to treating Fanny Creek AMD. The trial of SRBR, LLB and OLC treatment systems was designed to monitor treatment effectiveness of systems while influent AMD flow rates were adjusted and hydraulic retention times (HRT) shortened. Influent AMD chemistry for the trial is analysed and compared to AMD at the proposed treatment site (R12) to determine whether results represent treatment of appropriate AMD.

Treatment effectiveness for bench scale SRBR, LLB and OLC systems is established by analysis of metal removal efficiencies with a focus on effluent from treatment system settling ponds because these are indicative of final treatment performance. Metal removal efficiencies of effluent directly from treatment systems (prior to settling ponds) are provided in Appendix IV, A. Several aspects of AMD treatment are assessed including:

- The overall effectiveness of AMD treatment for each system is outlined by a description of metal removal efficiencies at different HRTs during the trial.
- The influence of settling ponds on final treatment performance. This is determined by comparing metal removal efficiencies before and after treatment system settling ponds.
- Whether changes in treatment performance occur over time. This is determined by comparison of metal removal efficiencies at control HRTs (similar HRTs at beginning, middle and end of the trial)
- The degree of sulfate removal and increase (export) in calcium concentrations in effluent relative to influent AMD. Sulfate removal and calcium export efficiencies reflect the extent of bacterial sulfate reduction and limestone dissolution, respectively.
- Identification of treatment trends, processes, failure thresholds and effective operating ranges of trial systems.

Treatment performance and processes operating to remediate AMD can be identified in each bench scale treatment system. In some systems mechanisms for neutralization of acidity and removal of metals are identified. Trends in data analysis (particularly metal removal) can be combined with other water chemistry (alkalinity) and quality (pH, dissolved oxygen) results to interpret physical, chemical and biological processes that act to treat AMD, and their response as HRT shortens. Data from autopsy analysis of systems is used to support these interpretations. Passive treatment systems are susceptible to problems that can reduce long term effectiveness of AMD treatment, therefore, limitations of each treatment system are addressed, with particular reference to autopsy analysis and system flushing results. Interpretation and understanding of processes that govern acidity and metal removal in passive treatment systems gives an insight into effectiveness and longevity of treatment systems. This interpretation assists with selection and design of optimal passive treatment strategies for Fanny Creek AMD.

Criteria for the design and implementation of passive AMD treatment systems are used to estimate the size of a treatment system needed to treat the AMD water chemistry and flow rate (PIRAMID, 2003). After interpretation of results, optimal acid neutralization and metal removal thresholds with respect to HRT are determined for SRBR, LLB and OLC systems in this study, along with other specific requirements for effective AMD treatment. These are used to derive HRT design criteria for each trial bench scale treatment system, which are compared to criteria suggested by other authors. The performance and design criteria established in this study are applied to future operations and AMD treatment at Island Block mine.

## 5.2 Bench Scale SRBR, LLB and OLC Treatment Systems

### 5.2.1 Influent AMD

The variation of influent AMD chemistry during laboratory trials of bench scale passive treatment systems occurred because AMD was collected on three different occasions from Fanny Creek (separated by about a month), and chemistry changed slightly in response to flow conditions in the catchment (Table 4.5 and Figure 4.16). Highest metal concentrations occurred during initial HRT periods, however, about half way through the trial (5<sup>th</sup> HRT period) influent chemistry became more stable, except for iron which was minimum at the 7<sup>th</sup> HRT period (Figure 4.16). Influent aluminium concentrations almost halved, from 17 mg/L initially to 9.6 mg/L (6<sup>th</sup> HRT period). Iron, copper and zinc concentrations decreased about an order of magnitude, from 1.9 to 0.14 mg/L, 0.24 to 0.059 mg/L, and 1.3 to 0.69 mg/L, respectively, throughout the trial. Similarly, influent acidity was greatest initially (1<sup>st</sup> and 4<sup>th</sup> HRT periods) with a measured concentration up to 125 mg CaCO<sub>3</sub>/L, but also varied as the trial progressed (85 - 100 mg CaCO<sub>3</sub>/L) (Figure 4.18). Influent acidity was primarily related to mineral acidity (generated during metal hydrolysis) as indicated by the similarity in measured and calculated acidity values (Table 4.5). This degree of variation in influent chemistry is not ideal for comparing the treatment performance of trial systems at different HRTs; however, it is representative of AMD conditions at Fanny Creek.

Influent AMD used for bench scale trials is representative of worst likely AMD at the proposed treatment site (R12). This is because minimum calculated acidity of influent during trials (72.3 mg CaCO<sub>3</sub>/L) is greater than the maximum acidity calculated from monthly monitoring at R12 (54.6 mg CaCO<sub>3</sub>/L). However, average acid soluble iron concentration during the trial was 0.59 mg/L, which is lower than the monthly Fanny Creek average at site R12 (1.8 mg/L). Average dissolved oxygen concentrations are also lower for the trial, (6.48 mg/L compared to 7.98 mg/L), which suggests influent for bench scale trials may contain more ferrous iron than at Fanny Creek.

### 5.2.2 Effluent Data Analysis

The purpose of data analysis was to standardize treatment performance of trial treatment systems in relation to influent and effluent metal concentrations. Data analysis focused primarily on treatment efficiencies for metal removal. Calculated acidity and metal loadings

and removal were also determined for the SRBR treatment systems to allow comparison with other studies.

Metal removal treatment efficiencies were considered on a percent basis and computed using the following equation where X represents metal concentrations (mg/L):

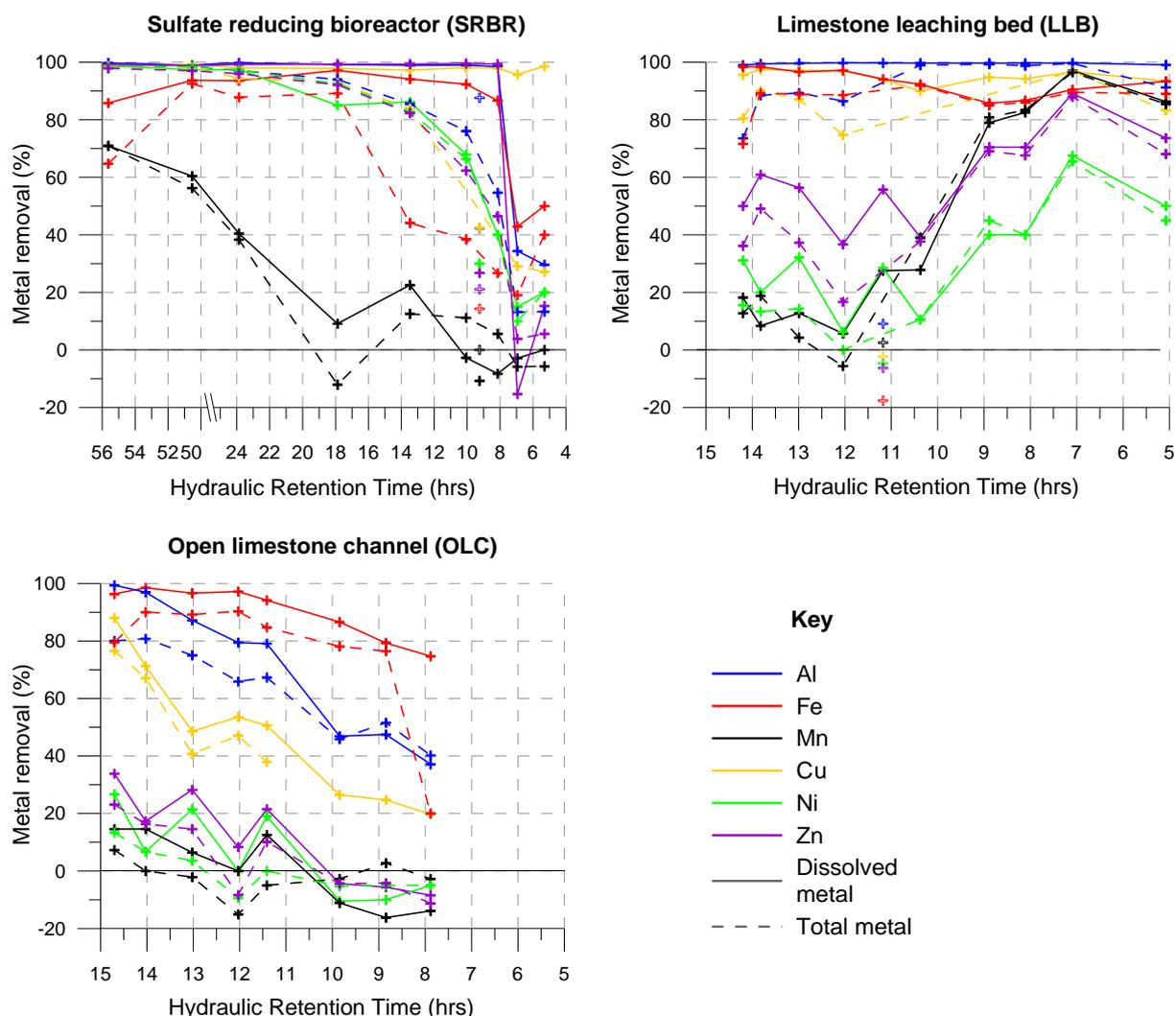
$$\text{Percent treatment efficiency} = 100(X_{\text{in}} - X_{\text{out}}) / X_{\text{in}}$$

For the bench scale SRBR system, calculated acidity is reported on a g CaCO<sub>3</sub> per m<sup>2</sup> of upper treatment system surface area per day basis. The formula used to calculate acidity is in section 2.2.2, but other metals such as copper, nickel, and zinc were included because precipitation of these metals occurred, although manganese was not included because of its high solubility (Watzlaf et al., 2003). Influent acidity was calculated assuming an iron composition of 80% ferric iron and 20% ferrous iron (based on spectrophotometer measurements). Effluent calculated acidity assumes dissolved iron is ferrous, due to the insolubility of ferric iron at effluent pH.

Influent metal loading and removal was determined for the SRBR treatment system on a moles of metals per cubic meter of substrate per day basis. Molar metal loading was calculated using average influent flow rate, along with iron, aluminium, manganese, copper, nickel, and zinc concentrations.

#### **5.2.2.1 Metal Removal Efficiencies**

The variation of influent water chemistry was incorporated into calculations by determining metal removal efficiencies for trial treatment systems at each HRT tested. In general, greater, more effective metal removal (almost 100%) occurs at longer HRTs for each system (Figure 5.1). In certain systems at shorter HRTs, net export of metal occurs (effluent concentrations greater than influent), indicated by negative removal efficiencies. Metal removal efficiencies are calculated from dissolved and total metal analysis, therefore, the difference between corresponding dissolved and total removal efficiencies for metals at each HRT indicates the proportion of metal particulate in effluent.



**Figure 5.1: Dissolved and total metal removal efficiencies (%) of effluent discharged from SRBR, LLB and OLC treatment system settling ponds for different hydraulic retention times (hours).**

Dissolved metal removal efficiencies for SRBR settling pond effluent are greatest for aluminum (99.8%), iron (>97.1%), and zinc (99.6%) at HRTs  $\geq 8$  hours, and for copper (99.3%) at  $\geq 5$  hours HRT (Figure 5.1). Aluminium and iron removal decrease markedly at HRTs < 8 hours, declining to 29.6% and 42.9%, respectively, while net export of zinc occurs (-15.4%). Maximum removal of nickel (98.7%) and manganese (70.9%) occurs at 56 hours HRT. However, removal decreases at shorter HRTs, to a minimum of 15.0% for nickel, while manganese concentrations in settling pond effluent are greater than in influent AMD (-8.3%) at HRTs < 10 hours. Total removal efficiencies are comparable at HRTs  $\geq 18$  hours, with maximum efficiencies of 98.5% (Al), 92.5% (Fe), 98.6% (Cu), and 97.8% (Zn). Although at shorter HRTs, total metal removal efficiencies decrease more rapidly than corresponding

dissolved removal (especially for iron), which indicates a greater proportion of metal particulate in settling pond effluent.

Dissolved metal removal efficiencies for LLB treatment system settling pond effluent are effective for aluminium, iron and copper at all HRTs tested ( $\geq 5$  hours), with maximum removal efficiencies of 99.8%,  $>98.4\%$ , and 97.1%, respectively. Removal of dissolved nickel, zinc and manganese is initially poor, with respective minimum efficiencies of 6.3%, 36.7% and 5.7% at 12 hours HRT (Figure 5.1). However, at shorter HRTs, removal efficiencies increase to maximums of 67.5% (Ni), 89.1% (Zn), and 97.1% (Mn) (7 hours HRT). In general, total metal efficiencies in settling pond effluent are slightly lower initially, however, at HRTs  $<12$  hours total removal efficiencies become more similar to dissolved, indicating a decrease in metal particulate in settling pond effluent. Although, at the shortest HRT tested (5 hours HRT) total removal efficiencies decrease slightly compared to dissolved removal for all metals.

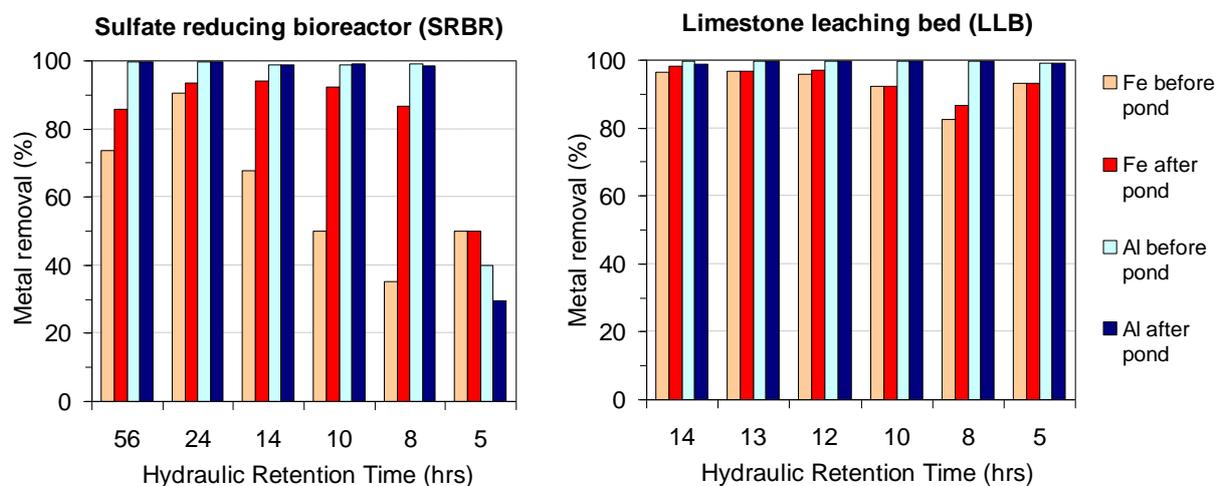
Dissolved metal removal efficiencies for the OLC treatment system settling pond effluent are greatest at HRTs  $\geq 14$  hours for aluminium (99.4%), iron ( $>98.5\%$ ), and copper (88.0%). Removal of these metals declines as HRT is shortened, especially for aluminium and copper, to minimum efficiencies of 37.1% (Al), 74.7% (Fe) and 19.7% (Cu) at 8 hours HRT. Dissolved nickel, zinc and manganese removal efficiencies are poorer than the SRBR and LLB systems, with maximum removal of only 26.7%, 33.9%, and 14.6% respectively. Net export of nickel, zinc and manganese occurs at HRTs  $\leq 10$  hours. Total metal removal efficiencies are initially lower than dissolved, especially for iron and aluminium. Total removal becomes more comparable over time however (HRTs  $<11$  hours), which indicates less metal particulate in settling pond effluent. Total iron removal efficiency of 20.0% at 8 hours HRT is attributed to sampling error (disturbance of settling pond before sampling).

A number of data in Figure 5.1 show total metal removal efficiencies greater than corresponding dissolved removal efficiency (e.g. manganese removal for the SRBR system at 10 and 8 hours HRT). This is incorrect because laboratory analysis of total metals includes both dissolved and particulate metal fractions, therefore, total removal efficiency should always be lower than dissolved. These discrepancies are attributed to laboratory analytical uncertainty. The analytical uncertainties for metal analysis were not determined as part of this study, however, laboratory service providers suggest uncertainty is about 10%. Dissolved and

total removal efficiencies for the SRBR at 9 hours HRT, and total removal efficiencies for the LLB system at 11 hours HRT depart from trends established from other close HRTs. These results probably reflect analytical error and are not considered further (although included as single data points on the graph with a solid symbol for dissolved metal removal, and a hollow symbol for total metal removal).

### 5.2.2.1.1 Affect of settling ponds on treatment performance

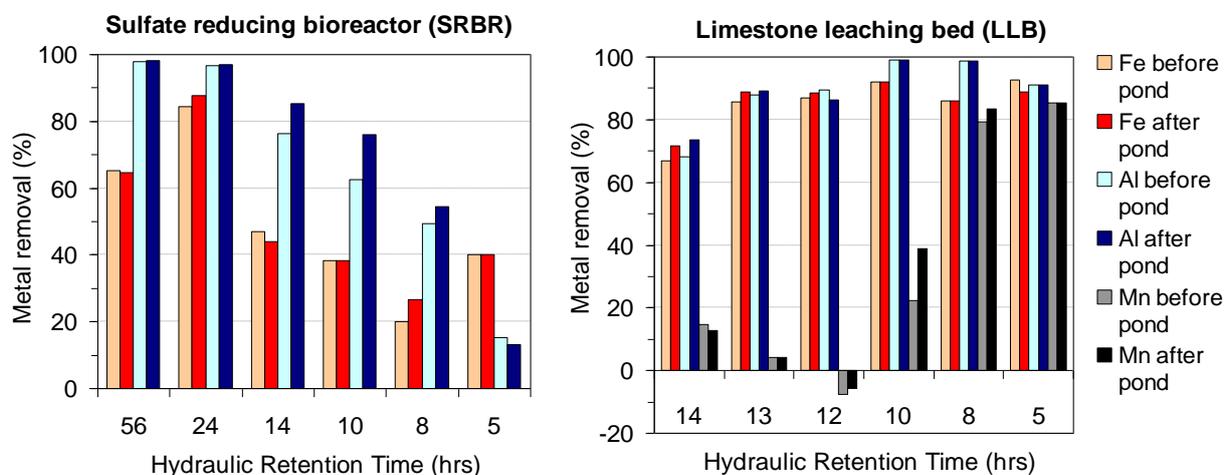
Metals that best indicate the affect of subsequent settling ponds on treatment performance are displayed (Figures 5.2 and 5.3). The largest difference exists for iron for the SRBR treatment system, with removal efficiency increasing once effluent passed through the settling pond (except at 5 hours HRT) (Figure 5.2). Removal efficiencies for other metals have little change (Appendix IV, A) and dissolved aluminium removal efficiencies are shown to demonstrate this. Differences in metal removal efficiencies before and after the settling pond for the LLB system are very small, which is also the case for other metals (Appendix IV, A).



**Figure 5.2: Comparison of SRBR and LLB dissolved iron and aluminium removal efficiencies (%) between effluent discharged directly from treatment systems (before pond), and effluent from settling ponds at different hydraulic retention times (hours).**

The SRBR system also displays the largest difference for total metal removal efficiencies in effluent before and after settling ponds. Removal of metal particulate increases slightly after effluent passed through the SRBR settling pond, especially for aluminium (except at 5 hours HRT) (Figure 5.3). Only small differences occur between effluent for the LLB treatment system, and this is similar to the trend for metals in the OLC system (Appendix IV, A). There

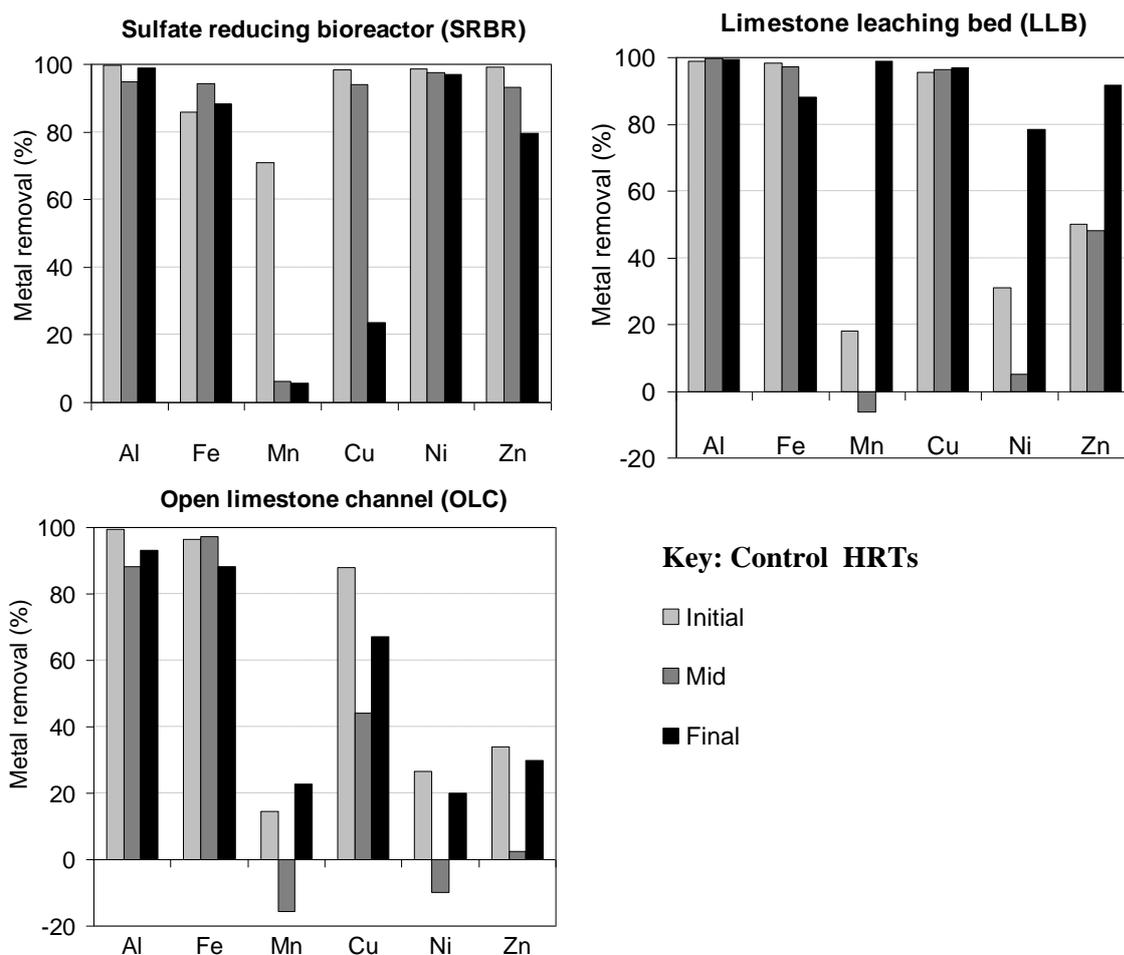
is however an increase in manganese removal in LLB settling pond effluent at 12, 10 and 8 hours HRT.



**Figure 5.3: Comparison of selected SRBR and LLB total metal removal efficiencies (%) between effluent discharged directly from treatment systems (before pond) and effluent from settling ponds at different hydraulic retention time (hours).**

#### 5.2.2.1.2 Changes in Treatment Performance Over Time (Control HRTs)

For the SRBR treatment system, removal efficiencies differ most between control HRTs for manganese (70.9% - 5.7%), copper (98.5% - 23.7%) and zinc (99.2% - 79.7%), with removal decreasing over time. For the LLB treatment system iron removal shows a slight downward trend in efficiency, reducing from 98.4% to 88.2%. However, removal efficiencies for other metals have increasing removal over time, especially for manganese, nickel and zinc. Removal efficiencies at control HRTs for the OLC system generally have a downward trend between initial and final control HRTs. Copper has the greatest decline in removal from 88.0 – 67.1%, and iron decreases from 96.3% to 88.2%, and aluminium drops from 99.4% to 93.1%.

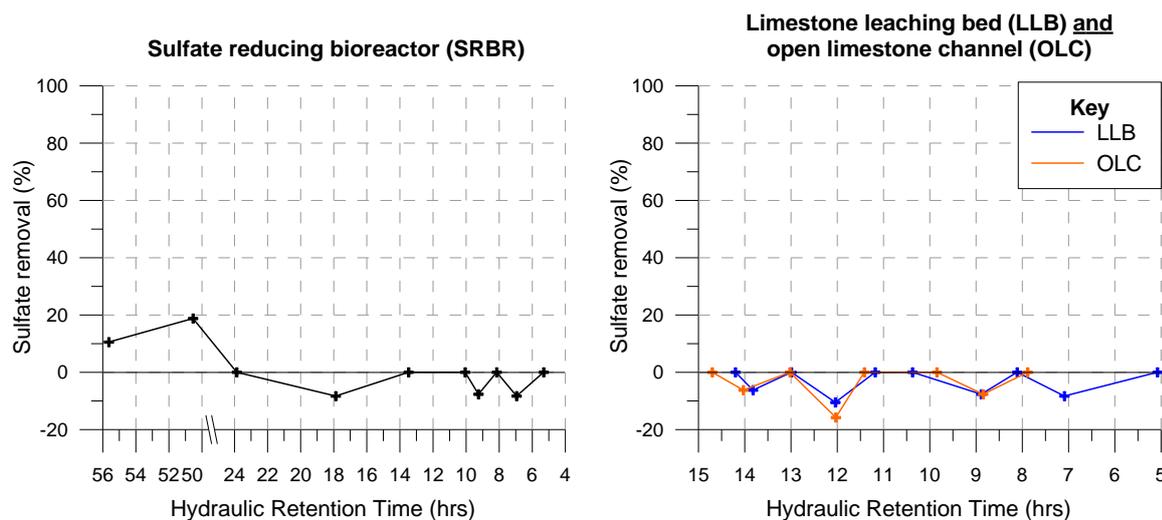


**Figure 5.4: Dissolved metal removal efficiencies at control HRTs for bench scale treatment systems.**

### 5.2.2.2 Sulfate Removal Efficiencies

Removal of sulfate in SRBR treatment systems gives an indication of bacterial activity and the degree of sulfate reduction (Johnson & Hallberg, 2005). Sulfate is removed by precipitation of either mono-sulfides and metal sulfides, or release of hydrogen sulfide gas (Dvorak, 1992). In limestone based treatment systems, sulfate can be removed by the formation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Watzlaf et al., 2003; Cravotta III & Ward, 2008).

The SRBR treatment system has the greatest sulfate removal, with a maximum of 18.8% at 51 hours HRT in settling pond effluent (Figure 5.5). At shorter HRTs however, removal decreases and net export occurs (maximum of -8.3%). LLB and OLC treatment systems display either no removal, or net export of sulfate.

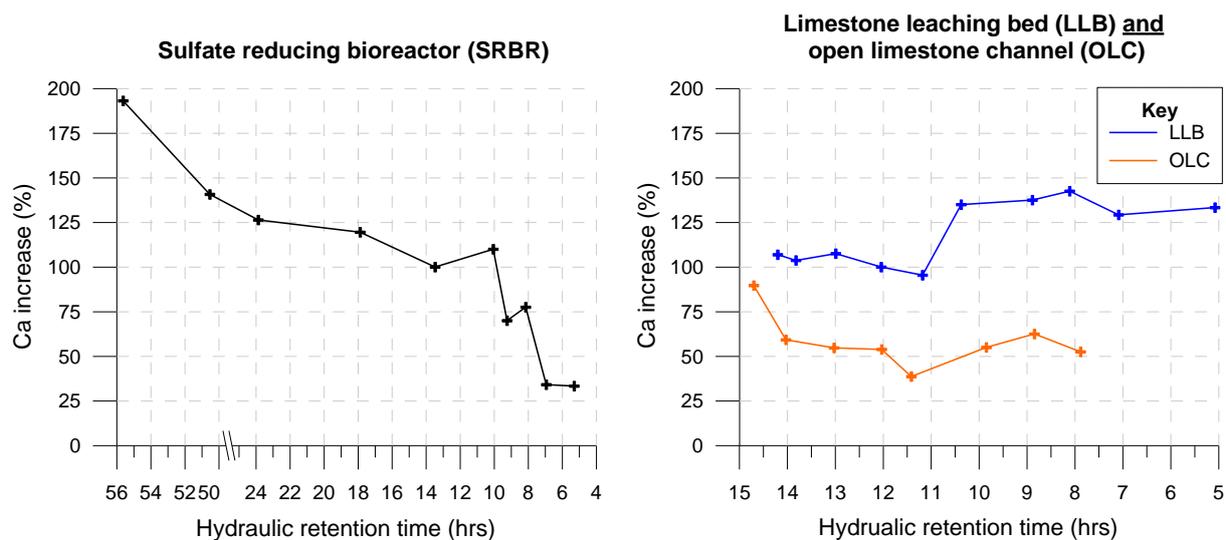


**Figure 5.5: Sulfate removal efficiencies (%) of effluent discharged from SRBR, LLB and OLC system settling ponds for different hydraulic retention times (hours).**

### 5.2.2.3 Calcium Export Efficiencies

Dissolution of carbonate minerals in treatment systems, such as limestone or mussel shells, is indicated by an increase (net export) in calcium concentrations in effluent from treatment system relative to influent AMD (Cravotta III, 2008).

The greatest export of calcium for treatment systems occurs for the SRBR system (Figure 5.6). A maximum export of 193.1% occurs at 56 hours HRT, however, this gradually declines as HRT is shortened, and rapidly drops at HRTs <10 hours to a minimum of 33% (5 hours HRT). Calcium export efficiencies for the LLB system decline slightly initially, from 106.9% to a minimum of 95.5% (14 - 11 hours HRT). However, at HRTs <11 hours calcium export increases markedly, to a maximum of 142.5% at 8 hours HRT and remains steady until the end of the trial. Export of calcium is lowest for the OLC treatment system, with a maximum of 89.7% at 15 hours HRT which declines to 52% at 5 hours HRT.



**Figure 5.6: Dissolved calcium export efficiencies in effluent discharged from SRBR, LLB and OLC system settling ponds for different hydraulic retention times (hours).**

## 5.2.3 Treatment Performance, Processes and Optimal Treatment Criteria

### 5.2.3.1 Sulfate Reducing Bioreactor

Studies show SRBR treatment systems can generate alkalinity and successfully remove dissolved metals from AMD (Rose, 2004; Tsukamoto et al., 2004; Gilbert et al., 2004; Zagury et al. 2006; Doshi, 2006; Gusek, 2002, 2004; McCauley et al., 2008). Hydraulic retention time is the key factor, with treatment performance generally decreasing at shorter retention time (Dvorak, 1992; Bechard et al., 1994; Jage et al 2001; Brenner et al., 2002; Gilbert et al. 2004; Neculita et al., 2008). Results for the bench scale SRBR treatment system agree, exhibiting comparable effectiveness and treatment better performance at longer HRTs tested (Figure 5.1).

The extent of bacterially mediated sulfate reduction in SRBR systems is indicated by sulfate removal (Johnson & Hallberg, 2005). Results of the trial SRBR system suggest sulfate removal only occurred during the initial two HRT periods, with a maximum of 18.8% at 51 hours HRT (Figure 5.5). Adsorption to organic materials likely contributed, but the increase in removal, from 10.5% (56 hours HRT) to 18.8% (51 hours HRT) indicates bacterial sulfate reduction was responsible, because adsorptive removal typically decreases with time (Younger et al., 2002). Supporting bacterial sulfate reduction is the coincident development of

suitable anaerobic conditions, with dissolved oxygen concentrations of 1.39 mg/L in effluent directly from the SRBR system (Figure 4.20). In addition, the increase in metal removal (Figure 5.1) and the development of an odour of hydrogen sulfide when operating at 51 hours HRT also support sulfate reducing conditions. Despite the apparent absence of sulfate removal at HRTs <51 hours it is thought sulfate reducing bacteria were active at shorter HRTs, in particular when operating at 24, 18 and 14 hours HRT. This is inferred primarily by a continued (and stronger) odour of hydrogen sulfide, metal removal, and anaerobic conditions (dissolved oxygen concentrations of 0.6 mg/L in effluent directly from the SRBR system at these HRTs). Bacterial sulfate reduction likely diminished at HRTs <14 hours due to unfavorable redox conditions (dissolved oxygen concentrations >1.62 mg/L) caused by higher flow rates forcing dissolved oxygen into anaerobic zones (McCauley et al., 2008). This is supported by a weakened odour of hydrogen sulfide at HRTs <10 hours.

#### **5.2.3.1.1 Alkalinity Generation**

Although bacterial sulfate reduction contributes to alkalinity generation, neutralization of acidity in the SRBR system is attributed primarily to dissolution of mussel shells within the reactive substrate mixture. This is inferred from the similarity in trends between effluent alkalinity (Figure 4.18) and calcium export efficiencies (Figure 5.6), implying a direct relationship with mussel shell dissolution. Mussel shell dissolution was greatest at longer HRTs (56 and 51 hours HRT), shown by maximum increases in calcium concentrations (193%) and effluent alkalinity (255 mg/L CaCO<sub>3</sub>). This is related to longer contact time with AMD and consequently greater mussel shell dissolution. Bacterial sulfate reduction undoubtedly made a minor contribution to alkalinity generation, shown at 51 hours HRT with alkalinity in effluent directly from the SRBR system increasing above and deviating from the linear trend of calcium export efficiencies. As a result of mussel shell dissolution, pH increases in effluent compared to influent AMD, with a maximum of pH of 7.12 in SRBR settling pond effluent at 51 hours HRT (Figure 4.19). HRT thresholds are apparent in the extent of mussel shell dissolution, as illustrated by effluent alkalinity and pH. For example alkalinity drops significant in effluent directly from the SRBR system at HRTs <51 hours, with a decline to 140 mg/L CaCO<sub>3</sub> at 24 hours HRT. Another decrease occurs at HRTs <18 hours, with alkalinity decreasing from 130 to 60 mg/L CaCO<sub>3</sub> (14 hours HRT), and at HRTs shorter than 8 hours pH decreases to below 5 and alkalinity generation is minimal (15 mg/L CaCO<sub>3</sub>).

### 5.2.3.1.2 Metal Removal

Metal removal efficiencies suggest bacterial sulfate reduction was responsible for removing iron, but removal of other metals such as copper, nickel, zinc and manganese occurred largely by adsorption to organic materials within the reactive substrate mixture.

The effectiveness of iron removal varied with HRT and the extent of bacterial sulfate reduction. Iron removal by sulfate reduction was caused by the formation of iron sulfides after reaction with bacterially generated hydrogen sulfide (Dvorak, 1992; Doshi, 2006). Initial low iron removal (~70% at 56 hours HRT) was caused by the lack of bacterial activity (only 10 days of operation). This correlates with the observation of other precipitate in the settling pond in the early stages of operation indicating that iron was not retained within the SRBR substrate mixture. A lag period is common in SRBR systems, caused by the delay of bacterial colonization of the substrate (Doshi, 2006; Neculita et al., 2007). Iron sulfide formation initiated with the onset of bacterial sulfate reduction at about 51 hours HRT. This correlates with an increase in dissolved and total iron removal efficiencies in settling pond effluent to 93.7% and 92.5%, respectively. Iron sulfide formation requires anoxic conditions to reduce influent ferric iron (FeII) to ferrous iron (FeIII), and both dissolved oxygen concentrations (<2 mg/L) and iron composition (83% ferrous iron) in treatment system effluent indicate anoxic conditions are present (Figure 4.20 and Figure 4.21).

Iron removal by bacterial sulfate reduction appears effective at HRTs as short as 18 hours, because corresponding total iron removal efficiency of 89.1% (97.1% dissolved) occurs in settling pond effluent at this HRT. At this HRT Fe removal is attributed to bacteria because the settling pond removes negligible iron particulate (Figure 5.3), and therefore, Fe must have been retained within the SRBR substrate. However, at 14 hours HRT, Fe removal declines, with dissolved (Figure 5.2) and total (Figure 5.3) removal efficiencies of 67.7% and 47.1%, respectively, in effluent directly from the SRBR system. This indicates 14 hours HRT is insufficient for complete formation of iron sulfide, with ~30% un-reacted FeII in effluent directly from the system, and that iron sulfide that had formed are increasingly discharged by increased flow velocity. At HRTs shorter than 14 hours, Fe removal in effluent directly from the SRBR system continues to decrease (minimum of 35.3% at 8 hours HRT) related to diminished sulfate reduction, as indicated by unsuitable anaerobic conditions for bacteria (DO >1mg/L). However, a concurrent decline in Fe removal in settling pond effluent is not

observed, with dissolved iron removal efficiencies  $\geq 86.7\%$  between 14 and 8 hours HRT (the reason for which is explained during discussion of aerobic SRBR removal processes).

Results suggest attenuation of copper, nickel and zinc occurred primarily by adsorption and formation of surface complexes on reactive substrate materials, or possibly onto other precipitates such as iron and aluminium oxyhydroxides. This is inferred largely from the dramatic decrease in dissolved zinc removal occurring simultaneously with a drop in pH of effluent from the SRBR system. At 8 hours HRT (when bacterial sulfate reduction considered relatively inoperative) dissolved zinc removal in settling pond effluent was 99.3%, and pH directly from the treatment system was 5.84. However, at the following HRT (7 hours) pH declines to 4.61, and net export of zinc is recorded (-15.4%). The relationship between pH and adsorption of cationic metals is well recognized, with adsorption generally becoming weaker for cations as pH declines (Younger et al., 2002; Gilbert et al., 2005). Gilbert et al. (2005) show a linear increase in metal sorption onto organic material with increasing pH, with a removal plateau at pH 6 for zinc, and pH 4 for copper. This corresponds well with SRBR treatment results. An abrupt decline in zinc removal occurs in effluent when pH is increasingly below 6, and copper removal remains high (98.6% at 5 hours HRT) as effluent remains above pH 4. Removal of nickel is also attributed primarily to adsorption to organic materials, however, adsorption appears to require a pH of  $\sim 7$  for greatest removal (97.4% dissolved removal at  $\sim 24$  hours HRT), which concurs with Younger et al. (2002). Attenuation of copper, nickel and zinc by other mechanisms also likely occurred, such as bacterial sulfate reduction (i.e. ZnS), co-precipitation with metal precipitates, and bio-absorption (Neculita et al, 2007).

Metal adsorption to organic materials is a common phenomena in the early stages of SRBR treatment systems (Gilbert et al., 2005; Younger et al., 2002; Neculita et al., 2008); however, this process is reversible and removal declines once organic materials become saturated with respect to metals (Younger et al., 2002). Results from control HRTs are consistent with the adsorptive removal mechanism with dissolved metal removal decreasing over time for copper, nickel and zinc (Figure 5.4). Therefore, it appears the long term effectiveness of copper, nickel and zinc removal by bacterial sulfate reduction is not clearly defined by this study.

In addition, total metal removal efficiencies in effluent from the SRBR settling pond indicate copper, nickel and zinc particulates are increasingly discharged at HRTs  $< 24$  hours (at 5 hours

HRT total copper removal is 27.1%). This indicates the organic substrate particles (or iron and aluminium oxyhydroxide precipitates) on which metals have sorbed become mobile at higher flow velocities caused by shorter HRT. This also indicates the subsequent SRBR settling pond was not large enough, and did not provide sufficient time for settling and removal of suspended solids in effluent from the SRBR system.

Autopsy investigations showed accumulations of black precipitate adhered loosely to the inside surfaces of mussel shells, while the reactive substrate mixture also contained similar precipitate or sludge (Figure 4.29). This observation supports the formation of metal sulfides, and is similar to other SRBR studies that document black precipitate (Chang et al., 2000; Christensen et al., 1996; Neculita et al., 2008). Black precipitate was verified as metal sulfide after precipitate faded once exposed to the atmosphere, indicating oxidation (Appendix III, E). Autopsy SEM analysis revealed areas of metal on mussel shell surfaces with elevated iron (Figure 4.30 and Figure 4.31) which verified the presence of iron sulfides, and subordinate proportions of zinc and copper suggest mono-sulfide or metal carbonate mineral formation occurred.

Aluminium removal in SRBR systems is controlled by pH, with the formation of insoluble aluminium hydroxides or sulfates (Gusek 2002; Thomas & Romanek, 2002; Gusek & Wildeman, 2002). SRBR results support this interpretation because settling pond dissolved removal efficiencies are >98.5% when effluent is above pH 5, whereas, only about 35% of aluminium removal occurs when effluent drops below pH 5 (HRTs <8 hours). Total metal removal efficiencies indicate aluminium solids are increasingly discharged from the SRBR system at HRTs <24 hours (Figure 5.1), however, some particulate settles and is removed in the subsequent pond, shown by an increase in total aluminium removal efficiencies in settling pond effluent compared to removal efficiency directly from the system (maximum increase of 13.5% at 10 hours HRT) (Figure 5.3). X-ray fluorescence analysis verifies SRBR pond sludge comprises mainly aluminium (Figure 4.40). This agrees with Gusek & Wildeman (2002) who propose SRBR systems prevent the formation of gibbsite ( $\text{Al}(\text{OH})_3$ ), a white, gelatinous aluminium precipitate (highly buoyant) which can clog treatment systems; rather, SRBR system produce denser, less voluminous aluminium compounds. The results of SRBR autopsy support this, with a absence of white precipitate observed amongst reactive substrate materials (Figure 4.28). In addition, areas of metal accumulation identified by SEM analysis on inner

mussel shell surfaces contain high concentrations of aluminium which may be related to the accumulations of black precipitate.

Manganese removal is not expected in SRBR treatment systems due to the high solubility of manganese sulfides in reducing conditions (Watzlaf et al., 2003; Zaluski et al., 2003; Hallberg & Johnson, 2005). This is supported by results, with poor manganese removal. Initial relatively high removal (70.9%) is due to adsorption of manganese to organic substrate materials, however, removal rapidly declines at shorter HRTs, and net export occurs at HRTs <10 hours (from -2.8% to -8.3%) as a result of saturation of substrate materials with respect to manganese.

#### **5.2.3.1.2.1 Aerobic Iron Removal**

Aerobic metal removal processes also occur in the SRBR treatment system, primarily to remove dissolved iron. This is evident by an accumulation of ochre precipitate on post peel at the SRBR surface (Figure 4.24), as a result of FeIII precipitation in the upper water column which has a pH that exceeds FeIII solubility (pH of about 3.75). Algae on the SRBR surface and associated photosynthesis reactions may have also catalyzed oxidation of FeII and subsequent precipitation of FeIII on the surface (Appendix III, E).

Aerobic precipitation of iron on the SRBR surface is an important removal process. This is indicated by removal of up to half of influent iron at the shortest HRT tested (50.0% at 5 hours HRT), when iron removal by anaerobic bacterial sulfate reduction was most likely inoperative. This result agrees with Watzlaf et al. (2003) who state iron removal on the surface of anaerobic systems can be significant. The temporary color change of precipitate at the SRBR surface from ochre to black is attributed to transient, localized anoxic conditions, which is also reported by Neculita et al. (2008). This could have caused precipitation of metal sulfide, or transformed oxide precipitates (i.e. iron) already present at the surface to sulfides, creating a black precipitate.

An equally, and perhaps even more important process was removal of dissolved Fe within the SRBR settling pond at shorter HRTs. This is ascribed to oxidation of FeII discharged from the SRBR system as it entered the settling pond, and subsequent precipitation of insoluble ferric iron hydroxides in the circum-neutral conditions of the pond (pH  $\geq$ 5.58 at HRTs  $\geq$ 8 hours).

For example, at 8 hours HRT, removal of dissolved iron increases from 35.3% in effluent directly from the SRBR system, to 86.7% in settling pond effluent (Figure 5.2). Effluent iron species composition also supports FeII oxidation (measured when operating at 58 hours HRT), with iron composition changing from >80% FeII in effluent directly from the SRBR system, to 100% FeIII in effluent from the SRBR settling pond (Figure 4.21). Oxidation of FeII was likely caused by either atmospheric exposure (Neculita et al., 2008) or by aeration as effluent dropped into the settling pond. This process was significant for interpretation of treatment performance because it obscured the decline in iron removal by bacterial sulfate reduction between 14 and 8 hours HRT (dissolved removal in settling pond effluent  $\geq 86.7\%$ ). This study highlights the importance of identifying where iron is removed in SRBR systems, because if incomplete sampling occurs, iron removal might be attributed to sulfate reduction processes, which is clearly not the case in the SRBR system studied. Although dissolved iron is removed from solution in the SRBR settling pond, the precipitated iron hydroxides remain in suspension are discharged and not retained in the pond, inferred from the negligible difference between total iron removal efficiencies before and after the settling pond (Figure 5.3).

However, at HRTs <8 hours, FeII oxidation and removal in the SRBR settling pond is clearly not as effective than at longer HRTs, with dissolved iron removal in pond effluent decreasing to  $\leq 50\%$  (from 86.7% at 8 hours HRT). This abrupt change is explained by the absence of abiotic iron oxidation at pH <5 (Younger et al., 2002), with the pH of the SRBR settling pond dropping to  $\leq 4.53$  at HRTs shorter than 8 hours.

#### **5.2.3.1.3 Potential SRBRs Limitations**

The SRBR organic substrate used in this study demonstrated its suitability as a carbon source for bacterial sulfate reduction, and consequent alkalinity generation and metal removal. This supports the study of McCauley et al. (2008) who determined optimal organic substrate materials and mixtures for SRBR systems treating AMD from Stockton Opencast mine near Westport. However, due to the relatively short duration of the trial, the long term effectiveness of the substrate to maintain microbial activity is uncertain, although less biodegradable materials such as post peel and bark are likely to sustain bacterial sulfate reduction (Gusek, 2004; Zagury et al., 2006).

Problems that can arise in SRBR systems and cause ineffective treatment relate to hydraulic properties of the reactive substrate, and include clogging, compaction and development of preferential flow paths (Younger et al., 2002). The accumulation of metal precipitates, biomass and metabolic products of bacterial activity can decrease porosity and permeability, potentially affecting long term treatment effectiveness (Neculita et al., 2007). Metal precipitates accumulated within the SRBR (Figure 4.28 - 4.30), however, no signs of preferential flow paths were observed. The trial duration was likely to short to determine the affect of metal solids and accumulation of other materials in the substrate mixture, indicated by similar iron and aluminium removal efficiencies during control HRTs (Figure 5.4). Flushing is recommend to maintain treatment performance in limestone and compost based systems (Kepler & McCleary, 1997), however, Skousen & Ziemkiewicz (2005) are skeptical and suggest only metal solids within drainage pipes are removed during flushing. This concurs with flushing results of the SRBR system that indicates removal of metal solids was relatively limited (compared to the LLB system (Table 4.6)). The color change of water during flushing (clear after 15 L discharged) supports the idea that the metal solids removed originated mainly from drainage piping and not from within the substrate mixture (Appendix III).

#### **5.2.3.1.4 Optimal Treatment and Design Criteria**

Optimal design criteria for a SRBR treatment system to treat Fanny Creek AMD include:

- Treatment of AMD by bacterial sulfate reduction requires  $\geq 14$  hours HRT. Optimal bacterial sulfate reduction requires  $\geq 51$  hours HRT, inferred from maximums in sulfate removal, alkalinity generation from SRBR system, and total iron removal efficiency.
- Maximum alkalinity generation occurs at 51 hours HRT (255 mg CaCO<sub>3</sub>/L directly from system) from a combination of mussel shell dissolution and bacterial sulfate reduction. Mussel shell dissolution requires a HRT of 10 hours to increase pH above 6, and a HRT of 8 hours to increase pH above 5.
- Metals display varying removal thresholds, depending on removal mechanisms. Iron removal by bacterial sulfate reduction requires a minimum of 18 hours HRT for effective formation of iron sulfide. Thresholds for removal of nickel, zinc, and copper by bacterial sulfate reduction are not established because these metals were probably removed primarily by adsorption processes. However, pH controlled removal efficiency, with

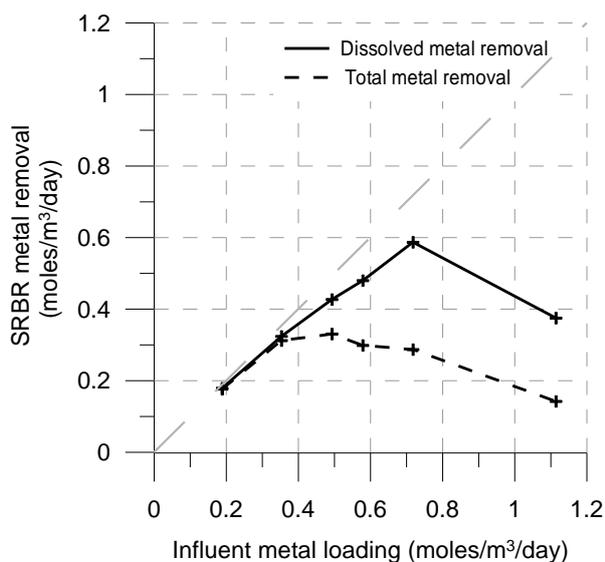
effective removal occurring at ~pH 7 for nickel ( $\geq 24$  hours HRT), ~pH 6 for zinc ( $\geq 8$  hours HRT), while it is presumed pH  $\geq 4$  is required for effective copper removal (5 hours HRT).

- Aluminium removal is controlled by pH. A HRT of  $\geq 8$  hours HRT is required for effective removal (increases pH above 5).
- Removal of aluminium, nickel, zinc and copper particulates within the SRBR substrate mixture requires  $\geq 24$  hours HRT.

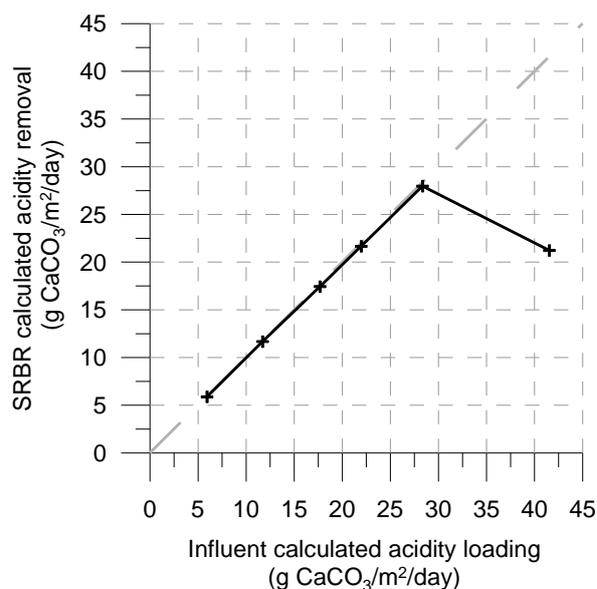
Optimal HRT criterion for a SRBR treatment system for Fanny Creek AMD is based on effective bacterial sulfate reduction. Therefore, a HRT of 51 hours (or two days) is recommended for design of a SRBR treatment system. This HRT represents a minimum criterion in order to achieve optimal bacterial sulfate reduction in a SRBR system, and thus maximum metal removal and alkalinity generation. However, for sub-optimal bacterial sulfate reduction, yet effective metal removal, a HRT of 24 hours HRT is sufficient. Design of future SRBR treatment systems based on these criteria requires similar reactive substrate mixture to that used in this study. Although the effectiveness of system flushing is uncertain, the inclusion of this feature is advised for potential removal of solids from the substrate to avoid hydraulic related problems.

#### **5.2.3.1.5 Metal and Acidity Design Criteria**

Optimal performance and design criteria for metal and acidity removal are also established for the SRBR treatment system in this study (Figure 5.7 and 5.8). Metal removal for effluent discharged directly from the SRBR system is compared to influent AMD metal loading, in terms of moles of metals/  $\text{m}^3$  of substrate/ day ( $\text{moles}/\text{m}^3/\text{day}$ ) (Figure 5.7). Most effective treatment occurs when metal removal loading is equivalent to influent AMD metal loading, which plots along the 45°, light grey dashed line (Figure 5.7). Conversely, less effective metal removal, or system stress, is indicated by lower metal removal compared to influent AMD metal loadings (some metals not removed in effluent), indicated by a departure of metal removal away from the 45° line of equal metal loading and removal. This interpretation also applies for Figure 5.8, which displays acidity removal for the SRBR treatment system based on the upper surface area of the system ( $\text{g CaCO}_3$  acidity/ $\text{m}^2$  /day).



**Figure 5.7: Molar volumetric influent metal loading and removal directly from the SRBR treatment system. Units are in moles of metal removed/m<sup>3</sup> of substrate/day. Dashed grey line indicates equal metal loading and removal.**



**Figure 5.8: Calculated acidity loading and removal (g CaCO<sub>3</sub>/m<sup>2</sup>/day) for the SRBR system. Dashed grey line indicates equal metal loading and removal.**

Influent molar volumetric metal loading for the SRBR treatment system ranged from 0.19 to 1.11 moles/m<sup>3</sup>/day (Figure 5.7). Maximum dissolved metal removal in effluent directly from the SRBR system is 0.59 moles/m<sup>3</sup>/day, while maximum total metal removal is 0.33 moles/m<sup>3</sup>/day, at influent metal loadings of 0.72 and 0.43 moles/m<sup>3</sup>/day, respectively. Metal removal for the SRBR system is almost equivalent as influent metal loading (almost 100% metal removal) at an influent loading rate of 0.35 moles/m<sup>3</sup>/day. At this loading rate dissolved and total metal removal is 0.32 and 0.31 moles/m<sup>3</sup>/day, respectively. However, metal removal is less effective at influent metal loading above 0.35 moles/m<sup>3</sup>/day, as indicated by the departure of the metal removal trend from the dashed line (equal influent metal loading and removal) at greater loading rates. This suggests the SRBR system is stressed and bacterial sulfate reduction is less effective at influent metal loading rates greater than 0.35 moles/m<sup>3</sup>/day.

Maximum acidity removal calculated from effluent directly from the SRBR treatment system is 28.0 g CaCO<sub>3</sub>/m<sup>2</sup>/day (98.6%), at an influent loading rate of 28.4 g CaCO<sub>3</sub>/m<sup>2</sup>/day (Figure 5.8). Acidity removal is almost equivalent to acidity loading (nearly 100% acidity removal) throughout the trial, except at the highest loading rate of 41.5 g CaCO<sub>3</sub>/m<sup>2</sup>/day, where acidity

removal drops to 21.2 g CaCO<sub>3</sub>/m<sup>2</sup>/day (51.1%). The marked decline in acidity removal at the highest acidity loading rate correlates with a decrease in effluent pH to below 5 at shorter HRTs (<8 hours HRT) and therefore an increase in dissolved aluminium concentrations in SRBR effluent. This explains the decrease in acidity removal because dissolved aluminium has the potential to generate acidity upon hydrolysis.

Metal and acidity removal design criteria for the SRBR treatment system are based on effective metal and acidity removal treatment performance. Therefore, metal removal criteria recommended for a SRBR treatment system to treat Fanny creek AMD is given as 0.30 moles of metals/ m<sup>3</sup> of reactive substrate/ day and an acidity removal criteria of 28.0 g as CaCO<sub>3</sub>/m<sup>2</sup> of treatment system surface area/day is recommended.

#### **5.2.3.1.6 Comparison of Design Criteria with Other Studies**

Overall, design criteria established for a SRBR treatment system for Fanny Creek AMD are comparable to criteria for similar anaerobic treatment systems (SRBRs and VFWs). Younger et al. (2002) suggest at least 40 hours HRT is needed for effective bacterial sulfate reduction, while Skousen and Ziemkiewicz (2005) recommend 24 hours HRT. However, Neculita et al. (2007) suggest a longer HRT, such as 3 to 5 days to allow for effective formation of metal sulfides.

Optimal metal removal values determined in this study are similar to Wildeman et al. (2006) who propose 0.3 moles metal removal/m<sup>3</sup> of substrate/day. However, performance is considerably lower than criteria given by McCauley et al. (2008) of 0.8 moles metal removal/m<sup>3</sup> substrate/day and acidity removal of 66g CaCO<sub>3</sub>/m<sup>2</sup>/day, for SRBRs using very similar organic substrate mixtures to this study. This difference could be because McCauley (2008) used much more concentrated AMD and thus had longer HRTs to achieve similar metal loadings compared to this study. However, the acidity removal criterion recommended from this study (28.0 g CaCO<sub>3</sub>/m<sup>2</sup>/day) is similar to the standard value suggested by others of around 20 – 25 g CaCO<sub>3</sub>/m<sup>2</sup>/day (Rose & Dietz, 2002; Rose, 2004; Watzlaf et al., 2003; Skousen & Ziemkiewicz, 2005).

### 5.2.3.2 Limestone Leaching Bed

Treatment of AMD in LLB passive systems occurs by limestone dissolution which neutralizes acidity and generates bicarbonate alkalinity, increasing pH which promotes aerobic removal of metals such as iron and aluminium (Younger et al., 2002; Cravotta III et al., 2008). The bench scale LLB treatment system demonstrates effective acidity neutralization and metal removal capability throughout the trial (Figure 5.1), and similar performance and treatment mechanisms to those documented by others (Black et al., 1999; Cravotta & Trahan, 1999; Means & Rose, 2005; Trumm et al., 2006; Cravotta III et al., 2008; Cravotta & Ward, 2008).

#### 5.2.3.2.1 Alkalinity Generation

The LLB treatment system demonstrates effective limestone dissolution by an increase in calcium concentrations of around 100 – 150% relative to influent AMD (Figure 5.6), and steady alkalinity generation with an average of 74 mg/L CaCO<sub>3</sub> in effluent (Figure 4.18). As a consequence, pH was increased to above 6.0 in settling pond effluent at all HRTs tested during the trial (Figure 4.19).

Hydraulic retention time is a critical factor in limestone bed systems because it affects the rate of limestone dissolution and alkalinity generation (Cravotta & Trahan, 1999; Younger et al., 2002; Watzlaf et al., 2003). Alkalinity generation is expected to decrease with shorter HRTs because the trend of limestone dissolution as a function of contact time with AMD is asymptotic (Watzlaf et al., 2003; Cravotta III, 2004). However, results indicate this was not the case for the LLB system, with relatively similar concentrations of alkalinity in effluent (60 - 90 mg CaCO<sub>3</sub>/L) at the different HRTs tested (14 - 5 hours). As a result, neutralization of acidity occurred at every HRT tested (alkalinity of 75 mg/L CaCO<sub>3</sub> at the shortest HRT).

Cravotta & Trahan (1999) suggest proton acidity released during metal hydrolysis can enhance limestone dissolution and alkalinity generation. This occurs in the LLB treatment system, indicated by the similarity in trends between influent acidity and effluent alkalinity (Figure 4.18) and by the increase in calcium export at HRTs <11 hours. The increase in calcium concentrations in LLB effluent correlates with the onset of manganese removal in the system, which during precipitation releases acidity that then reacts with limestone and enhances dissolution. However, the acidity produced by hydrolysis and precipitation with

aluminium, iron and manganese is sufficiently neutralized in the LLB system, because circum-neutral pH conditions occur in effluent at every HRT tested.

Surface area affects limestone dissolution and the time taken for neutralization of acidity (Cravotta III, 2008). The limestone clasts used in the bench scale system (10 – 30 mm) are small compared to clast sizes recommended for full scale treatment systems (50 - 100 mm) (Cravotta III & Trahan, 1999; PIRAMID Consortium, 2003). Therefore, limestone used in the bench scale LLB system is more reactive, and as a result neutralization and alkalinity generation rates likely represent maximum potential values at respective HRTs for this kind of system.

The lack of sulfate removal (Figure 5.5) indicates that gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) formation did not occur in the LLB system. This is because high sulfate concentrations ( $>2000$  mg/L) are required to saturate solution with respect to gypsum (Santomartino & Webb, 2007), and the maximum sulfate concentration in influent AMD was 569 mg/L.

#### **5.2.3.2.2 Metal Removal**

Iron removal primarily occurred by hydrolysis and precipitation of iron hydroxides, because ferric iron was predominant in influent AMD (Figure 4.21) and is insoluble above pH 3.5 (Younger et al., 2002). Iron hydroxide precipitation was rapid, shown by the accumulation of ochre precipitate near inflow piping (Figure 4.32). Settling pond dissolved oxygen concentrations (Figure 4.20) confirmed aerobic conditions were present, with an average of 6.16 mg/L. Iron oxidation is apparent by the accumulation of ochre precipitate on limestone clasts at the surface of the LLB system, attributed to greater oxygen exchange at the water interface (Means & Rose, 2005). However, results indicate not all FeII was oxidized, indicated by minimum iron removal of 85.7% in settling pond effluent at 9 hours HRT, while pH was 6.43 which is above the solubility of FeIII. This correlates with minimum dissolved oxygen concentrations (3.89 mg/L) in influent AMD during the trial, which explains why FeII is maximum at this HRT. In addition, maximum dissolved iron removal (98.4%) and influent dissolved oxygen concentrations (8.79 mg/L) occur at the same HRT. This emphasizes that aeration is necessary to achieve optimal iron removal in an LLB system.

Aluminium removal is dependant on pH, with low solubility of aluminium hydroxide at pH above 5. This explains removal efficiencies of  $\geq 98.9\%$  at all HRTs tested because pH remained above 6. The white precipitate observed on the surface and throughout the LLB system (Figure 4.25) was most likely aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ). Greater accumulations of white precipitate occur near inflow piping, and diminished with distance as reported in other studies (Cravotta III & Trahan, 1999).

The high solubility of manganese, nickel and zinc in carbonate based systems can result in poor removal (Watzlaf et al., 2003; PIRAMID Consortium, 2003). However, the LLB system in this study removed these metals. Initial attenuation of nickel and zinc was probably due to adsorption and co-precipitation with iron and aluminium hydroxides (Stumm & Morgan, 1996). Copper removal is high ( $\geq 90.0\%$ ) because it readily absorbs to iron and aluminium hydroxides (PIRAMID Consortium, 2003) which were abundant within the limestone bed. The marked increase in manganese removal at HRTs <12 hours is caused by precipitation of manganese oxides (Cravotta III & Trahan, 1999; Means & Rose, 2005) by an autocatalytic process. Abiotic oxidation of manganese only occurs at pH >8 (Stumm & Morgan 1996), therefore, manganese precipitation was catalyzed by either co-precipitation and adsorption to iron and manganese oxide surfaces (Stumm & Morgan, 1996) or by microbial activity (Means & Rose, 2005). A lag period for manganese removal is described by authors during which manganese removal is low (Cravotta III & Trahan, 1999; Denholm et al., 2003). However, with increased accumulation of iron hydroxides, or establishment of bacterial, greater adsorption and precipitation of manganese occurs, which in turn generates more manganese oxide surfaces that further accelerate manganese removal (autocatalytic). Therefore, iron hydroxides, or bacteria, are required to initially catalyze manganese oxidation and precipitation, but once initiated, manganese oxides are a more effective catalyst for continued manganese precipitation. Removal efficiencies in settling pond effluent reflect the rapid acceleration in manganese precipitation, with an removal increasing from 27.8% to 78.9% within a timeframe of one week (10 and 9 hours HRT). At the same time, a dark color appeared on clasts within the limestone bed, along with black precipitate in the settling pond (Figure 4.25). The correlated increase in nickel and zinc removal (occurring just after the increase in manganese removal) is attributed to co-precipitation (Stumm & Morgan, 1996) and absorption (Watzlaf et al., 2003) to manganese oxides. Zinc removal with manganese appears more effective because removal efficiencies for nickel are lower.

Autopsy of the LLB system revealed a black precipitate, typical of manganese oxide, adhered to many limestone clasts (Figure 4.32). SEM analysis identified manganese on the surface of a limestone clast, in distinct nodules containing about 50% manganese (Figure 4.35 and 4.38), together with high concentrations of iron (~25 %). This supports the autocatalytic removal process, along with rounded nodule morphology that implies a nucleus for precipitation. Manganese nodules on the surfaces of limestone clasts has not been documented in other studies. More effective zinc removal is apparent in elemental compositional analysis because this shows zinc was incorporated within nodules in higher concentrations (10%) than nickel (~1 %).

Greatest removal of dissolved manganese (97.1 %), nickel (67.5%) and zinc (89.1%) occurs at 7 hours HRT. However, this is due to the affect of trial duration associated lag period for manganese precipitation, rather than HRT. However, the decrease in removal of these metals at 5 hours HRT is related to AMD contact time, and explained by the requirement of strong circum-neutral conditions (pH >6) for manganese precipitation (Younger et al., 2002; Watzlaf et al., 2003). The pH of treatment system effluent between 7 and 5 hours HRT drops slightly, (from 6.2 to 5.93), therefore, the shortened contact time for acid neutralization likely caused less favorable conditions for manganese precipitation, and associated nickel and zinc removal. The reason for the pH dependence of manganese precipitation include the intolerance of catalyzing microbes at pH <6, or the increased solubility of manganese oxides at lower pH (Younger et al., 2002).

X-ray fluorescence and SEM analysis of LLB settling pond sludge indicates a composition rich in aluminium and manganese (Figure 4.25 and Figure 4.40). SEM analysis show settling pond sludge contained manganese nodules (Figure 4.41) which is reflected in total manganese removal efficiencies by an improvement in removal (from 22.2% to 38.9% at 10 hours HRT) once effluent has passed through the settling pond (Figure 5.3). Despite the retention of aluminium particulate in the pond, the similarity in total metal removal efficiencies before and after the settling pond indicate minimal precipitate was actually retained, likely due to the buoyant nature of aluminium solids. This shows that the settling pond was too small to provide effective settling of aluminium precipitates.

Greater retention of metal particulates within the limestone bed occurred approximately half way through the trial, inferred by the increase in total metal removal efficiencies, and

therefore, less particulate was discharged in effluent (Figure 5.1). This is unexpected because higher flow velocities at shorter HRTs were anticipated to entrain more precipitates which would result in discharge of more particulate, and thus lower total metal removal efficiencies. The absence of reduced total metal removal efficiencies is probably due to the physical filtration of precipitated metals by accumulated metal solids which slowly built up in the LLB system. In addition, the small limestone clast size would have lowered transmissivity and reduced the potential for transport of metal solids (Cravotta III et al., 2008). Flow velocities of  $>0.1$  m/min are required to keep metal hydroxide precipitates in suspension in similar treatment systems (Cravotta III & Trahan, 1999). Maximum flow velocities during the LLB trial were significantly less (0.00215 m/min at 5 hours HRT) which also explains why precipitates accumulated in the LLB system. However, the slight decline in total aluminium removal efficiency at 5 hours HRT suggest maximum velocities reached in this trial did entrain metal hydroxide precipitates to a small degree which resulted in removal from the LLB system.

#### **5.2.3.2.3 Potential Limitations for LLBs**

Precipitation of iron and aluminium hydroxides in LLB systems can cause armouring of limestone clasts and clogging, leading to short circuiting and treatment failure (Younger et al., 2002; Watzlaf et al., 2003; Cravotta III, 2008). Observations during autopsy indicate that very little iron armouring occurred on clasts. This is partially supported by SEM analysis, with minimal iron present on a limestone clast sample from near the LLB inflow (Figure 4.33). However, the surface of a limestone clasts from near the outflow was largely covered in iron (Figure 4.36) suggesting some amour formation. Trumm et al., (2008) conclude that the potential for iron armouring is low for a small scale LLB system that treated similar iron concentrations ( $\sim 1.4$  mg/L), and in some cases limestone dissolution can be effective even after armouring (Ziemkiewicz et al., 1994; Cravotta III et al., 2004; Santomartino & Webb; 2007). It is possible that manganese oxides, which strongly adhered to clasts, could hinder limestone dissolution if treatment continued, but this has not been documented elsewhere; and results actually indicate that manganese precipitation enhance limestone dissolution. Manganese precipitates within the pore spaces of the limestone bed could however contribute to clogging of a treatment system. Accumulation of aluminium hydroxides within the LLB system also indicate a reduction in permeability and porosity of the limestone bed, and possibly the initial stages of clogging, particularly at the inflow. Regardless of the

accumulation of precipitates, control HRTs show performance was not affected over time (Figure 5.4), rather, an overall increase in removal was recorded, except for iron for which removal decreased probably due to the presence of more ferrous iron in influent AMD.

Flushing results show more metal precipitates were removed from the LLB system compared to the SRBR system (Table 4.6). Flushed water was light grey for the entire flush, which suggests solids were removed from the entire limestone bed, and not just from drainage piping. White and ochre precipitate remaining on and within the limestone bed after flushing (Figure 4.27) suggest the effectiveness flushing is limited. Observations of aluminium precipitates in motion during flushing are encouraging because this shows precipitates can be dislodged and potentially removed from treatment systems. Overall, results concur with other authors who are uncertain about the benefits of flushing to maintain treatment performance (Cravotta III & Ward, 2008; Cravotta III et al., 2008), although system flushing is recommended to prolong treatment longevity (Cravotta & Trahan, 1999).

#### **5.2.3.2.4 Optimal Treatment and Design Criteria**

Optimal design criteria for a LLB treatment system to treat Fanny Creek AMD include:

- Effective limestone dissolution and alkalinity generation occurs at HRTs  $\geq 5$  hours. Influent acidity was sufficiently neutralized and effluent was net alkaline ( $>60$  mg  $\text{CaCO}_3/\text{L}$ ) with final pH above 6 for all HRTs tested.
- Removal of ferric iron and aluminium occurred at HRTs  $\geq 5$  hours. This occurred because pH was sufficiently raised to exceed metal hydroxide solubility. Oxidation and removal of ferrous iron requires aeration and high dissolved oxygen concentrations in AMD.
- Manganese removal requires the presence of either iron hydroxide and manganese oxide surfaces, or bacteria to catalyze oxidation and removal. Optimal removal requires pH  $\geq 6$  which was achieved by a HRT of 7 hours in the bench scale LLB system. The absence of ferrous iron is also required for manganese removal.
- Most effective removal of nickel and zinc requires precipitation of manganese oxides for these metals to absorb to or co-precipitate.
- Effective copper removal occurred at HRTs  $\geq 5$  hours and require the presence of either iron or aluminium hydroxides

- Flow velocities associated with HRTs <5 hours are necessary to keep iron and aluminium hydroxides in suspension for transport out of the LLB system. Longer HRTs result in accumulation of iron and aluminium solids within the LLB system, which can lead to limestone armouring and clogging, potentially limiting AMD treatment effectiveness.
- Treatment system flushing indicated potential for removal of accumulated iron, aluminium and manganese precipitates from the LLB system.

Optimal HRT criteria for a LLB treatment system for Fanny Creek AMD are based on effective neutralization, removal of dissolved metals and transport of metal precipitates from the system. Therefore, a HRT of 5 hours is recommended for design of a LLB system. This criterion represents a conservative HRT for effective acid neutralization, alkalinity generation, and removal of dissolved ferric iron and aluminium. It is possible that shorter HRTs (i.e. 3 hours) could also achieve such treatment. However, 5 hours is a minimum HRT to achieve circum-neutral pH conditions (pH>6) for precipitation of manganese oxides, and promote removal of dissolved nickel and zinc. The flow rate associated with 5 hours HRT represents sub-optimal flow velocity to keep metal precipitates in suspension to avoid problems such as limestone armouring and clogging. Therefore, the inclusion of drainage piping to enable system flushing is advised. Full scale LLB treatment systems should employ larger limestone clasts sizes (75 – 100 mm) to permit greater transmissivity and flow velocity for improved transport of metal solids.

Overall, treatment performance of the bench scale LLB treatment system exceeds conservative design criteria for limestone bed treatment systems. Design criteria established in this study is 1/5 of the criteria (15 hours) recommended for effective limestone dissolution and alkalinity generation by some authors (Kepler & McCleary, 1997; Watzlaf et al., 2003; Skousen & Ziemkiewicz, 2005). These authors also advise against using limestone bed systems to treat AMD that contains concentrations of dissolved oxygen, ferric iron and aluminium above 1mg/L. However, a design criteria of 5 hours HRT is similar to other studies that suggest shorter HRTs ( $\leq 3$  hours) are sufficient to treat oxic AMD containing moderate acidity (<90 mg/L) and iron and aluminium concentrations (2 – 20 mg/L) (Cravotta & Trahan, 1999; Mukhopadhyay et al., 2007; Santomartino & Webb, 2007; Cravotta & Ward, 2008). The flow rates associated with 3 hours HRT is also suggested as a minimum in order

for suspension and removal of metal hydroxide precipitates from limestone bed treatment systems (Cravotta & Trahan, 1999).

### **5.2.3.3 Open Limestone Channel**

Treatment of AMD in OLC systems occurs by dissolution of limestone which neutralizes acidity and generates alkalinity, increasing pH of mine water. This causes the aerobic removal of dissolved metals (Younger et al., 2002). The bench scale OLC treatment system had comparable treatment performance and processes to OLCs reported elsewhere (Skousen & Ziemkiewicz, 2005; Ziemkiewicz et al, 1994, 1996, 1997).

#### **5.2.3.3.1 Alkalinity Generation**

Limestone dissolution and neutralization of acidity occurred as AMD flowed through the bench scale OLC treatment system. Calcium concentrations in effluent increased by at least 39% (Figure 5.6), and bicarbonate alkalinity was generated, averaging 15 mg/L CaCO<sub>3</sub> (Figure 4.18) in effluent from the OLC settling pond. This caused a gradual increase in pH with distance along the channel (Figure 4.22). However, the effectiveness of neutralization declined as HRT was shortened, shown by an overall decline in pH with distance along the channel, and effluent decreasing to <pH 5 at HRTs shorter than 13 hours (Figure 4.19). Therefore, the extent of limestone dissolution decreased with reduced contact time with AMD in the OLC system (Watzlaf et al., 2003; Younger et al., 2002; Cravotta, 2004). Reduced limestone dissolution is demonstrated by a rapid decline in calcium export efficiencies,, decreasing from 90% at the longest HRT tested (15 hours HRT) to 39% at 11 hours HRT (Figure 5.6). Effluent alkalinity concentrations are relatively low compared to the SRBR and LLB bench scale systems, which is explained by the bicarbonate alkalinity generating reactions only occurring at pH values above 5 (Younger et al., 2002). The increase of pH at approximately 7 – 10 m distance along the channel is related either to a contact time threshold for limestone dissolution and alkalinity generation (inducing greater pH) or by generation of acidity by metal hydrolysis that increases limestone dissolution causing a localized increase of pH.

### 5.2.3.3.2 Metal Removal

Iron and aluminium were increasingly removed with distance along the channel by precipitation of metal hydroxides as increased pH (Figure 4.23). Removal of FeIII was rapid, as pH was increased above 3.5 at all HRTs by 1.0 m distance along the channel. This is supported by an accumulation of ochre precipitate on limestone clasts at 0 - 0.25 m (Figure 4.26), and iron removal of almost 50% at 1.0 m distance while operating at HRTs >13 hours. Oxidation of FeII and consequent removal also occurred as aerobic conditions prevailed within the channel, with dissolved oxygen concentration of 6.26 mg/L measured in the settling pond. Oxidation of FeII was most evident by another accumulation of ochre precipitate immediately below where AMD dripped from the upper to middle channel tier, at 2 m distance. The drop into the channel below aerated AMD enough to oxidize soluble FeII, which then precipitated as ferric hydroxide due to the elevated pH in the channel (pH >4 at HRTs >8 hours). This is supported by a change in the composition of iron species between drip points (Figure 4.21), with the proportion of FeII in AMD decreasing from 38% to 0% from the upper to middle channel tier (at 2 m distance), along with a slight increase in dissolved oxygen concentrations immediately after drip points (Appendix III, E). This process is reflected in iron removal efficiencies along the channel (Figure 4.23), with greatly increased iron removal at 3 m distance along the channel at HRTs >11 hours, after AMD had dropped between tiers. No noticeable increase in iron removal occurs after the drop from the mid to lower tier (between 6 m and 9 m sampling locations) because most iron had been removed at this distance. Iron removal in the OLC system declined as HRT was shortened, with removal decreasing from >98.5% at 14 hours HRT to 74.7% at 8 hours HRT (Figure 5.1). Lower removal during the latter stage of the trial is attributed to more soluble FeII in influent AMD, as pH of settling pond effluent remains above 3.5 throughout the trial which should remove all ferric iron from solution.

Aluminium was removed gradually along the OLC system (Figure 4.23), up to approximately 7 - 8 m distance, as the solubility of aluminium decreased as pH increased due to limestone dissolution. This is supported by white precipitate on limestone clasts and within the channel downstream of 0.25 m distance. At longer HRTs (>14 hours HRT) pH is increased to remove most dissolved aluminium, with 98.8% removal at 8 m distance, and almost 100% removal by 12 m distance along the channel (15 hours HRT). The zone of increased aluminium precipitation between 8.25 m and 9.75 m distance (Figure 4.26) is due to rapid precipitation of aluminium as a pH of 5 was reached. Over time aluminium precipitate and sludge filled the

channel, completely covering limestone clasts in this zone. Hydrolysis reactions during aluminium precipitation generates proton acidity. At longer HRTs ( $\geq 13$  hours) hydrolysis generated acidity is buffered by reaction with limestone and bicarbonate alkalinity, and there is a continued rise in pH downstream of the sludge zone. However, at HRTs  $< 13$  hours, increased metal loading from higher flow rates caused more hydrolysis related acidity that was not sufficiently neutralized by limestone dissolution due to shorter contact time. This caused the pH in the channel to decrease downstream of 9 m. For example, when the OLC system operated at 9 hours HRT the pH decreased from 5.35 at 9 m, to 4.8 at 10 m distance along the channel. Similar to iron, removal of dissolved aluminium in the OLC system declines at shorter HRTs ( $< 14$  hours), with about 40% removal at 8 hours HRT (Figure 4.23 and Figure 5.1). This is related to the higher solubility of aluminium as pH decreases to below 5 in channel due to shorter time for neutralization of AMD, and therefore less aluminium is precipitated. In addition, dissolution of aluminium precipitates previously deposited in the channel in the lower pH conditions at shorter HRTs also likely contributed to lower removal efficiencies. The poor treatment performance at shorter HRTs was the reason why metal analysis of effluent was ceased.

Removal of manganese, nickel and zinc is poor in the OLC system because of their high solubility in carbonate based treatment systems (PIRAMID Consortium, 2003). Initial removal is likely caused by adsorption and co-precipitation with iron and aluminium hydroxides (Younger et al., 2002; Watzlaf et al., 2003). Copper removal is relatively high (88% at 15 hours HRT) and is likely removed by adsorption to aluminium precipitates indicated by a very similar removal trend to aluminium. Net export of dissolved manganese, nickel and zinc at HRTs  $< 10$  hours (particulate export occurs earlier) is caused by dissolution of absorbed metals as pH decreases and metals are remobilized (Younger et al., 2002). Autopsy investigation revealed limestone clasts in the OLC system had a black, spotty appearance, that increased in abundance with distance along the channel (Figure 4.37). This appearance was mostly obscured during operation of the OLC system because of the covering of aluminium precipitates on limestone clasts, but must have developed in the latter stages of the trial. Similar to the LLB system the black precipitate on limestone clasts indicates precipitation of manganese oxide by a similar mechanism as described. High magnification SEM images of a limestone clast from OLC outflow show a manganese rich coating on the surface of the limestone (~50% manganese) together with nodules of similar composition (Figure 4.38). Therefore, had metal analysis continued an improvement in manganese nickel

and zinc removal likely would have occurred. However, the extent of removal of these metals would be limited in the OLC system at shorter HRTs (pH <5) because a pH above 6 is required for optimal precipitation of manganese (Younger et al., 2002).

Aluminium and iron particulates are increasingly retained within the channel as the trial progressed because there is increasingly similarity between dissolved and total removal efficiencies (Figure 5.1). Similar to the LLB system this is most likely related to increased filtration and retention of metal solids as a result of the build up of precipitates within the channel.

#### **5.2.3.3.3 Potential Limitations for OLCs**

Open limestone channels are recommended to have a slope of between 10 and 20% to maintain high flow velocities to carry away iron and aluminium precipitates and minimize limestone armouring or channel clogging (Ziemkiewicz et al., 1994; 1996; Skousen & Ziemkiewicz, 2005). This recommendation is supported by results, as OLC trial system was constructed sub-horizontal and limestone clasts had initial iron armouring at distances of 0, 1 and 2 m (Figure 4.37) and were covered with aluminum hydroxide precipitate further down the channel (Figure 4.26). Iron armouring probably had little impact on treatment performance because it was restricted to a very short section of channel, however, the potential for more armouring is clear. The extent of aluminium solids accumulation undoubtedly had an adverse affect on treatment performance of the OLC system, reducing porosity within the limestone clast layer and promoting preferential flow over limestone clasts instead of between clasts. This would have reduced HRT in the system and contact time of limestone clasts with AMD for neutralization. The latter factor contributed to reduced effectiveness because limestone burial is probably a more significant problem than armouring (Ziemkiewicz et al., 1994). Decreases treatment effectiveness is confirmed by results for control HRTs that show metal removal effectiveness decreased over time (Figure 5.4) and therefore the accumulation of iron and aluminium precipitates could severely impact the long term effectiveness of an OLC treatment system.

Although the gradient of the trial OLC treatment system (<1%) is significantly less than recommended, it is considered more representative of a full scale OLC system at Fanny Creek than a 10 – 20% slope. This is because an OLC system would be constructed following a

sedimentation pond to prevent burial of limestone by sediment, and this would occur on the valley floor in the Waitahu valley where the gradient is relatively shallow (Figure 1.2).

#### 5.2.3.3.4 Optimal Treatment and Design Criteria

Optimal design criteria for a OLC treatment system to treat Fanny Creek AMD include:

- Effective limestone dissolution and neutralization of acidity requires at least 13 hours HRT. Settling pond effluent was raised to above pH 5.15, and alkalinity generation ranged between 15 and 20 mg/L CaCO<sub>3</sub>.
- Effective removal of ferric iron occurred at HRTs  $\geq 5$  hours as solubility of metal hydroxide was exceeded. Ferrous iron oxidation and removal requires aeration and increased dissolved oxygen concentrations in AMD.
- Effective removal of aluminium requires  $\geq 14$  hours HRT, related to the low solubility of aluminium above pH 5.
- Most effective copper removal requires 15 hours HRT and the presence of iron and aluminium hydroxides.
- Effective removal of manganese, nickel and zinc requires HRTs  $> 15$  hours.
- Channel gradient must be steeper than sub horizontal ( $> 1\%$ ) to enable sufficient flow velocity to prevent accumulation of iron and aluminium hydroxides which can limit treatment effectiveness.

Optimal HRT criteria for an OLC treatment system for Fanny Creek AMD are based on effective neutralization, removal of dissolved metals, and transport of metal precipitates from the system. Therefore, a HRT of 15 hours is recommended for design of an OLC treatment system. This is a conservative HRT for neutralization of acidity and removal of dissolved ferric iron, however, 15 hours HRT represents a minimum value for effective removal of dissolved aluminium. Criterion does not provide for effective removal of manganese, nickel and zinc. The channel gradient should be at least 10% to remove iron and aluminium precipitates. A full scale OLC system should employ limestone clasts approximately 150 – 300 mm in size to maximize flow velocity.

Criteria developed from the bench scale OLC treatment system are similar to design criteria suggested in the literature (Ziemkiewicz et al., 1994; Skousen & Ziemkiewicz, 2005). However, it is suggested that a time frame of days may be needed for effective treatment in OLC passive AMD treatment systems Ziemkiewicz et al. (1996).

### **5.3 The Waitahu River Mixing Option**

The viability of this option depends on whether the Waitahu River could neutralize Fanny Creek AMD, and if river water could be transferred to the treatment area for mixing with AMD.

#### **5.3.1 Waitahu River Buffering Capacity and Metal Removal**

Data from monthly monitoring in Fanny Creek catchment indicate the Waitahu River is capable of neutralizing Fanny Creek AMD because river water has natural buffering capacity (15 – 30 mg CaCO<sub>3</sub>/L) (Table 4.7). Neutralization of AMD was confirmed by an increase of pH to above 5 when water from the Waitahu River was added to Fanny Creek AMD from site R12 (Appendix III, D). The pH increases because alkalinity in river water quickly reacts to neutralize acidity in AMD and acidity generated by metal hydrolysis is also buffered.

No metal analysis was completed for the mixture of Fanny Creek AMD and Waitahu River water after neutralization to pH 5 occurred. At the circum-neutral pH, however, dissolved ferric iron or aluminium are removed from solution by precipitation as metal hydroxides. Other metals at elevated concentrations in Fanny Creek AMD such as copper, nickel, zinc and manganese likely remain in solution as they have higher solubility. However, some removal of these metals may occur by adsorption and co-precipitation with iron or aluminium precipitates (PIRAMID Consortium, 2003; Watzlaf et al., 2003).

#### **5.3.2 Waitahu River Flow Volume Required to Neutralize AMD**

Monthly monitoring of acidity (pH 5) and flow rate in Fanny Creek, along with alkalinity of the Waitahu River enabled a calculation of the flow volume of river water required to neutralize AMD to pH 5 for each monthly occasion using a acidity and alkalinity ratio (Table

4.7). Comparison of calculated ratios to those derived from actual mixing of Waitahu River water with AMD in October, November and January indicate ratios are mostly comparable (Table 4.8). However, only three occasions are compared, and the ratios of samples collected in November are slightly different (1.52 compared to 1.00), but this difference is probably due to titration inaccuracy. Therefore, results of actual mixing of river water with Fanny Creek AMD verify the calculated monthly ratios to neutralize acidity, and consequently the monthly estimates of flow volume required from the Waitahu River.

The average acidity and alkalinity ratio calculated from monthly monitoring is 1.1 for AMD at R12 and 2.7 for more acidic AMD at IB5c (). However, assuming worst case AMD conditions with maximum acidity at R12 (32.5 mg CaCO<sub>3</sub>/L) and IB5c (70 mg CaCO<sub>3</sub>/L), along with maximum R12 flow rate (30 L/s), ratios of river water to neutralize AMD are about twice as much, with 2.2 and 4.7 at R12 and IB5c respectively. Therefore, the estimated flow volume of river water required for neutralization during worst case conditions is significantly greater than the average from all monthly occasions and correspond to flows of 65 L/s for neutralization at R12, and 140 L/s at site IB5c (compared to monthly averages of 16 L/s and 39 L/s, respectively). This occurred because of a low alkalinity concentration in the Waitahu River on the occasion in July (15 mg CaCO<sub>3</sub>/L) caused by rainfall dilution (river level elevated at time of sampling). Lower alkalinity in the Waitahu River meant more river water was needed to neutralize acidity during worst case conditions. Fanny Creek AMD is not diluted to a large extent during high flow conditions (section 2.5.5.3); therefore, it is appropriate to combine minimum alkalinity of the Waitahu River water and maximum Fanny Creek acidity concentrations, and so worst case flow volumes needed for neutralization are realistic. This is supported by calculated volumes of river water required to neutralize AMD in July of 45 L/s at R12, and 120 L/s at IB5c, which are comparable to estimates during worse case conditions.

Therefore, the design criteria range for the Waitahu River Mixing option to neutralize likely worst case Fanny Creek AMD to pH 5 include:

- A ratio of Waitahu River water to Fanny Creek AMD between 2.2 and 4.7.
- A minimum Waitahu River water flow volume of ~65 L/s
- A maximum Waitahu River water flow volume of ~140 L/s.

These flow volumes could be easily obtained from the large Waitahu River (approximately 15 - 20 cumecs) without significantly reducing downstream flow between site R8 and R5 (water would re-enter the Waitahu River after mixing with AMD).

Although an increase of Fanny Creek AMD to pH 5 is reported, actual mixing of Fanny Creek and Waitahu River water in January indicate pH can be increased above pH 5, with a maximum of pH 7 reached on this occasion (Appendix III, D).

Effective treatment of Fanny Creek AMD requires sufficient retention of mixed waters within settling ponds so that metal precipitates (especially buoyant aluminium hydroxides) can settle from the water column and be retained in ponds. Baffle structures and wetland vegetation can increase the retention time of water in settling ponds, increasing removal of metal solid. This is particularly necessary during worse case conditions where the combined flow volumes through the settling ponds could reach more than 170 L/s.

### **5.3.3 Transfer Method for Mixing Waitahu River Water with AMD**

The overall down gradient from monitoring site R8 to site R12 means water from the Waitahu River can be transferred to the AMD treatment site by gravity flow. This requires construction of a channel to divert flow from the river to be directed along the inside toe of the sediment fan for mixing with Fanny Creek AMD.

Investigation of a passive method to lift water from the Waitahu River to avoid channel construction identified the Hydraulic Ram Pump System. However, the flow volume required for neutralization exceeds the practical capability of a such as system, and it is probably less economic compared to construction of a channel (Appendix III, E).

### **5.3.4 Potential Limitations**

Limitations of this passive treatment option include:

- Removal of elevated trace metals such as manganese, nickel and zinc is likely to be poor. There is however potential to dilute AMD significantly so that elevated metal concentrations are adequately lowered.

- Removal of precipitated metals within settling basins could be difficult with increased flow rates through settling basins, with construction of additional ponds likely.
- The river water alkalinity to acidity ratio is currently well defined, however, flow rate measurement limitations at R12 could affect criteria values of Waitahu River water required for neutralization (i.e. more flow volume water required).

## **5.4 Comparison of Trial Passive Treatment Systems**

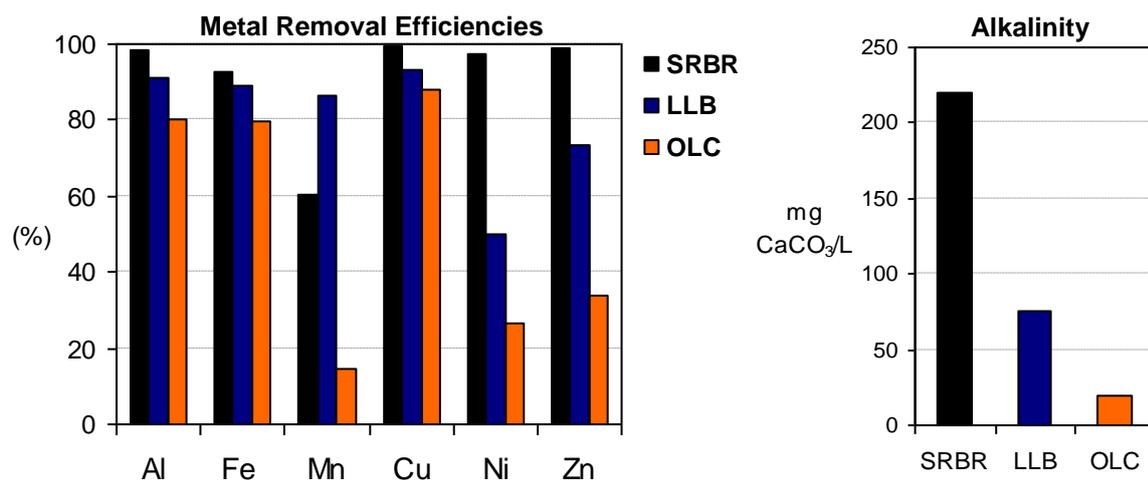
Comparison of laboratory trial options enabled optimal passive treatment strategies for Fanny Creek AMD to be determined. The four AMD treatment options trialed are compared in terms of water chemistry treatment effectiveness and implications for scale up at the site. Comparison of water chemistry primarily compares bench scale SRBR, LLB and OLC systems because detailed analysis was completed for these options, although scale up implications for the Waitahu River Mixing option is compared to other options.

### **5.4.1 Water Chemistry Treatment Effectiveness**

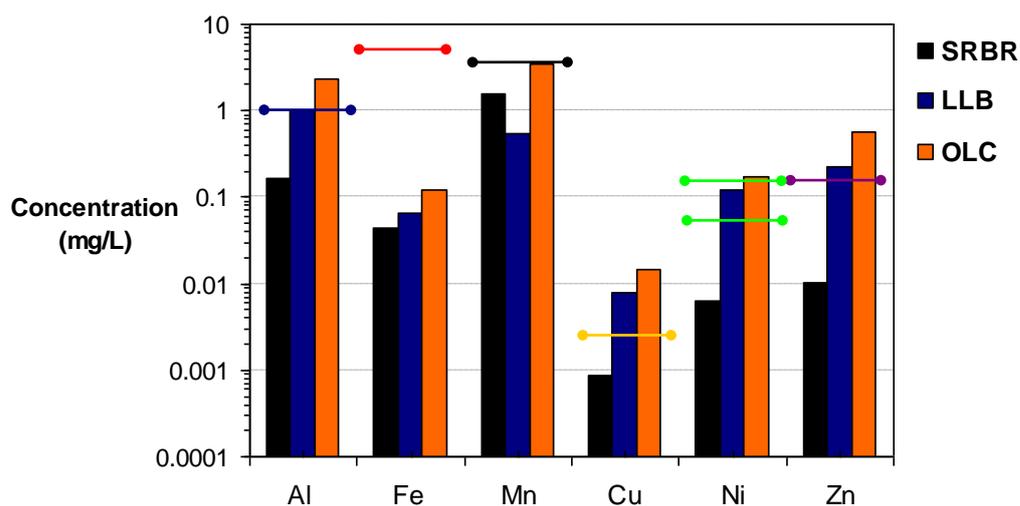
Comparison of water chemistry treatment effectiveness for bench scale SRBR, LLB and OLC systems uses final treatment performance at optimal HRTs. Therefore, water chemistry of SRBR, LLB and OLC settling pond effluent is compared when systems operated at 51 hours, 5 hours, and 15 hours, respectively (Figure 5.9). Comparison and evaluation of treatment effectiveness is based principally on the capability of each system to achieve water quality criteria for Cypress Mine. Cypress Mine is a recently consented coal mine on the West Coast and it is likely future mining would have similar consent conditions (Figure 5.10).

Metal removal efficiencies and effluent alkalinity (pH 3.7) concentrations for treatment systems are measurements of effluent at optimal HRTs (Figure 5.9). However, to enable comparison of metal removal performance effluent metal concentrations at optimal HRTs were calculated to normalize results and minimize the effect of influent AMD chemistry variation during the trial (Figure 5.10). Effluent metal concentrations were normalized by applying settling pond metal removal efficiencies at optimal HRTs to average metal concentrations of influent AMD during the trial. Effluent is compared related to Cypress Mine consent water quality criteria (Table 2.1), therefore, calculated metal concentrations for aluminium and iron were calculated from total metal analysis (comparable to acid soluble),

and manganese, copper, nickel and zinc concentrations were calculated from dissolved metal analysis at optimal HRTs. No criteria are specified for manganese and copper for Cypress Mine, so ANZECC guideline values are used. Water quality criteria for each metal are shown as colored horizontal lines which provides direct evaluation of treatment system metal removal performance (Figure 5.10).



**Figure 5.9: Final metal removal efficiency and alkalinity generation treatment performance for bench scale SRBR, LLB and OLC systems at optimal HRTs.**



**Figure 5.10: Calculated effluent metal concentrations for bench scale SRBR, LLB and OLC treatment systems at optimal HRTs. Water quality limits for Cypress Mine (Al, Fe, Ni, Zn) and ANZECC guideline values (Mn, Cu) indicated by horizontal lines. Effluent metal concentrations calculated from removal efficiencies at optimal HRTs and average influent AMD metal concentrations.**

Overall, the SRBR system has most effective metal removal efficiencies at optimal HRTs for trial systems (Figure 5.9). The SRBR system removed  $\geq 92.5\%$  of all elevated metals, except for manganese (60.4%). The LLB system was next most effective with removal  $\geq 86.3\%$  for all metals apart for nickel and zinc, however the LLB had highest manganese removal (86.3%) of all trial systems. The OLC system had poorest metal removal performance, with lowest efficiencies for all metals compared to other systems. Removal efficiencies for nickel and zinc differed most between trial systems. The SRBR removed almost 100% of influent nickel and zinc, while the LLB respectively removed 50.0% and 73.6%. The OLC system removed only about a third of the nickel (26.7%) and zinc (33.8%) removed by the SRBR system.

The SRBR system had greatest alkalinity concentrations (220 mg CaCO<sub>3</sub>/L) at optimal HRTs, followed by the LLB system (75 mg CaCO<sub>3</sub>/L), while the OLC system had lowest alkalinity (20 mg CaCO<sub>3</sub>/L). All treatment systems increased pH above the median limit (pH 4.5) stipulated for Cypress Mine. In accord with alkalinity, the SRBR increased pH the most (7.12), however, the pH of effluent for the LLB system was lowest (6.08), with a pH of 6.62 measured for the OLC system at optimal HRT. It is highly unlikely that a relatively lower pH occurs at higher alkalinity concentrations, therefore, pH measurements for the LLB and OLC are probably erroneous (pH of 5.65 directly from OLC system is more likely the correct value).

Normalized effluent metal concentrations for SRBR, LLB and OLC treatment systems at optimal HRTs have the same trend as metal removal efficiencies, and display treatment effectiveness relative to Cypress Mine and ANZECC water quality limits (Figure 5.10). The SRBR system was most effective at decreasing influent metal, with effluent metal concentrations well below Cypress and ANZECC limits, with 0.17 mg/L aluminium, 0.044 mg/L iron, 1.6 mg/L manganese, 0.00085 mg/L copper, 0.0063 mg/L nickel, and 0.010 mg/L zinc. The LLB system demonstrates next most effective treatment, with effluent at the limit for aluminium (1.0 mg/L), below for iron (0.065 mg/L) and manganese (0.55 mg/L), and slightly below the maximum for nickel (0.12 mg/L) although the lower limit is exceeded. However, concentration for zinc (0.23 mg/L) marginally exceed Cypress Mine limits, and copper (0.0079 mg/L) is above the ANZECC guideline value. Treatment of the OLC treatment system was least effective, with calculated effluent metal concentrations above water quality limits for aluminium (2.3 mg/L), copper (0.014 mg/L), nickel (0.18 mg/L) and

zinc (0.58 mg/L), although effluent is below for iron (0.12 mg/L), and just under the limit for manganese (3.42 mg/L).

Metal removal effectiveness for the Waitahu River Mixing Option can not be quantitatively compared to other trial systems because no metal analysis for this option was completed. However, alkalinity in river water has the capability to neutralize Fanny Creek AMD and increase pH to above 5. At this pH dissolved ferric iron and aluminium are removed along with their metal hydroxide precipitates given sufficient retention time in settling ponds, and a minor amount of dissolved trace metal removal will also probably occur. Therefore, because the Waitahu River can provide an abundant supply of alkaline water, this option most likely has the capability to remove metals and significantly dilute AMD to the point where Cypress Mine and ANZECC water quality criteria limits are achieved.

#### **5.4.1.1 Optimal AMD Treatment Options based on Water Chemistry**

Comparison of effluent water chemistry for SRBR, LLB and OLC treatment systems at optimal HRTs indicates the SRBR system performs best and is capable of most effective AMD treatment. The SRBR system achieves Cypress or ANZECC water quality criteria for all metals, generates greatest alkalinity and increases pH the most compared to LLB and OLC systems. Treatment by the LLB system decreases metals so that effluent concentrations only slightly exceed the lower limit for nickel, and slightly for zinc and copper. Alkalinity generation in the LLB system was roughly a third that for the SRBR system, and effluent pH was lowest of all options but is above pH 6. The OLC system has worst treatment performance at optimal HRTs of the trial treatment systems. Metal concentrations in effluent were above water quality limits for all metals (except iron) and alkalinity generation was minimal, having less than a third of that generated by the LLB system.

Although the SRBR system demonstrates superior performance the following factors are considered when selecting optimal treatment options for Fanny Creek AMD:

- Results suggest attenuation of copper, nickel and zinc in the SRBR system may be from short-term adsorptive processes, therefore, the long term removal effectiveness for these metals is inconclusive and may be limited. However, SRBR systems are reported to effectively removal such metals (Gusek, 2002, 2004; Neculita et al., 2007).

- The LLB system has effective treatment capability at a significantly shorter optimal HRT design criteria (5 hours) compared to the SRBR system (51 hours). This has implications for full scale system size requirements and costs.
- The Waitahu Mixing Option has the potential to neutralize acidity, remove metals, and significantly dilute AMD so that water quality limits are achieved.

Therefore, comparison of trial AMD treatment system water chemistry treatment performance suggests the following systems could be adequate for passive remediation of Fanny Creek AMD:

- Sulfate reducing bioreactor
- Limestone leaching bed
- Waitahu River Mixing

#### **5.4.2 Implications for Treatment System Scale up at Fanny Creek**

The application of passive AMD treatment options at Fanny Creek requires that the implications of scale up of the different options be considered because this relates to AMD treatment costs. Adequate treatment options, SRBR, LLB and Waitahu River Mixing determined from evaluation of water chemistry treatment performance are compared in terms of size and construction requirements, and factors that may affect the long term treatment effectiveness of systems are also considered in order to determine optimal treatment options for Fanny Creek AMD.

##### **5.4.2.1 SRBR and LLB Treatment Systems**

A simplified sizing method described by Younger et al. (2002) was used to estimate the volume of a full scale SRBR and LLB system required to treat AMD, and thus, approximate full scale treatment system size can be established (Table 5.1). The sizing calculation is based on optimal HRTs, maximum flow rate at Fanny Creek and assumed porosity of reactive treatment materials (Appendix IV, B). The dimensions of full scale systems (Table 5.1) satisfy the calculated volumes, but are arbitrary and only intended to give an approximate sense of scale for full sized systems (i.e. for the LLB system,  $35\text{ m} * 18\text{ m} * 2\text{ m} = 1260\text{ m}^3$ , instead of  $1\ 200\text{ m}^3$ ).

**Table 5.1: Volume and size estimates for full scale SRBR and LLB treatment systems based on optimal HRTs.**

	Volume of reactive material required m <sup>3</sup>	Number of units	Dimensions		
			Length	Width	Thickness
<b>SRBR</b>	13 770	4	62	28	2
<b>LLB</b>	1 200	1	35	18	2

Note: Dimensions are approximate. The full scale SRBR system includes four separate SRBR units in parallel.

Sizing estimates indicate a full scale SRBR system operating at optimal HRT (~two days) requires an organic substrate volume of 13 700 m<sup>3</sup>. A SRBR system that has four parallel SRBR units with approximate dimensions of 62 m long, by 28 m wide, with a 2 m thick substrate mixture, satisfies this volume. The total size of the four SRBR units would be about 120 m by 65 m long. The system comprises separated treatment units because this is standard design practice for SRBR systems to distribute flow of AMD (Watzlaf et al., 2003; PIRAMID Consortium, 2003). A full scale LLB system operating at optimal HRT (5 hours) requires a limestone clasts volume of 1 200 m<sup>3</sup>. A single limestone bed with dimensions of 35 m long, by 18 m wide, with a 2 m limestone clasts thickness satisfies this volume. Sizing estimates indicate the area available on the Waitahu Valley floor (1000 m across by 150 m wide) can accommodate either a full scale SRBR or LLB passive treatment system.

Construction of a full scale SRBR or LLB treatment system for Fanny Creek AMD requires engineered retaining walls to contain drainage piping and reactive treatment materials. The design of a SRBR system is relatively more complicated compared to a LLB system, due to the requirement of separate SRBR units, and different layers that include drainage gravel and overlying geo-textile, organic substrate mixture, and upper post peel and surface water. Safety measures to restrict access to the saturated SRBR surface are also required (i.e. to exclude fauna such as deer).

Scale up of SRBR and LLB treatment systems to treat Fanny Creek AMD indicates the size of a full scale SRBR system is about an order of magnitude larger than the size of a full scale LLB system. The substantial difference in size has implications for AMD treatment costs and therefore it is highly likely the treatment costs of a SRBR system to will be much greater compared to the cost of implementation of a LLB system. This is caused by initial costs associated with construction of the more complicated SRBR system and delivery of materials

to the relatively isolated treatment site, even though waste materials are employed in the SRBR system.

#### **5.4.2.2 Waitahu River Mixing Option**

Size estimation for the Waitahu River Mixing option is not possible with the data available, however, sizing is briefly discussed. The size of this treatment option relates to the area of settling pond required to enable sufficient removal of metal precipitates from the water column. Neutralization of acidity will proceed quickly once AMD and river water mix, however, water will require a certain residence time within ponds for settling of aluminium and iron hydroxide solids. Cypress Mine water quality criteria for aluminium and iron is based on acid soluble analysis which includes the particulate fraction of metals, therefore, metal solids need to be removed to achieve criteria. The size of the settling ponds for the Waitahu River Mixing option will be controlled by the size required for settling of metal precipitates during highest combined Waitahu River and Fanny Creek flow volumes (~170 L/s).

Design considerations for the Waitahu River mixing option are relatively simple with construction of a channel to divert water from the Waitahu River to be transferred to the AMD treatment are near monitoring site R12. The primary design considerations for this option are:

- The elevation of the sediment fan adjacent to the Waitahu River is above the river level by about 2 m (at site R8). Channel construction along the toe of the sediment fan requires a reasonable degree of earth removal to create downward gradient for water transfer, and the level of the first settling basin will also likely need to be lowered to allow flow from the Waitahu River.
- The water level of the Waitahu River has considerable seasonal variation (~0.5 m) and therefore channel design has to account for such fluctuations. This may involve a mechanism to restrict flow from the Waitahu River during high flow conditions (flood events) to prevent excessive flow through settling ponds which could entrain sediment and metal precipitates and cause water quality criteria to be exceeded.

### 5.4.2.3 Long Term Treatment Performance Factors

Factors that may affect the long term treatment performance and economic viability of adequate passive treatment options for Fanny Creek are considered:

- **Reactive Treatment Material Depletion:** Infrequent but regular addition of both organic substrate and limestone is required to maintain bacterial sulfate reduction and limestone dissolution, respectively.
- **Hydraulic Problems:**

**SRBR System:** Compaction and clogging of organic substrate materials by solids (sediment, metal precipitates, biomass) can reduce porosity and permeability and cause development of preferential flow paths and system failure.

**LLB system:** Accumulation of iron, aluminium and manganese precipitates may reduce porosity and permeability and lead to short circuiting and inefficient limestone dissolution. Limestone may become armoured with metal precipitates which can reduce limestone dissolution (Ziemkiewicz, et al., 1997).
- **Fanny Creek flow variability:** Low flow conditions in Fanny Creek will cause greatly increased HRTs in SRBR and LLB treatment systems that can exacerbate hydraulic problems mentioned above. This may also accelerate depletion of the organic substrate mixture in the SRBR system (Neculita et al., 2008).

## 5.5 Optimal Passive Treatment Options for Fanny Creek AMD

A summary of advantages and disadvantages of options selected as most suitable from water chemistry treatment effectiveness (SRBR, LLB or Waitahu River Mixing) illustrates the basis on which optimal passive treatment strategies for Fanny Creek AMD were chosen (Table 5.2). The evaluation includes both general and site specific factors that relate to AMD treatment performance and economic viability of selected options.

**Table 5.2: Advantages and disadvantages of passive treatment options for Fanny Creek AMD.**

Advantages	Disadvantages
<b>Sulfate Reducing Bioreactor</b>	
Effective removal of most metals	Large size requirement and cost
Prevention of aluminium clogging	Relatively complicated design
High alkalinity generation	Fanny Creek flow variability
Utilisation of waste material	Clogging and compaction
	Short circuiting of flow
	Carbon source depletion
	Long term trace metal removal uncertain
<b>Limestone Leaching Bed</b>	
Metal removal and alkalinity generation capability	Relatively lower metal removal
Relatively small size and cost	Clogging
Simple design	Short circuiting of flow
Limited iron armouring (low iron concentrations)	Limestone armouring
Flushing mechanism	Limestone depletion
<b>Waitahu River Mixing</b>	
Simple design	Removal of trace metals uncertain
River water provides constant, large supply of alkalinity	Potentially large settling pond requirements
Capability for effective metal removal and dilution	Waitahu River flow variability

In view of treatment system advantageous and disadvantageous, optimal passive treatment options for remediation of Fanny Creek AMD are:

- Limestone leaching bed; or
- Waitahu River Mixing

These options are chosen because they have the capability to achieve applicable water quality criteria, are relatively simple, and likely offer most cost effective AMD treatment due to smaller size requirements and measures to mitigate problems (i.e. flushing of precipitates for the LLB system). The SRBR system is most likely less cost effective compared to a LLB system and the Waitahu River Mixing option because of its greater size and design requirements. In addition, long-term treatment effectiveness could be limited as a result of flow variability in Fanny Creek which may cause accelerated substrate depletion and hydraulic related problems which can not be easily mitigated.

However, the uncertainty of AMD treatment effectiveness in relation to water quality criteria, and potential disadvantages of the LLB system and Waitahu River Mixing options can not be

overlooked, and the benefits of a SRBR system should not be disregarded. For this reason further investigation of all three options is required in a field context to accurately determine optimal the passive treatment strategy for Fanny Creek AMD.

## **5.6 Full Scale AMD Treatment System Considerations**

Full scale passive AMD treatment systems incorporate a ‘treatment train’ with the primary treatment unit preceded by a settling pond for sediment removal, followed by settling ponds and wetlands that act to polish and removal residual components in treatment system effluent prior to discharge from the site. Before and after settling ponds need to be appropriately designed to accommodate high flow conditions.

The valley floor is an ideal location for implementation of treatment system components. A suitable site for the primary unit (e.g. a LLB system) is immediately prior to existing settling basins (site R12), with preceding sediment removal ponds situated on the flat fan area. The current series of settling basins and wetland system can be incorporated and optimized for final polishing of treatment system effluent prior to discharge into the Waitahu River (Appendix IV, C).

Passive treatment designs should incorporate and optimize input of alkalinity from un-impacted drainage within the catchment. Alkaline drainage from sites U5 and U4 should be utilized before and after the primary AMD treatment unit, respectively.

Subsurface loss of flow from Fanny Creek to the Waitahu River should be minimized within the AMD treatment area either by compaction of underlying earth or by addition of impermeable material. This is particularly important for preceding sedimentation ponds in a treatment system.

A factor of safety in treatment system design should be included to account for the variable West Coast climate. This involves greater treatment system size of approximately ~50% than estimated.

## **5.7 Future Work**

### **5.7.1 Pilot Scale Testing**

The next step for design of optimal passive treatment strategies for Fanny Creek AMD is to complete pilot scale testing of SRBR, LLB and Waitahu River Mixing treatment systems at Island Block mine. Pilot scale application of AMD treatment options will determine the response of remediation processes, particularly microbial, to Island Block site variables such as AMD chemistry, flow rate, and temperature.

The data from pilot treatment systems will resolve uncertainties surrounding the long term treatment performance and verify optimal HRT and design criteria. This will allow more accurate sizing and cost estimates for full scale passive systems. Field testing will determine the economic viability of different treatment options and ultimately enable selection and design of the optimal AMD treatment system.

#### **5.7.1.1 Implementation of Pilot Scale Passive Treatment Systems**

A portion of Fanny Creek can be diverted for use in pilot scale AMD treatment systems. The current second settling basin is a suitable location for pilot SRBR and LLB systems because it can provide for sediment removal (Appendix IV, C).

Pilot scale SRBR and LLB systems are recommended to have a reactive treatment material volume of about 10 m<sup>3</sup> (~2.5 m wide, 4 m long, 1 m deep). Pilot system designs should be comparable to bench scale systems, although the SRBR should have horizontal down-flow because this replicates full scale design. The LLB system should employ limestone clast sizes used in full scale systems (75 – 100 mm). Pilot systems are advised to include a drainage mechanism to enable periodic flushing of systems. Effluent should discharge into separate settling ponds to simulate a full scale treatment system.

A pilot scale Waitahu River Mixing system can be simulated by construction of a series of small ponds (10 m<sup>3</sup> capacity) for mixing a portion of Fanny Creek AMD with un-impacted alkaline drainage from site U5 (using appropriate flow ratios). The alkalinity of drainage from the hillside at U5 is very similar to Waitahu River water, therefore, it is representative of a full scale system.

Sustained water chemistry and flow monitoring for about one year is required to obtain robust data to evaluate and compare metal removal performance and alkalinity generation of pilot systems during varying flow conditions and thus different hydraulic retention times.

## **5.7.2 Research Requirements for Pilot and Full Scale Treatment Systems**

### **5.7.2.1 SRBR System**

Aspects of the SRBR treatment system option that require investigation are:

- The long-term suitability of pilot scale organic substrate mixture to sustain bacterial sulfate reduction. This is indicated by the extent of sulfate removal over time.
- Whether removal of copper, nickel and zinc occurs in the pilot SRBR system by short term adsorptive processes as suggested by laboratory results, or by long term bacterial sulfate reduction. This will be determined by the effectiveness of metal removal over time.
- Changes of SRBR substrate mixture porosity and hydraulic conductivity as a result of accumulation of metal solids, particularly in relation to increased residence time in the system (i.e. porosity testing after low flows). The effectiveness of flushing and assessment of organic substrate compaction is recommended.
- In general, better understanding is required of metal removal processes and biogeochemical dynamics in SRBR systems. Improved understanding of sulfur reactions and mass balances in SRBR systems is required to help interpret sulfate and metal removal relationships.

### **5.7.2.2 LLB System**

Aspects of the LLB treatment system option that require investigation are:

- Whether manganese precipitation occurs in field conditions in the pilot scale LLB system. This has implications for removal of nickel and zinc in this system. The exact mechanism for manganese removal and initiation of this process requires further examination.
- The extent and affect of limestone armouring in the pilot LLB system, especially by iron or manganese precipitates.
- The potential for accumulation of metal solids, clogging and associated short circuiting problems. It is crucial pilot testing ascertains the effectiveness of flushing precipitates

from the limestone bed. Different drainage pipe configurations for most effective flushing is an important research aspect.

- A more accurate sizing method for larger scale LLB systems. Sizing should account for the smaller, more reactive limestone clast sizes used in the laboratory trial, with calculation of limestone surface area per unit volume. A comparison of between bench and pilot scale alkalinity generation will verify optimal HRT and design criteria.
- Prediction of limestone depletion rate and limestone mass for long term neutralization of AMD. This methodology and calculations are described by Cravotta III, 2008.
- The inclusion of lower quality limestone, dolomitic limestone, or mussel shells in the LLB system.
- The potential to include an SRBR component in a full scale system to increase removal of trace metals.

### **5.7.2.3 Waitahu River Mixing System**

Aspects of the Waitahu River Mixing option that require investigation are:

- The residence time of Fanny Creek AMD after neutralization with Waitahu River water in settling ponds to allow settling and removal of iron and aluminium precipitates. This directly controls the size requirement for this treatment option and can be determined by laboratory or pilot scale experiments.
- Pilot scale testing likely requires single analysis on one occasion. Regulation of flow rates of alkaline water (U5) and AMD from Fanny Creek will test a range of HRTs through constructed ponds and completion of total metal analysis will indicate the approximate time required for settling and effective removal of metal precipitates.
- Surveying of site topography from site R8 to R12 to determine the feasibility of channel construction for transfer of Waitahu River water to the AMD treatment site. This will quantify the amount of earth removal required.
- An effective flow control mechanism to restrict the flow of water from the Waitahu River into settling ponds during flood events.

## CHAPTER SIX

### Summary

#### 6.1 Project Outline

Fanny Creek is impacted by acid mine drainage (AMD) from Island Block opencast coal mine, owned by Solid Energy New Zealand Limited. Solid Energy is currently investigating ways to mitigate AMD by passive treatment methods such as constructed wetlands. There is limited data on drainage chemistry and flow rate in Fanny Creek catchment, and this information is required to design effective passive AMD treatment systems. The objectives of this study were to characterize drainage chemistry in Fanny Creek catchment and determine optimal passive treatment strategies for remediation of Fanny Creek AMD. Characterization of drainage in Fanny Creek catchment was achieved by monthly monitoring to collect drainage chemistry and flow data between February 2008 and January 2009. Laboratory scale trials of four suitable passive AMD treatment systems were conducted and their treatment performance assessed to select and design optimal passive treatment strategies for future pilot or full scale implementation at Fanny Creek.

#### 6.2 Characterization of Drainage Chemistry in Fanny Creek Catchment

##### 6.2.1 Upper Catchment

Characterization of drainage in upper Fanny Creek catchment occurred on three occasions between February and April, 2008. Detailed metal analysis was completed on samples collected in during March.

- Fanny Creek is primarily sourced from a number of AMD seeps on the steep eastern waste slope slopes of Island Block mine.
- Pyrite oxidation in overburden and Brunner Coal Measure waste rock sediments is the cause of AMD in Fanny Creek.
- AMD seep drainage chemistry varies considerably and is typical of drainage from opencast coal mines hosted in Brunner Coal Measures. The pH of drainage was low (average <3.62), enriched with aluminium and iron and contains elevated concentrations

of trace metals such as manganese, copper, nickel, zinc and cadmium relative to applicable water quality criteria (i.e. ANZECC guidelines).

- Seeps on mid and northern waste rock slopes had lower pH and higher metal concentrations compared to seeps on the southern waste rock slope.
- The AMD seeps on the northern waste rock slope contribute most acidity and metal to Fanny Creek, followed by AMD seeps on mid waste rock slopes. The contribution to Fanny Creek AMD from seeps on the southern slope is relatively negligible.
- The composition of seep chemistry differs between slopes. Seeps on mid and northern waste rock slopes contain primarily aluminium, whereas manganese is dominant in seeps on the southern slope. This is likely related to the different age and source of waste rock.

### **6.2.2 Mid Catchment**

AMD seeps on the northern waste rock slope form a northern tributary, and seeps on mid and southern slopes form a southern tributary. Tributaries combine midway in the catchment (monitoring site IB5) to form the main Fanny Creek channel. Monitoring occurred from February to July with metal analysis completed on samples collected in March.

- Fanny Creek AMD is mostly sourced from the northern waste rock slope with the northern tributary contributing the majority of acidity (~70%) and metal (~60%).
- Northern tributary drainage also dissolves additional metals upon mixing with the southern tributary.

### **6.2.3 Lower catchment**

- The most suitable location for a passive AMD treatment system is on the relatively large, flat Waitahu valley floor (site R12), because this allows for sediment removal prior to a AMD treatment system.
- Natural attenuation of AMD in Fanny Creek occurs in the lower catchment as a result of dilution with surface and ground waters, neutralization by un-impacted alkaline run-off, and by oxidation and precipitation, and sorption reactions.
- A number of un-impacted alkaline streams drain from adjacent hillsides. At confluence site IB7 the addition of alkalinity neutralizes acidity, which increases pH and causes a

decrease in downstream dissolved ferric iron and aluminium concentrations (solubility decreases at higher pH).

- Alkalinity in un-impacted drainage is likely derived from carbonate minerals in Greenland Group basement rocks comprise the hillsides below Island Block mine.
- Any future passive treatment designs should incorporate alkaline drainages to optimize natural conditions.

Monitoring site R12 is situated prior to existing settling basins and is the locality preferred for AMD treatment. Monthly monitoring characterized Fanny Creek in detail because this information is valuable for effective passive treatment selection and design. Monthly analysis was completed for metals identified as elevated within the catchment.

- Flow rate at R12 varied seasonally and ranged between 1.5 and ~30L/s. Drainage had an average pH of 3.95, average calculated acidity of 42.7 mg CaCO<sub>3</sub>/L and average dissolved concentrations of 6.0 mg/L for aluminium, 1.3 mg/L for iron, 3.1 mg/L for manganese, 0.49 mg/L for zinc, 0.14 mg/L for nickel, 0.0071 mg/L for copper and 0.00048 mg/L for cadmium.
- Drainage chemistry at R12 is largely independent of flow rate and primarily geochemically controlled. Rainfall dilution does not have a significant affect as indicated by minimal variation in chemistry at a range of flow rates.
- The rate of AMD generation from Island Block mine is proportionate to drainage, with acidity and metal loading increasing linearly with flow at R12.
- Rapid dissolution of secondary minerals from pyrite oxidation stored within waste rock are likely the source of increased acidity and metals during increased flow conditions.

Monitoring site R5 is after the series of settling basins and represents discharge to the receiving environment, the Waitahu River. Monthly analysis was completed for elevated metals.

- Flow of through settling basins from R12 to R5 is complex. On certain occasions loss of flow to the subsurface occurs (no surface flow at R5), while at other times flow is increased by un-impacted drainage.

- Water quality improves as AMD passes through settling basins due to input of alkaline drainage, natural wetland attenuation processes, and loss to subsurface flow. The pH at R5 is increased to an average of 4.33, and concentrations of acidity and metal are about half that at R12.
- Average metals concentrations (parenthesis) that exceed applicable ANZECC water quality guidelines are aluminium (2.68 mg/L), copper (0.0039 mg/L), nickel (0.076 mg/L), zinc (0.27 mg/L) and cadmium (0.00026 mg/L).
- Acid mine drainage discharged into the high flow, slightly alkaline Waitahu River has no detectable impact on downstream river water chemistry.

#### **6.2.4 Future Work**

Further investigation of Fanny Creek catchment chemistry and aspects for future mining include:

- Compilation of accurate flow data for passive treatment system design.
- Characterization of flush drainage chemistry during and after heavy rainfall.
- Increased monitoring once mining resumes to determine any changes in drainage chemistry occurs and whether this affects optimal passive AMD treatment options for Fanny Creek.
- Analysis of leach column testing and geochemical data of Island Block overburden units to characterize the acid producing potential of different lithologies and predict drainage chemistry. These results have implications for waste rock management and AMD mitigation.

### **6.3 Laboratory Trials and Optimal Passive AMD Treatment Options for Fanny Creek AMD**

A selection flow chart specific to New Zealand suggested either a sulfate reducing bioreactor (SRBR), limestone leaching bed (LLB), and open limestone channel (OLC) could be suitable passive AMD treatment systems to treat Fanny Creek AMD. A fourth, site specific Waitahu River Mixing option was also identified as potentially suitable and involved mixing alkaline

Waitahu River water with Fanny Creek to neutralize AMD. A phased selection and design approach to passive treatment was adopted, therefore, laboratory trials of ‘bench’ scale SRBR, LLB and OLC systems and the Waitahu River Mixing option were conducted. The treatment performance of laboratory trial systems was interpreted and assessed to identify optimal treatment options for Fanny Creek AMD and to obtain data to size and configure future pilot or full scale passive treatment systems.

### **6.3.1 Laboratory Trial Experimental Design**

Laboratory trials of bench scale SRBR, LLB and OLC treatment systems were held over a duration of about four months in Christchurch, and the Waitahu River Mixing option was tested in Reefton laboratory. The AMD used for trial systems was sourced from Fanny Creek and simulated worst likely AMD at the proposed treatment site at R12.

- The hydraulic retention time (HRT) within bench scale SRBR, LLB and OLC treatment systems was systematically decreased and treatment effectiveness was assessed by analysis of effluent after each HRT. The HRT for the SRBR system was reduced from 56 to 5 hours, and the HRT for LLB and OLC systems was respectively decreased from about 15 hours to 5 hours.
- The SRBR system comprised an organic substrate mixture of mussel shells, post peel, bark, and compost. The LLB and OLC systems were composed entirely of small limestone clasts. Treatment systems discharged into small plastic containers to simulate settling ponds following AMD treatment.
- The Waitahu River Mixing option used acidity and alkalinity data from monthly catchment monitoring to calculate a ratio of alkaline river water required to neutralize AMD to pH 5. The calculated ratio was combined with Fanny Creek flow rate data to determine the flow volume of river water required to neutralize AMD.

## 6.3.2 Bench Scale SRBR, LLB and OLC Passive Treatment Systems

### 6.3.2.1 Treatment Effectiveness

The treatment effectiveness of bench scale SRBR, LLB and OLC systems was established primarily by metal removal efficiencies in settling pond effluent for each system. Effluent from settling ponds was used because it reflected final treatment of AMD at each HRT for trial systems. Alkalinity generation and pH of effluent was also indicative of treatment systems effectiveness. Overall, as the HRT in treatment systems was shortened, the AMD treatment effectiveness of trial systems also decreased:

#### ▪ SRBR Treatment System

- Greatest removal of dissolved aluminium (99.8%), iron (>97.1%) and zinc (99.6%) occurs at HRTs  $\geq 8$  hours, and at  $\geq 5$  hours HRT for copper (99.3%). Most effective removal of nickel (98.7%) and manganese (70.9%) occurs at a much longer HRTs (56 hours). At HRTs <8 hours dissolved removal decreases for aluminium (29.6%), iron (42.9%), and nickel (15.0%), and net export of zinc (-15.4%) and manganese (-8.3%) occurs. Sulfate removal only occurs at HRTs  $\geq 51$  hours ( $\leq 18.8\%$ ).
- Total metal removal efficiencies are comparable to dissolved removal efficiencies initially; however at shorter HRTs (<24 hours) total metal removal decreases more rapidly which indicates metal precipitates are increasingly discharged from the SRBR system at higher flow rates.
- Maximum alkalinity generation (255 mg CaCO<sub>3</sub>/L) and pH (7.12) occurs at 51 hours HRT. Alkalinity steadily decreases with shorter HRT to a minimum of 15 mg CaCO<sub>3</sub>/L and pH decreases to below 5 at HRTs <8 hours.
- Metal removal decreases over time for all metals except iron, decreasing most for manganese, copper and zinc.

#### ▪ LLB Treatment System

- Removal is most effective at HRTs  $\geq 5$  hours for dissolved aluminium (99.8%), iron (>98.4%) and copper (97.1%). Removal is relatively poorer initially for dissolved nickel (6.3%), zinc (36.7%) and manganese (5.7%); however, removal increases to 67.5% (Ni), 89.1% (Zn), and 97.1% (Mn) at shorter HRTs (7 hours HRT).

- Total metal removal efficiencies are more similar to dissolved efficiencies at shorter HRTs and faster flow rates which indicates greater retention of metal particulates within the LLB system. Removal slightly decreases at the shortest HRT tested (5 hours).
  - Alkalinity generation for the LLB system is steady (60 - 90 mg CaCO<sub>3</sub>/L) and effluent pH is increased above 6.0 at all HRTs tested ( $\geq 5$  hours HRT).
  - Metal removal mostly increases over time, especially for manganese, nickel and zinc.
- **OLC Treatment System**
- Removal is most effective at HRTs  $\geq 14$  hours for dissolved aluminium (99.4%), iron (>98.5%) and copper (88.0%); however, removal declines at shorter HRTs to 37.1% (Al), 74.7% (Fe) and 19.7% (Cu) at 8 hours HRT. Maximum removal is relatively poor for dissolved nickel (26.7%), zinc (33.9%) and manganese (14.6%), and net export of these metals occurs at HRTs <10 hours.
  - Total metal removal efficiencies are more similar to dissolved efficiencies at shorter HRTs, especially for iron and aluminium. This indicates more metal particulate is retained in the OLC system.
  - Alkalinity generation is relatively low at all HRTs tested ( $\leq 25$  mg CaCO<sub>3</sub>/L). The pH of effluent is increased to a maximum of 6.62 at 15 hours HRT, but drops to below 5 at HRTs <13 hours.
  - Metal analysis was not completed for effluent at HRTs <8 hours because of poor performance.
  - In general, metal removal decreases over time, particularly decreasing for copper and also for aluminium and iron.

### 6.3.2.2 Treatment Processes

Certain AMD treatment processes in bench scale SRBR, LLB and OLC treatment systems were identified. This helped to determine optimal HRTs for AMD treatment in systems and evaluation of long term treatment effectiveness.

### ▪ **SRBR Treatment System**

- Bacterial sulfate reduction occurred in the SRBR system at longer HRTs as indicated by sulfate and metal removal, an odour of hydrogen sulfide and suitable anaerobic conditions. This process was optimal at 51 hours HRT, but bacteria were less active and diminished at shorter HRTs (<14 hours) due to unsuitable anaerobic conditions.
- Alkalinity was generated primarily by dissolution of mussel shells in the organic substrate mixture, rather than by bacterial sulfate reduction.
- Dissolved iron was removed by formation of black iron sulfide in the SRBR system, and by aerobic removal with precipitation of ochre iron hydroxide on the SRBR surface and in the settling pond (up to 50% removed).
- Removal of dissolved aluminium was controlled by pH. The SRBR system prevented the formation of gibbsite with minimal white precipitate in substrate after AMD treatment.
- Removal of manganese, copper, nickel, and zinc was likely caused by short term adsorption processes to organic substrate materials and metal precipitates because removal of these metals decreased over time. Therefore, long term removal of these metals by bacterial sulfate reduction was inconclusive.
- Metal precipitates accumulated in the organic substrate mixture but flushing the SRBR system had relatively little affect of removing metal solids from the substrate.

### ▪ **LLB Treatment System**

- Neutralization of acidity and generation of alkalinity in the LLB system occurred by limestone dissolution at all HRTs tested. This is indicated by net export of calcium in effluent, and an increase of pH relative to influent AMD.
- Removal of dissolved aluminium and iron occurred by precipitation of white and ochre oxyhydroxides, respectively, on the surface and within the LLB system. Copper was most likely removed by adsorption to aluminium and iron precipitates.
- Increased manganese removal at shorter HRTs was caused by precipitation of black manganese oxides by an autocatalytic processes. Manganese removal was catalyzed by either co-precipitation and adsorption to iron and manganese oxides, or by microbial activity. Most limestone clasts in the LLB system had black precipitate adhering to the

surface, and SEM analysis identified precipitate and nodules on a clast surface rich in manganese (~50%) and iron (~25%).

- Removal of nickel and zinc correlated with manganese removal, and occurred by co-precipitation and absorption to manganese oxides. Removal of zinc by this process was more effective than for nickel, as indicated by greater metal removal efficiencies for zinc. This is apparent in SEM analysis as zinc is more concentrated in manganese nodules than nickel.
  - Aluminium and iron precipitates are retained in the LLB system because flow velocities are not high enough to keep metal solids in suspension. Metal particulates are increasingly retained at shorter HRTs likely because of filtration by precipitates already accumulated in the system. However, minimal iron armouring of limestone clasts occurs, and flushing indicates potential for removal of metal solids from the LLB system.
- **OLC Treatment System**
- Neutralization of acidity in the OLC system occurred by limestone dissolution, indicated by a net export of calcium in effluent and a pH increase along the channel.
  - Neutralization of AMD decreased with shorter HRT caused by insufficient time for effective limestone dissolution. This caused pH to decrease below 5 which limited alkalinity generation reactions.
  - Removal of dissolved aluminium and iron occurred by precipitation of white and ochre oxyhydroxides along the OLC system, respectively. Oxidation and precipitation of ferrous iron occurred as AMD was aerated as it dropped between channel tiers.
  - A zone of increased aluminium precipitation occurred between 8.25 m and 9.75 m distance along the OLC system distance because a pH of 5 was reached. At shorter HRTs acidity generated by hydrolysis caused pH to decrease downstream of 9 m which likely resulted in dissolution of metals previously precipitated in the channel.
  - Precipitation of manganese occurred in the OLC system probably by the same mechanism as for the LLB system. This was indicated by a black, spotty precipitate on limestone clasts in the channel, and SEM analysis identified manganese rich precipitate and nodules on the surface of a clast. Therefore, had metal analysis continued at shorter HRTs an improvement in manganese, nickel and zinc removal would likely have occurred.

- The OLC system has clear potential for iron armouring of limestone clasts, and clogging by accumulation of aluminium hydroxides, which can limit the effectiveness of AMD treatment. These problems occurred because the gradient of the trial system was not steep enough to create sufficient flow velocity to keep metal precipitates in suspension for removal from the system. This gradient is however representative of a full scale system at Fanny Creek..

### **6.3.2.3 Optimal Treatment Criteria**

Optimal AMD neutralization and metal removal thresholds with respect to HRT were determined for bench scale SRBR, LLB and OLC systems in this study. These are used to derive optimal HRT design criteria for future pilot or full scale treatment systems for Fanny Creek AMD. Optimal HRT design criteria are:

- 51 hours HRT for the SRBR system
- 5 hours HRT for the LLB system
- 15 hours for the OLC system

### **6.3.3 The Waitahu River Mixing Option**

The viability of this option depended on whether Waitahu River water could neutralize Fanny Creek AMD, and if river water could be transferred to the AMD treatment area site R12 for mixing.

- Waitahu River water is slightly alkaline and can neutralize Fanny Creek AMD.
- Calculated ratios from monthly acidity and alkalinity monitoring data indicate the ratio of Waitahu River water required to neutralize Fanny Creek AMD to pH 5 during worst likely AMD conditions are:
  - 2.2 (AMD from site R12)
  - 4.7 (more acidic AMD from site IB5c)

- The worst likely alkalinity and acidity ratios for neutralization of AMD correspond to Waitahu River water flow volumes between:
  - 65 L/s (at site R12); and
  - 140 L/s (at site IB5c)
- These flow rates can be easily supplied by the large volume Waitahu River.
- Ratios calculated from monthly monitoring were verified by actual mixing of Waitahu River water with Fanny Creek AMD.
- The gradient from the proposed transfer site at R8 (upstream of Island Block mine) to the AMD treatment area at R12 is downhill. Therefore, river water can be transferred by a channel from the Waitahu River under gravity for mixing with Fanny Creek.
- No metal analysis was completed for this treatment option, however, at pH 5 ferric iron and aluminium are removed. There is potential for the extent of dilution to decrease concentrations of other metals significantly.

#### **6.3.4 Comparison of Treatment Options for Fanny Creek AMD**

The four trial passive AMD treatment options are compared in terms of water chemistry treatment effectiveness and implications for scale up at Fanny Creek. Water chemistry primarily compares bench scale SRBR, LLB and OLC systems because detailed metal analysis was completed for these options. Comparison of trial treatment systems enabled optimal passive AMD treatment strategies for Fanny Creek AMD to be determined.

#### **6.3.5 Water chemistry Treatment Effectiveness**

The water chemistry treatment effectiveness of SRBR, LLB and OLC system settling pond effluent was compared at optimal HRTs for each system (51, 5 and 15 hours). Treatment effectiveness was evaluated primarily on the capability of each system to achieve water quality criteria for recently consented Cypress Mine and ANZECC guideline values, which will likely apply to Island Block mine.

- The SRBR system had most effective AMD treatment of the options trialed. Metal concentrations are decreased to achieve criteria for all metals, alkalinity generation is greatest, and pH is increased the most.

- The LLB system decreased metals so that concentrations only slightly exceed criteria for nickel, zinc and copper. Alkalinity generation was about a third of the SRBR system, and pH was lower compared to SRBR and OLC system, but was above 6.
- The OLC system had worst treatment performance at optimal HRTs for trial systems. Metal concentrations were above water quality criteria for all metals except iron, and alkalinity generation is less than a third generated by the LLB system.
- The Waitahu River Mixing option has the capability to effectively remove iron and aluminium, and significantly dilute AMD so that water quality criteria are achieved for other metals.
- Comparison of water chemistry treatment performance of trial options indicates either a sulfate reducing bioreactor, limestone leaching bed, or the Waitahu River mixing option could be adequate for passive remediation of Fanny Creek AMD.

### **6.3.6 Long-term Performance Factors and Implications for Treatment System Scale Up**

Factors that may affect long term performance and implications of a full scale SRBR, LLB or Waitahu River Mixing treatment system at Fanny Creek are considered because this affects AMD treatment costs.

- A full scale SBRB system to treat Fanny Creek AMD has a significantly greater size requirement compared to a full scale LLB system (about an order of magnitude) due to the large difference in optimal HRT design criteria, and also has a relatively more complicated design.
- Long term treatment performance of a SRBR system may be limited by short term removal processes, hydraulic problems such as clogging and compaction, and accelerated depletion of the organic substrate mixture caused by the variability of flow in Fanny Creek.
- A full scale LLB system is significantly smaller, and problems relating to long term effectiveness (clogging and iron armouring) can be mitigated by appropriate design such as inclusion of a flushing mechanism.
- The Waitahu River Mixing option is relatively simple because the system primarily involves construction of a channel and settling pond system.
- Although the SRBR system has superior water chemistry treatment effectiveness other treatment options may provide more cost-effective treatment of AMD.

### **6.3.7 Optimal Passive Treatment Options for Fanny Creek AMD**

In view of the advantages and disadvantages of trial passive treatment systems, the options determined as optimal for passive remediation of Fanny Creek AMD are:

- Limestone leaching bed; or
- Waitahu River Mixing option

Either a LLB system or the Waitahu River Mixing options likely provide most cost effective treatment for Fanny Creek AMD. However, there is still uncertainty about their ability to successfully achieve water quality criteria, and around full scale sizing requirements of these options. In addition, the treatment capability of a SRBR system should not be disregarded; therefore, this option should also be included in future investigations of optimal passive treatment options for Fanny Creek AMD.

### **6.3.8 Future Work**

Pilot scale testing of SRBR and LLB treatment systems, and the Waitahu River Mixing options is recommended.

- Pilot scale testing of SRBR and LLB systems could occur in the second settling basin on the Waitahu Valley floor. The Waitahu River Mixing option can be simulated by mixing AMD with alkaline drainage from the hillside.
- Pilot scale testing of treatment systems will determine their response to site variables, resolve uncertainties about long-term treatment effectiveness, and enable more accurate sizing and cost estimates of full scale systems.

Future investigation should focus on:

- Long term AMD treatment effectiveness of pilot scale systems, the affect of accumulated solids on hydraulic properties of the SRBR and LLB treatment systems and the ability of flushing to maintain treatment performance.
- More accurate full scale treatment system sizing methods. Sizing a LLB system should account for the small limestone clast size used in laboratory trials. The Waitahu River Mixing option requires the residence time for effective settling of iron and aluminium precipitates in settling ponds to be determined.

- The potential to combine different components of different treatment system options to utilize specific AMD treatment benefits.

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## **Appendix I**

### **Characterization of Fanny Creek Catchment Drainage Chemistry: Methods, Raw Data and Results**

#### **A) Previous Monitoring Data**

#### **B) Methods**

- Water Monitoring Sites and Fanny Creek Catchment Environs
- Flow Rate Measurement: V-notch weir
- Data Analysis: Acidity and Metal Loading Calculations

#### **C) Raw Data and Analysis**

- Results in raw data format collected during monthly monitoring of Fanny Creek catchment stored on CD-ROM

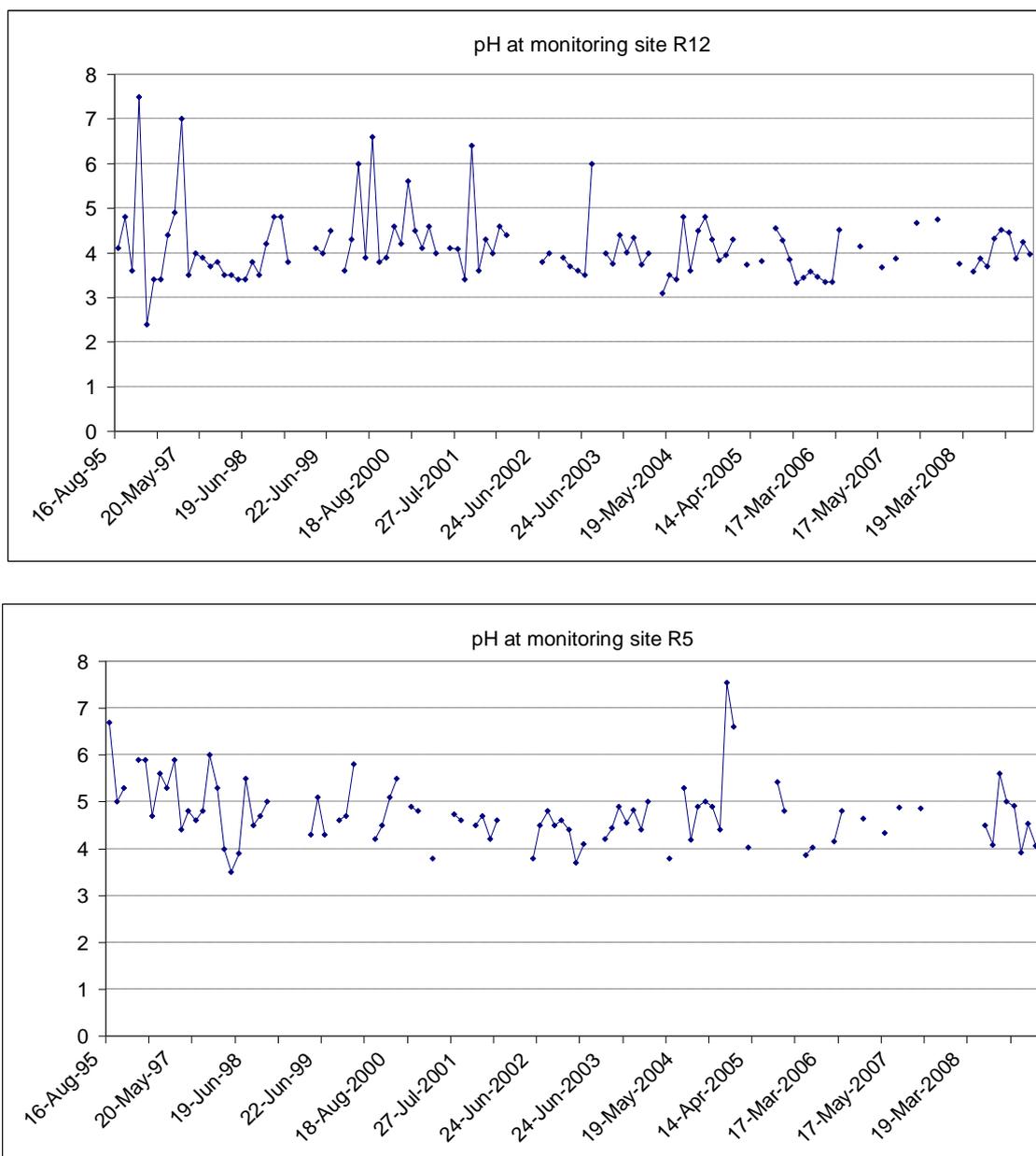
#### **D) Results**

- Monthly Monitoring Results at Fanny Creek Outflow
- Alkalinity Loadings at Un-impacted Drainage Sites and Fanny Creek Outflow
- Fanny Creek Flow Complexity Within Valley Floor Settling Basin

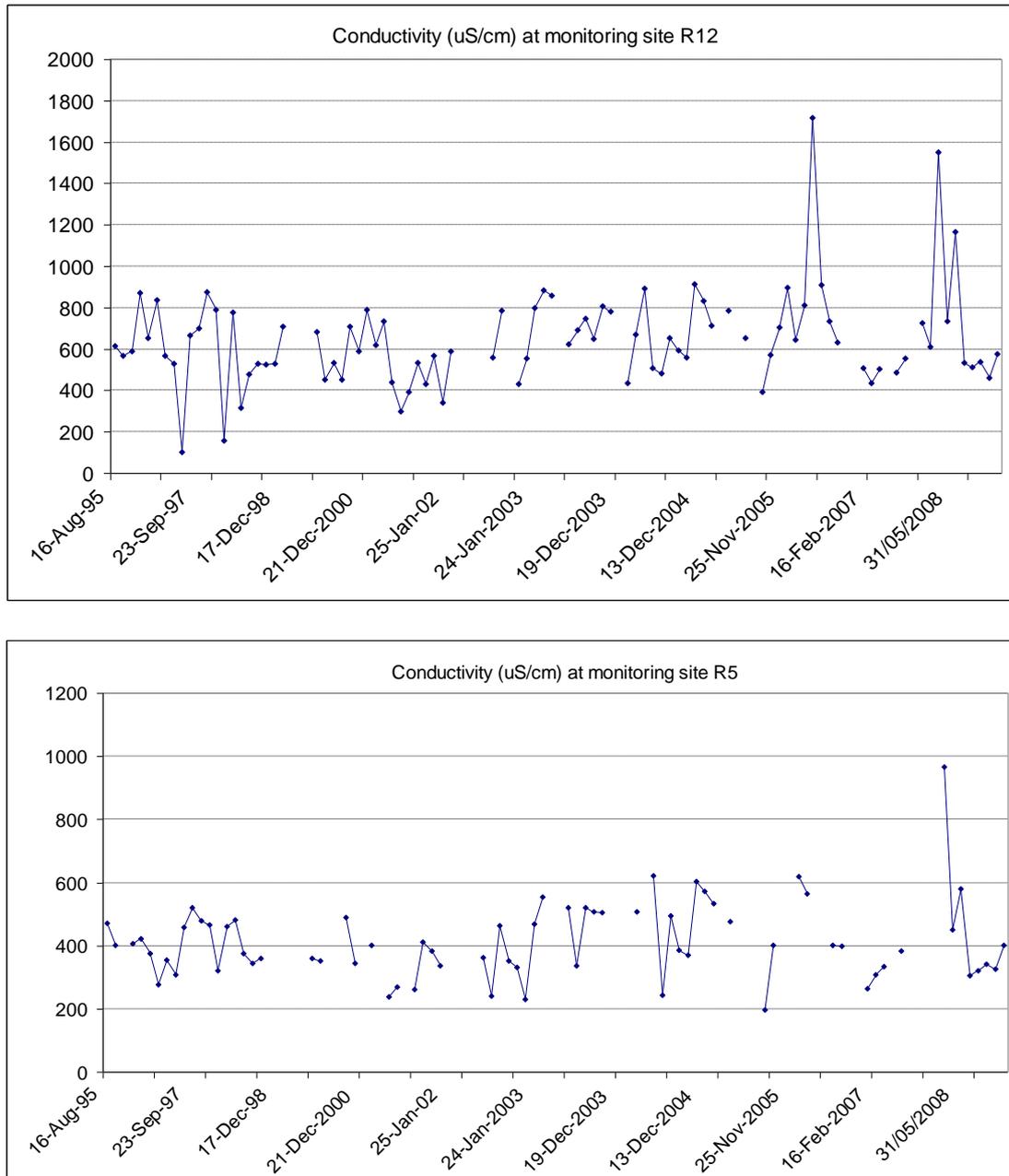
#### **E) Environmental Geology Work**

## Appendix I. (A): Previous Water Monitoring Data

**Table 1.1: Previous water monitoring data at Island Block mine. Data for pH, EC ( $\mu\text{S}/\text{cm}$ ), Turbidity (NTU) and Suspended Solid are collated from previous monitoring by Solid Energy since August 1995. These data stored on CD-ROM located at the back cover.**



**Figure 1.1: pH at R12 and R5 measured between August 1995 and January 2009. Gaps in data indicate no monitoring occurred.**



**Figure 1.2: Electrical Conductivity ( $\mu\text{S}/\text{cm}$ ) at R12 and R5 between August 1995 and January 2009. Gaps in data indicate no monitoring occurred.**

## Appendix I. (B): Methods

### Water Monitoring Sites and Fanny Creek Catchment Environs

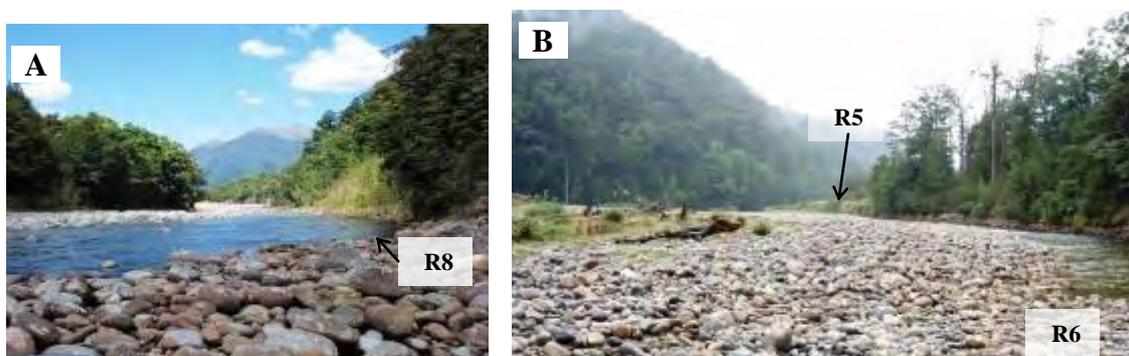


Figure 1.3: Waitahu River monitoring sites R8 (a) and R6 (b). Site R8 is located just upstream of the Island Block fan area, and site R6 is 200 m downstream of where Fanny Creek outflow into the Waitahu River (site R5).

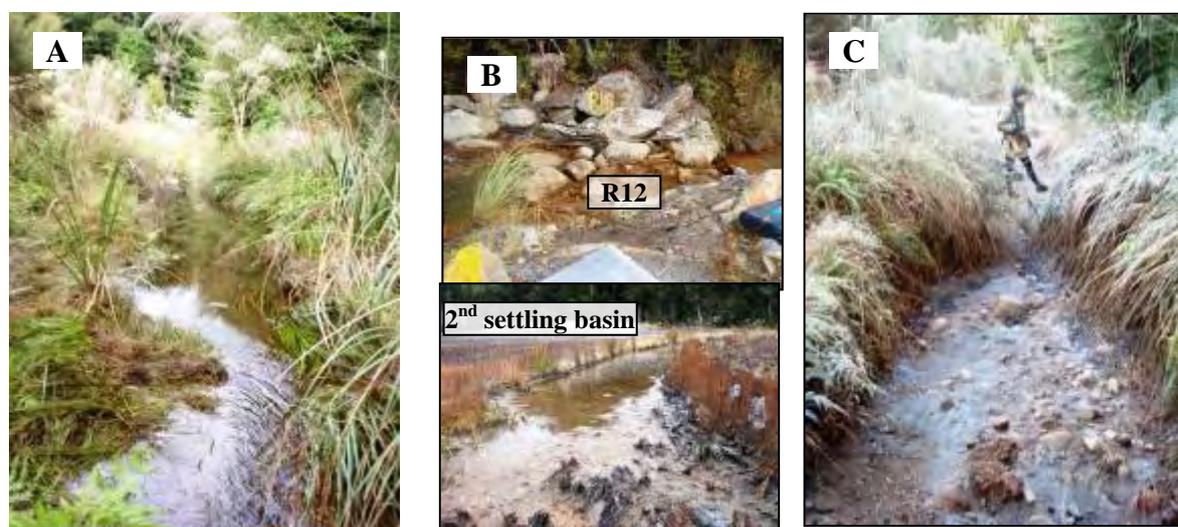


Figure 1.4: Fanny Creek outflow monitoring site R5, before AMD enters the Waitahu River. A) Fanny Creek at site R5 on 7<sup>th</sup> March, 2008. B & C) Low flow conditions on 31 May 2008 showing no surface flow at site R5 (C) despite flow at upstream site R12 (B). This indicates subsurface flow loss occurs as Fanny Creek flow through the settling basins, in the second settling basin where Fanny Creek ‘dries up’ (B).



**Figure 1.5: Monitoring site IB6. Site IB6 is where Fanny Creek ponds in the second settling basin.**



**Figure 1.6: Monitoring site U4. Site U4 is un-impacted alkaline drainage just before it enters Fanny Creek AMD in the second settling basin.**



**Figure 1.7: Monitoring site U6 (A). Site U6 is un-impacted alkaline drainage that has ponded behind the first settling basin, at the toe of the Fanny Creek fan. It is fed by stream U5 but during low flow conditions U5 has subsurface loss and does not reach ponded water (B).**



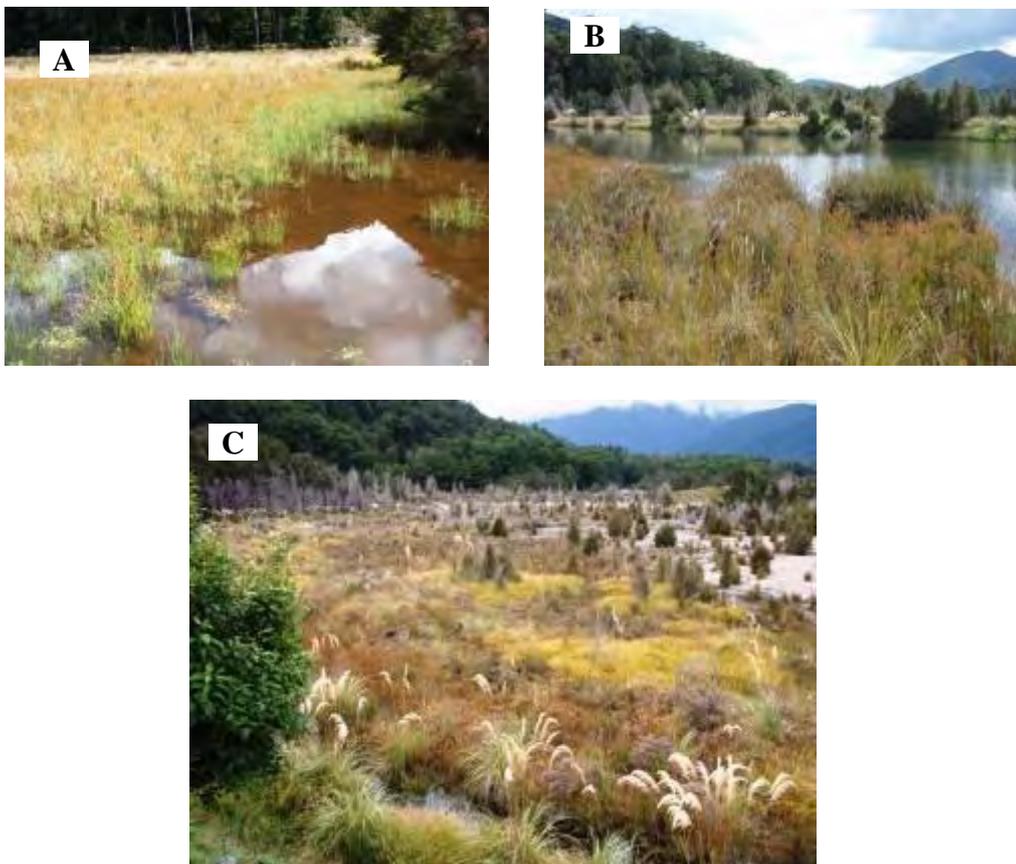
**Figure 1.8: Mixing of un-impacted alkaline drainage from site U2a with Fanny Creek AMD at confluence IB5 during different flow conditions. The different affect of alkalinity on neutralization is illustrated by difference in metal precipitation. Alkalinity input during May had the greatest affect on Fanny Creek, with aluminium precipitation stretching 100 m downstream of the confluence.**



**Figure 1.9: Fanny Creek ~100 m upstream of site R12. This site was used for flow measurements using bucket and timer method. A) flow during February (4.9 L/s). B) maximum flow conditions during July (estimated 30 L/s).**



**Figure 1.10: Confluence IB8a. Fanny Creek mixes on some occasions with alkaline drainage from site U1.**



**Figure 1.11: Fanny Creek wetland system within the series of settling basins on the Waitahu Valley floor. A & B) Large pond and wetland vegetation (cattails) within the second settling basin. C) Vegetation in the third settling basin.**



**Figure 1.12: Sediment fines from Island Block waste rock slopes in the first settling pond, immediately downstream of site R12.**

### Flow Rate Measurement: V-notch weir

**Table 1.2: Formula for calculation of flow (Q) from measurements of head (h) behind V-notch weirs (Berkman, 1995)**

V-notch weir (90°)	$= (0.17556 * (h)^{2.48}) / 3600$	H = head measured above the apex of the 'V'. Yield Q in L/s if 'h' is in mm.
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(Berkman, 1995).



**Figure 1.13: Measurement of flow rate by V-notch weir method. A) V-notch weir measurement during the lowest flow in May just upstream of R12. B) Measurement in March during moderate flow at Fanny Creek outflow (site R5).**

### Data analysis: Acidity and Metal Loadings

**Table 1.3: Acidity and metal loading calculations. Acidity loading is unit weight of calcium carbonate required per day for neutralization (kg CaCO<sub>3</sub>/day). Metal loading is in unit mass of metal per day (kg/day), and in moles of metal per day (moles metal/day).**

#### Acidity and metal loading calculation

$$\begin{aligned}
 &= \frac{C \text{ (mg/L)}}{1000} = \text{g/L} && \text{(convert units to g/L)} \\
 &= \text{g/L} \quad \times \quad \text{L/day} \\
 &= \text{g/day} && \text{(Loading of acidity (g CaCO}_3\text{/day)} \\
 &&& \text{or metal (g/day) )}
 \end{aligned}$$

Where C = metal concentration. Either acidity (mg CaCO<sub>3</sub>/L) or dissolved metal (mg/L).

Loadings referred to in either grams of kilograms per day.

#### Molar metal loading calculation

$$\begin{aligned}
 &= \frac{C \text{ (mg/L)}}{1000} = \text{g/L} && \text{(convert units to g/L)} \\
 &= \frac{\text{g/L}}{C \text{ atomic mass (g/mol) } * } = \frac{\text{g}}{\text{L}} \times \frac{\text{mol}}{\text{g}} = \text{mols/L (moles of metals /L)} \\
 &= \text{mols/L} \quad \times \quad \text{flow rate} \quad \frac{(\text{L})}{\text{day}} \\
 &= \text{mols/day} && \text{(Metal loading (moles metals/day))}
 \end{aligned}$$

Where C = dissolved metal (mg/L).

## **Appendix I. (C): Raw Data and Analysis**

Tables 1.4 – 1.11 are results in raw data format from monitoring drainage in Fanny Creek catchment. Data analysis primarily involves calculation of acidity and metal loadings, along with contributions of acidity and metal components to total loadings (%). These tables are stored on Appendix I on CD-ROM, located at the back cover. Cypress Mine Resource Consent conditions are stored in Appendix I on CD-ROM.

**Table 1.4: Water sampling data of monitoring sites in Fanny Creek catchment, collected between February 2008 and January 2009. Data include pH, electrical conductivity, flow rate (L/s), dissolved oxygen concentrations, and measured acidity (pH 3.7) and alkalinity (pH 7) concentrations. Acidity and alkalinity loadings also included. Notes for monitoring sites provided.**

**Table 1.5: Water sampling data of un-impacted alkaline drainage in Fanny Creek catchment. These data are included in Table 1.4, but are also provided separately here to collate data. Average alkalinity loadings (kg CaCO<sub>3</sub>/day) for samples collected during monitoring period included, bars indicate maximum and minimum loadings.**

**Table 1.6 and Table 1.7: Acidity (pH 4, 5, 7) and alkalinity (5, 4, 3.7) titration data for water samples collected in Fanny Creek catchment between February 2008 and January 2009. Measured acidity and alkalinity reported in mg/L as CaCO<sub>3</sub> equivalent. Methodology and calculation given by Lewis & McConchie (1994).**

**Table 1.8: Metal analysis completed on samples collected in Fanny Creek catchment (mg/L). Data includes monthly metal concentrations measured at sites R12 (dissolved and total) and R5 (dissolved) for elevated metals (Al, Fe, Mn, Cu, Ni, Zn, Cd) and calcium and sulfur. Detailed dissolved metal analysis completed for samples collected during March 2008 at upper catchment monitoring sites (AMD seeps) and at confluences along Fanny Creek (IB5 and IB7) are provided (this also includes detailed metal analysis at sites R12 and R5 in March). Selected metal analysis (Al, Fe, Ca) for samples collected from IB7 confluence during May and July shown.**

**Table 1.9: Metal and acidity loadings calculated on a monthly basis for sites R12 (A) and R5 (B). Metal loading given in units mass of metal per day (Kg/day), and in moles of metal per day**

(moles metal/day). Acidity loadings are in units of calcium carbonate per day for neutralization (kg CaCO<sub>3</sub>/day). Component contributions to acidity and metal loadings are also calculated.

**Table 1.10: Acidity (kg CaCO<sub>3</sub>/day) and metal (kg/day) loadings calculated from detailed metal analysis completed for samples collected in March (and of IB7 confluence data collected in May and July). These include acidity (calculated and measured) and metal (kg/day) loadings of AMD seeps, important confluences (IB5 and IB7), and loadings along Fanny Creek. Acidity and metal contributions (%) are calculated for southern and northern tributaries. pH along Fanny Creek given.**

**Table 1.11: Metal loadings (moles metal/day) calculated from detailed metal analysis completed for samples collected in March. Molar loadings are used to determine to metal flux individual metal contributions to total metal loading. The relative southern and northern metal contributions (%) to metal in Fanny Creek are shown.**

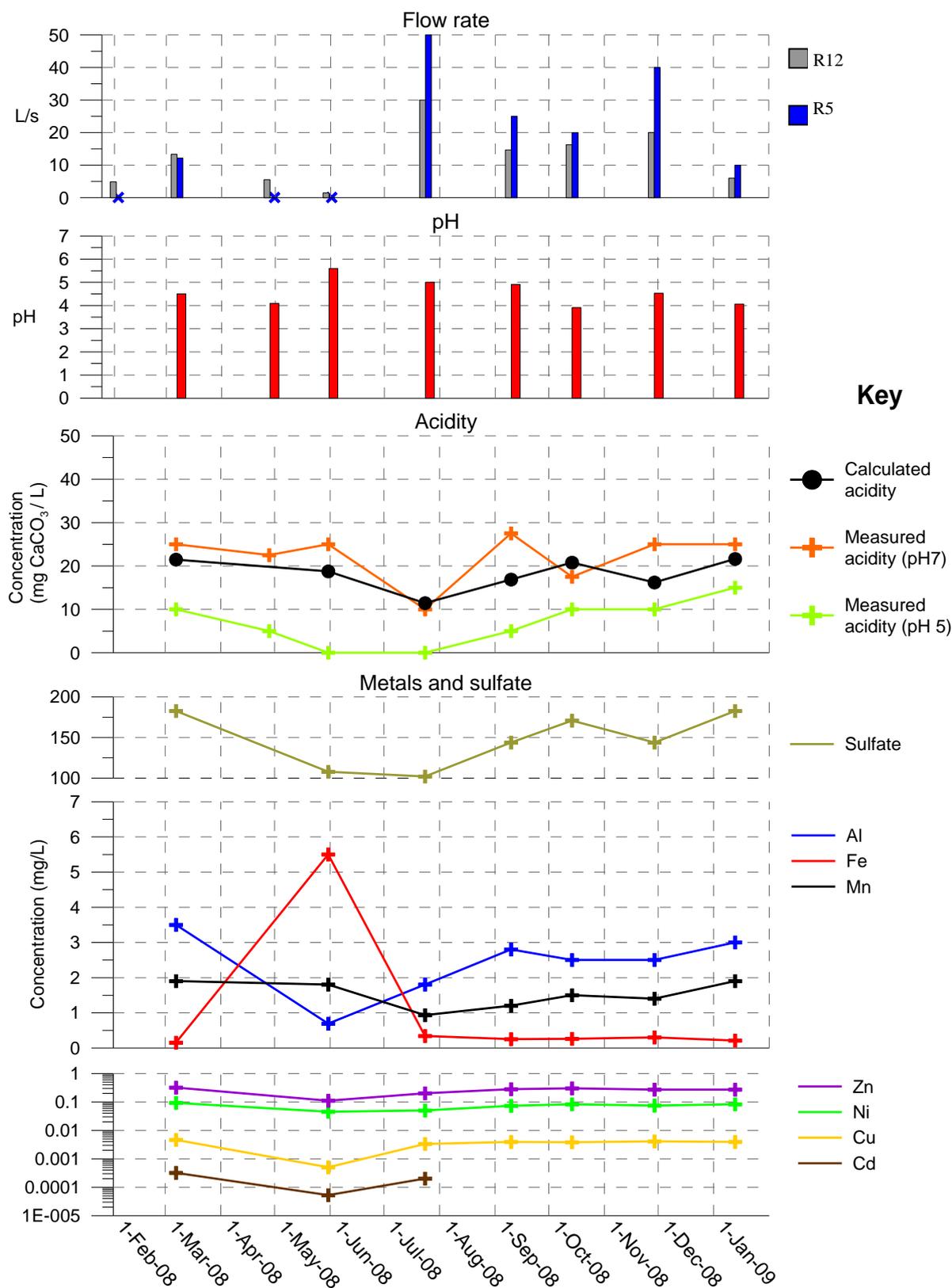
## Appendix I. (D): Results

### Monthly Monitoring Results for Fanny Creek Outflow (R5)

Figure 1.14 displays monthly monitoring data for Fanny Creek outflow to the Waitahu River (site R5) between 2 February 2008 and 13 January 2009. Average flow rate was 17.5 L/s, with a maximum estimated flow of 50 L/s, and a minimum of 0 L/s (no surface flow in the channel occurred). Flow rate at R5 had to be mostly estimated (except in March) due to difficulty using v-notch weir method. The pH at R5 ranged from 3.91 (Oct) to 5.6 (May), with a median of 4.51. The high pH measurement in May was of ponded water in the channel (no surface flow).

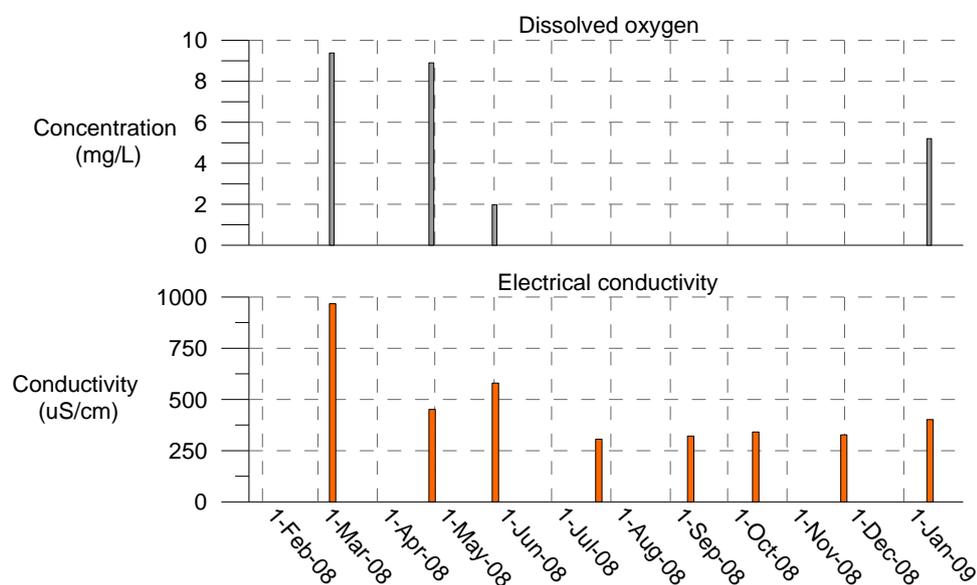
When AMD flowed in the channel at site R5 measured acidity (pH 7) averaged 21.7 mg CaCO<sub>3</sub>/L and ranged between 10 and 27.5 mg CaCO<sub>3</sub>/L. Average calculated acidity was 18.1 mg CaCO<sub>3</sub>/L (11.4 - 21.6 mg CaCO<sub>3</sub>/L) (calculated acidity measured in May was omitted because the sample was taken from a ponded area within the outflow channel and iron concentration was likely erroneous due to analytical error).

Average dissolved metal concentrations at R5 measured 2.4 mg/L for aluminium (0.69 - 3.5 mg/L), 0.25 mg/L for iron (0.15 - 0.34 mg/L), 1.5 mg/L for manganese (0.93 - 1.9 mg/L), 0.0034 mg/L for copper (<0.0005 - 0.0046 mg/L), 0.071 for nickel (0.045 - 0.092 mg/L), 0.25 mg/L for zinc (0.11 - 0.32 mg/L), and 0.00019 for cadmium (0.000052 - 0.00032 mg/L). Sulfate concentrations averaged 148 mg/L (102 - 183 mg/L). High iron concentration in May departs from trend and is likely due to analytical error which also occurs for measurement at site R12 on the same occasion. Therefore, iron measured in May is omitted from analysis.



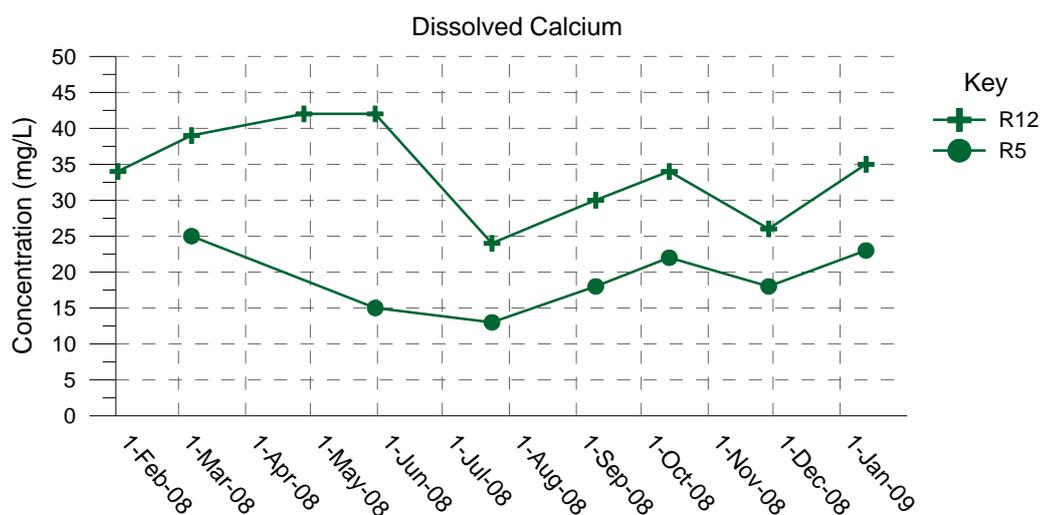
**Figure 1.14: Monthly flow rate, pH, acidity, sulfate and metal concentration data collected from sampling site R5 (Fanny Creek outflow to Waitahu River) between 2 February 2008 and 13 January 2009. Flow rate upstream at R12 (before settling basins) shown for comparison.**

When AMD flowed in the channel at site R5 dissolved oxygen averaged 7.83 mg/L (5.2 - 9.38 mg/L) and conductivity valued averaged 444  $\mu\text{S}/\text{cm}$  (306 – 967  $\mu\text{S}/\text{cm}$ ) (Figure 1.15). Dissolved oxygen of ponded water (no flow) during May was lowest and measured 1.98 mg/L.



**Figure 1.15: Monthly dissolved oxygen concentration and electrical conductivity data collected from the R5 sampling site between 2 February 2008 and 13 January 2009.**

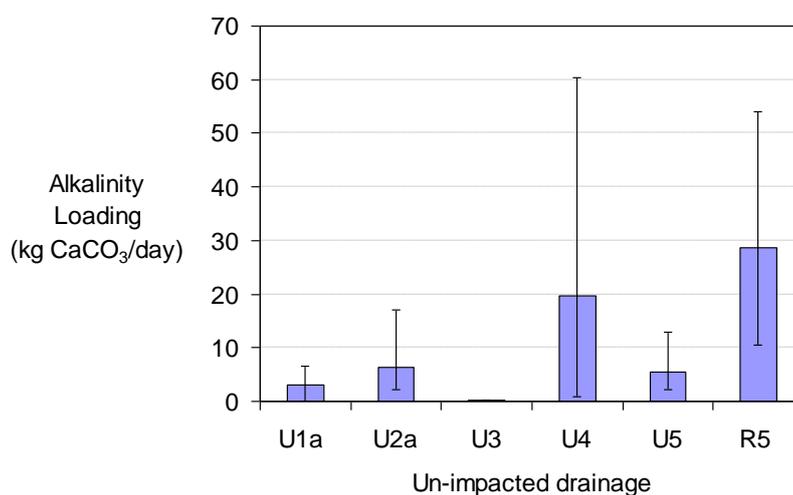
Calcium concentrations at site R12 averaged 34 mg/L and ranged from 24 to 42 mg/L, while at site R5, concentrations averaged 19 mg/L (13 - 25 mg/L) (Figure 1.16).



**Figure 1.16: Dissolved calcium concentrations at sites R12 and R5 between 2 February 2008 and 13 January 2009.**

### Alkalinity Loadings of Un-impacted Drainage and at Fanny Creek Outflow

Alkalinity loadings of alkaline streams that drain into Fanny Creek vary considerably ((Figure 1.17). Alkaline drainage from site U4 has the greatest average alkalinity loading of alkaline tributaries between February 2008 and January 2009, averaging 19.6 kg CaCO<sub>3</sub>/day (0.864 - 60.5 kg CaCO<sub>3</sub>/day). Next greatest alkalinity loading is at site U2a, with 6.33 kg CaCO<sub>3</sub>/day (2.1 - 17.1 kg CaCO<sub>3</sub>/day), followed by U5 with 5.4 kg CaCO<sub>3</sub>/day (2.2 - 13 kg CaCO<sub>3</sub>/day) and U1a with 3.06 kg CaCO<sub>3</sub>/day (0.0781 - 6.5 kg CaCO<sub>3</sub>/day). Alkalinity loading of drainage from site U3 is minimal, with an average of 0.14 kg CaCO<sub>3</sub>/day. Alkalinity loading at R5, the outflow of Fanny Creek to the Waitahu River averages 28.7 kg CaCO<sub>3</sub>/day (10.5 - 54.0 kg CaCO<sub>3</sub>/day).



**Figure 1.17: Average alkalinity loading of un-impacted drainages (U1a – U5) and Fanny Creek outflow (R5). Loadings of un-impacted drainage (U1 – U5) are given for drainage immediately before entering Fanny Creek. Bars indicate minimum and maximum loadings.**

**Fanny Creek Flow Complexity Within the Valley Floor Settling Basins (between site R12 and R5)**

The complexity of Fanny Creek drainage within the settling basins is illustrated by Figure 1.18 and 1.19. On monitoring occasions in February, April and May, loss of flow to the subsurface results in no surface flow of Fanny Creek at R5 (outflow). This is shown in Figure 1.18 where Fanny Creek flow ends or ‘dries up’. During higher flow conditions the greater flow volume in Fanny Creek overcomes the volume lost to subsurface flow, and surface flow at the outflow the Waitahu River occurs. During these conditions Fanny Creek flow is increased by alkaline drainage that enters in the second settling pond (site U4). These factors create flow differences between R12 and R5.



**Figure 1.18: Loss of Fanny Creek flow to the sub surface within settling basins on the Waitahu Valley Floor. Image shows water in Fanny Creek drying up in the first settling basin.**



**Figure 1.19: Difference in flow conditions in Fanny Creek illustrated by the confluence of Fanny Creek with alkaline drainage from site U4. A) during very low flow conditions in May with no flow at the confluence. B) Higher flow conditions.**

## **Appendix I. (E): Environmental Geology Work**

**Results stored on CD – ROM in Appendix I, E.**

**This contains:**

- Detailed Stratigraphic Column of the Island Block High Wall.
- Acid-base accounting data of samples collected from Island Block and Echo Mine highwalls.

## **Appendix II**

### **Literature Review: Passive Treatment of Acid Mine Drainage**

#### **A) Introduction and Passive AMD Treatment Principles**

- Introduction
- Acid Mine Drainage Treatment
- Active Treatment
- Passive Treatment

#### **B) Metal Removal Processes**

- Iron Removal
- Aluminium Removal
- Removal of Other Metals

#### **C) Proton Acidity Neutralization**

- Carbonate Mineral Dissolution
- Bacterial Sulfate Reduction

#### **D) Selection of Passive Treatment Systems**

#### **E) Review of Selected Passive Treatment Systems**

- Sulfate Reducing Bioreactor
- Limestone Leaching Bed and Open Limestone Channel
- Summary

## **Appendix II. (A): Introduction and Passive AMD Treatment Principles**

### **2.1 Introduction**

This section reviews the remediation of acid mine drainage (AMD) impacted water, focusing on passive treatment methods. The principles of passive treatment are reviewed along with metal and acidity neutralization processes operating within treatment systems.

The selection of three suitable passive AMD treatment systems for remediation of Fanny Creek AMD necessitated a detailed review of these systems. Selected treatment systems are: sulfate reducing bioreactor, limestone leaching bed and open limestone channel. The process used to select these systems is initially described. The review then includes a description of remediation processes for these systems, factors that influence performance, design criteria, and lifespan. To avoid repetition the review combines limestone leaching bed and open limestone channel treatment systems because these two systems have similar remediation processes.

### **2.2 Acid Mine Drainage Treatment**

Negative environmental impacts associated with AMD have led to the development of various treatment technologies (Younger et al., 2002). The primary goals of such treatment are to:

- Neutralize acidity; and
- Remove metals

(Brown et al., 2002)

AMD treatment systems are categorized as either 'active' or 'passive' depending on the type of remediation process involved (Brown et al., 2002; Younger et al., 2002).

### **2.3 Active treatment**

Active AMD treatment systems require ongoing inputs of energy and/or (bio)chemical reagents (Younger et al., 2002).

Active AMD treatment involves the operation and maintenance of machinery, and generally requires the constant addition of alkaline materials (Brown et al., 2002; Trumm et al., 2007). Active systems are often expensive to operate compared to passive treatment options (Younger et al., 2002; Watzlaf et al., 2003), and are suited to active mining operations where land area is limited and the scale of AMD may be significant (Brown et al., 2002). Common examples include lime dosing and sludge treatment plants (Figure 2.1). This study focuses on the passive treatment of AMD, thus, no further review of active treatment is provided.



**Figure 2.1: Example of an active AMD treatment system. Photo shows a lime dosing plant at Stockton Mine open cast coal mine, owned by Solid Energy NZ.**

## **2.4 Passive Treatment**

Passive AMD treatment systems exploit and enhance naturally occurring biological, chemical and physical processes to remediate contaminated mine water (Younger et al., 2002; Watzlaf et al., 2003). These systems are defined as the deliberate improvement of water quality using a natural energy source (e.g. gravity, microbial metabolic energy, photosynthesis) in systems which require infrequent (albeit regular) maintenance to operate effectively over the system lifetime (Younger et al. 2002).

Passive treatment systems have been used to remediate AMD from mine sites for over 20 years (Ziemkiewicz et al., 2003). The idea originated from two independent studies that

observed an improvement in coal mine water quality as it flowed through *sphagnum* moss bogs (Huntsman, 1978; Wieder & Lang, 1982). Since then, much attention has been given to passive treatment technologies for mine water remediation (Younger et al., 2002; PIRAMID Consortium, 2003; Watzlaf et al., 2003; Johnson and Hallberg, 2005; Ziemkiewicz et al., 2003).

There are numerous advantages to using passive methods for treatment of AMD, although there can also be drawbacks (Table 2.1). Nevertheless, problems can be minimized or prevented through design and selection of appropriate systems (Younger et al., 2002; Trumm, 2007).

**Table 2.1: Advantages and disadvantages of passive AMD treatment systems**

<b>Advantages</b>	<b>Disadvantages</b>
Relatively inexpensive	Short circuiting of flow
Minimal maintenance	Limestone armouring
Avoid continuous addition of neutralizing agents	Clogging with precipitate
Avoid power requirements	Vulnerable to variation of flow and dissolved constituent concentrations
Operation in remote areas	Require periodic maintenance or renewal
Use of recycled materials	Large space requirements

(Younger et al., 2002; Brown et al., 2002; Doshi, 2006; Trumm, 2007).

There is limited research of passive AMD treatment systems in New Zealand (O'Sullivan, 2005; Trumm 2005, 2006, 2007, 2008; McCauley et al., 2008, 2009), and it is considered by McCauley et al (2008) to be at the development stage.

## Appendix II. (B): Metal Removal Processes

### 2.5 Metal Removal

Metals in AMD can be removed by various chemical and biological processes operating in passive treatment systems (Watzlaf et al., 2003). The mechanisms currently considered most important in achieving metal removal are:

- Oxidation and hydrolysis reactions; and
- Reduction reactions

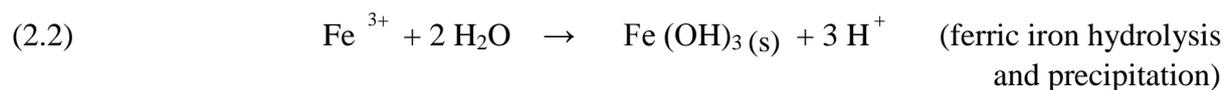
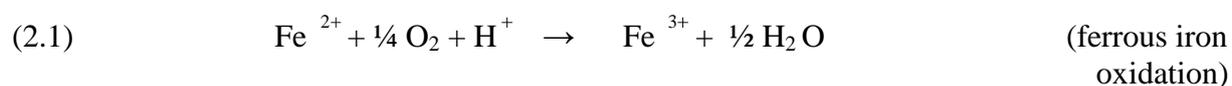
(Brown et al., 2002; Younger et al., 2002)

Passive treatment systems can be categorized as being either oxidizing or reducing, depending on the primary removal mechanisms (Trumm et al., 2007). Other metal removal processes include: exchange of metals by organic substrate, adsorption by other metals, metal uptake by plants, physical filtering and settling of suspended solids, alkalinity generation by organic matter decay, and metal adsorption or exchange onto algal materials (Doshi, 2006). The critical factor for metal removal is pH, because it affects metal solubility, speciation, and kinetics of hydrolysis reactions (Watzlaf et al., 2003).

#### 2.5.1 Iron Removal

##### 2.5.1.1 Aerobic Iron Removal

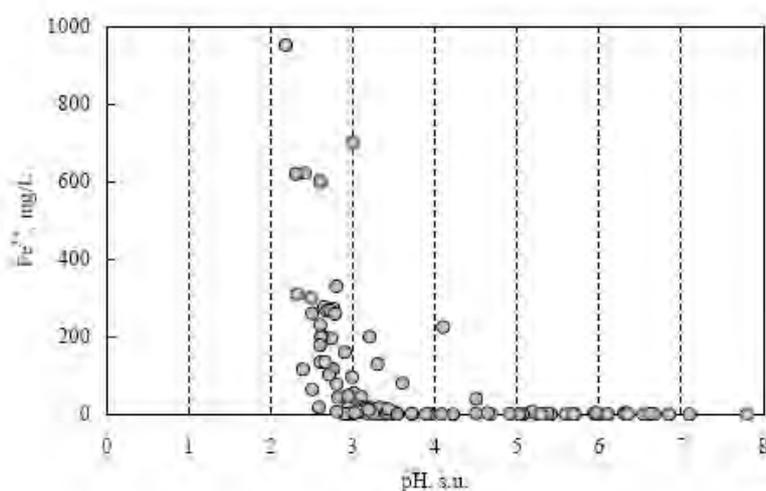
In aerobic passive treatment systems, oxidation, hydrolysis and precipitation reactions are the primary removal mechanisms of ferrous iron (Younger et al., 2002):



In the above reactions, ferrous iron ( $\text{Fe}^{2+}$ ) is removed from mine water by oxidation to ferric iron ( $\text{Fe}^{3+}$ ) (2.1), followed by hydrolysis and precipitation as iron hydroxide ( $\text{Fe}(\text{OH})_3$ ) (2.2). Iron hydroxide solids are then retained in treatment systems (Brown et al., 2002). Oxidation of ferrous iron occurs either chemically (abiotic) and/or catalyzed by microbial (biotic)

processes, and the predominance of either is controlled by pH. Abiotic oxidation involves aeration to increase dissolved oxygen, and is most important for oxidation ferrous iron between pH 6 and 7. Conversely, biotic oxidative processes (e.g. iron oxidizing *thiobacillus ferrooxidans*) dominate iron oxidation at pH below 5 (Johnson & Hallberg, 2005).

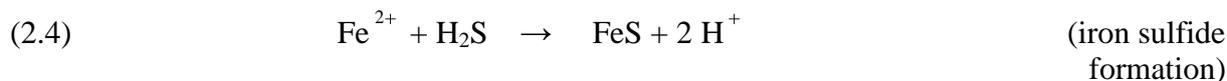
Hydrolysis and precipitation reactions also depend on pH. Dissolved ferric iron is insoluble above pH 3.5 and can precipitates as iron hydroxide, oxyhydroxide or hydroxysulfate, however, at pH below 3 ferric iron becomes soluble (Figure 2.2). Conversely, dissolved ferrous iron is soluble at acidic and circum-neutral pH (up to pH ~8). Aerobic systems aim to oxidize ferrous iron to take advantage of the lower solubility of ferric iron. However, ferric iron hydrolysis releases  $H^+$  ions into solution (2.2), therefore aerobic treatment systems require sufficient alkalinity to neutralize this acidity. If not, pH will decrease leading to an undesirable increase in ferric iron solubility (Brown et al., 2002).



**Figure 2.2: Dissolved ferric iron concentration against pH from 150 coal mine discharges (Watzlaf et al., 2003).**

### 2.5.1.2 Anaerobic Iron Removal

In anaerobic passive treatment systems, the principle iron removal mechanism is bacterially mediated sulfate reduction. Sulfate reducing bacteria such as *Desulfovibrio* are responsible for this process, performed as part of their metabolic function (Cocos et al., 2002). These bacteria are found in many natural anaerobic environments, such as wetland sediment (Postgate, 1965). The typical reactions for this process are:

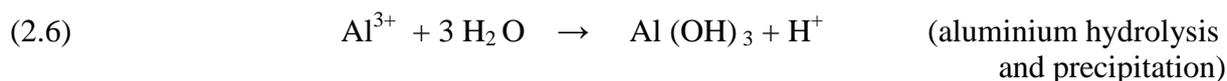


(Neculita et al., 2007; Younger et al., 2002)

Sulfate reducing bacteria metabolize organic carbon compounds ( $\text{CH}_2\text{O}$ ), and at the same time reduce sulfate ions ( $\text{SO}_4^{2-}$ ) in AMD, which produces hydrogen sulfide ( $\text{H}_2\text{S}$ ) and bicarbonate alkalinity ( $\text{HCO}_3^-$ ) (2.3). These by-products react with dissolved ferrous iron ( $\text{Fe}^{2+}$ ) in mine drainage to form iron sulfide ( $\text{FeS}$ ) and/or iron carbonate ( $\text{FeCO}_3$ ) (reactions 2.4 and 2.5 respectively) which precipitate in treatment systems, removing iron from solution (Zagury et al., 2006; Cocos et al., 2002). Proton acidity ( $\text{H}^+$ ) created during reactions is buffered by the generation of alkalinity (2.3). This process only operates under anaerobic and circum-neutral pH conditions (Younger et al., 2002; Doshi, 2006).

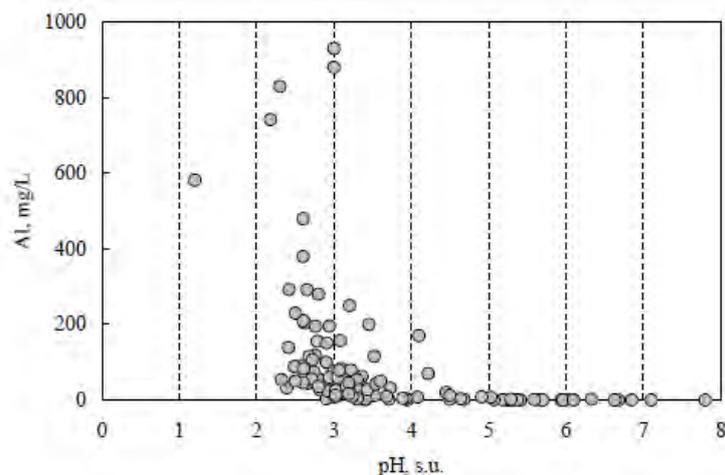
### 2.5.2 Aluminium Removal

Aluminium is removed by hydrolysis reactions in both aerobic and anaerobic passive treatment systems, operating by hydrolysis reactions (2.6).



(Younger et al., 2002)

In equation 2.6, dissolved aluminium ( $\text{Al}^{3+}$ ) hydrolyses in water to form insoluble aluminium hydroxides ( $\text{Al}(\text{OH})_3$ ) that precipitate, removing aluminium from solution (Younger et al., 2002). Aluminium occurs in mine drainage in only one oxidation state ( $\text{Al}^{3+}$ ), therefore; an oxidation step is not required and removal depends only on pH (Watzlaf et al., 2003). Elevated concentrations only occur at  $\text{pH} < 4$ , and dissolved aluminium is insoluble above  $\text{pH} 4.5$  (Figure 2.3) (Younger et al., 2002). Thus, aluminium can precipitate in either aerobic or anaerobic conditions, but similar to ferric iron, hydrolysis produces proton acidity which can lower pH (Younger et al., 2002). In addition to hydroxides, aluminium hydroxysulfate and other minerals can form when high sulfate concentrations or other anions are present (Gusek and Wildeman, 2002).



**Figure 2.3: Dissolved aluminium concentrations against pH in 150 coal mine discharges (Watzlaf et al., 2003)**

### 2.5.3 Removal of Other Metals

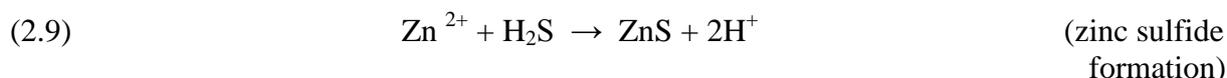
Other metals commonly present in mine drainage include manganese, arsenic, copper, nickel, zinc, cadmium, and lead. Oxidation and reduction reactions are important for removal of these metals (PIRAMID Consortium, 2003). Oxidative removal of manganese is described in the literature (Brown et al., 2002; Watzlaf et al., 2003). Removal occurs primarily by oxidation and hydrolysis reactions, resulting in precipitation of manganese hydroxides (Younger et al., 2002):



Chemical oxidation of  $\text{Mn}^{2+}$  (2.7) and precipitation of manganese oxides ( $\text{MnO}_2$ ) (2.8) only occurs at  $\text{pH} > 8$  (Younger et al., 2002). However, oxidation of manganese can be catalyzed by bacteria, and iron and manganese hydroxide solids, allowing hydrolysis and precipitation in lower pH conditions (Watzlaf et al., 2003; Rose, 2006). Other metals such as copper, lead, and zinc can also be removed via oxidation processes in alkaline solutions to form carbonate minerals (Stumm and Morgan, 1996; Watzlaf et al., 2003).

In addition, trace metals such as copper, nickel, zinc and also arsenic are commonly removed by adsorption to ferric iron solids during ferric iron hydrolysis reactions, or by adsorption to clays and organic matter at circum-neutral pH (Brown et al., 2002).

In anaerobic treatment systems, the primary metal removal mechanism is by bacterial sulfate reduction and precipitation of sulfide minerals (Younger et al., 2002). Metal sulfide compounds often have lower solubility compared to their oxides, making anaerobic systems valuable treatment options (Younger et al., 2002). For example, zinc removal (2.9):



## **Appendix II. (C): Proton Acidity Neutralization**

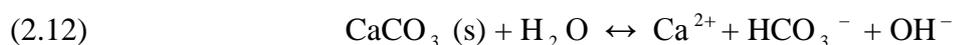
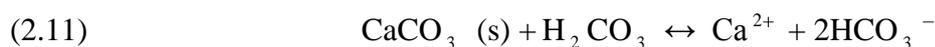
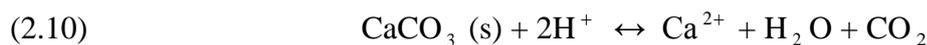
### **2.6 Proton Acidity Neutralization**

Passive treatment systems also neutralize proton acidity associated with AMD. Neutralization of proton acidity ( $\text{H}^+$ ) causes a corresponding increase in mine water pH (Younger et al., 2002; Ziemkiewicz et al., 1996). Acidity neutralization removes metal ions from solution because they generally become less soluble as pH increases (Skousen & Ziemkiewicz, 2005). The two main processes that remove acidity in passive treatment systems are (Younger et al., 2002):

- Carbonate mineral dissolution; and
- Bacterial sulfate reduction

#### **2.6.1 Carbonate Mineral Dissolution**

The most commonly used carbonate mineral in passive treatment systems is calcite ( $\text{CaCO}_3$ ). Calcite is common in limestone and removes mine drainage acidity by dissolution reactions (Younger et al., 2002; Cravotta III & Trahan, 1999):



Calcite dissolution consumes proton acidity ( $\text{H}^+$ ) (2.10) in AMD, and at  $\text{pH} > 5$  generates bicarbonate ( $\text{HCO}_3^-$ ) and hydroxyl ( $\text{OH}^-$ ) alkalinity (2.11 and 2.12). The  $\text{HCO}_3^-$  produced then either consumes more acidity (2.13) or remains un-reacted, providing an increase in buffering capacity (Cravotta III et al., 2008). Generally, dissolution of carbonate minerals is indicated by elevated calcium concentration (Cravotta III et al., 2004). Overall, the effect of reactions 2.10 – 2.13 is the consumption of proton acidity and generation of alkalinity, resulting in an increase of mine water pH (Younger et al., 2002).

### 2.6.2 Bacterial Sulfate Reduction

A variety of biological processes can influence pH, however, with respect to passive mine water treatment, bacterial sulfate reduction is most important (Younger et al., 2002; Gusek, 2002). This is described previously (reactions 2.3 - 2.5) and involves generation of bicarbonate alkalinity ( $\text{HCO}_3^-$ ) which neutralizes proton acidity ( $\text{H}^+$ ) (2.13) and increases pH.

## **Appendix II. (D): Selection of Passive AMD Treatment Systems**

### **2.7 Selection of Passive AMD Treatment Systems**

Selection of the most appropriate passive AMD treatment system for a specific AMD site is crucial in order to achieve successful remediation (Gusek, 2002). Flow charts are recommended as a decision making tool for selection of treatment systems (PIRAMID, 2003; Watzlaf et al., 2003). Various flow charts have been developed, incorporating variables such as flow rate and drainage chemistry (dissolved oxygen content, ferrous and ferric iron ratio, aluminium concentrations and pH) (Hedin & Nairn, 1992; Skousen et a., 2000; Watzlaf et al., 2003). Recently, Trumm (2007) developed a flow chart specific for New Zealand that incorporates mine drainage chemistry, topography and available land area. Many authors suggest that various passive treatment methods be used in combination with each other for most effective remediation (Skousen, 2000; Gusek, 2002; Younger et al., 2002; Watzlaf et al., 2003; PIRAMID Consortium, 2003).

## Appendix II. (E): Review of Selected Passive AMD Treatment Systems:

### 2.8 Sulfate Reducing Bioreactor

#### 2.8.1 Introduction

Sulfate reducing bioreactors (SRBRs) are a promising technology for removing dissolved metals and acidity from mine drainage (Doshi, 2006; Neculita et al., 2007; McCauley et al., 2008; 2009). SRBRs are described as using a simple flow-through design, with AMD fed into a solid reactive mixture which provides a carbon source for bacteria, and a physical support for microbial activity and metal sulfide precipitation (Neculita et al., 2007). SRBRs operate by passing mine water through an inorganic and/or organic reactive mixture, termed 'substrate' (Gusek, 2002; Neculita et al., 2007). Flow is usually vertical, either up or down (Neculita et al., 2007), however, horizontal flow orientations have been used less commonly (Zaluski et al. 2003; McCauley et al., 2008; 2009). SRBRs can be applied to highly acidic mine drainage, containing a wide range of dissolved metals (Gusek, 2002; Gusek and Wildeman, 2002). The schematic in Figure 2.4 displays a typical SRBR design, and Figure 3.2 shows a SRBR system operating on-site.

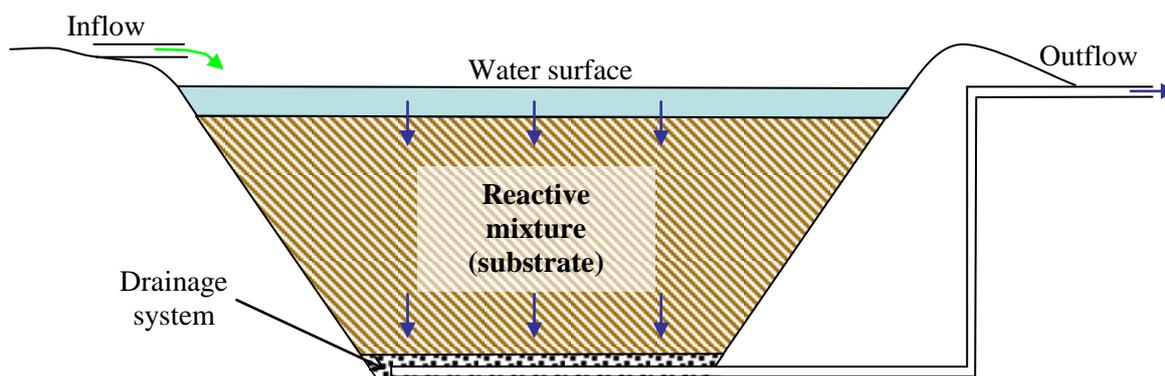


Figure 2.4: Schematic of the design of a sulfate reducing bioreactor passive treatment system. Adapted from Gusek (2002).



**Figure 2.5: Photo of a typical on-site sulfate reducing bioreactor (Gusek, 2002).**

## **2.8.2 Remediation Processes**

SRBR passive treatment systems remediate mine water by utilizing the naturally occurring chemical and biological processes associated with microbial sulfate reduction. (Doshi 2006; McCauley et al., 2008). Bacterially mediated sulfate reduction is the primary mechanism for immobilizing metals and generating alkalinity in SRBR systems (Gusek, 2002; Watzlaf et al., 2003; Gilbert et al., 2004; Doshi, 2006; Neculita et al., 2007) (reactions 2.3 - 2.5). Recent reviews by Doshi (2006) and Neculita et al. (2007) conclude sulfate reduction can effectively transform dissolved metals into immobile minerals such as sulfides, sulfates, and carbonates. Metal sulfide formation is preferable due to their higher density, and lower solubility and bio-availability compared to more common metal hydroxides (Gazea et al., 1996; Cocos et al., 2002). Dissolved metals that precipitate as metal sulfides in SRBRs include divalent cations: iron, copper, nickel, zinc, cadmium, lead, and mercury (Doshi, 2006; Gusek, 2002, 2004). Aluminium can also be precipitated, however removal processes differ from typical sulfide formation and are not well understood (Gusek and Wildeman, 2002).

Other important metal removal mechanisms include adsorption, bio-absorption, co-precipitation, and metal precipitation on the surface of substrate materials and bacteria (Neculita et al., 2007; McCauley et al., 2008; 2009). Dissolved metals that SRBRs do not always remove include manganese and arsenic (Dvorak et al., 1992; Watzlaf et al., 2003;

Zaluski et al., 2003). Additionally, SRBRs have a lag period after initial construction, before bacterial sulfate reduction becomes well established. During this time, adsorption onto substrate materials is the dominant metal removal mechanism (Willow & Cohen, 2003; Zaluski et al., 2003; Zagury et al., 2006), and treatment may not be complete.

### **2.8.3 Factors that Influence Performance**

The success of SRBR systems is largely dependant on the activity of sulfate reducing bacteria, because they reduce sulfate in AMD and generate alkalinity (Doshi, 2006; Neculita et al. 2007). To achieve optimal treatment, SRBR systems must be designed to promote conditions where these bacteria thrive (Gazea et al., 1996; Gusek, 2002). The most crucial factor is the availability of carbon from an organic source (2.3) (Neculita et al., 2007). Secondary factors that influence bacterial activity include redox conditions, pH, water chemistry, temperature, and reactive substrate materials (Watzlaf et al., 2003; Gilbert et al., 2004; Tsukamoto et al., 2004; Doshi, 2006; Zagury et al. 2006; Neculita et al., 2007).

#### **2.8.3.1 Organic Carbon Source and Substrate**

The availability of liable carbon is the most critical factor limiting bacterial activity and therefore sulfate reduction (Gilbert et al., 2004; Zagury et al., 2006). Effective AMD treatment only occurs if a suitable organic carbon source is present (Tsukamoto et al., 2004; Neculita et al., 2007). Consequently, suitable organic substrate must be selected to ensure treatment is feasible (Neculita et al., 2007), and for this reason substrate mixture has been extensively studied (Waybrant et al., 1998; Cocos et al., 2002; Ingvorsen et al., 2003; Gilbert et al., 2004; Tsukamoto et al., 2004; Zagury et al., 2006; McCauley et al., 2008).

Sulfate reducing bacteria only utilize simple organic carbon compounds such as methanol, ethanol, lactate. Zagury et al. (2006) and Ingvorsen et al. (2003) successful demonstrate treatment using these compounds in laboratory experiments and an active chemical plant, respectively. However, these compounds are rapidly consumed and require constant addition which makes these carbon sources unsuitable for long term use (Doshi, 2006; McCauley et al., 2009). Complex organic compounds have been incorporated because carbon sources to sustain bacterial sulfate reduction. These are usually industrial waste products as they are relatively inexpensive to acquire and include: sawdust, hay, alfalfa, wood chips, bark, walnut

shells, paper, peat, pulp mill, compost and animal manure (Younger et al, 2002; Gusek, 2004; Zagury et al., 2006, Doshi, 2006; Neculita et al., 2007; McCauley et al. 2008). Numerous laboratory and field studies have investigated different carbon sources and substrate mixtures, evaluating treatment performance to determine the most efficient sources and substrate mixtures (Cocos et al., 2002; Gilbert et al., 2004; Zagury et al., 2006; Waybrant et al., 1998; Tsukamoto et al., 2004; McCauley et al., 2008). Cocos et al. (2002) and Gilbert et al. (2004) both found manure to be a critical variable for optimal sulfate reduction, but this differs to results by Zagury et al. (2006) who found wood chips were better at promoting sulfate reduction than poultry manure. However, comparison between experiments is difficult because factors such as residence times, duration and others are often poorly quantified (Neculita et al., 2007).

A mixture of organic materials promote increased bacteria activity and sulfate reduction, compared to individual organic materials alone (Cocos et al., 2002; Zagury et al., 2006; McCauley et al., 2008b). For example, Zagury et al. (2006) demonstrate a mixture of compost (30%), poultry manure (18 %), and wood chips (2 %) promoted sulfate reduction and metal removal more than respective materials alone. The relative composition of materials influences treatment performance, for example, McCauley et al. (2008) report better treatment in small scale SRBRs containing a higher proportion of wood chips (post peel) than bark. It is thought that substrates containing multiple organic materials are more effective because sulfate reducing bacteria rely on a symbiotic relationship with other micro-organisms to break down complex organic materials to simpler carbon compounds which they can then use (Watzlaf et al., 2003; Gilbert et al., 2004; Zagury et al., 2006; McCauley et al., 2008). The biodegradability of substrate materials is important as it determines the rate of bacterial degradation and carbon availability to sustain bacterial sulfate reduction (Gilbert et al., 2004; Zagury et al., 2006). The inclusion of both easily biodegradable organic materials (manure, compost) and more resistant sources such as sawdust, hay, alfalfa, or wood chips is required. This provides a source of carbon during initial SRBR start-up, and also a long term supply to sustain bacterial activity (Cocos et al 2002; Zagury et al., 2006). The chemical composition of organic materials is assumed to control biodegradability, however there is no reliable method for predicting degradation rate, and current substrate mixtures are based on intuitive comparisons of the biodegradability of organic materials (Gilbert et al., 2004; Gusek, 2004). McCauley et al. (2008) state there is currently no agreement on the optimal organic substrate

mixture for SRBR systems, and attribute this to the complexity of interactions associated with microbial degradation and bacterial consumption of organic materials.

Many authors recommend the inclusion of a material inoculated with sulfate reducing bacteria, to accelerate bacterial colonization within SRBR substrates (Gusek, 2004; Doshi, 2006; Zagury et al., 2006). Materials suggested include compost, manure, or material from natural anoxic environments (Zagury et al., 2006; Gilbert et al., 2004).

Limestone can also be added to the substrate mixture as a source of additional alkalinity (Reisinger et al., 2000; Thomas and Romanek, 2002; Cocos et al., 2002; Zaluski et al., 2003). Recently, McCauley et al. (2008; 2009) integrated mussel shells into small scale SRBRs to achieve a similar affect, to promote metal precipitation and conditions suitable for bacterial activity.

### **2.8.3.2 Redox Conditions**

Anoxic, reducing conditions are required for sulfate reducing bacteria to survive and flourish (Doshi, 2006). These conditions are promoted in substrate mixtures by the high oxygen demand of organic materials (Watzlaf et al., 2003). Optimal conditions for sulfate reducing bacteria are dissolved oxygen concentrations  $<1\text{mg/L}$  (Doshi, 2006) and an oxidation-reduction (Eh) potential lower than  $-100$  (Neculita et al., 2007).

### **2.8.3.3 pH**

Maximum sulfate reducing bacterial activity requires circum-neutral pH conditions (pH 5 - 8) (Gusek & Wildeman, 2002; Willow & Cohen; 2003; Doshi, 2006). At lower pH, bacterial activity decreases, lowering the rate of sulfate reduction and thus SRBR treatment performance (Neculita et al., 2007). However, effective bacterial sulfate reduction has been documented in acidic conditions, at pH  $<4$  (Elliot et al., 1998; Tsukamoto et al., 2004). Watzlaf et al. (2003) suggest bacteria can be very active at  $<5$  pH, although this could be attributed to acid tolerant bacterial strains and alkaline microenvironments.

#### **2.8.3.4 Water Chemistry**

Bacterial sulfate reduction requires the presence of sulfate ions ( $\text{SO}_4^-$ ) which is an abundant component in AMD (typically  $>500$  mg/L) (Gusek, 2002). The effect of dissolved metals on bacterial activity can be either beneficial or detrimental (Neculita et al., 2007). Studies show that high metal concentrations can inhibit bacteria, with toxic thresholds ranging from just 1 mg/L to as high as 100 mg/L, and can have synergistic effects (Poulson et al., 1997; Utgikar et al., 2002). High concentrations of hydrogen sulfide (477 – 617 mg/L) can also be harmful (Neculita et al., 2007). Alternatively, low concentrations can be stimulatory, and promote increased sulfate reduction and metal removal (Utgikar et al., 2002). Importantly, sulfate reducing bacteria require the absence of oxidizing agents such as dissolved oxygen, ferric iron ( $\text{Fe}^{3+}$ ) and manganese ( $\text{Mn}^{4+}$ ) (Watzlaf et al., 2003).

#### **2.8.3.5 Temperature**

Doshi (2006) and Neculita et al. (2007) conclude that lower temperatures generally slow down bacterial activity. Doshi (2006) reported a 25% reduction in treatment performance during winter months in a RAPS. However other studies at both laboratory (Tsukamoto et al., 2004) and field scale have shown SRBR efficiency is not significantly impacted at cooler temperatures (1 - 8 °C) (Rose & Dietz; Gusek, 2002; Zaluski et al., 2003; Kuyucak et al., 2006). Lower temperatures can affect bacterial colonization of SRBRs, but once acclimatized bacteria are not critically affected and treatment performance is maintained (Tsukamoto et al., 2004; Neculita et al., 2007).

#### **2.8.3.6 Other Factors**

Other factors that influence SRBR treatment performance is system configuration and hydraulic properties (Lyew and Sheppard, 1997; Neculita et al., 2007; McCauley et al., 2008). System configuration refers to the flow direction through SRBRs which can affect metal transport and AMD interaction with substrate (Neculita et al., 2007). Down flow systems may develop preferential flow paths (McCauley et al., 2008), while Zaluski et al. (2003) and McCauley et al (2008) both report successful laboratory and field scale horizontal flow systems. Hydraulic retention time is important as it can affect the reaction rate of sulfate reduction and metal sulfide formation. If retention time is too short, this process may not run to completion, or bacteria could be flushed out (Neculita et al., 2007), while unnecessary long

retention time can accelerate consumption of organic materials (Dvorak et al., 1992). Hydraulic conductivities of substrate are also important as this affects retention times (McHaffie et al., 2007). Clogging with metal precipitates such as hydroxides, sulfides and carbonates and compaction of SRBR reactive substrate mixture can reduce porosity and permeability and potentially lead to preferential flow paths (short circuiting), and eventually system failure (Neculita et al., 2007; Younger et al., 2002).

#### **2.8.4 Design Criteria**

Three main types of design criteria recommended for sizing SRBR treatment systems are: metal molar volumetric loadings, acidity areal loadings, and hydraulic retention time. These criteria are conservative values because of the recent development of SRBR systems and limited field validation of criteria (Younger et al., 2002). Design criteria established for other passive AMD treatment systems (vertical flow wetlands) can be used for SRBR design, as these systems are very comparable, but have been in use longer and thus design criteria and performance are better established (PIRAMID Consortium, 2003).

##### **2.8.4.1 Metal Removal**

Design criteria for SRBR systems in terms of metal molar volumetric loadings are provided by Wildeman et al. (2006) and McCauley et al. (2008). Wildeman (2006) recommends a design criteria of 0.3 moles of metals removed per cubic meter of substrate per day (moles metals/m<sup>3</sup>/day), using a substrate mixture that consisted of organic materials and crushed limestone. However, McCauley et al. (2008) report greater metal removal criteria from small scale trials that incorporate mussel shells with organic materials. McCauley (2008) gives a conservative metal removal criteria of 0.4 moles metals/m<sup>3</sup>/day (for partial sulfate removal), while a criteria of 0.8 moles metals/m<sup>3</sup>/day is given for minimal sulfate removal. Metal removal design criteria are more recently used for sizing SRBR treatment systems (Wildeman et al. 2006; McCauley et al., 2008; 2009).

##### **2.8.4.2 Acidity Removal**

SRBRs can also be designed according to areal acidity loading criteria. This criteria is based on the amount of acidity removed, in units of CaCO<sub>3</sub>, per unit of surface area per day. Acidity removal criteria specifically for SRBR systems is provided by McCauley et al. (2008), who

recommend a conservative criteria of 66g CaCO<sub>3</sub> of acidity removal/m<sup>2</sup>/day based on several small scale systems. Acidity removal criteria for comparable systems such as VFWs are well established, and can be applied to the sizing of SRBR systems (McCauley et al., 2008, 2009). Many authors adhere to a value of 20 – 25 g CaCO<sub>3</sub>/m<sup>2</sup>/day (Rose & Dietz, 2002; Rose, 2004; Watzlaf et al., 2003), however, greater areal acidity removal rates have also been documented (Thomas and Romanek, 2002; Ziemkiewicz et al., 2003).

#### **2.8.4.3 Hydraulic Retention Time**

Hydraulic retention time (HRT or residence time) is another design for SRBRs. HRT refers to the length of time mine drainage is in contact with the reactive substrate materials within SRBR treatment systems (Younger et al., 2002). HRT design criteria specified for SRBR treatment systems varies considerably. According to a 2003 URS Report (Neculita et al., 2007) and Kuyucak et al. (2006), a HRT of at least 3 to 5 days is required for precipitation of metal sulfides. Similarly, Younger et al. (2002) propose a minimum retention time of 40 hours for effective sulfate removal, but at least four days for effective metal removal in highly acidic AMD. Alternatively, Skousen and Ziemkiewicz (2005) recommend a HRT of only 24 hours is needed for effective treatment.

#### **2.8.5 Lifespan**

The long term effectiveness of SRBR treatment systems is uncertain due to their relatively recent development and few field examples to verify predicted life expectancy. Factors that influence longevity are well identified however, which include organic substrate and its degradation, AMD chemistry, microbial activity, and hydraulic issues such as preferential flow paths, plugging, and compaction (Reisman et al., 2003; Gilbert et al., 2004; Neculita et al., 2007). Hedin et al. (1992) and Wildeman et al. (2006) predict about 20-30 years operation based on sulfate reduction and organic carbon degradation, however, Reisman et al. (2003) state the variability of sulfate reduction rates make predictions very difficult. Long term treatment requires addition of more carbon sources to sustain bacterial activity (Neculita et al. 2007). However, reported operating lifetimes are between 3 and 5 years (URS Report, 2003; Neculita et al., 2007) with some examples of older SRBR systems performing effectively (Doshi et al. 2006; Watzlaf et al. 2003; Gusek, 2002).

### **2.8.6 Sulfate Reducing Bioreactor Summary**

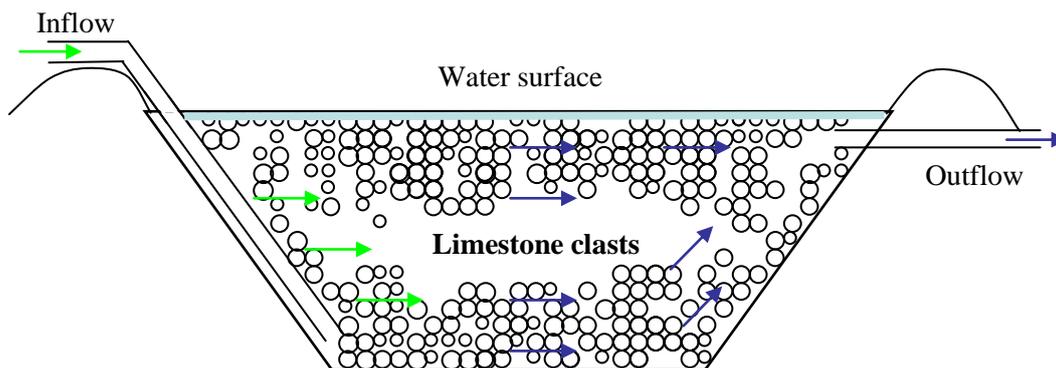
Despite the large number of studies on biological passive AMD treatment, many aspects require further investigation. Much remains to be understood about the fundamental interactions and complex chemical and biological processes in SRBR treatment systems, in order to improve on-site designs and performance. A key issue is the biodegradability of organic substrates and suitability of substrate mixtures (Gilbert et al., 2004; Doshi, 2006; Zagury et al. 2006; Neculita et al., 2007). More reliable techniques are required to characterise substrate materials in terms of carbon content and depletion rate and its ability to promote sulfate reduction (Gilbert et al., 2004; Zagury et al., 2006; Neculita et al, 2007). Research to assess and differentiate the various mechanisms for metal removal is needed, particularly for aluminium. Investigation of precipitated metals through geochemical modelling, solid phase species analysis and mineralogical characterization is also required (Neculita et al., 2007; McCauley et al., 2008).

## **2.9 Limestone Leaching Bed and Open Limestone Channel**

### **2.9.1 Introduction**

Passive treatment of AMD can occur by employing limestone to neutralize acidity and generate alkalinity (Younger et al., 2002). Various passive treatment systems utilize limestone because it is inexpensive, widely available, and it is relatively cheap to construct and maintain limestone based systems (Sasowsky et al., 2000).

Limestone leaching beds (LLBs) consist of an open, rectangular bed of limestone clasts (10 – 100 mm) that allow horizontal flow of AMD through pore spaces to remediate acidic drainage (Figure 3.3 and 2.7). The limestone bed is exposed to the atmosphere interacts with oxygen (Cravotta & Trahan, 1999). Skousen & Ziemkiewicz (2005) consider LLBs as simply limestone filled ponds. Cravotta III & Ward (2008) describe a bed of limestone clasts continuously flooded with AMD, and Denholm et al. (2003) indicate horizontal flow through these systems.



**Figure 2.6: Schematic of the basic design of a Limestone Leach Bed passive treatment system. Adapted from Skousen (1997).**



**Figure 2.7: Limestone leaching bed receiving low pH water in West Virginia, USA (Skousen & Ziemkiewicz, 2005).**

On the other hand, open limestone channels (OLCs) transmit water along a channel or ditch lined with an impermeable material over which are placed coarse, limestone clasts (Ziemkiewicz et al., 1994; O'Sullivan, 2005) (Figure 2.8). AMD is directed into the channel, travelling downhill in contact with limestone, aerating mine drainage along the way (Cravotta III et al., 2004; O'Sullivan, 2005).



**Figure 2.8: Open limestone channel passive treatment systems operating in Alabama (left) and West Virginia (right), USA (Ziemkiewicz et al., 1994; Skousen and Ziemkiewicz, 2005).**

### 2.9.2 Remediation Processes

Limestone leaching beds and open limestone channels are aerobic passive treatment systems (Ziemkiewicz et al. 1997; Younger et al., 2002). The most important metal removal mechanisms are oxidation and hydrolysis reactions (Cravotta III & Trahan, 1999). LLBs and OLCs use limestone for calcite dissolution to neutralize acidity and generate alkalinity (equations 2.10 – 2.13) with a resultant increase in pH. This promotes metal removal as metal solubility generally decreases with increasing pH (Younger et al., 2002; Cravotta III & Trahan, 1999).

The main purpose of aerobic passive treatment systems is to aerate mine drainage, oxidizing any ferrous iron to ferric iron, allowing greater removal within the systems (Younger et al., 2002). Limestone based treatment systems can increase the pH of mine water to between 6.0 – 7.5 (Ziemkiewicz et al., 1996). At this pH, common dissolved metals ions such as ferric iron and aluminium are not soluble (Figure 2.2, 2.3), and are removed from solution by hydrolysis and precipitation reactions (reactions 2.2 and 2.6) (Younger et al., 2002). Limestone based systems are also documented to remove manganese by surface catalyzed hydrolysis reactions (2.7, 2.8) (Cravotta III & Trahan, 1999; Denholm et al., 2003) and microbial activity (Younger et al, 2002; Means & Rose, 2005). The precipitation of solid hydroxides (especially iron) also removes other metals such as copper, nickel, zinc, cadmium, and arsenic, via adsorption and co-precipitation processes (Younger et al., 2002; Cravotta III & Trahan, 1999; Cravotta III, 2008; Rait et al., In press). Ideally, high flow velocities (>0.1 m/min) keep metal

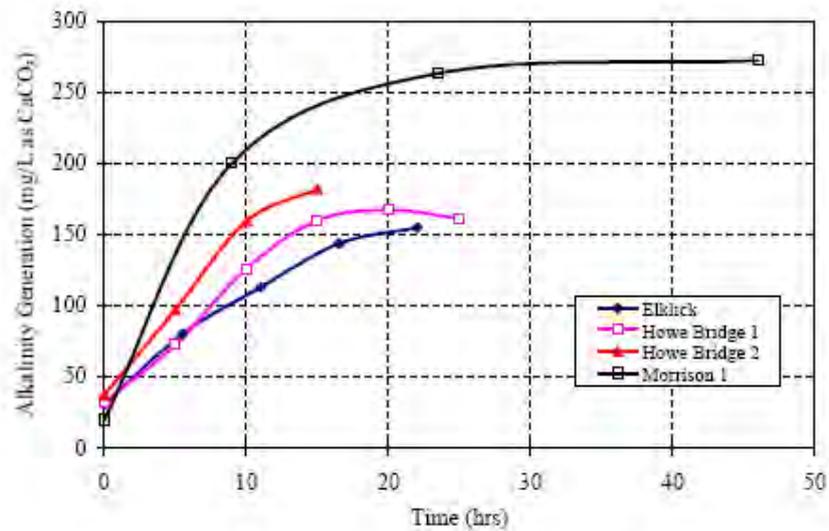
precipitates in suspension, flushing solids out for collection in settling ponds or aerobic wetlands (Ziemkiewicz et al., 1997; Cravotta III & Trahan, 1999).

### **2.9.3 Factors that Influence Performance**

A major factor influencing the performance of LLB and OLC treatment systems is the precipitation of metals within systems, which can affect limestone dissolution (Cravotta III & Trahan, 1999; Younger et al., 2002; Watzlaf et al., 2003). Limestone clasts can become encrusted and covered by iron and aluminium hydroxides, hydroxysulfates, or calcium-sulfate (gypsum), causing limestone to become 'armoured'. Armouring potentially reduces the rate and extent of limestone dissolution (Cravotta III & Trahan, 1999; Skousen & Ziemkiewicz, 2005; Santomartino & Webb, 2007) by up to 80% (Pearson & McDonnell, 1975), however, dissolution was not prevented entirely. Other authors have shown armoured limestone dissolves at a significant rate (Cravotta III et al., 2004; Ziemkiewicz et al., 1994) depending on pH and armour thickness (Skousen & Ziemkiewicz, 2005). Additionally, metal precipitates can accumulate within limestone beds or channels, clogging pore spaces and reducing permeability which can lead to short circuiting of AMD (channelization) and failure due to reduced limestone contact time for neutralization (Ziemkiewicz et al., 1994; Cravotta III & Ward, 2008). Some authors recommend installing a scour or flush pipe in limestone bed systems to dislodge metals from limestone surfaces and pore spaces and flush accumulated precipitates (Cravotta III & Trahan, 1999), however, no consensus is reached on whether flushing maintains treatment effectiveness (Cravotta III et al., 2008). Many limestone based systems fail prematurely due to the affects of limestone armouring and clogging (Skousen & Ziemkiewicz, 2005; Watzlaf et al., 2003; Cravotta III, 2008), therefore, these problems have to be mitigated by appropriate system designs (Cravotta III & Trahan, 1999).

The rate of limestone dissolution also can be influenced by factors such as temperature, pH, dissolved and suspended constituent concentrations, reactive surface area (limestone clasts size), microbial activity, and limestone quality (Younger et al., 2002; Cravotta III et al., 2008; Cravotta III & Ward, 2008). Dissolution is enhanced by higher carbon dioxide partial pressure (Plummer et al., 1979), a by-product of dissolution. Cravotta III & Trahan (1999) suggest hydrolysis of dissolved iron and aluminium also promotes dissolution by generation of proton acidity which subsequently reacts with limestone. Conversely, limestone dissolution decreases with increased pH and dissolved calcium and bicarbonate concentrations (Cravotta

III & Trahan, 1999). A positive logarithmic relationship between AMD contact time and alkalinity generation exists. In the initial hours of AMD contact, calcite dissolution occurs rapidly; however, the dissolution rate slows with time as water reaches saturation with respect to calcite (Rose, 2004; Jage et al., 2001). Watzlaf et al. (2003) demonstrate this by an exponential increase in alkalinity generation until a maximum is reached after 15 - 20 hours contact time with AMD in anoxic limestone treatment systems (Figure 2.9).



**Figure 2.9:** Alkalinity concentration as mine water flows through ALD treatment systems (Watzlaf et al., 2003).

## 2.9.4 Design Criteria

### 2.9.4.1 Limestone Leaching Bed

Design guidelines for LLB treatment systems are tentative due to the variable rate of limestone dissolution (Cravotta III et al., 2008). Design criteria for other limestone based passive treatment systems can be used, such as anoxic limestone drains and oxic limestone drains (Younger et al., 2002). Criteria are based on influent AMD concentrations, hydraulic retention time (HRT) and limestone dissolution rates.

Influent AMD design criteria focuses on dissolved iron, aluminium and oxygen concentrations. Traditionally criteria have been conservative, with authors recommending limestone bed treatment is only suitable for AMD containing <1 mg/L of ferric iron, aluminium, or dissolved oxygen (Hedin et al. 1992; Black et al., 1999; PIRAMID Consortium, 2003; Watzlaf et al., 2003). However, Cravotta III & Trahan (1999) suggest

treatment can be successful with moderate concentrations of DO, <5 mg/L of Fe and Al, and 90 mg/ L CaCO<sub>3</sub> total acidity, while Santomartino and Webb (2007) suggest limestone bed systems can treat up to 10 – 20 mg/L of iron.

Hydraulic retention time is a commonly suggested design criteria, and authors generally recommend 12 - 15 hours contact time, based on the rate of calcite dissolution and maximum (>85%) alkalinity generation (Skousen & Ziemkiewicz, 2005; Watzlaf et al., 2003; Younger et al., 2002). Mukhopadhyay et al. (2007) developed equations based on the kinetics of limestone dissolution to determine retention time and the mass of limestone required in treatment systems. This author, along with Cravotta III & Trahan (1999) report effective treatment of AMD with only 1 – 3 hrs retention time. Therefore, it appears optimal design criteria for limestone beds remains provisional, though conservative criteria are established.

Limestone clast sizes recommended for limestone bed systems vary. PIRAMID Consortium (2003) recommend 10 – 20 mm sized clasts for sites with high hydraulic gradient, but 50 – 75 mm aggregate for flatter sites. Cravotta & Trahan (1999) recommend tabular clasts (100 mm by 30 mm) in order for adequate hydraulic conductivity, but regardless of size, a restricted size range is required to maintain porosity (Younger et al., 2002).

#### **2.9.4.2 Open Limestone Channel**

Criteria for the design of OLCs are generalized and poorly established. Similar to LLBs, HRT is a critical parameter (Skousen & Ziemkiewicz, 2005). Ziemkiewicz et al. (1996) advise that HRT must be as at least 10 hrs, up to several days may be necessary to achieve adequate treatment. However, water velocity must remain high to keep metal precipitates in suspension and avoid clogging and armouring of limestone clasts (Ziemkiewicz et al., 1996). Therefore, channel length is important, and it is advised OLCs be constructed on steep slopes having a gradient of 10 – 20% (Skousen & Ziemkiewicz, 2005; Cravotta III et al., 2004). Ziemkiewicz et al. (1994) developed a model to estimate limestone volumes and channel dimensions, proposing channels are built five times larger to account for the effects of armouring. The long channel lengths suggested (>600 m) seem impractical in some mine environments. In general, coarse limestone clasts should be used (15 to 30 cm), to maximize flow velocity and minimize accumulation of metal precipitates (Ziemkiewicz et al., 1996).

### **2.9.5 Lifespan**

Eventually LLB and OLC systems will fail due to depletion of limestone from calcite dissolution in acidic drainage, and consequently, occasional addition of limestone is required (Cravotta III et al., 2008). Alternatively, treatment can end prematurely due to armouring or clogging by iron and aluminium hydroxides. Santomartino & Webb (2007) report the amount of ferric iron is a crucial factor for lifespan, rather than consumption of limestone. Generally, the literature prescribes a design lifespan of 20 – 30 years for limestone based systems (Ziemkiewicz et al., 1994; PIRAMID Consortium, 2003; Trumm et al., 2006).

### **2.9.6 Limestone Leaching Bed and Open Limestone Channel Summary**

Additional research is required for LLB and OLC passive treatment systems so that criteria can be developed to optimize AMD treatment efficiency. Research into effective design concepts relating to prevention of metal precipitate accumulation in systems, effective flushing mechanisms, and limestone armouring is required (Cravotta III & Ward, 2008; Ziemkiewicz et al., 1997). Design concepts need to be trailed under field conditions and evaluated. Studies to improve understanding of optimal hydraulic retention times, limestone dissolution rate and trace metal sorption are also recommended (Cravotta III & Trahan, 1999).

## **2.10 Summary**

Much research overseas has focused on the passive treatment of AMD during the last two decades. Passive treatment systems utilise naturally occurring processes to remediate AMD, and are less expensive in the long term than active treatment options. Passive systems are considered a proven treatment technology by many authors, provided they are appropriately selected and designed for AMD sites (Younger et al, 2002). The primary acidity and metal removal processes operating to treat AMD are relatively well understood, and these are reviewed.

Despite a number of studies that characterise and describe affects of AMD in New Zealand, little research has focussed on remediation of acidic mine drainage (O'Sullivan, 2005; Trumm et al. 2005, 2006, 2008; Trumm, 2007; McCauley et al. 2008, 2009). McCauley et al. (2006) consider New Zealand to be in the initial stages of remediation, with specific passive

treatment methods yet to be proven. The implementation of passive treatment systems and evaluation of their performance will enable validation and design improvements for different passive technologies (McCauley et al., 2006).

## **Appendix III**

### **Laboratory Trials of Passive AMD Treatment Systems: Methodology, Raw Data and Results**

#### **A) Selection of Suitable Passive AMD Treatment Systems for Fanny Creek**

#### **B) Laboratory Trial Design Methodology**

- Calculation of AMD Volume for Determination of Influent Flow Rates
- Hypothetical Bench Scale Sizes for the Design of Appropriate Flow Rates
- Porosity Testing (AMD Volume)

#### **C) Construction and Operation of Bench Scale Passive Treatment Systems**

- AMD Supply
- Sulfate Reducing Bioreactor
- Limestone Leaching Bed and Open limestone channel
- Settling Ponds
- Data Collection

#### **D) Raw Data**

- Tables in raw data format stored on CD-ROM

#### **E) Results**

- Summary Tables of Bench Scale Treatment System Effluent Water Quality and Chemistry
- Metal analysis of Effluent Discharged Directly from Bench Scale Treatment Systems
- Electrical Conductivity Influent and Effluent Measurements for Bench Scale Treatment Systems
- Dissolved Oxygen Concentrations along the OLC Treatment System
- SRBR Treatment System Upper Water Surface 24 hour Investigation
- Autopsy Analysis of Bench Scale Treatment Systems
- Waitahu River Mixing Option: Hydraulic Pump System

### **Appendix III. (A): Selection of Suitable Passive AMD Treatment Systems for Fanny Creek**

Suitable passive treatment options for Fanny Creek AMD were determined by a selection flow chart developed by Trumm (2007), specific to New Zealand conditions. Parameters required for the flow chart such as water chemistry (iron and aluminium concentrations, ferrous/ferric iron ratio and dissolved oxygen content), topography, and available land area were established from initial monthly water sampling data, and a visual evaluation of the Fanny Creek catchment. Parameters were assigned both numeric values and qualitative descriptors, according to that required by the flow chart. To properly characterise AMD water chemistry, a sampling program of approximately one year is preferred (P Weber, pers comm., 2008). However, due to time constraints and the need to commence laboratory trials, potentially suitable treatment options were selected after only four months of field-site water sampling. Water chemistry parameters were derived from monitoring site R12 (just prior to the settling ponds at the valley bottom). Parameters were taken from R12 because this was the preferred locality for a passive treatment system within the catchment (P Weber, pers comm, 2008). The necessary flow chart parameters, specific numeric value or descriptors assigned to each parameter according to Fanny Creek, and the respective actual data or catchment characteristic used to derive parameters are shown in Table 3.1

**Table 3.1: Parameters used in the flow chart developed by Trumm (2007) for the selection of suitable passive treatment systems (from initial four months sampling occasions).**

Flow chart parameter	Specific parameter for flow chart	Data and catchment characteristics used to derive flow chart parameters
Iron concentration	low	3.55* mg /L
Aluminium concentration	low	6.4 mg / L
Ferrous / Ferric Iron ratio	N/A	N/A
Dissolved oxygen content	> 2 mg/L	8.2 mg/L
Topography	Steep <i>and</i> Not steep	Figure 1.1 in thesis
Available land area	Large flat area <i>and</i> Long narrow area	Figure 1.1 in thesis

\* The initial four month average iron concentration is elevated compared to the average (1.3 mg/L) over the entire sampling period from February 2008 – January 2009 due to an erroneously high concentration in May (8.0 mg/L).

Iron and aluminium concentrations were relatively low and were therefore assigned the descriptor 'low' (D Trumm, pers comm., 2008). Average dissolved oxygen concentrations were 8.7 mg/L, therefore this parameter was well defined ( $> 2$  mg/L). The parameters topography and available land area were assigned both options, as the Fanny Creek catchment exhibits both of these characteristics.

## **Appendix III. (B): Laboratory Trial Design Methodology**

### **Calculation of AMD Volume for Determination of Influent Flow Rates**

To design appropriate flow rates for bench scale treatment systems, two variables were required: AMD Volume ( $m^3$ ) and Hydraulic Retention Time (HRT). HRTs were predetermined from the trial design; however, AMD Volume for bench scale treatment systems required determining. AMD volume is the amount of AMD ( $m^3$ ) in contact with solid reactive materials facilitating remediation within passive treatment systems, and essentially represents the porosity of such materials (with the exception of the OLC as explained below). An excel spread sheet comprising various sizes and/or volumes of hypothetical SRBR, LLB and OLC treatment systems was developed (Table 3.2). AMD Volumes within respective bench scale systems sizes were calculated on a spread sheet using estimated solid reactive mixture porosities and simple volume calculations, illustrated by the equation below:

**Table 3.2: Contained on Appendix III, CD-ROM. Spread sheet demonstrating the process used to select appropriate bench scale treatment system sizes and flow rates for laboratory trials. Hypothetical SRBR, LLB and OLC bench scale system sizes (or reactive material volumes) are shown by 'Total Volume'. Flow rates for the prescribed hydraulic retention times are based on actual AMD Volumes, measured once bench scale treatment systems were constructed.**

$$\text{Eq.1) AMD Volume (m}^3\text{) = (Volume * Porosity) + X (m}^3\text{)}$$

*Where:*

- i) Volume is the volume of solid reactive materials (m<sup>3</sup>) facilitating remediation within passive treatment systems;
- ii) Porosity is the pore space available within such solid reactive materials that AMD can occupy;
- iii) 'X' is any other additional volume of AMD not contained within the pore spaces of solid reactive materials facilitating remediation, yet still designed to receive treatment by solid reactive materials (this applies to the OLC)

To calculate the AMD Volumes of different sized, hypothetical bench scale treatment systems on the spreadsheet, porosities of the solid reactive materials employed had to be estimated (as this exercise occurred prior to construction of bench scale systems). Porosity for the SRBR reactive substrate mixture was assumed to be 48%, based on previous studies of similar substrates by McHaffie (2007). Porosity of limestone aggregate within LLB and OLC treatment systems was assumed to be 50%, as this is commonly suggested at laboratory scales (Watzlaf et al., 2003). Using assumed porosities, and the various hypothetical bench scale system sizes / volumes, estimated AMD Volumes were calculated (Eq.1).

This was relatively straightforward for the SRBR and LLB, and involved a simple multiplication; however, AMD Volume for the OLC bench scale treatment system not only included the amount of AMD within the pore space of limestone aggregate (or clasts) in the channel, but also the amount of AMD above limestone clasts (the OLC was designed to simulate a stream channel, and as such limestone clasts were submerged). In the equation above, 'X' represents the amount of AMD overlying limestone clasts, and is only applicable to the OLC bench scale system (SRBR and LLB systems only designed to treat AMD within pore spaces of reactive substrate materials and limestone aggregate, respectively). The total AMD Volume for the OLC system was calculated based on simple volumetric calculations, and varied according to different lengths of hypothetical OLCs. The length of channel determined the volume of limestone clasts and total AMD Volume within the system (Table 3.2). The amount of AMD within the pore spaces of limestone clasts was accounted for by applying the assumed 50% porosity to the volume of limestone aggregate (or clasts) in the

channel. To calculate the additional volume of AMD above limestone clasts, the depth of AMD in the channel was assumed uniform, then using the given channel lengths, and fixed channel width, the overlying amount of AMD was calculated. These two AMD volumes were added to give an estimated AMD Volume within the OLC bench scale treatment system. The specific equation used is provided below:

$$\text{Eq.2) OLC AMD Volume (m}^3\text{)} = ((T * W * L) * 0.5) + (D * W * L)$$

Where:

T = assumed thickness of limestone clasts within the channel (0.02 m)

W = channel width (0.09 m)

L = channel length (Xm)

0.5 = assumed porosity of limestone clasts (%)

D = assumed depth of AMD above limestone clasts (0.005 m)

**Table 3.3: Various hypothetical OLC lengths evaluated, and their associated calculated limestone clast volume and AMD Volume.**

Channel length (m)	Volume of Limestone clasts in channel (m <sup>3</sup> )*	AMD Volume (L)
8	0.0144	0.0108
12	0.0216	0.0162
15	0.027	0.02025
20	0.036	0.027

\*Limestone clast volume calculated based on a fixed channel width of 90 mm, and an assumed limestone clast thickness of 20 mm in the channel.

### **Hypothetical Bench Scale Sizes for the Design of Appropriate Flow Rates**

The process employed to select appropriate SRBR, LLB and OLC bench scale treatment system flow rates and sizes is shown in Appendix IV, Figure 2. Hypothetical bench scale sizes and their respective flow rates were assessed to select those most appropriate for laboratory trials. Size and flow rates determined the amount of AMD required to supply the trial and therefore had to be defined appropriately so that the amount of AMD requiring collection from Fanny Creek and transportation to Christchurch was feasible. The different, hypothetical bench scale sizes in Table 3.2 are shown in terms of the total volume (Total Volume) of reactive materials facilitating AMD treatment. The AMD Volumes shown are derived from actual measured porosities and volume measurements once bench scale systems were constructed. However, during the design of the trial, prior to construction of treatment systems, AMD Volume had to be estimated (as described above in the calculation of AMD Volumes) to enable the selection of appropriate flow rates and sizes, so construction of bench scale treatment systems could proceed. Therefore, the flow rates shown Table 3.2 are the actual flow rates designed for the prescribed HRTs (unnecessary to show original approximated flow rates used to gauge treatment system sizes). Flow rates were used to extrapolate the total amount of AMD needed for each system (shown at the end of each flow rate row), which were then added together to assess the total amount of AMD required for all three systems. SRBR, LLB and OLC sizes were chosen on the basis of being representative of larger scale treatment system processes, yet requiring feasible amounts of AMD to supply the trial. These sizes and/or reactive material volumes chosen, along with their corresponding HRT flow rates, are those highlighted in Table 3.2

### Porosity Testing (AMD Volume)

To design appropriate flow rates the volume of AMD in contact with the solid reactive materials facilitating remediation within passive treatment systems had to be determined. This volume essentially represents porosity of reactive materials however for the OLC the quantity of AMD overlying limestone aggregate is also included. Following construction of bench scale treatment systems, porosity testing and measurements to determine actual AMD Volumes were conducted and these are described below for each treatment system.

#### ▪ Sulfate Reducing Bioreactor

To determine the porosity of the reactive substrate mixture in the SRBR bench scale treatment system, the substrate was fully saturated with tap water (filled from the bottom to avoid air pockets) and then drained via the flushing outflow, with the volume of water discharged measured (Figure 3.1). However, the portion of water volume contained within the lower gravel layer had to be quantified (the flushing outlet level was below the level of the reactive substrate mixture layer). This was done prior to placing the substrate mixture on top of the gravel layer within the SRBR container. The volume of water required to fully submerge the gravel layer from the flushing outflow water level (water that could not drain) was measured by inputting known volumes of water. This volume (plus the calculated water volume contained within the external piping) was then subtracted from the total volume drained from the saturated reactive substrate material. Porosity testing was conducted three times to derived average porosity and AMD Volume (Table 3.4).

**Table 3.4: Porosity testing of the SRBR reactive substrate mixture for determination of AMD Volume.**

	Measured water volume drained from SRBR substrate (L)	Porosity
	29	0.59
	26.5	0.53
	27	0.54
<b>Average</b>	27.5	0.55

Note: Measured water volumes have had surplus water volume contained within the gravel layer (3.95L) subtracted.



**Figure 3.1: Porosity testing of the reactive substrate mixture in the bench scale SRBR treatment system.**

- **Limestone Leaching Bed**

To determine the porosity of the limestone clast bed, the bed was filled with tap water fully saturating all limestone clasts, and then drained via the flushing outflow with the discharged volume of water measured (). However, because the level of the flushing outlet was elevated off the bottom of the container (30 mm), not all water within the limestone bed could drain and be measured. Therefore, this volume was quantified prior to placing all the limestone clasts into the LLB container. This was done by inputting known volumes of water into the LLB container (along with wetted limestone clasts up to the flushing outflow level) until the water level reached the flushing outflow level. This volume was then added to the measured volume drained from the LLB treatment system. Porosity testing was conducted three times, and the average porosity and AMD Volume derived (Table 3.5).

**Table 3.5: Porosity testing of the LLB limestone clast bed for determination of AMD Volume.**

	Measured water volume drained from limestone clast bed (L)	Porosity
	24.5	0.48
	25	0.51
	24	0.48
<b>Average</b>	24.5	0.49

Note: The water volumes shown have had the additional water volume that could not drain (4.5 L) added.



**Figure 3.2: Porosity testing of the limestone clast bed in the bench scale LLB treatment system.**

- **Open Limestone Channel**

To determine the volume of water contained within the OLC bench scale treatment system, the system was filled with tap water and operated as it would have during treatment of AMD. The volume of water contained within the channel was then measured by manually tipping the water out of each gutter and measuring the volume of water drained. Measured volumes of water for each tier were added together and this formed the quantity used for AMD Volume. Measurement of AMD Volume was conducted three times, with the average water volume derived from these measurements (Table 3.6).

**Table 3.6: Water volume testing of the OLC channel for determination of AMD Volume.**

Measured water volume drained from the OLC channel (L)	
	19.1
	18.5
	18.1
<b>Average</b>	18.5

## Appendix III. (C): Construction and Operation of Bench Scale Passive Treatment Systems

### AMD supply



Figure 3.3: Collection of Fanny Creek AMD for use in laboratory trials of bench scale SRBR, LLB and OLC passive treatment systems.



Figure 3.4: Header tank and inflow and overflow tubing. Outlet tubings feeding down into bench scale treatment systems also shown.



**Figure 3.5: Fuller™ metal clamps used as the influent AMD flow rate control mechanism for bench scale SRBR, LLB and OLC systems.**

### **Sulphate reducing bioreactor (SRBR)**



**Figure 3.6: Previously used SRBR substrate sample from trials conducted by McCauley et al. (2008). This material was included in the reactive substrate mixture in the current SRBR study, for the purpose of promoting bacterial colonisation.**

## Limestone Leaching Bed (LLB) and Open Limestone Channel (OLC)

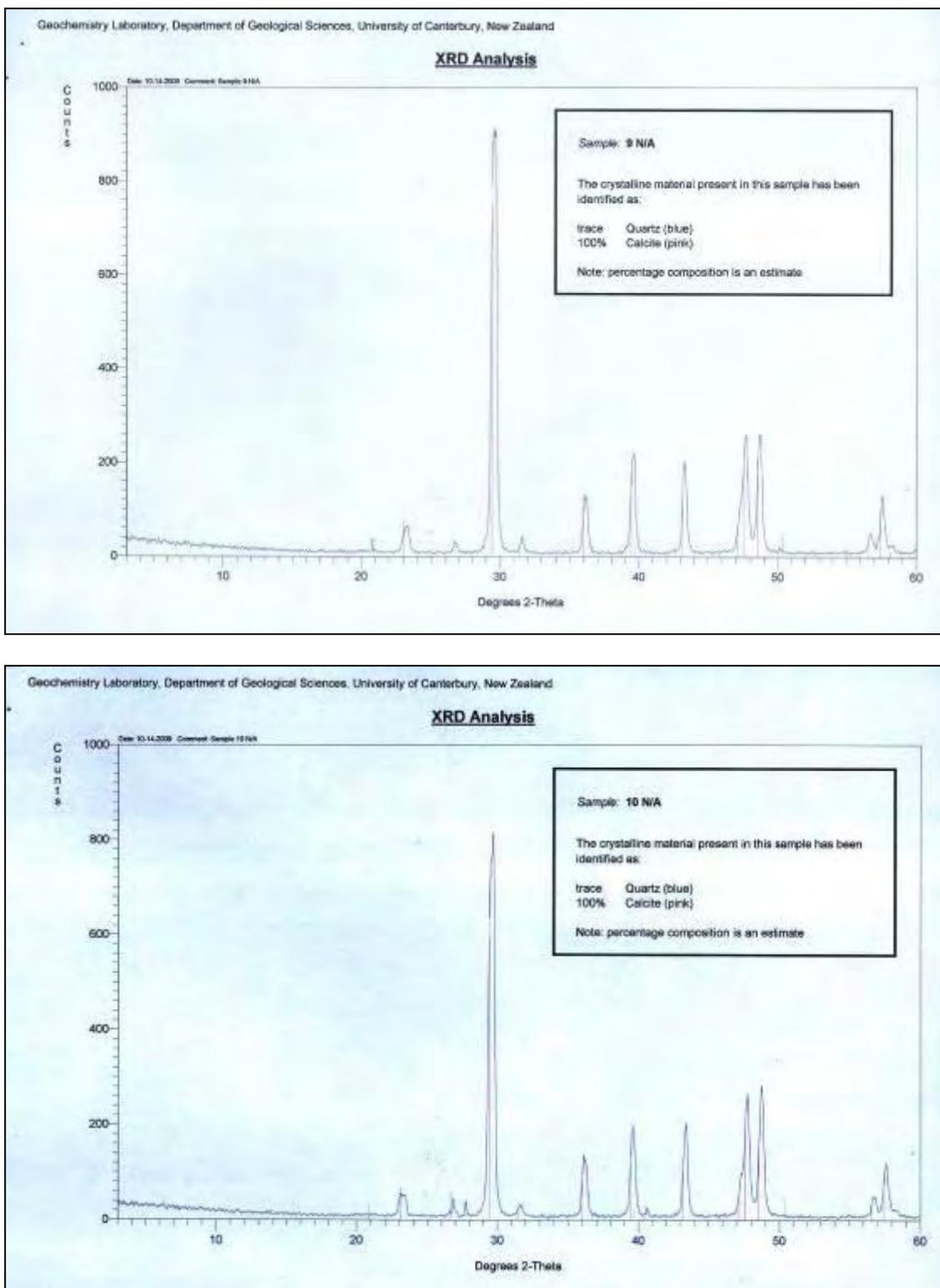
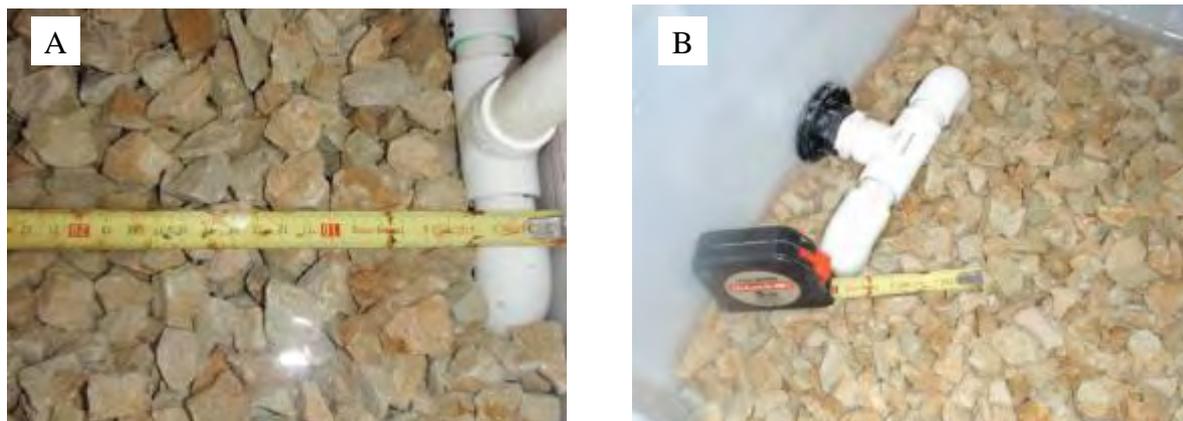


Figure 3.7: X-ray Powder Diffraction patterns of two samples of limestone clasts used in bench scale LLB and OLC treatment systems.



**Figure 3.8: Inflow (A) and outflow (B) pipe structures of the bench scale LLB system. Photos shows the level at which pipe structures are set in relation to the water level within the system. The horizontal segment of inflow piping (A) is set just below the water level in the system to prevent preferential flow down any one side. The level of the outflow pipe structure (B) determined the water elevation within the system, and is set so the depth of AMD overlying limestone clasts is approximately 10 mm.**

### Settling Ponds



**Figure 3.9: Figure 11: Settling pond outlet structure consisting of a lower threaded bung that could be unscrewed to enable direct water sampling of settling pond effluent.**

### Data Collection



**Figure 3.10: Measurement of influent AMD flow rates. Photo shows the LLB system during flow rate testing. Influent AMD was diverted and collected in a cylinder over a measured time period to determine the influent flow rate.**

## Appendix III. (D): Raw Data

Tables 3.7 – 3.21 contain results in raw data format collected during laboratory trials of bench scale treatment systems. Tables are stored on CD-ROM, located at the back cover.

**Table 3.7: Designed and measured experimental parameters for bench scale SRBR, LLB and OLC treatment systems. Table shows measured and average influent AMD flow rates (L/day) and associated hydraulic retention times, and notes for bench scale treatment systems. Notes indicate when water sampling to assess treatment performance was conducted and also observations over the trial duration.**

**Table 3.8: Measured water quality parameters pH, electrical conductivity, dissolved oxygen and temperature during laboratory trials of SRBR, LLB and OLC bench scale treatment systems. Measurements taken of influent AMD, effluent discharged directly from treatment systems, effluent discharged from respective settling ponds, water contained in settling ponds and upper water surfaces (SRBR and LLB treatment systems only).**

**Table 3.9: Acid soluble influent and dissolved and total effluent Al, Fe, Mn, Ca, Cu, Ni, Zn, and sulfate concentrations (mg/L) (a), and corresponding removal efficiencies (b) during laboratory trials of bench scale SRBR, LLB and OLC treatment systems. Dissolved Al and Fe concentrations and removal efficiencies along the OLC treatment system also provided.**

**Table 3.10: Acidity titrations for influent AMD during bench scale trials of SRBR, LLB and OLC passive treatment systems. Measured influent AMD acidity (pH 4, 5, and 7) is reported in mg/L as CaCO<sub>3</sub>. Methodology and calculation given by (Lewis and McConchie, 1994).**

**Table 3.11: Alkalinity titrations of bench scale SRBR, LLB and OLC passive treatment system effluent discharged both directly from treatment systems and from respective settling ponds. Measured effluent alkalinity (pH 5, 4, 3.7) is reported in mg/L as CaCO<sub>3</sub> equivalent. Methodology and calculation given by (Lewis and McConchie, 1994).**

**Table 3.12: Influent and effluent iron species composition (% ferrous or ferric) for SRBR, LLB, and OLC treatment systems.**

**Table 3.13: Investigation of the upper water surface of the SRBR treatment system over a 24 hour period. Water chemistry analysed included ferrous and ferric iron composition and water quality parameters measured included dissolved oxygen (mg/L), pH, and temperature.**

Measurements were obtained approximately every 2.5 hours, with the SRBR operating at ~58 hrs HRT.

**Table 3.14:** pH and electrical conductivity (EC) and with distance along the OLC treatment system for each hydraulic retention time tested. Measurements obtained at approximately 1 m intervals.

**Table 3.15:** Dissolved oxygen (a) and sulfur concentrations (b) with distance along the bench scale OLC treatment system. Measurements have units in mg/L and were obtained when the system was operating at ~15 hrs HRT.

**Table 3.16:** Calculated areal influent acidity (acid soluble), and calculated areal acidity removal (dissolved and total) both directly from bench scale SRBR, LLB and OLC treatment systems and from respective settling ponds during laboratory trials. Acidity is measured on a g CaCO<sub>3</sub> / m<sup>2</sup> of treatment system surface area/ day basis.

**Table 3.17:** Sulfate reducing bioreactor molar volumetric influent metal loading (acid soluble), and molar volumetric metal removal (dissolved and total) both directly from the SRBR treatment system and from the SRBR settling pond. Molar volumetric metal loading and removal are measured on a moles of metals per cubic meter of substrate per day basis (mols/m<sup>3</sup>/day). Conversion from metal concentration data (mg/L) to molar loading values provided.

**Table 3.18:** Hach Spectrophotometer iron speciation analysis of influent and effluent of SRBR, LLB and OLC bench scale treatment systems at different HRTs.

**Table 3.19:** Waitahu River Mixing Option Investigation. Calculation of Waitahu River water required to neutralize Fanny Creek AMD (from both R12 and IB5c) to pH 5.

**Table 3.20:** Waitahu River water and Fanny Creek AMD (R12) titration mixing data.

**Table 3.21:** Scanning Electron Microscopy elemental composition analysis of bench scale SRBR, LLB and OLC autopsy samples

## **Appendix III. (E): Results**

### **Summary Tables of Bench Scale SRBR, LLB and OLC Treatment System** **Effluent Water Quality and Chemistry**

Table 3.22 – 3.24 summarize effluent water quality and chemistry for bench scale SRBR, LLB and OLC treatment systems. Data are separated into effluent discharged directly from the treatment system (before entering settling ponds and labelled ‘system’) and effluent discharged from subsequent settling ponds (labelled ‘pond’).

**Table 3.22: Summary of effluent water quality parameters and water chemistry for the bench scale sulfate reducing bioreactor treatment system. Units are in mg/L unless otherwise specified. Alkalinity units are in mg/L as CaCO<sub>3</sub>. N is equal to 6 for metal concentration data labelled 'system'. For all other data n is equal to 10.**

	Sulfate reducing bioreactor (SRBR)							
	Mean		Median		Min		Max	
	System	Pond	System	Pond	System	Pond	System	Pond
<b>pH</b>	-	-	5.89	6.02	4.61	4.45	6.97	7.12
<b>Electrical Conductivity (µS/cm)</b>	846	860	764	816	665	672	1270	1259
<b>Dissolved oxygen</b>	1.86	2.63	1.73	2.74	0.6	1.22	3.57	4.04
<b>Alkalinity (pH 3.7)</b>	95	92	57	77	15	15	255	250
<b>Dissolved Al</b>	1.1	2.0	0.11	0.12	0.032	0.035	5.9	6.9
<b>Total Al</b>	3.4	2.8	3.1	1.4	0.34	0.19	8.3	8.6
<b>Dissolved Fe</b>	0.17	0.094	0.12	0.060	0.056	<0.020	0.50	0.27
<b>Total Fe</b>	0.23	0.18	0.17	0.14	0.091	0.072	0.66	0.67
<b>Dissolved Mn</b>	3.2	3.1	3.5	3.3	1.7	1.6	4.0	4.1
<b>Total Mn</b>	3.3	3.1	3.6	3.5	1.5	1.6	4.1	3.7
<b>Dissolved Cu</b>	0.0012	0.0063	0.0011	0.0024	0.00074	0.00084	0.0018	0.042
<b>Total Cu</b>	0.012	0.023	0.0054	0.0079	0.0024	0.0029	0.042	0.078
<b>Dissolved Ni</b>	0.067	0.073	0.065	0.046	0.0049	0.0058	0.16	0.17
<b>Total Ni</b>	0.069	0.074	0.070	0.050	0.0059	0.0048	0.16	0.18
<b>Dissolved Zn</b>	0.097	0.21	0.014	0.010	0.0034	0.0031	0.49	0.90
<b>Total Zn</b>	0.27	0.29	0.29	0.20	0.031	0.028	0.59	0.75
<b>Dissolved Ca</b>	97	93	80	86	54	52	170	170
<b>Sulfate</b>	432	409	419	390	360	360	509	509

**Table 3.23: Summary of effluent water quality parameters and water chemistry for the bench scale limestone leaching bed treatment system. Units are in mg/L unless otherwise specified. Alkalinity units are in mg/L as CaCO<sub>3</sub>. N is equal to 6 for metal concentration data labelled 'system'. For all other data n is equal to 10.**

	Limestone leaching bed							
	Mean		Median		Min		Max	
	System	Pond	System	Pond	System	Pond	System	Pond
<b>pH</b>	-	-	6.23	6.21	5.92	6.01	6.73	6.63
<b>Electrical conductivity (µS/cm)</b>	903	874	824	831	740	756	1359	1105
<b>Dissolved oxygen</b>	-	6.16	-	6.09	-	4.62	-	8.79
<b>Alkalinity (pH 3.7)</b>	74	74	70	70	60	60	90	90
<b>Dissolved Al</b>	0.056	0.20	0.053	0.039	0.025	0.030	0.10	1.5
<b>Total Al</b>	1.7	2.0	1.3	0.49	0.092	0.046	5.4	10
<b>Dissolved Fe</b>	0.030	0.033	0.023	0.020	<0.020	<0.020	0.067	0.14
<b>Total Fe</b>	0.14	0.12	0.053	0.028	<0.021	<0.021	0.63	0.54
<b>Dissolved Mn</b>	3.1	2.5	3.55	2.75	0.50	0.099	5.3	5.0
<b>Total Mn</b>	3.2	2.7	3.7	3.1	0.51	0.12	5.7	5.6
<b>Dissolved Cu</b>	0.0069	0.0069	0.0067	0.0046	0.0042	0.0037	0.012	0.024
<b>Total Cu</b>	0.018	0.030	0.014	0.018	0.005	0.0035	0.048	0.089
<b>Dissolved Ni</b>	0.21	0.18	0.20	0.16	0.11	0.065	0.34	0.31
<b>Total Ni</b>	0.22	0.20	0.20	0.20	0.11	0.069	0.39	0.38
<b>Dissolved Zn</b>	0.50	0.39	0.51	0.39	0.20	0.085	0.83	0.76
<b>Total Zn</b>	0.57	0.50	0.57	0.43	0.22	0.094	0.97	1.0
<b>Dissolved Ca</b>	107	102.7	98.5	96	90	86	140	130
<b>Sulfate</b>	467	447	419	404	360	360	629	629

**Table 3.24: Summary of effluent water quality parameters and water chemistry for the bench scale open limestone channel treatment system. Units are in mg/L unless otherwise specified. Alkalinity units are in mg/L as CaCO<sub>3</sub>. N is equal to 5 for metal concentration data labelled ‘system’, and equal to 8 for data labelled ‘pond’. For all other data n is equal to 10.**

	Open limestone channel							
	Mean		Median		Min		Max	
	System	Pond	System	Pond	System	Pond	System	Pond
<b>pH</b>	-	-	4.81	4.75	4.44	4.82	5.89	6.62
<b>Electrical conductivity (µS/cm)</b>	803	813	744	769	696	680	1014	1026
<b>Dissolved oxygen</b>	-	6.26	-	6.03	-	4.89	-	9.98
<b>Alkalinity (pH 3.7)</b>	15	14	15	12	5	10	25	25
<b>Diss Al</b>	3.1	3.1	4.2	2.9	0.19	0.11	5.6	6.1
<b>Total Al</b>	5.1	4.3	5.2	4.2	3.4	2.5	6.6	5.8
<b>Diss Fe</b>	0.056	0.032	0.036	0.025	0.023	<0.020	0.11	0.070
<b>Total Fe</b>	0.14	0.11	0.085	0.066	0.061	0.033	0.38	0.39
<b>Diss Mn</b>	4.8	4.3	4.5	4.2	4.2	3.5	5.6	5.3
<b>Total Mn</b>	4.9	4.5	4.6	4.5	4.3	3.6	6.1	6.1
<b>Diss Cu</b>	0.053	0.056	0.049	0.054	0.034	0.024	0.088	0.079
<b>Total Cu</b>	0.061	0.071	0.056	0.079	0.047	0.047	0.092	0.090
<b>Diss Ni</b>	0.27	0.25	0.23	0.22	0.20	0.17	0.37	0.33
<b>Total Ni</b>	0.27	0.27	0.24	0.24	0.20	0.20	0.39	0.39
<b>Diss Zn</b>	0.90	0.82	0.79	0.78	0.76	0.62	1.2	1.1
<b>Total Zn</b>	0.93	0.89	0.83	0.86	0.74	0.71	1.2	1.3
<b>Diss Ca</b>	80	78	81	74	60	61	100	110
<b>Sulfate</b>	503	476	479	449	419	390	629	659

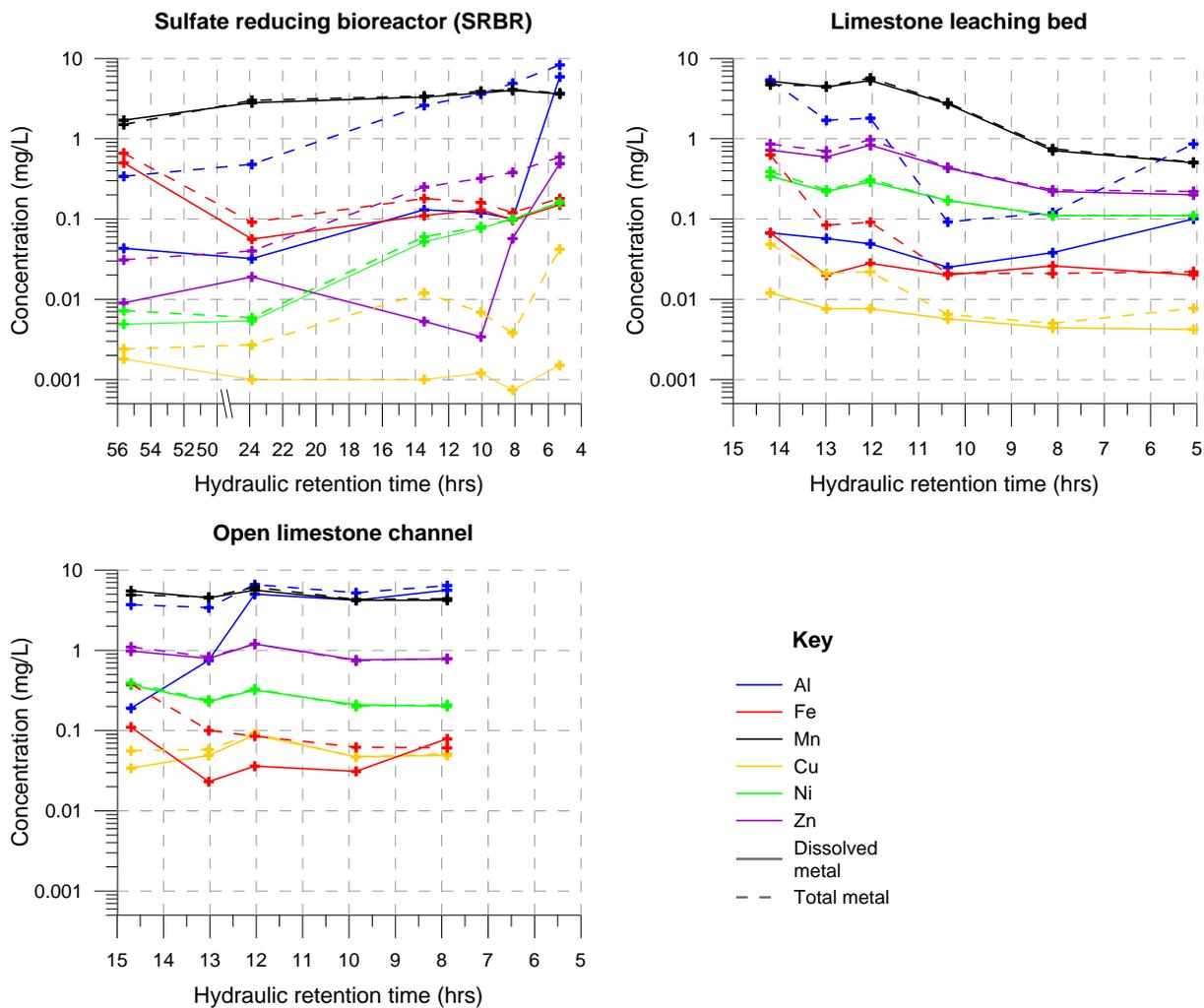
**Metal Analysis of Effluent Discharged Directly from Bench Scale SRBR, LLB  
and OLC Treatment Systems (prior to settling ponds)**

Dissolved and total metal concentrations (mg/L) of effluent discharged directly from bench scale treatment systems (before subsequent settling pond) are shown for each HRT during laboratory trials (Figure 3.11). Overall, metal concentrations in effluent increase as HRTs decrease for each system.

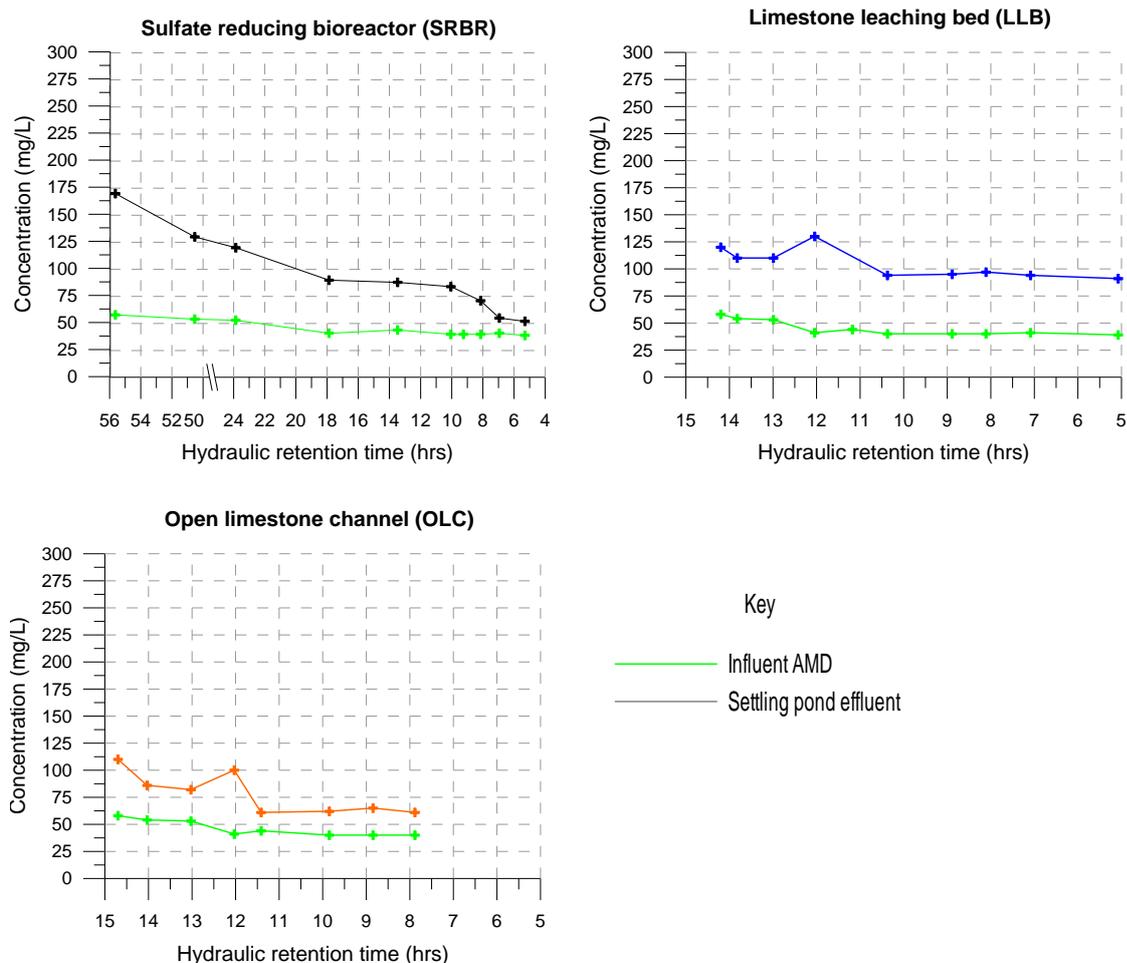
Minimum dissolved metal concentrations in effluent discharged directly from the SRBR treatment system were 0.032 mg/L for aluminium, 0.056 mg/L for iron, 1.7 mg/L for manganese, 0.00074 mg/L for copper, 0.0049 for nickel, and 0.0034 mg/L for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 5.9 mg/L (8.3 mg/L) for aluminium, 0.50 mg/L (0.66 mg/L) for iron, 4.0 mg/L (4.1 mg/L) for manganese, 0.0018 mg/L (0.042 mg/L) for copper, 0.16 mg/L (0.16 mg/L) for nickel, and 0.49 mg/L (0.59 mg/L) for zinc.

Effluent discharged directly from the LLB treatment system had minimum dissolved metal concentrations of 0.025 mg/L for aluminium, <0.020 mg/L for iron, 0.50 mg/L for manganese, 0.0042 mg/L for copper, 0.11 mg/L for nickel, and 0.20 mg/L for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 0.10 mg/L (5.4 mg/L) for aluminium, 0.067 mg/L (0.63 mg/L) for iron, 5.3 mg/L (5.7 mg/L) for manganese, 0.012 mg/L (0.048 mg/L) for copper, 0.34 mg/L (0.39 mg/L) for nickel, and 0.83 mg/L (0.97 mg/L) for zinc.

Minimum dissolved metal concentrations in effluent discharged directly from the OLC treatment system were 0.19 mg/L for aluminium, 0.023 mg/L for iron, 4.2 mg/L for manganese, 0.034 mg/L for copper, 0.20 for nickel, and 0.76 mg/L for zinc. Maximum dissolved and total (parentheses) effluent concentrations were 5.6 mg/L (6.6 mg/L) for aluminium, 0.11 mg/L (0.38 mg/L) for iron, 5.6 mg/L (6.1 mg/L) for manganese, 0.088 mg/L (0.092 mg/L) for copper, 0.37 mg/L (0.39 mg/L) for nickel, and 1.2 mg/L (1.2 mg/L) for zinc.



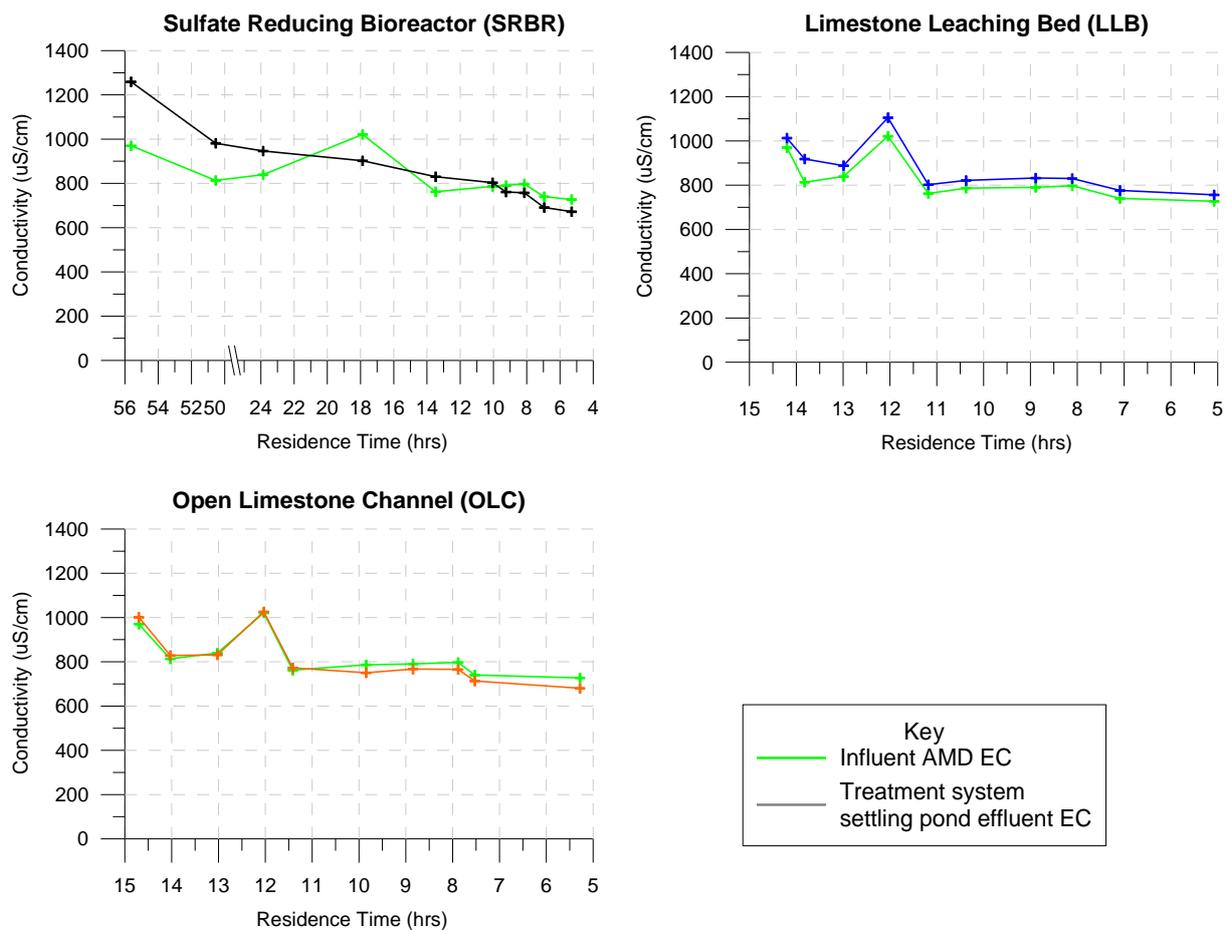
**Figure 3.11: Dissolved and total metal analysis (mg/L) of effluent discharged directly from SRBR, LLB and OLC treatment systems (before settling ponds) at different hydraulic retention times (hours).**



**Figure 3.12: Calcium concentrations (mg/L) of influent AMD and bench scale treatment system settling pond effluent against hydraulic retention time (hours).**

### **Electrical Conductivity of Influent and Effluent for Bench Scale Treatment Systems**

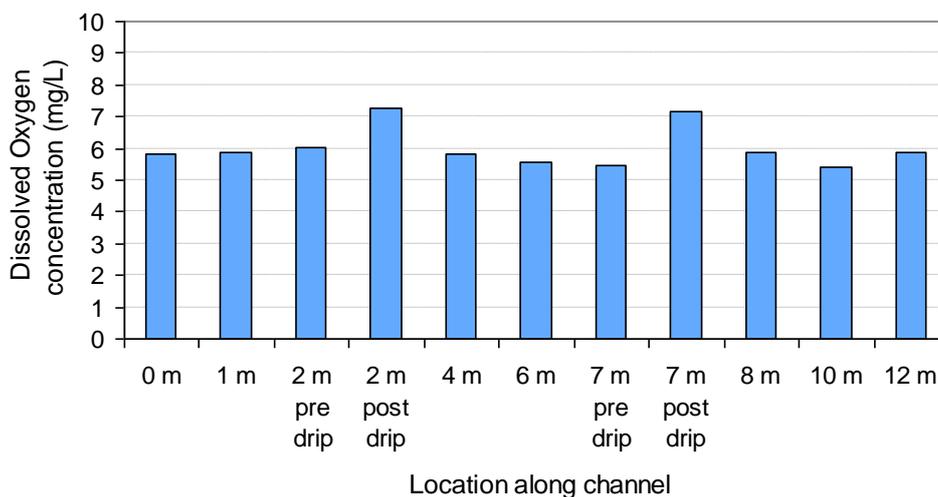
Electrical conductivity (EC,  $\mu\text{S}/\text{cm}$ ) of influent AMD and of effluent from treatment system settling ponds at different HRTs (Figure 3.13). Influent AMD conductivity averaged 824  $\mu\text{S}/\text{cm}$ . Highest effluent EC is exhibited by the SRBR treatment system, with 1259  $\mu\text{S}/\text{cm}$ , however, EC declines to a minimum of 672  $\mu\text{S}/\text{cm}$  at 5 hours HRT. EC for the LLB and OLC treatment systems is relatively constant (except at 12 hrs HRT), averaging 874 and 813  $\mu\text{S}/\text{cm}$ , respectively.



**Figure 3.13: Electrical conductivity ( $\mu\text{S/cm}$ ) of influent AMD and effluent discharged from SRBR, LLB and OLC treatment system settling ponds at different hydraulic retention time (hours).**

### Dissolved Oxygen Concentrations along the OLC Treatment System

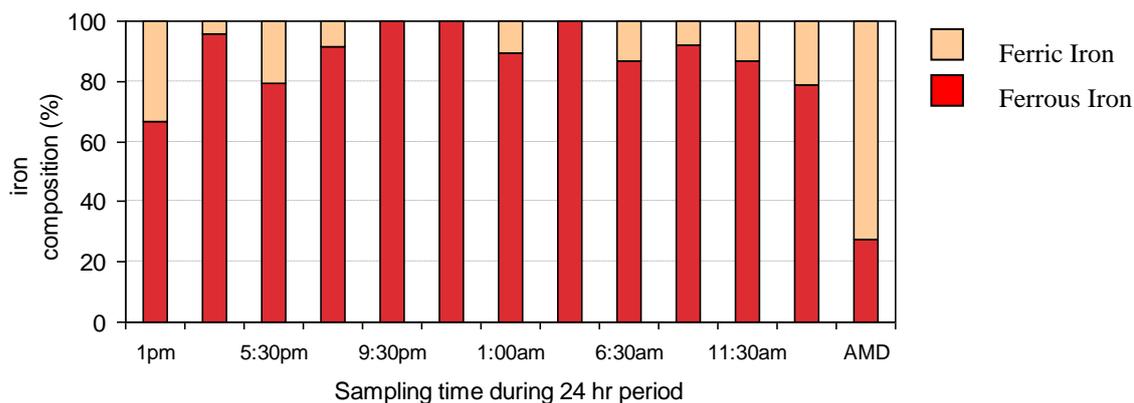
Dissolved oxygen concentrations (mg/L) were measured at approximately 2 m intervals along the OLC treatment system when operating at ~15 hrs HRT (Figure 3.14). Dissolved oxygen concentrations averaged 6.02 mg/L within the channel, with maximum concentrations of 7.26 mg/L and 7.14 mg/L occurring at post drip sampling points, 2 m and 7 m respectively. This indicates that aeration of AMD occurred which supports the process of oxidation, hydrolysis and precipitation of ferrous iron as AMD drips from the channel tier above to the channel tier below.



**Figure 3.14: Dissolved oxygen concentrations (mg/L) with distance along the OLC treatment system, while operating at 15 hrs HRT.**

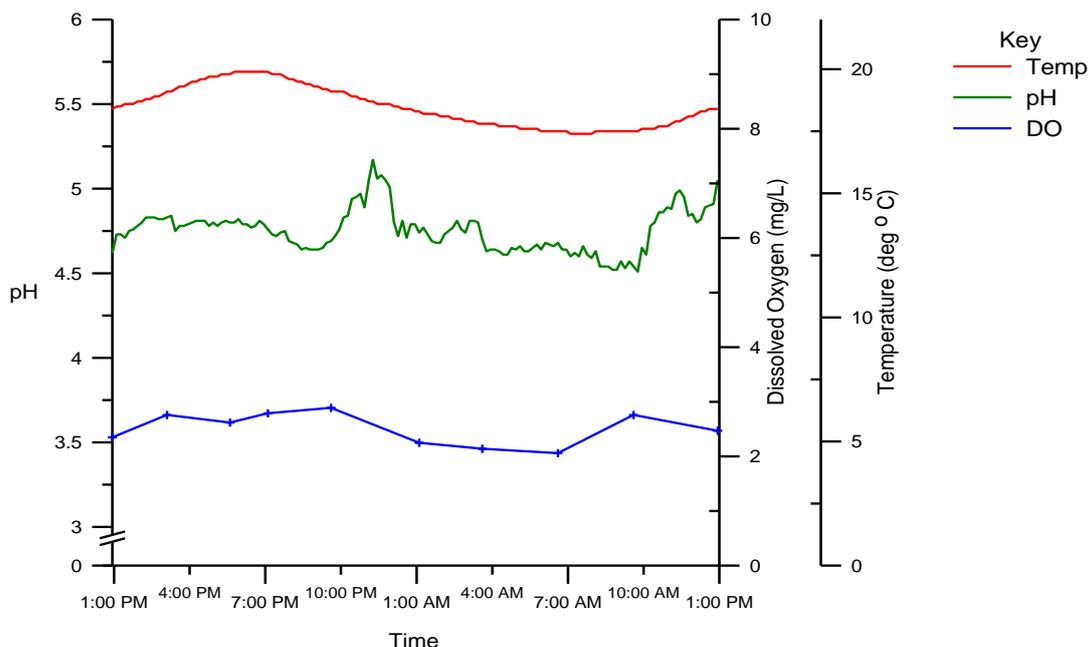
### SRBR Treatment System Upper Water Surface 24 hour Investigation

Iron species composition of the SRBR upper water surface varied over a 24 hr sampling period (Figure 3.14). Iron is predominately ferrous, with 100% at 9 pm, 11:30 pm and 3:30 am, while ferric iron comprises a maximum of only 33.3% (initial sample at 1pm). Influent AMD iron composition is provided at the end of the graph.



**Figure 3.15: Iron species composition (% ferric or ferrous) of the upper water surface of the SRBR treatment system over a 24 hour period, beginning at 1 pm. Measurements obtained approximately every 2.5 hours, with the SRBR system operating at ~ 58 hrs HRT.**

Water quality parameters DO, pH and temperature at the upper water surface of the SRBR treatment system show a rhythmic pattern over a 24 hour time period (Figure 3.16). Dissolved oxygen concentrations range from a maximum of 2.89 mg/L at 9:30 PM to a minimum of 2.06 mg/L, measured at 6:30 AM. pH ranges from maximum of 5.17 at 11:16 PM to a minimum of 4.51 at 9:46 AM. Temperature of the upper water surface varies uniformly with the inside laboratory temperature.



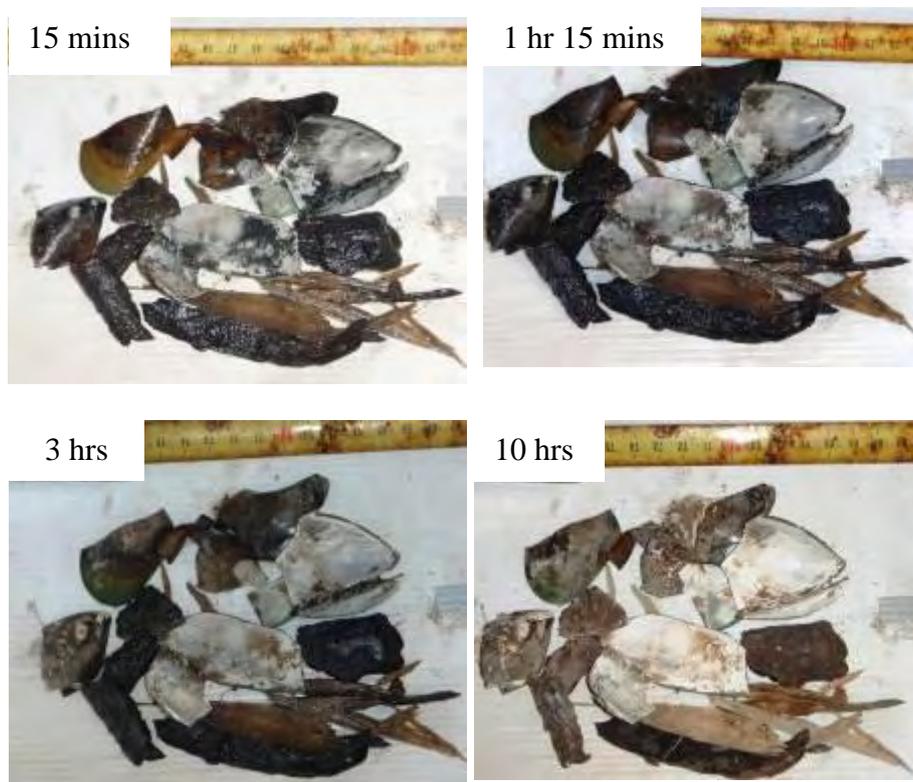
**Figure 3.16: Dissolved oxygen concentration (mg/L), pH and temperature (°C) of the upper water surface of the SRBR treatment system over a 24 hour period. Measurements obtained approximately every 2.5 hours, with the SRBR operating at ~58 hrs HRT.**

These results (Figures 3.15 and 3.16) indicate that algae growing on post peel at the SRBR surface may have influenced water chemistry and perhaps contributed to removal of iron by photosynthesis reactions oxidising any ferrous iron present, which enabled precipitation of ferric hydroxides at the surface (pH >3.7). This is inferred from increase in ferrous iron proportions during the night when algae are presumed to have stopped photosynthesis (and generally supported by an overall decrease in dissolved oxygen concentrations at the surface).

## Autopsy Analysis of Bench Scale Treatment Systems

### 3.1.1.1 Precipitate on SRBR reactive substrate mixture materials after AMD treatment

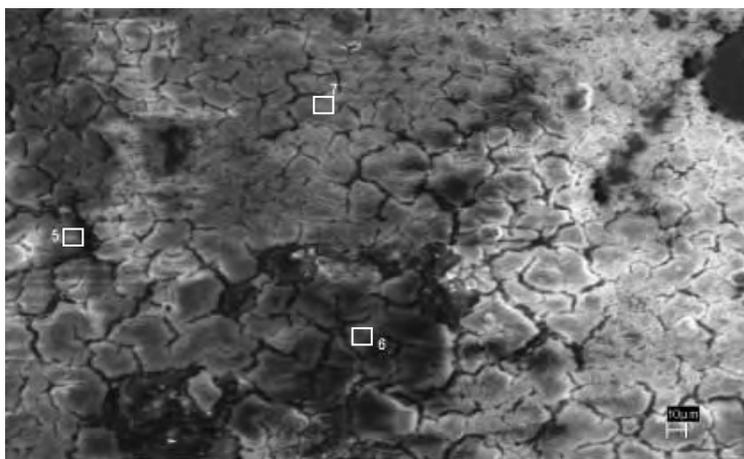
Black precipitate on the surfaces of mussel shells faded after exposure to the atmosphere during autopsy analysis (Figure 3.17). This indicates the black precipitate is likely metal sulfide with the fading indicating oxidation (D Trumm, 2009, pers. com).



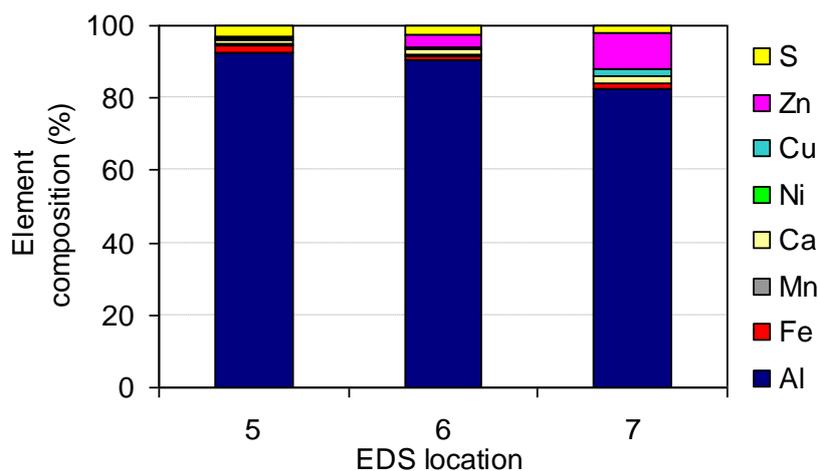
**Figure 3.17: Reactive substrate materials obtained from the SRBR treatment system after AMD treatment and exposed to the atmosphere over a 10 hour period. Samples were obtained prior to system flushing.**

### 3.1.1.2 Scanning Electron Microscopy (SEM) Analysis of Settling Pond Sludge

SEM image of SRBR treatment system settling pond sludge shows a fine, flaky precipitate with no distinctive textural features (Figure 3.18). Elemental composition analysis (Figure 3.18) at locations 5, 6, 7 indicates aluminium is the predominant metal with a maximum of 92.5% (location 5). Zinc comprises has the next greatest concentration with 10.3% (location 7), while other metals comprise < 3.7%.



**Figure 3.18: SEM image of a sample of SRBR settling pond sludge. Numbers 5, 6 and 7 indicate locations of EDS analysis.**



**Figure 3.19: Quantitative elemental analysis of SRBR settling pond sludge at locations 5, 6, and 7.**

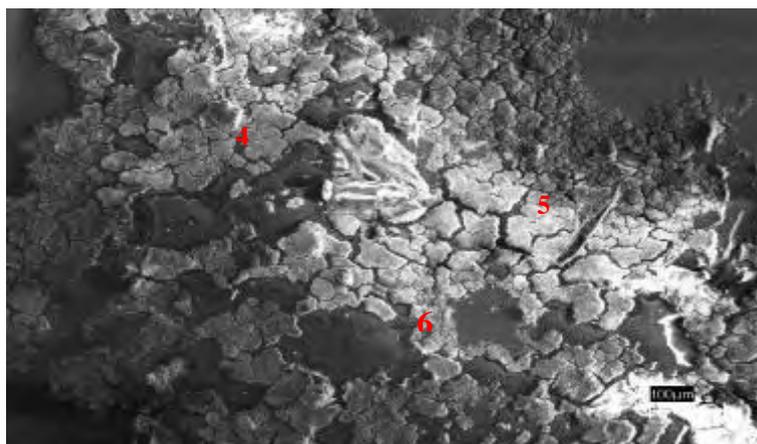


Figure 3.20: SEM image of OLC settling pond sludge. Numbers 4, 5, and 6 indicate locations of EDS analysis.

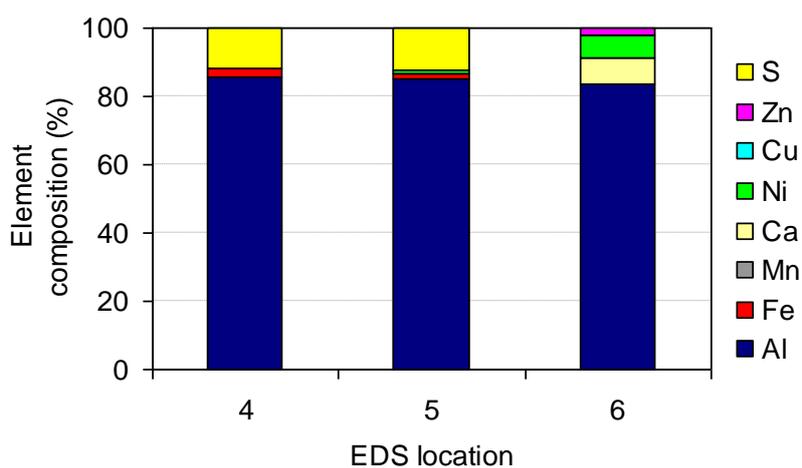


Figure 3.21: Quantitative elemental analysis of OLC settling pond sludge at locations 4, 5, and 6.

### 3.1.1.3 X-Ray Diffraction of Treatment System Sludge Samples

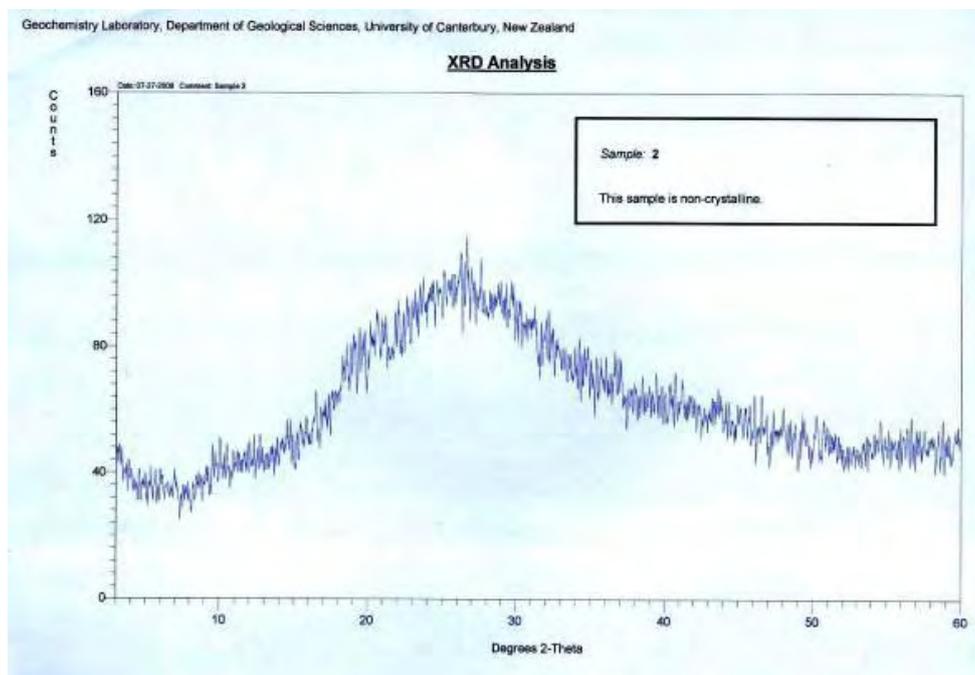


Figure 3.22: X-ray power diffraction pattern of a sludge sample from the LLB treatment system settling pond.

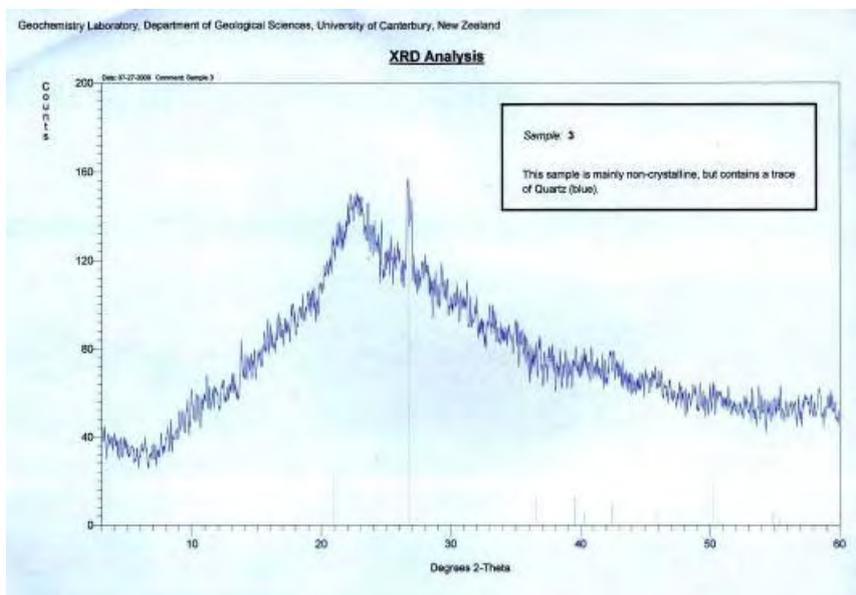
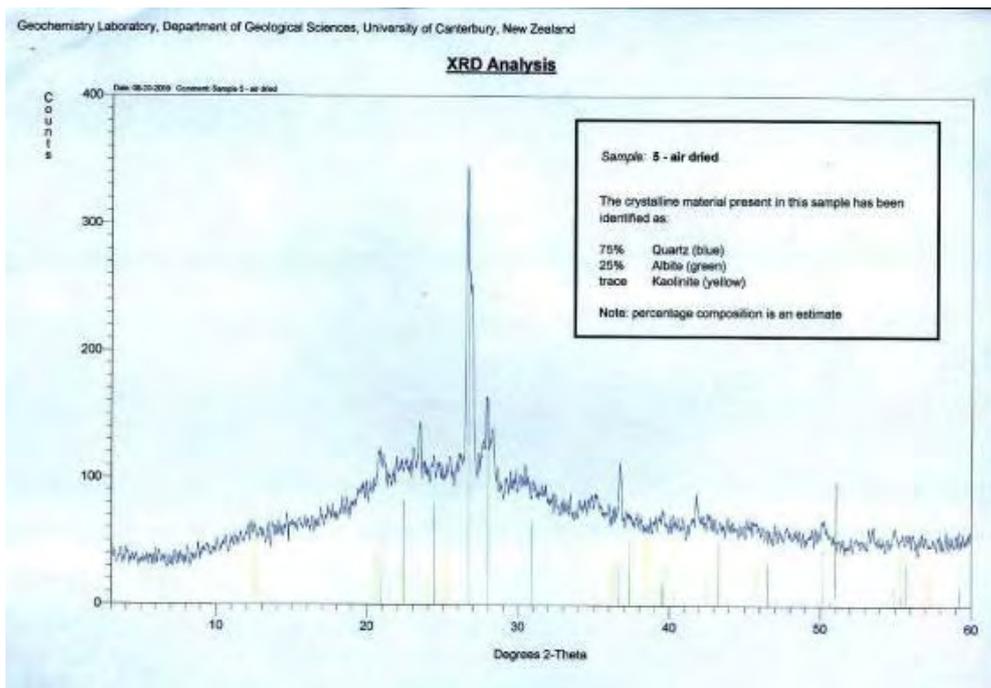
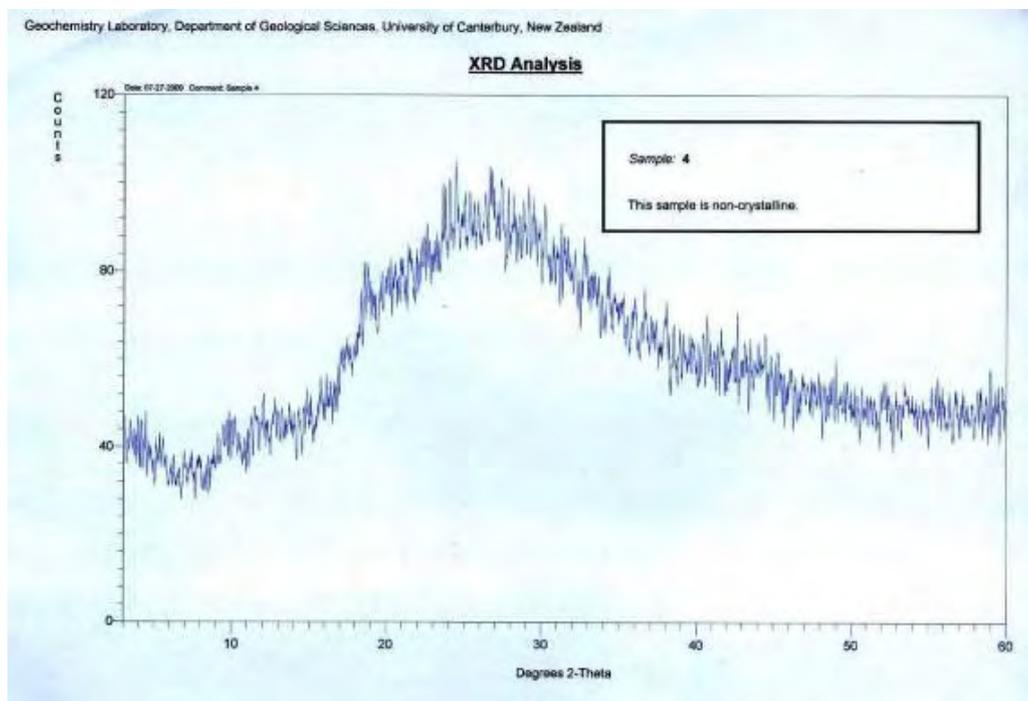


Figure 3.23: X-ray power diffraction pattern of a sludge sample from the OLC treatment system settling pond.



**Figure 3.24:** X-ray power diffraction pattern from a sludge sample flushed from the SRBR bench scale treatment system.



**Figure 3.25:** X-ray power diffraction pattern from a sample of sludge flushed from the LLB bench scale treatment system.

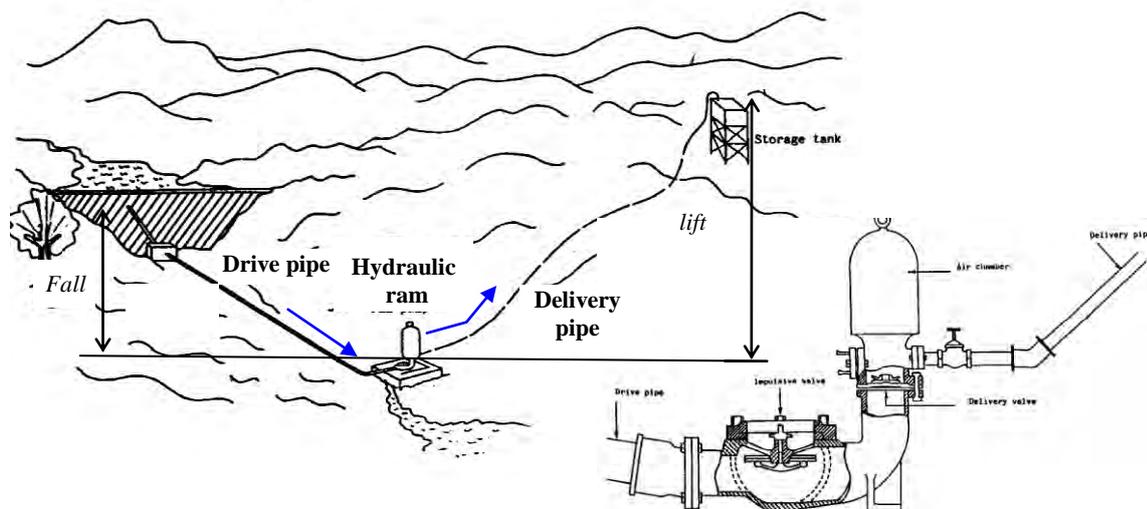
### **Waitahu River Mixing Option: Hydraulic Pump System**

Field observations suggest that the elevation along the toe of the sediment fan where Waitahu River water is proposed to travel, along with the area around R12 (settling pond one), is higher than the elevation of the Waitahu river bed at site R8 (water extraction point). This implies water would have to flow uphill (unless significant earth moving occurred), which precludes a gravity transferal system (a channel from R8 - R12). This is despite a desk top study of elevations in the area that shows an overall downward gradient from R8 to R12. These data are taken from Google Earth and may not in fact be representative of current field site topography, or have margins of error too large to precisely determine the gradient from the Waitahu River stream bed at site R8 to the proposed treatment site around R12.

Therefore, given the possibility that water may need to be transferred uphill, or that considerable channel construction costs would incur to transfer water under gravity, a desk top investigation of potentially more economic passive methods to achieve water transfer was undertaken.

The desktop investigation identified the hydraulic ram pump as a potential method for transferring water uphill from the Waitahu River for mixing with Fanny Creek AMD (Figure 3.26). This device is powered entirely by the energy of falling water, instead of using electricity or fuel for operation (WOT, 2010). The pump utilizes the ‘water hammer’ effect, and operates by taking in water at one hydraulic head and flow rate and transferring water to a higher hydraulic head but at a relatively lower flow-rate at the other end (Jennings, 1996).

The components of a hydraulic ram pump system include a drive pipe that supplies water to the pump, and a delivery pipe that transports a portion of water to a higher elevation (Figure 3.26) (Group ITD, 2009). Hydraulic rams can generally pump 10% of the flow through the drive pipe to a height 10 times greater than the difference in head between the drive pipe inlet and the pump (Jennings, 1996).



**Figure 3.26: Hydraulic ram pump system (Group ITD, 2009).**

To design a hydraulic ram pump system site specific information is required by pump manufactures to determine whether a system can transfer water at the desired flow rate to the desired height (Table 3.25). Field parameters were estimated from the stretch of Waitahu River upstream of the Fanny Creek fan, around monitoring site R8. This was deemed the only suitable location along the Waitahu River for a water extraction system (because is provided the least difference in elevation between water had to be transferred). Water could be drawn up from this location river and transported (via pipe or channel) along the inside toe of the fan to the designated mixing site (local gradient shows water flows towards R12, as indicated by un-impacted stream U5).

**Table 3.25: Information required by hydraulic ram pump manufactures for installation of a pump system, and corresponding Fanny Creek field site parameters.**

Information required by hydraulic ram pump manufactures	Field site parameters
The quantity of water available from the water source (Q)	~ 15 000L/s
The quantity of water required at the point of use (Q)	65 - 140 L/s
The elevation difference between the water source and the pump (fall)	~ 2 m
The elevation difference between the pump and the point of use (lift)	~5 m
The horizontal distance in which the Fall is obtained	~50 m
The distance from the pump water has to be transported.	~50 m

(Green and Carter, 2010; Rife, 2010).

The viability of the Waitahu River Mixing option was investigated by determining whether a hydraulic ram pump system could deliver the estimated flow rate of Waitahu River water to neutralize Fanny Creek using worst case scenario data (consistent with bench scale laboratory trials). Relevant site specific information to determine the suitability of a pump system were used to consult two leading manufacturers of hydraulic ram pumps about the applicability of a pump system: Green and Carter in England (Green and Carter, 2010), and Rife in Pennsylvania, US (Rife, 2010). The relevant information provided by pump manufacturers in relation to worst case scenario estimates are (Table 3.26):

**Table 3.26: Information provided by hydraulic ram pump manufacturers. Waitahu River water flow rate requirements are included.**

<b>Waitahu River flow rate required for neutralization to pH 5 (L/s)</b>	<b>R12</b>		<b>R8</b>	
	65		140	
<b>Maximum delivery flow rate of Hydraulic Ram Pumps supplied (L/s)</b>	<b>Carter and Green</b>		<b>Rife</b>	
	5.8		15.1	
<b>Number of pumps needed</b>	<b>R12</b>	<b>R8</b>	<b>R12</b>	<b>R8</b>
	12	25	5	10
<b>Cost per pump (NZ\$)</b>	50 000.0		26 000.0	

The maximum possible delivery flow rate of hydraulic ram pumps supplied by the two manufacturers was 5.8 L/s (Green and Carter) and 15.1 L/s (Rife). These are greatest achievable flow rates for hydraulic ram pumps (C Doble, pers comm., 2010) but are far lower than the minimum flow rate required for sufficient neutralization (65 L/s). Using the maximum delivery flow rate supplied by Rife, a total of 5 pumps are needed for neutralization of AMD at R12, while 10 pumps are needed for IB5c AMD (multiple pumps are possible). This would entail installation expertise which is limited in New Zealand, while the associated costs of purchasing pumps are not as economic as first thought.

Furthermore, the length of drive pipe for hydraulic ram pumps is related to the fall of the system, with the optimal pipe length 3 – 12 times the fall distance (Jennings, 1996; Group ITD, 2009). Delivery flow rates quoted by Rife require 1.5 m of fall, which therefore assumes a maximum drive pipe length of 18 m. The maximum fall at the proposed pump site is estimated to be 2 m, over a distance of approximately 50 m (Table 3.21). Thus, the shallow

gradient of the Waitahu River would result in lower actual delivery flow rates than those suggested by Rife. Therefore, an even greater number of hydraulic ram pumps would be needed to achieve desired volumes of Waitahu River water for sufficient neutralization to pH 5.

Hydraulic ram pump units are recommended to be situated above flood river levels (Group ITD, 2009), and can become blocked if the water source has suspended sediment or plant material (Jennings, 1996; WOT, 2010). The Waitahu River is a sub-alpine active river with regular high flow events, during which suspended material in the water column occurs.

Therefore, the amount of river water required to provide effective remediation during a realistic worst case AMD appears to exceed the capability of a hydraulic ram pump system. The cost, implementation and sustainability of a hydraulic ram pump system is also problematic, due to the availability of pumps, necessary expertise, and the active nature of Waitahu River. For these reasons, this treatment option is precluded as a viable passive treatment solution for remediation of Fanny Creek AMD.

## **Appendix IV**

### **Additional Discussion of Passive AMD Treatment System Laboratory Trials**

#### **A) Additional Analysis**

- Metal Removal Efficiencies of Effluent Discharged Directly from Bench Scale Treatment Systems
- Metal Removal in Settling Ponds
- Sulfate Removal Efficiencies in Effluent Directly from Treatment Systems

#### **B) Preliminary Sizing of Suitable Full Scale Passive Treatment Systems**

#### **C) Full Scale Treatment System Considerations**

## Appendix IV. (A): Additional Analysis

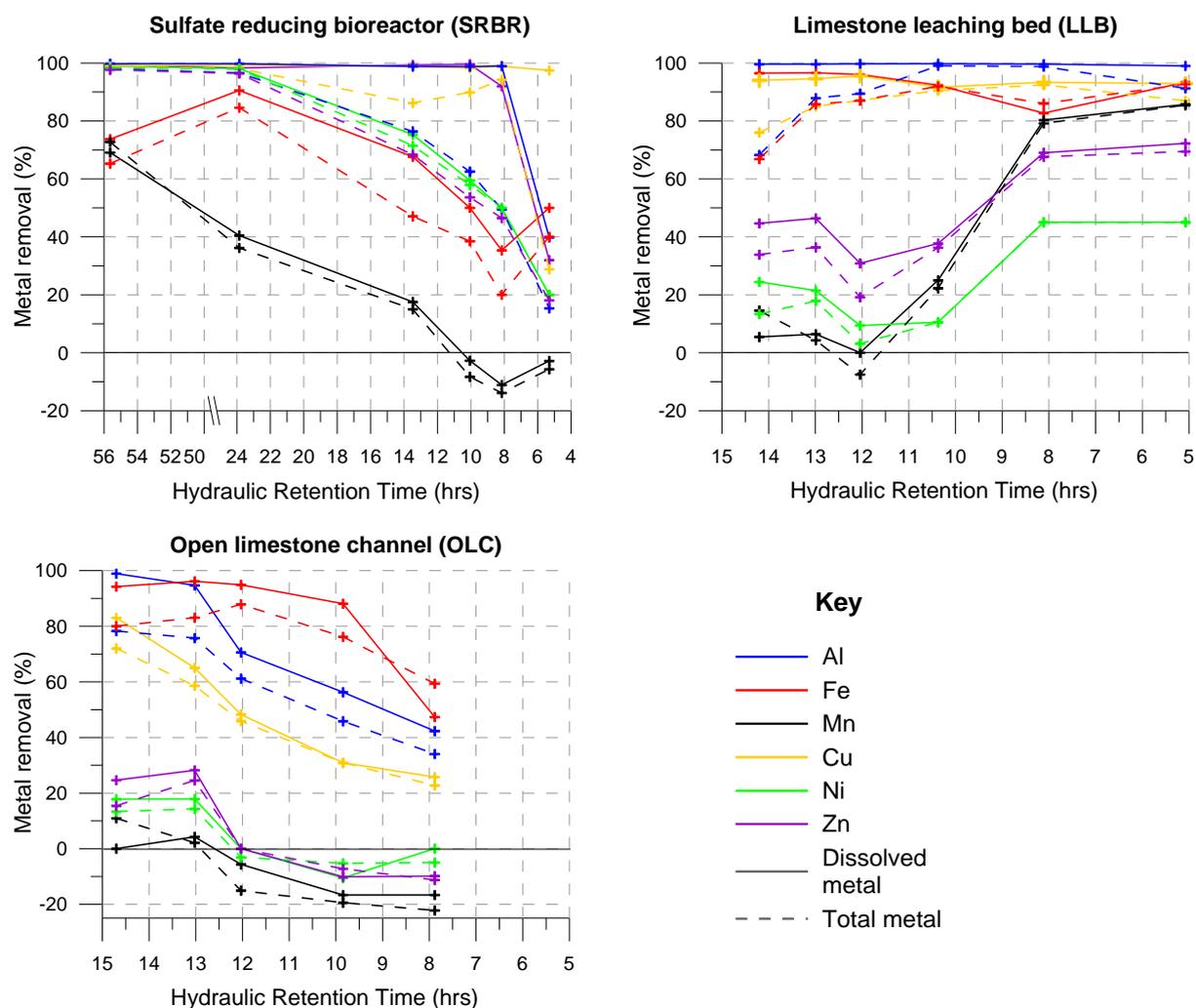
### Metal Removal Efficiencies of Effluent Discharged Directly from Bench Scale Treatment Systems

Figure 4.1 displays dissolved and total metal removal efficiencies (elevated metals) for effluent discharged directly from bench scale treatment systems for different HRTs.

Dissolved metal removal efficiencies for effluent discharged directly from the SRBR treatment system are greatest for dissolved Cu, with effective removal (>97.5%) at all HRTs tested. Removal of Al (99.8%) and Zn (99.3%) are greatest at HRTs  $\geq 8$  hrs, however at shorter HRTs (5 hrs) removal decreases to a minimum of 39.8% and 31.9%, respectively. Maximum removal of Ni (98.9%), Mn (69.1%) and Fe (90.5%) occurs at HRTs of 56 hrs and 24 hrs, respectively. As HRT is shortened removal gradually decreases to minimums of 20.0% for nickel and 35.5% for iron, and net export of manganese occurs (-11.1%). Total metal removal efficiencies for SRBR treatment system effluent vary most for Al, Zn, Fe and Cu compared to corresponding dissolved metal removal efficiencies. Initially total metal removal is comparable, with maximum efficiencies of 98.0% (Al), 97.6% (Zn), 84.6% (Fe), and 98.8% (Cu) at HRTs  $\geq 24$  hrs. However with shorter HRTs total metal removal decreases more rapidly (increasing metal particulate fraction) to minimum efficiencies at the tested HRTs of 8 hrs and 5 hrs.

Dissolved metal removal efficiencies for effluent discharged directly from the LLB treatment system are effective for Al, Fe and Cu at all HRTs tested (> 5 hrs), with maximum removal efficiencies of 99.7%, 96.6% and 95.5%, respectively. Removal of dissolved Ni, Zn and Mn is initially poor, with minimum efficiencies of 9.4%, 30.8% and 0.0%. However, removal increased as the trial progressed (decreasing HRTs) resulting in maximum removal at 5 hrs HRT with efficiencies of 45.0% (Ni), 72.2% (Zn), and 85.7% (Mn). Initially, total metal removal efficiencies for LLB treatment system effluent are lower for all metals (particularly Al, Fe, Cu); however, at HRTs  $\leq 10$  hrs total removal efficiencies are effectively equivalent to dissolved metal removal (negligible metal particulate).

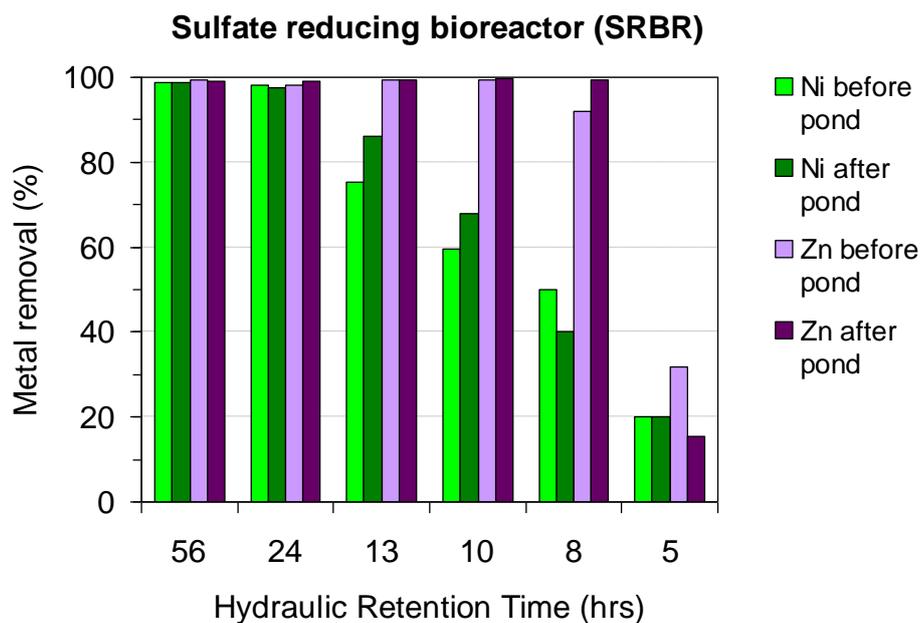
OLC treatment system effluent demonstrates greatest dissolved metal removal efficiencies for Al (98.9%), Fe (96.1%) and Cu (83.0%) at initial HRTs (15 hrs and 13 hrs). Removal of these metals declines however with decreasing HRT (especially for Cu and Al), to minimum efficiencies of 42.3% (Al), 47.3% (Fe) and 25.8% (Cu) at 8 hrs HRT (water chemistry analysis ceased due to poor performance). Removal of dissolved Ni, Zn and Mn is very poor, with maximum efficiencies of only 17.9%, 28.2% and 4.3%, respectively, with zero removal or net export occurring at HRTs shorter than 13 hrs. Initially, total metal removal efficiencies for OLC treatment system effluent are noticeably lower than dissolved removal efficiencies for metals Al, Fe, Cu and Zn. However, total removal becomes slightly more comparable with dissolved removal at shorter HRTs (decreasing metal particulate fraction).



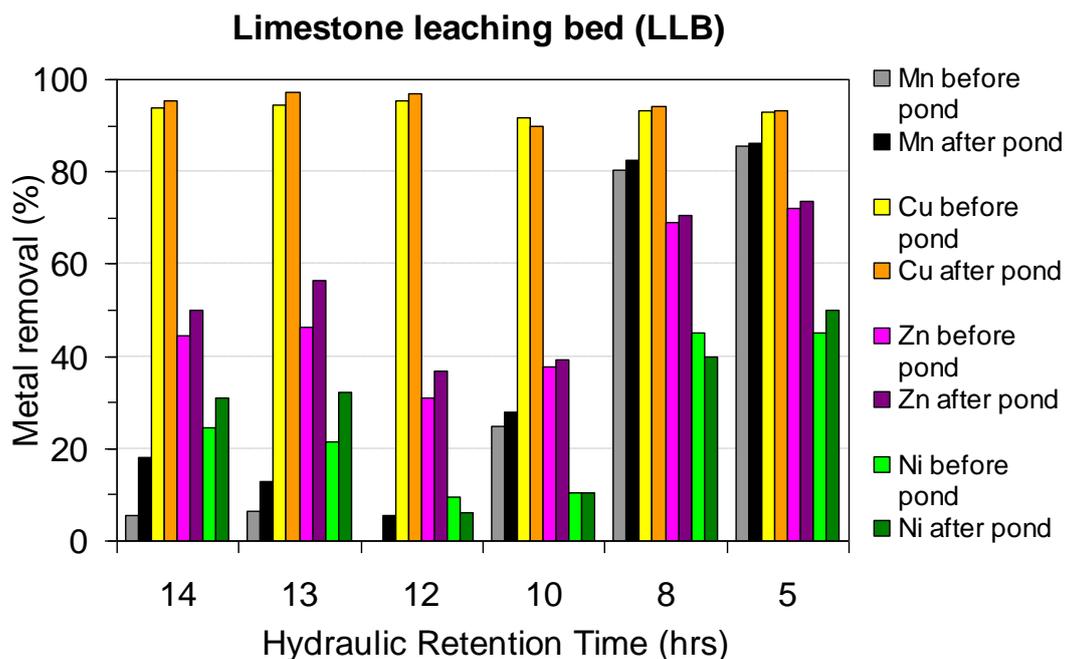
**Figure 4.1: Dissolved and total metal removal efficiencies (%) of effluent discharged directly from SRBR, LLB and OLC treatment systems against hydraulic retention time (hours).**

### Metal Removal In Settling ponds

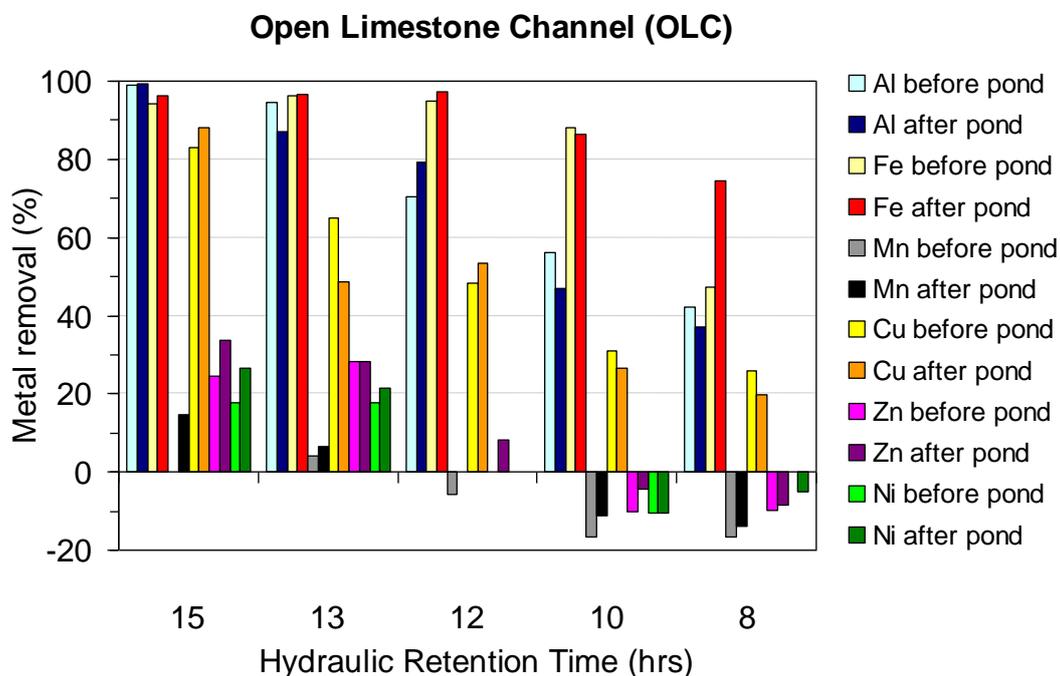
Metal removal efficiencies in effluent before and after SRBR, LLB and OLC settling ponds display no obvious trends for most metals (Figures 4.2 – 4.4). This indicates that overall the subsequent settling ponds did not significantly influence the final treatment performance of bench scale systems (i.e. little settling of metal precipitates).



**Figure 4.2: Dissolved Ni and Zn removal efficiencies (%) in effluent discharged directly from SRBR treatment systems (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**

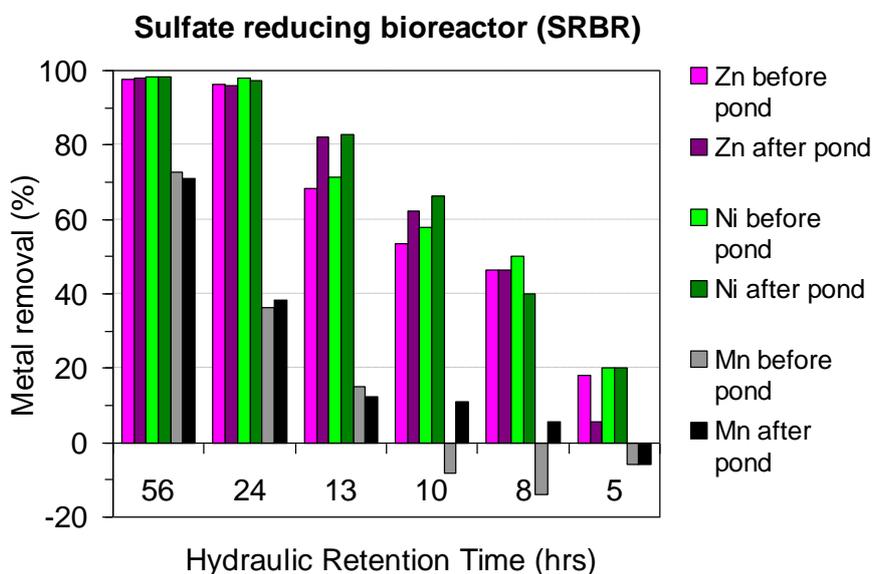


**Figure 4.3: Dissolved Mn, Cu, Zn, and Ni removal efficiencies (%) in effluent discharged directly from the LLB treatment system (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**

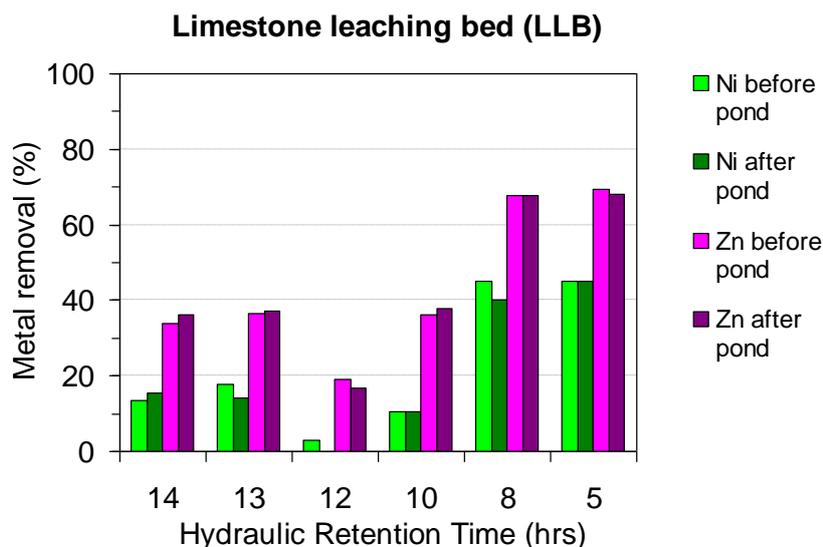


**Figure 4.4: Dissolved Al, Fe, Mn, Cu, Zn, and Ni removal efficiencies (%) in effluent discharged directly from the OLC treatment system (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**

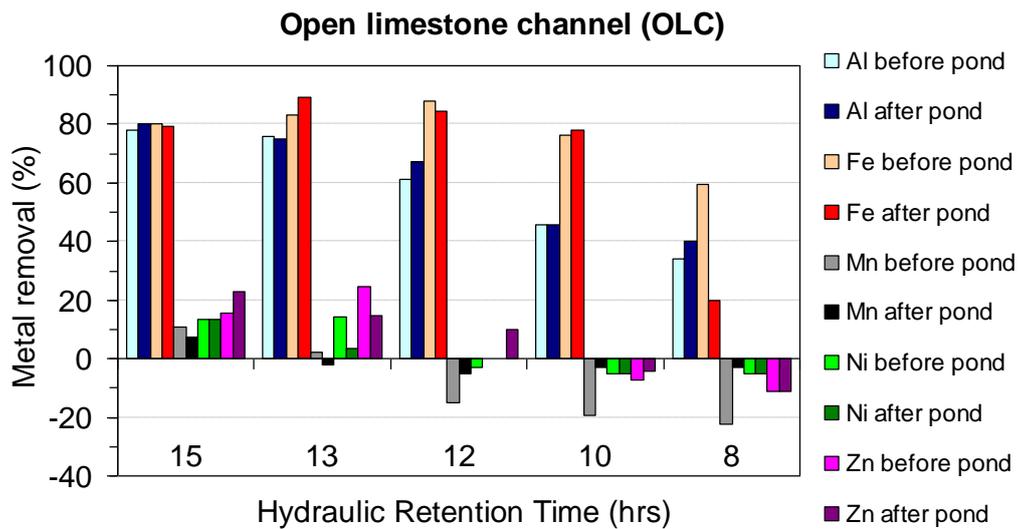
Figures 4.5 – 4.7 show the difference in total metal removal efficiencies in effluent before and after SRBR, LLB and OLC settling ponds. Differences in removal efficiencies display no obvious trends, and for most metals little or no removal occurs in settling ponds, except for a slight improvement in manganese at shorter HRTs for SRBR and OLC treatment systems.



**Figure 4.5: Total Zn, Ni and Mn removal efficiencies (%) of effluent directly from the SRBR treatment system (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**

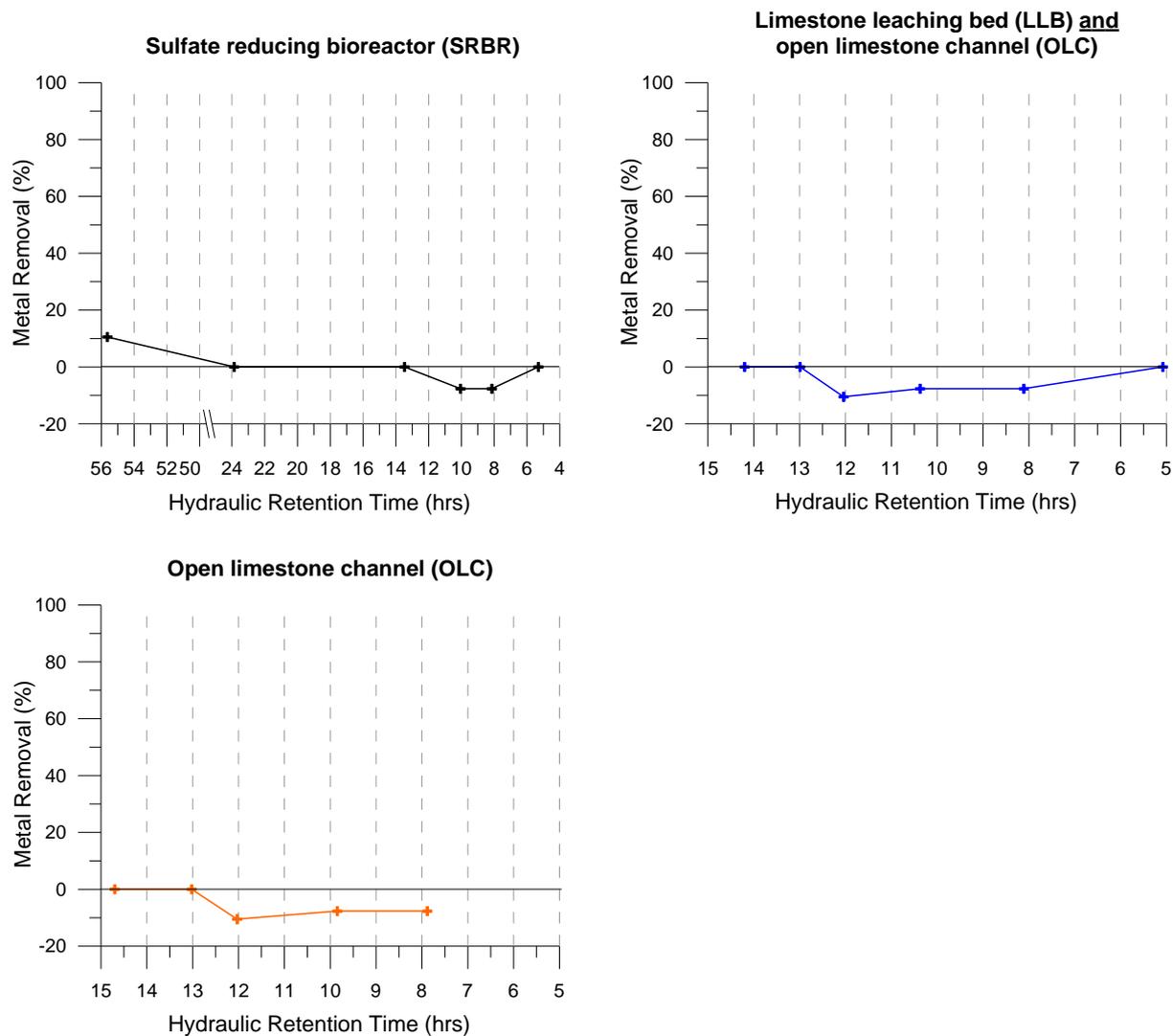


**Figure 4.6: Total Ni and Zn removal efficiencies (%) of effluent directly from the LLB treatment system (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**



**Figure 4.7: Total Al, Fe, Ni and Zn removal efficiencies (%) of effluent directly from the LLB treatment system (before pond) and effluent from the settling pond for different hydraulic retention time (hours).**

## Sulfate Removal Efficiencies Directly from Bench Scale Treatment Systems



**Figure 4.8: Sulfate removal efficiencies (%) of effluent discharged directly from SRBR, LLB and OLC treatment systems for different hydraulic retention times (hours).**

## **Appendix IV. (B): Preliminary Sizing of Suitable Full Scale Passive Treatment Systems**

The feasibility of a full scale SRBR or LLB treatment system in relation to available land area was evaluated by a preliminary estimation of treatment systems sizes (Table 4.1). Sizing systems used methodology described by Younger et al. (2002) based on optimal HRTs, maximum Fanny Creek flow rate and estimated porosities of treatment system materials.

Maximum flow determined from monthly monitoring (30L/s) was used to calculate full scale treatment system volumes because systems are required to treat AMD during high flow events. This flow rate is considered representative of high flow conditions during winter months (after rainfall), and therefore to achieve desirable treatment and water quality, systems should to be designed based on such flow rates. It is likely higher flows occurred, but were not observed due to the frequency of water sampling. Therefore, sizes calculated are conservative estimates. In addition, treatment system sizes are based on rectangular prisms volumes, whereas actual systems have sloped sides.

**Table 4.1: Calculation for estimating full scale SRBR and LLB passive AMD treatment system sizes to remediate Fanny Creek. The methodology used is described by Younger et al. (2002).**

<b>Optimal HRT:</b>	<b>Maximum Fanny Creek flow</b>	=	30 L/s
SRBR = 51 hours		=	108 m <sup>3</sup> /hr
LLB = 5 hours			

**Method\* for sizing recommended by Younger et al. (2002) p. 336**

\*Method used for ALD systems however same principles apply. Units adjusted to hours

- i) The volume of void space ( $V_v$ ) needed to store the required volume of water for the desired length of time :
- $$V_v = Q_d * HRT$$

Where  $Q_d$  is the design flow in m<sup>3</sup>/hr,  $V_v$  is in m<sup>3</sup>, and the HRT is equal to optimal HRT (hours)

- ii) Calculate the minimum total volume ( $V_t$ ) of the active part of the system (voids plus reactive treatment material) as follows:

$$V_t = V_v / n$$

Where  $V_t$  is the total volume of the system in m<sup>3</sup>, and  $n$  is equal to the effective porosity of the reactive treatment material (expressed as a decimal)

<b>SRBR treatment system</b>	
HRT =	51 hours
Porosity (n) =	0.4 (Average n for = 40%* (Neculita et al., 2008; McCauley et al., 2008))
	*represents a maximum porosity for field based SRBRs
$V_v = Q_d * HRT$	
$V_v = 108 * 51$	
5508 m <sup>3</sup>	
$V_t = V_v / n$	
$V_t = 5508 / 0.4$	
= 13770 m <sup>3</sup>	<b>Total volume of SRBR treatment system</b>

<b>LLB treatment system</b>	
HRT =	5 hours
Porosity (n) =	0.45 (Average n for = 45% (Younger et al., 2002; Watzlaf et al., 2003))
$V_v = Q_d * HRT$	
$V_v = 108 * 5$	
540 m <sup>3</sup>	
$V_t = V_v / n$	
$V_t = 540 / 0.45$	
= 1200 m <sup>3</sup>	<b>Total volume of LLB treatment system</b>

**Table 4.2: Volume and size estimates for full scale SRBR and LLB treatment systems for treatment of Fanny Creek AMD.**

	Total volume of reactive material required (m <sup>3</sup> )	Number of systems	Dimensions		
			Length	Width	Depth
<b>SRBR</b>	13770	4	62	28	2
		1	125	55	2
<b>LLB</b>	1200	1	35	18	2

Note: dimensions for the SRBR and LLB treatment system are approximate and only give a sense of scale (i.e.  $35 * 18 * 2 = 1260 \text{ m}^3$ ).

The SRBR full scale treatment system is shown in thesis text as requiring four separate, side by side units, instead of one single unit. This requires arbitrary dimensions of each SRBR unit of 62 m long, 28 m wide, with a 2 m thick substrate. The dimensions of a single SRBR unit would measure about 125 m long, 55 m wide, with a 2 m thick substrate. The full scale SRBR system is consists of separate units because authors recommend flow into SRBR treatment systems be minimised and dispersed (Watzlaf et al., 2003; PIRAMID Consortium, 2003). This is achieved by construction of multiple units, and reduces the risk of failure of an entire treatment system. Estimates of the maximum flow received by each treatment system are based on maximum flow estimates for Fanny Creek (30 L/s), therefore, the individual SRBR units operating a optimal HRT (~51 hours) would receive 7.5 L/s during a maximum flow event.

In addition, sizing estimates for the full scale SRBR system only account for reactive substrate mixture, and not other layers such as the underlying gravel drainage layer, upper flow equalisation post peel layer, or the overlying water surface (~0.5 m). Inclusion of these volumes would result in larger size estimates, and requirement of additional land area. Nevertheless, even with this extra size the land area available on the Fanny Creek sediment fan and settling ponds is most likely sufficient to accommodate this (1000 m across by 150 m wide).

## Appendix IV. (C): Full Scale Treatment System Considerations

Full scale passive AMD treatment systems comprise a ‘treatment train’ of different components. The settling basins at Fanny Creek provide a starting point for implementation of full scale treatment system components (Figure 4.9):

- Upstream sediment removal ponds on the sediment fan area ‘A’; full scale system in area ‘B’; final settling pond and wetland components in area ‘C’ .
- The red cross (1) indicates a suitable location for pilot scale testing of SRBR and LLB treatment systems.



**Figure 4.9: Locations for components of a full scale passive AMD treatment system to treat Fanny Creek AMD (1, 2). 1) Red cross indicates recommended location for pilot scale testing of SRBR and LLB treatment systems. 2) Aerial view of treatment area, looking down valley.**

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