PERFORMANCE OF MESOCOSM-SCALE SULFATE-REDUCING BIOREACTORS FOR TREATING ACID MINE DRAINAGE IN NEW ZEALAND

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Abstract: Water chemistry was monitored monthly for ten months from an acid mine drainage (AMD) seep emanating at Stockton Coal Mine within the Mangatini watershed in New Zealand. Metal concentrations of the seep water were Fe (4.31-146 mg/L), Al (7.43-76.7 mg/L), Cu (0.0201-0.0669 mg/L), Ni (0.0629-0.261 mg/L), Zn (0.380-1.39 mg/L), Cd (0.000540-0.00134 mg/L) and Pb (0.0049-0.0056 mg/L), pH was 2.49-3.34 and total acidity (pH 8.3) was 78.5-626 mg/L as $CaCO_3$. Water chemistry signature prompted laboratory mesocosm studies measuring the effectiveness of sulfate-reducing bioreactors (SRBRs) for generating alkalinity and sequestering metals.

Alkaline materials utilized in the SRBRs included industrial waste products such as mussel shells, nodulated stack dust (NSD) derived from the cement industry, and limestone. Organic substrate materials included post peel, a by-product from fence post manufacture, *Pinus radiata* bark and compost. Seven SRBRs comprised of varying substrate mixes received aerated AMD for nearly four months. AMD was sourced from the pond that collected the seep water. The SRBR containing NSD successfully removed all metals, but effluent was caustic with pH>9. Bioreactors consisting of 20-30% mussel shells were most successful at immobilizing metals and generating circumneutral effluent. Systems containing mussel shells sequestered more than 0.8 moles of metals/m^3 of substrate/day at stable operating conditions and yielded effluent concentrations (removal efficiencies) of 0.120-3.46 mg/L Fe (96.5-99.8%), 0.0170-0.277 mg/L Al (99.5-99.9%), <0.0005-<0.001 mg/L Cu (>99.7->99.9%), <0.0005-0.0020 mg/L Ni (99.3->99.7%), <0.001-0.005 mg/L Zn (99.7-99.9%), < 0.00005 Cd (>98.3->98.9%) and <0.0001-0.0001 Pb (99.5-<99.7%). The system consisting of limestone as the only alkalinity generating material was less effective (15.4-64.3 mg/L Fe). Results from duplicate systems but different reactor shapes indicated reactor dimensions influence flow characteristics and therefore treatment efficacy.

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Introduction

Numerous watersheds in New Zealand are impacted from acid mine drainage (AMD) typically containing high concentrations of acidity and metals. As a result, biodiversity and ecological health has been significantly altered (Harding and Boothryd, 2004; Harding, 2005). The majority of AMD-impacted streams are located on the West Coast of the South Island within or receiving drainage from estuarine coal formations including the Brunner Coal Measures (Trumm et al., 2005). The Brunner Coal Measures were formed in a marginal marine setting and consist of carbonaceous mudstones and coal containing abundant sulfide and subsequently high acid generating capabilities (Black et al., 2005; Trumm et al., 2005).

Coal mining operations at Stockton Mine commenced in the 1950's. Leachate from acid-generating waste rock has impacted the Mangatini, and subsequently the Ngakawau Watersheds (Lindsay et al., 2003; Black et al., 2005). The active mine is located on the Stockton Plateau within the Brunner Coal Measures about 35 km (22 miles) north of Westport (Figs. 1 and 2). The mine site is situated on rugged and undulating terrain 500-1100 m (1600-3600 ft) above sea level overlooking the Tasman Sea and receives an average of 6000 mm (236 in.) of precipitation annually (Solid Energy New Zealand Ltd., 2007). Such environmental extremities coupled with high intensity rain events and occasional snow add additional complexity to AMD remediation strategies on operational mine sites.

AMD Chemistry

The primary metals associated with AMD within the Mangatini watershed include Fe and Al, which consistently accounted for over 98% of metal loading (molar basis) from the seep monitored for this study. Secondary metal pollutants of concern include Cu, Ni, Zn and Cd. Acidity is generated from the oxidation of sulfide (pyrite (FeS_2)) minerals within the overburden. Iron is primarily leached during pyrite oxidation. As a result of acidity created during pyrite oxidation, Al leaches from the ubiquitous micaceous and feldspathic-rich rocks within the carbonaceous mudstones, in itself generating additional metal acidity (Black et al., 2005).

Figure 1. Project site location (Stockton Mine, West Coast, South Island, New Zealand).
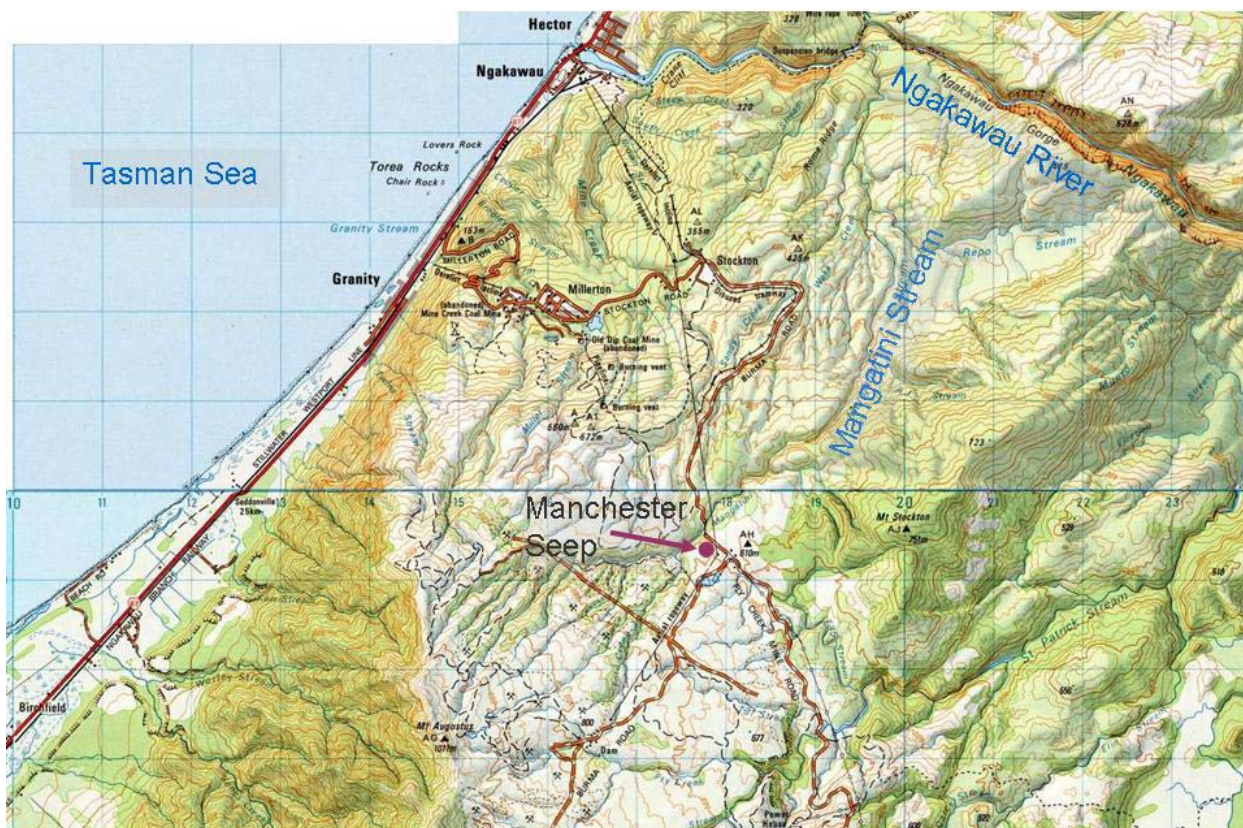
Figure 2. Topographic map of Mangatini and Ngakawau Watersheds (TopoNZ, 2007).


Passive Treatment and Sulfate Reduction

   Mine-water chemistry and numerous passive treatment options and design criteria specific to mine-water treatment are well documented (Younger et al., 2002; PIRAMID Consortium, 2003; Watzlaf et al., 2003; Wildeman and Schmiermund, 2004; Johnson and Hallberg, 2005). The focus of this study concerns systems based on SO_4^{2-} reduction including sulfate-reducing bioreactors (SRBRs) and vertical-flow wetlands (VFWs). Sulfate-reducing bioreactors were chosen as the most promising passive treatment technology for treating AMD at the project site because of their capability to sequester Fe, Al, Cu, Ni, Zn and Cd in AMD (Gusek, 2002; Gusek and Wildeman, 2002; Wildeman et al., 2006).

   Doshi (2006) and Neculita et al. (2007) recently published reviews critiquing SRBRs and summarizing case studies. They indicated that SO_4^{2-} reduction is a successful means of transforming dissolved/mobile metals into immobile minerals such as sulfates, carbonates and metal sulfides within reducing substrates. The primary mechanisms of sequestering metals via SO_4^{2-} reduction are typically simplified as shown in Equations 1 and 2.

$$2 \text{ CH}_2\text{O} + \text{SO}_4{}^{2-} \rightarrow \text{H}_2\text{S} + 2 \text{ HCO}_3{}^- \qquad \textbf{(1)}$$

organic carbon + sulfate → hydrogen sulfide + bicarbonate

$$\text{Me}^{2+} + \text{H}_2\text{S} + 2 \text{ HCO}_3{}^- \rightarrow \text{MS}\downarrow + 2 \text{ H}_2\text{O} + 2 \text{ CO}_2 \qquad \textbf{(2)}$$
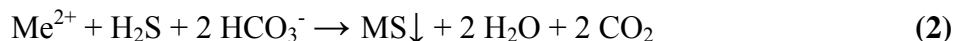
divalent metal + hydrogen sulfide + bicarbonate → metal sulfide (ppt) + water + carbon dioxide

Examples of divalent metal species include ferrous iron (Fe^{2+}), Cd, Cu, Ni and Zn. Aluminum, a trivalent metal cation, is typically precipitated as a silicate, $\text{SO}_4{}^{2-}$ or hydroxide in mine-water treatment applications (Gusek, 2002 and 2004; Wildeman et al., 2006).

In general, $\text{SO}_4{}^{2-}$ reduction occurs in environments where sulfate-reducing microorganisms flourish. Conditions include pH≥3 and adequate quantities of labile C and $\text{SO}_4{}^{2-}$ (Elliot et al., 1998; Doshi, 2006). Metal removal from mine waters tends to occur most efficiently at more circumneutral pH's (5.0-8.0) and at higher temperatures. Zagury et al. (2006) found that $\text{SO}_4{}^{2-}$ reduction was most effective when incorporating a mixture of organic substrates as opposed to using an individual substrate. Numerous SRBRs and VFWs have incorporated various organic waste products ranging from simple carbon sources such as lactate and ethanol to more complex carbon sources such as hay, alfalfa, sawdust, paper, woodchips, etc. (Younger et al, 2002; Gusek, 2004; Zagury et al., 2006). It is also recommended to include an organic source already naturally inoculated with sulfate-reducing bacteria such as compost or manure (Gusek, 2004; Doshi, 2006).

Design criteria typically recommended for SRBRs and VFWs are based on metal molar volumetric and acidity areal loadings. Wildeman et al. (2006) recommended a design criteria of 0.3 moles of metal removal/m^3 of substrate/day for SRBRs with a mixture of organic materials and crushed limestone. They also indicated that removal efficiencies are reduced by about 25% in cold climates. Watzlaf et al. (2003) recommended applying areal removal rates of 25-30 g acidity as CaCO_3/m^2 surface area/day in VFWs. Rose (2004) proposed a non-Mn acidity design criteria of about 35 g CaCO_3/m^2/day for VFWs.

Minimal research has been conducted on passive treatment systems for ameliorating AMD in New Zealand. O'Sullivan (2005) summarized AMD chemistry and potential passive-treatment options viable in New Zealand. Trumm et al. (2005 and 2006) summarized AMD assessment and mesocosm field studies for remediating AMD from Sullivan Mine, an abandoned coal mine

within the Brunner Coal Measures. The mesocosm field experiments were performed for 38 days. Results indicated that a VFW comprised of a 150 mm layer of limestone overlain by a 130 mm layer of mushroom compost was successful at generating alkalinity and removing metals. Influent Fe concentrations were about 38-62 mg/L, and Al concentrations were about 13-16 mg/L. Removal efficiencies at day 22 of system operation and five-hour calculated hydraulic residence time were 100% acidity, 97% Fe, 100% Al and 66% Ni. A small-scale VFW was also employed at Pike River, located on the West Coast of the South Island, yielding successful acidity and metal removal (Trumm et al., 2006). Removal efficiencies by day 58 of this system with an average hydraulic residence time of 20 hours were 100% acidity, 99% Fe, 96% Al, 95% Ni and 99% Zn. The system operated for 151 days.

Purpose and Scope

This paper reports preliminary research outcomes for developing the most appropriate and effective passive treatment option for ameliorating AMD from Manchester Seep at Stockton Mine. Data includes characterization of flow and water chemistry of the seep water. Results of the mesocosm-scale SRBRs treatment efficiencies are also presented.

Methods

Site Selection

Numerous AMD-impacted seeps were sampled during the preliminary stages of this research. Stockton Mine was chosen as the research field site for numerous reasons. Historic and active mining induced AMD at Stockton has significantly altered ecological health of numerous local streams and their receiving water bodies. Water chemistry, although variable across the mine, is representative of many AMD-impacted streams in New Zealand and considered appropriate for passive treatment. Sufficient land area and readily available logistical support were also considered because of future research plans to construct and assess pilot-scale passive treatment systems and potential to expand to a full-scale system. Manchester Seep was chosen as the primary focus of research efforts. Figures 3 and 4 show Manchester Seep and its associated sedimentation pond receiving AMD seepage. Current and future mining activities were not expected to alter water chemistry and associated flow at the site during this study.
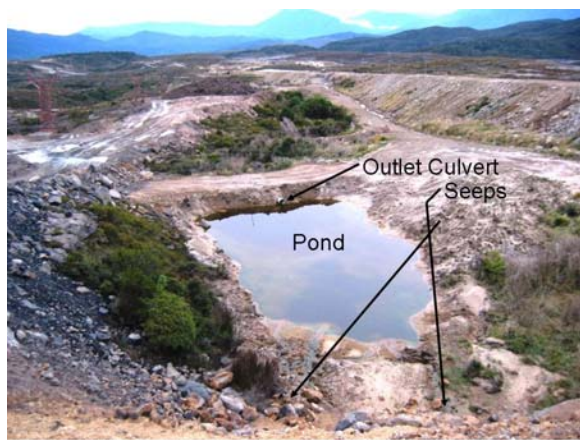
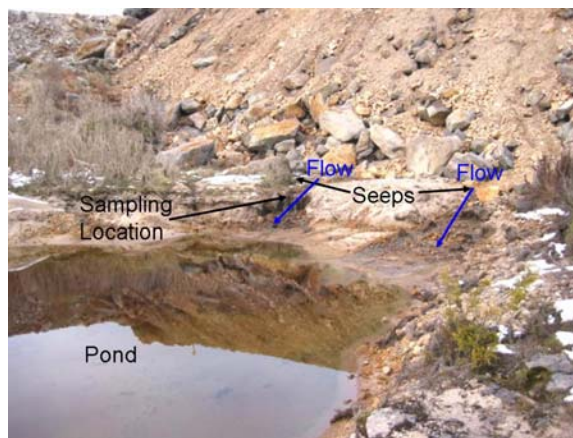Figure 3. Overview of Manchester Seep and Manchester Pond. Flow exits the pond via the outlet culvert.

Figure 4. Manchester Seep emanating from the toe of an overburden embankment.

Water Chemistry Sampling and Analyses

Manchester Seep was sampled following applicable criteria denoted in the Australian and New Zealand Environment and Conservation Council (ANZECC) Water Quality Guidelines (2000). Samples were collected about three meters downgradient of where the seeps daylighted at a location convenient for sample collection. Water quality parameters were measured with calibrated portable meters and coupled probes at the same location.

In the laboratory experiment, effluent from the SRBRs was collected directly into method-specified sample bottles and chilled at 2-6°C until analyzed. Samples for the water quality parameters measured using portable instruments were collected in high-density polyethene (HDPE) sampling bottles. Data was recorded when readings stabilized. AMD samples were collected from influent into the SRBRs. Water quality parameters were measured *in-situ* directly in the AMD feed tank using portable meters.

Water quality parameters including pH, conductivity, dissolved oxygen (DO), oxidation-reduction potential (ORP) and turbidity were measured at the time of sampling using portable water quality instruments. Instruments were calibrated just prior to sample collection using fresh standards and validated to ensure they maintained calibration following measurements. Sample pH was measured using a YSI Model 60 pH meter field calibrated with pH 4.01 and 7.00 standards (and pH 10.00 standard when applicable) and checked with a pH 1.68 standard. Conductivity was measured with a Hach sension 156 multiparameter meter field calibrated to a 0.01 M (1413 μS/cm at 25°C) KCl solution and checked with a 0.1 M (12,890 μS/cm at 25°C)

KCl solution. Dissolved oxygen was measured utilizing a YSI 550A DO instrument. Percent oxygen saturation was adjusted to account for temperature, salinity and barometric pressure as specified in YSI Inc. (1999). The DO meter was calibrated with oxygen-saturated water in the laboratory prior to transport to the research site and checked with oxygen-saturated water on arrival back from the field. Dissolved oxygen was recalibrated on site in the instrument's calibration chamber maintained at 100% water-saturated air. Barometric pressure was measured using a Silva Alba Windwatch equipped with a barometer. Oxidation-reduction potential was measured with a YSI pH 100 portable instrument equipped with an ORP probe and values standardized to a hydrogen electrode (Eh). Calibration was validated with solutions of quinhydrone saturated pH 4 and pH 7 solutions. Turbidity measurements were performed using a Hach Model 2100P portable turbidimeter. Calibration was performed with either Hach StablCal$^®$ calibration standards or freshly prepared formazin standards (<0.1, 20, 100 and 800 NTU). Calibration was performed when validation exceeded five percent of a standard. Calibration validation was either determined using Hach StablCal$^®$ calibration standards or three Gelex$^®$ standards whose values were determined during instrument calibration.

Metals, with the exception of Fe^{2+}, sulfur, cation, fecal coliform and five-day biochemical oxygen demand (BOD_5) concentrations were determined by R.J. Hill Laboratories (Hill Labs), an International Accreditation New Zealand (IANZ) certified lab. Acidity (pH 3.7), total acidity (pH 8.3) and alkalinity (pH 4.5) were either analyzed by Hill Labs or at the University of Canterbury Environmental Engineering Laboratory. Total suspended solids (TSS) were measured following American Public Health Association APHA Method 2540D (APHA, 1998).

Metal samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Dissolved metals were analyzed by APHA Method 3125B (APHA, 1998). Acid-soluble metals were analyzed by APHA Method 3125B (APHA, 2005) with dilute HNO_3 extraction. Total metals were analyzed by APHA Method 3125B with HNO_3 digestion (APHA, 1998). Metal samples were collected head-space free in HDPE sample bottles preserved with 1:1 HNO_3 to reduce pH to less than 2.0. Dissolved metal samples were filtered during sample collection either through 0.45 μm nitrocellulose filters encapsulated in a Pall 47 mm polycarbonate in-line filter holder or Waterra WAT45 groundwater filters containing polyethersulphone 0.45 μm filter media. All components of the Pall filters were decontaminated by washing in an Alconox solution followed by a tap water rinse, deionized water rinse, a 24 to 72 hour immersion in a

5% HNO$_3$ solution followed by a tap water rinse and a final deionzed water rinse. Waterra WAT45 filters are disposable so no decontamination was required.

Ferrous iron was measured at the time of sample collection following Hach Method 8146 (1, 10 Phenanthroline Method) and analyzed using a Hach Spectrophotometer at 510 nm (Hach Company, 2003). Ferric iron (Fe^{3+}) was calculated as the difference between total Fe and Fe^{2+}. Total S was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Total S concentrations were computed as mg/L of SO$_4^{2-}$ for comparative purposes only. Calcium samples were collected in unpreserved HDPE containers, filtered by Hill Labs and analyzed following APHA Method 3125B (APHA, 1998). Fecal coliform samples were collected in sterile and unpreserved polycarbonate containers and analyzed by Hill Labs the same day as sample collection following APHA Method 9222D (APHA, 2005). Samples for BOD$_5$ analysis were collected in unpreserved HDPE containers and analyzed following APHA Method 5210B (APHA, 1998).

Alkalinity (pH 4.5) was analyzed using a modified version of APHA Method 2320B (APHA, 2005). Acidity (pH 3.7) and total acidity (pH 8.3) were analyzed using a modified version of APHA Method 2310B (APHA, 2005). Titrants used were 0.1 N HCl and 0.02 N NaOH. Sample pH endpoints for titrations performed by Hill Labs were determined using a radiometer autotitrator and method specified indicators. Alkalinity (pH 4.5), acidity (pH 3.7) and total acidity (pH 8.3) were determined from titration curves for samples analyzed at the University of Canterbury. Hot peroxide treatment was performed on all AMD samples to oxidize iron by adding five drops of 30% H$_2$O$_2$ and boiling the solution in a covered Erlenmeyer flask for two to three minutes. Samples were allowed to cool to room temperature prior to titration. An EDT Instruments RE357 TX pH meter calibrated with pH 4, 7 and 10 standards was used to measure pH when determining titration curves. Calculated acidity was computed using the following equation where C$_{Fe}$$^{2+}$, C$_{Fe}$$^{3+}$, C$_{Al}$, C$_{Cu}$, C$_{Ni}$ and C$_{Zn}$ represent their respective metal concentrations in mg/L (modified from Watzlaf et al., 2003).

$$\text{total calculated acidity (mg/L as CaCO}_3) = 50.045(2\,C_{Fe}^{2+}/55.85 + \qquad \textbf{(3)}$$
$$3\,C_{Fe}^{3+}/55.85 + 3\,C_{Al}/26.98 + 2\,C_{Cu}/63.55 + 2\,C_{Ni}/58.71 + 2\,C_{Zn}/65.38 + 1000(10^{-pH}))$$

Ferric iron concentration was assumed to be zero from SRBR effluent samples due to Fe^{3+} solubility at effluent pH values (lowest recorded was 5.17 but typically >6.1) and low DO (<1.0

mg/L) and Eh (0 to 80 mV). Other metals (i.e. Cd, As and Pb) contributed minimal acidity (<0.4%).

<u>Flow Measurements</u>

Flow was monitored at the research site to ascertain flow rates emanating from Manchester Seep. Flow was typically monitored monthly from the outlet culvert of Manchester Pond (Fig. 3) using the bucket and stopwatch method. A minimum of five replicates were taken and averaged to determine mean flow. The bucket volume was 12.7 L as verified by filling with 2000 and 1000 mL graduated cylinders.

Influent into each laboratory SRBR was measured typically on a daily basis using 25 mL graduated cylinders and a stopwatch. Calibration-curve relationships were developed for two graduated cylinders at 5 mL increments using deionized water and a microbalance since graduated cylinder volumes were deemed sufficiently accurate only at the 25 mL marks. Influent flow into each SRBR was measured using the same graduated cylinder throughout the experiments for consistency.

<u>Preparation, Operation and Experimental Design of Mesocosm Sulfate-Reducing Bioreactors</u>

Mesocosm treatability tests were performed in a controlled laboratory setting at the University of Canterbury to ascertain treatment effectiveness of different substrate mixtures used in SRBRs. Substrate materials included predominately industrial-waste products. Alkaline materials included mussel shells, from mussel farm waste, nodulated stack dust (NSD), derived from the cement industry, and 20-70 mm diameter limestone, which was mined offsite. Organic substrate materials included post peel from untreated fence post manufacture, *Pinus radiata* bark and compost comprised of degraded forestry waste products such as bark and wood chips (Fig. 5).
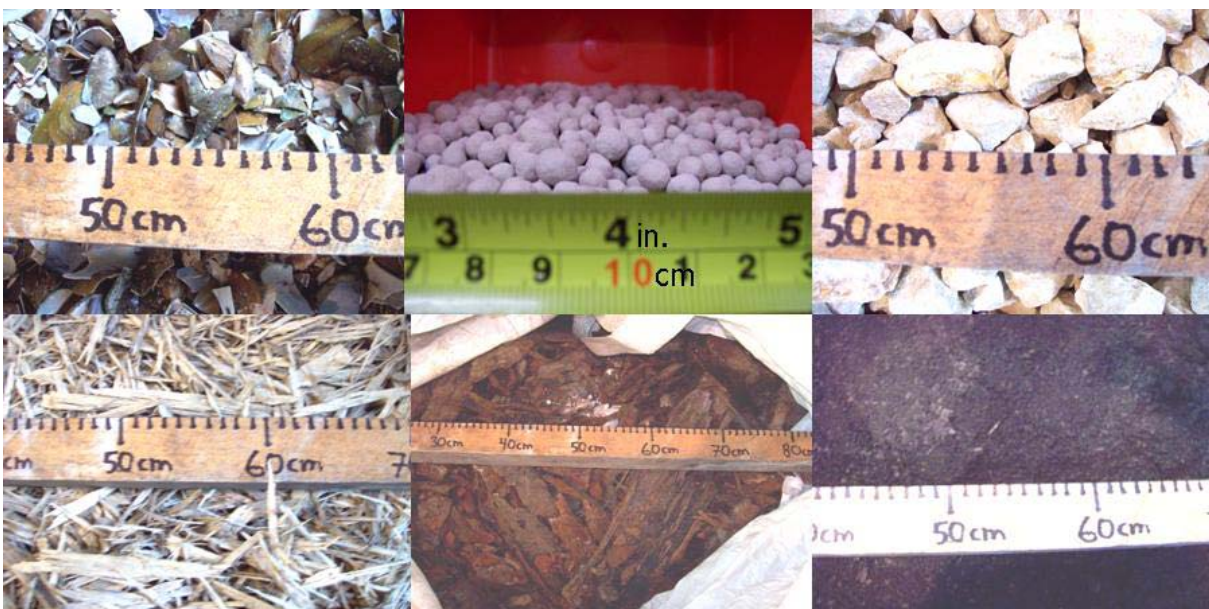
Figure 5.   Bioreactor substrate materials from upper left: mussel shells, NSD, limestone, post
peel, *Pinus radiata* bark and compost.

Each SRBR contained bedding material comprised of 20-40 mm diameter rounded and sub-rounded gravel (0.241 weight percent Ca) as the drainage layer. Shade cloth was placed on top of the bedding material to filter substrate particles. The substrate mixture was placed on top of the shade cloth.   Substrate mixture composition for each SRBR was predetermined on a volumetric basis. Known volumes of each substrate in each SRBR were measured using 22-liter buckets and mixed uniformly on an asphalt slab with shovels prior to placement into their respective SRBR container. Substrates were hand compacted and saturated with a mixture of tap water and AMD in approximately 150-200 mm lifts. The pH of the tap water/AMD mixture was 4.5 as measured with a calibrated YSI Model 60 pH meter. Post peel was placed on top of the substrate to promote flow equalization.   Water elevation in each reactor was controlled by adjusting the height of the 32 mm ID polyvinyl chloride (PVC) outlet tubing (Fig. 6 and 7). Water level was maintained at about 50 mm above the upper post peel surface.
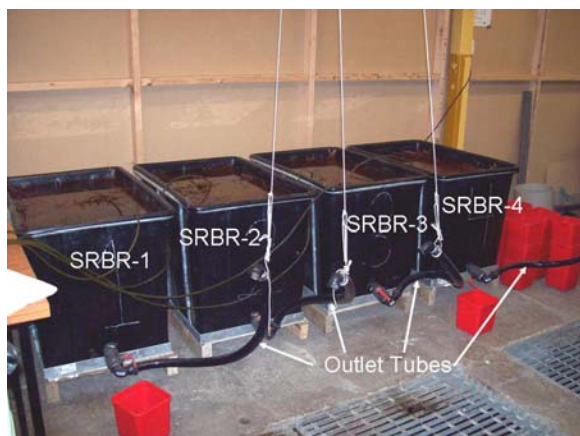
Figure 6. Mesocosm SRBRs (SRBR-1, SRBR-2, SRBR-3 and SRBR-4).

Figure 7. Mesocosm SRBRs (Perm-1, Perm-2 and Perm-3) and AMD feed tank.

Seven mesocosm SRBRs were trialed. Four of these reactors consisted of Stowers E4 low-density polyethene (LDPE) trapezoidal prism containers. Each E4 container was 337 liter capacity with upper dimensions of 900 mm X 600 mm, lower dimensions of 830 mm X 545 mm and a height of 680 mm (Fig. 6). Bedding material thickness was 90 mm, and volume was 0.0408 m^3. Substrate material thickness was 440 mm with a midpoint surface area of 0.491 m^2 and substrate volume of 0.216 m^3. Post peel thickness was 50 mm with a volume of 0.0262 m^3. Three of the reactors consisted of 138 liter HDPE drums with an average diameter of 465 mm and average surface area of 0.170 m^2 (Fig 7). Bedding material thickness was 14.8 cm containing a volume of 0.0183 m^3. Substrate thickness was 562 mm with a volume of 0.0994 m^3. Post peel layer thickness was 50 mm containing a volume of 0.00785 m^3.

Each SRBR contained a different substrate mixture, with exception of two systems, as summarized in Table 1. SRBR denotes 337 L (E4) trapezoidal prism reactors. Perm specifies 138 L drum reactors. SRBR-1 utilized only limestone for alkalinity generation. SRBR-2 and SRBR-3 contained equal quantities of mussel shells (20.0%) and compost (15.0%) but differing amounts of bark (30.0-40.0%) and post peel (25.0-35.0%). Reactors SRBR-4 and Perm-2 contained identical substrate mixtures incorporating both mussel shells (12.0%) and limestone (5.0%) for alkalinity generation. However, they were operated in different sized containers to determine how reactor dimensions affect treatment efficacy. Perm-1 contained the highest percentage of mussel shells (30.0%) of all reactors. Perm-3 trialed NSD (5.0%) mixed with limestone (2.5%) and mussels shells (12.0%).

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Table 1. Substrate composition of each mesocosm SRBR in volumetric percent.

	SRBR-1	SRBR-2	SRBR-3	SRBR-4	Perm-1	Perm-2	Perm-3
	337 L				138 L		
Limestone	12.5	0.0	0.0	5.0	0.0	5.0	2.5
Mussel Shells	0.0	20	20	12	30	12	12
NSD	0.0	0.0	0.0	0.0	0.0	0.0	5.0
Bark	35	40	30	30	30	30	30
Post Peel	37.5	25	35	38	25	38	35
Compost	15	15	15	15	15	15	15

Multiple batches of AMD were sourced from the mine site near the outlet of the sedimentation pond that captures Manchester Seep water (Fig. 3) and transported to the University of Canterbury lab (Fig. 6 and 7). The mine water was stored and left undisturbed in 1000 liter HDPE tanks and pumped into the 1000 liter HDPE feed tank when additional AMD was required. The AMD in the feed tank was aerated continuously with an open tube to better simulate DO conditions measured at the research site. Flow was conveyed into each mesocosm SRBR and flow rate controlled with a Masterflex peristaltic pump and speed controller equipped with Easy-Load pump heads, and No. 16 Tygon® tubing connected to 5 mm ID polyurethane tubing. A separate pump and pump head configuration was used for trapezoidal prism and drum reactors due to differences in substrate volumes and design flow rates.

Influent AMD flow rates were increased incrementally (0.05-1.44 moles of metals/m^3 substrate/day) throughout the experiment to test system limits. Reactors operated for nearly 17 weeks with exception of SRBR-1 (12.4 weeks) due to less effective metal removal compared with other SRBRs and Perm-3 (11.3 weeks) due to caustic effluent. The operation of these less effective systems were also terminated to reduce AMD shipments required. Sampling was typically conducted on a weekly or biweekly basis and prior to increasing AMD flow rate. The dissolved-metal fraction was sampled for the first six sampling periods (or 9.5 weeks of system operation). The acid-soluble fraction was sampled thereafter since TSS in reactor effluent stabilized at that point.

Results and Discussion

Manchester Seep Water Chemistry

Chemistry and flow of Manchester Seep AMD were monitored on a monthly basis between May 2006 and February 2007 (Fig. 8 and Table 2). Data measured was stochastic and likely influenced by precipitation, surface water runoff and infiltration, geochemical reactions of groundwater within fractured bedrock prior to daylighting and possibly activities associated with active coal mine operations.

A suspected site disturbance (December 2006) involving maintenance on an upgradient sediment pond likely contributed to the highest flow rate recorded (10.5 L/s). During this sampling event, a relatively instantaneous (within minutes) increase in turbidity from 30.9 to 4250 NTUs and TSS from 157 to 2960 mg/L was noted. Differences between total and dissolved Fe and total and dissolved Al also reflected the site disturbance relative to other sampling occasions (Fig. 8). Maximum flow (excluding December 2006 data) was measured at 5.96 L/s. Turbidity and TSS concentrations during other sampling events were comparable or less than the lower values recorded in December 2006.

Iron and Al contributed the majority of metal acidity. Hydrogen, Fe and Al cations contributed to over 99.9% of calculated acidity for all samples. Median percent contributions to calculated acidity were 37.1% Fe (10.0-53.8%), 35.3% Al (26.5-64.3%) and 19.3% H^+ (11.6-54.8%).

Dissolved and total metal concentrations were similar for all samples, with exception of the sample collected in December 2006 (site disturbance). Excluding the December 2006 anomaly, comparison of total and dissolved Fe yielded a linear best-fit slope of 0.991 with an R^2 of 0.993. Dissolved Fe decreased from 12.2 to 11.1 mg/L during the December 2006 sampling event, whereas total Fe increased from 14.3 to 116 mg/L. Ferric iron accounted for a median and average of 82% of Fe (72-92%) indicating most iron was oxidized. Dissolved oxygen and Eh values (Table 2) also indicated the prevalence of oxidized conditions.
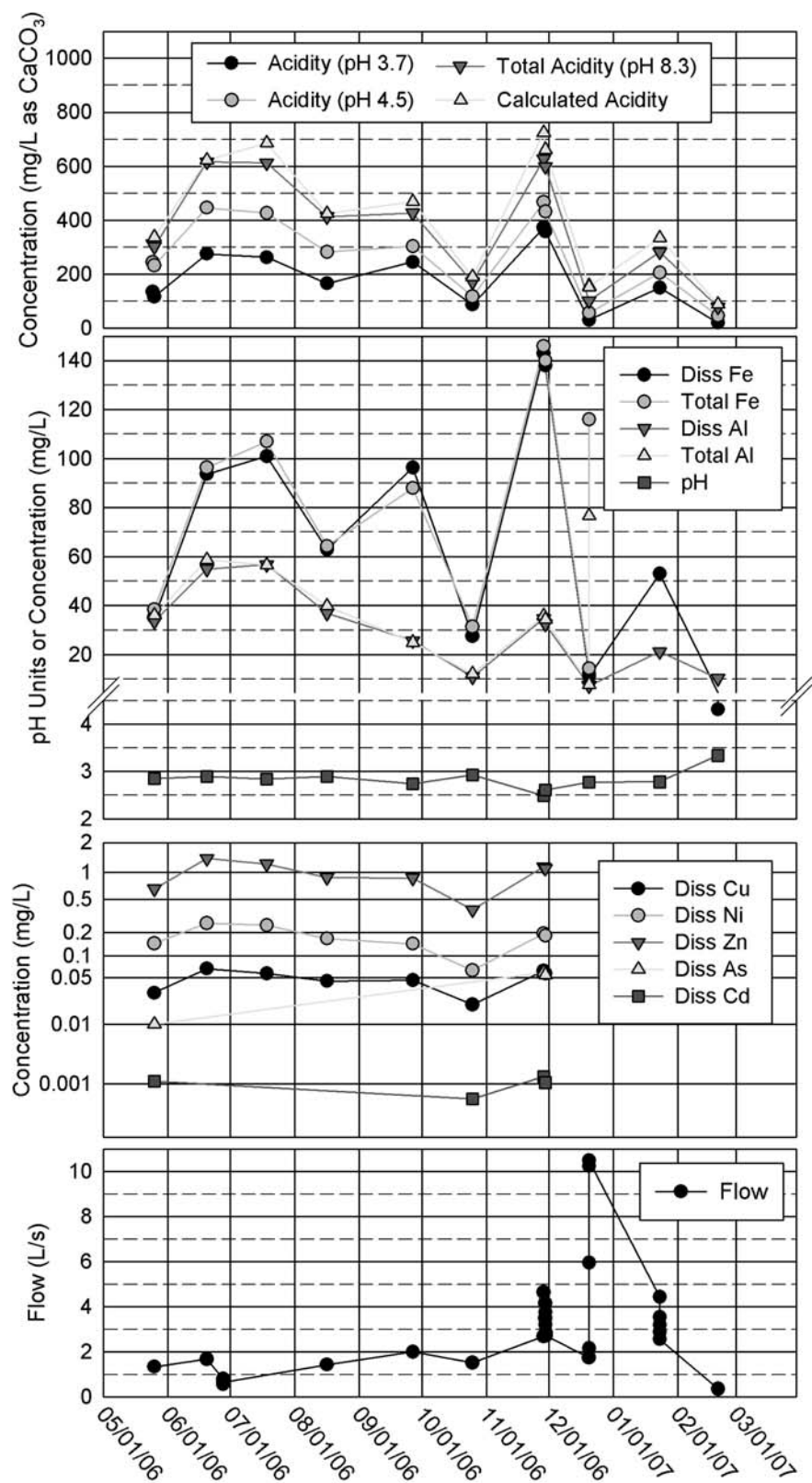
Figure 8. Manchester Seep acidity, metal concentrations, pH and flow monitoring data collected on a monthly basis prior to designing and initiating mesocosm-scale treatability tests.

Table 2. Manchester Seep water chemistry (May 2006-February 2007). All units in mg/L unless otherwise specified. Acidity units are mg/L as $CaCO_3$.

	n	Mean	Median	Min	Max	Std. Dev.
Flow (L/s)	12	2.97	1.84	0.35	10.5	2.82
Flow (gal/min)	12	47.1	29.2	5.55	166	44.8
Temp (^{o}C)	11	9.8	9.6	7.9	12.6	1.5
pH	12	2.82	2.81	2.49	3.34	0.21
Eh (mV)	9	715	709	691	744	19.2
Conductivity (μS/cm)	11	689	673	256	1033	267
Specific Conductance (25^oC) (μS/cm)	11	979	968	335	1500	390
DO	11	9.47	9.59	8.12	10.93	0.72
DO (% sat)	11	84.0	82.1	73.4	94.3	6.96
Turbidity (NTUs)	9	479	2.45	0.43	4250	141
TSS	11	298	18.8	0.51	2960	883
Calc Acidity	11	468	447	88.8	742	213
Acidity (pH 3.7)	12	378	363	78.5	626	203
Total Acidity (pH 8.3)	12	378	363	78.5	626	203
Total Fe	10	84.2	92.2	14.3	146	45.7
Diss Fe	11	69.7	62.9	4.31	143	48.2
Fraction Fe^{3+}	9	0.82	0.82	0.72	0.92	0.07
Total Al	10	38.3	36.0	7.85	76.7	21.2
Diss Al	11	29.5	32.5	7.43	56.7	16.7
Total Cu	3	0.0509	0.0585	0.0302	0.0640	0.0181
Diss Cu	8	0.0480	0.0514	0.0201	0.0669	0.0162
Total Ni	3	0.222	0.257	0.148	0.261	0.0641
Diss Ni	8	0.176	0.175	0.0629	0.261	0.0641
Total Zn	3	1.08	1.23	0.609	1.39	0.412
Diss Zn	8	0.957	0.993	0.380	1.39	0.327
Total Cd	1	0.00106	0.00106	0.00106	0.00106	
Diss Cd	4	0.00101	0.00109	0.00054	0.00134	0.000338
Total Pb	1	0.0056	0.0056	0.0056	0.0056	
Diss Pb	1	0.0049	0.0049	0.0049	0.0049	
Total As	1	0.011	0.011	0.011	0.011	
Diss As	3	0.041	0.055	0.010	0.059	0.027
Total Mn	1	0.877	0.877	0.877	0.877	
Diss Mn	4	0.819	0.801	0.727	0.947	0.0956

Aluminum concentrations were generally less variable than Fe concentrations. During December 2006 sampling, dissolved Al decreased from 7.61 to 7.24 mg/L following the site disturbance. Total Al increased from 7.85 to 76.7 mg/L. Excluding data from this sampling event, comparison of total and dissolved Al concentrations yielded an R^2 value of 0.994 with a linear best-fit slope of 1.032. Total Fe and Al and dissolved Fe and Al concentrations correlated poorly yielding R^2 values of 0.336 and 0.480, respectively, indicating no strong relationship between Fe and Al concentrations.

Other metals (Fig. 8 and Table 2) measured from Manchester Seep AMD at concentrations exceeding ANZECC guidelines for protection of 80% of aquatic species in freshwater, with guideline concentrations in parenthesis, included Cu (0.0025 mg/L), Ni (0.0017 mg/L), Zn (0.031 mg/L) and Cd (0.0008 mg/L). Arsenic (0.360 mg/L), Mn (3.600 mg/L) and Pb (0.0094 mg/L) were measured at concentrations below ANZECC guidelines. There are no ANZECC guideline values for Fe and Al (pH<6.5).

Treatment Performance of Mesocosm-Scale Sulfate-Reducing Bioreactors

Data analysis of the SRBR experiments focused primarily on metal and acidity loading and removal with an emphasis on Fe and Al treatment efficiencies. Metal removal was considered on a moles of metals/m^3 of substrate/day basis. Calculated acidity removal was determined on a g $CaCO_3$/m^2 of upper reactor surface area/day basis. Molar metal and acidity loading were computed from Fe, Al, Cu, Ni, Zn and H^+ concentrations. Manganese contribution was excluded since its removal in SRBRs in not expected due to the high solubility of MnS (Watzlaf et al., 2003; Wildeman et al., 2006). It typically accounted for <1% of molar loading and <0.6% of acidity loading (median concentration was 1.65 mg/L (1.40-2.61 mg/L)). Treatment efficiencies were calculated using the following equation where X represents loading rates (moles/m^3/day or g acidity/m^2/day) or concentrations (mg/L):

$$\text{percent treatment efficiency} = 100(X_{in}-X_{out})/X_{in} \tag{4}$$

Numerous literature sources have recommended design criteria and proven implementation of SRBRs and VFWs as effective means of sequestering Fe, Al and other metals commonly associated with AMD (Gusek and Wildeman, 2002; Rose and Dietz, 2002; PIRAMID, 2003; Watzlaf et al., 2003; Rose, 2005; Skousen and Ziemkiewicz, 2005; Rose, 2006). Results

presented from this study concur with these other studies with most reactors in our study exhibiting treatment efficacy greater than recommended design criteria reported elsewhere.

Area plots illustrating influent and effluent metal loading for the seven reactors, in units of moles of metals/m^3 of substrate/day, are presented in Fig. 9 on a probability scale. Black-shaded areas represent metals stored in each reactor. Areas shaded gray display effluent metal discharge. Therefore, plots showing less gray shading (i.e. Perm-3) indicate better metal sequestration. Conversely, plots displaying more gray shading (i.e. SRBR-1) indicate less effective metal removal. Figure 10 illustrates metal removal versus influent metal loading for each reactor on a moles of metals/m^3 of substrate/day basis. The dashed line shown in Fig. 10 represents equal loading and removal. Data points where loading and removal are most similar indicate the best metal sequestration (i.e. Perm-1 and Perm-3). Conversely, data deviating the most from the dashed line indicate less effective metal removal and, consequently, system stress or failure (i.e. SRBR-1 and SRBR-4).

Area plots showing influent and effluent calculated acidity amounts for each reactor on an areal basis are presented in Fig. 11 on a log scale. Area plots shown in Fig. 11 are interpreted in the same way as Fig. 9 except areas represent calculated acidity areal loading (g CaCO$_3$/m^2/day) instead of molar metal loading (moles/m^3/day). Figure 12 illustrates acidity areal removal rates versus acidity areal loading for each reactor on a g of CaCO$_3$ acidity/m^2 of reactor surface area/day basis.

A summary of influent and effluent metal concentrations from each reactor during stable operating conditions (weeks 5-16, metal loading rates 0.23-0.83 moles/m^3/day and acidity loading rates 21-80 g CaCO$_3$/m^2/day) are shown in Table 3. Data excludes the first three and final sampling events (unstable operating conditions), except for Perm-3 and SRBR-1. Effluent data from Perm-3 and SRBR-1 includes samples collected from week five until bioreactor operation ceased (during week 11 for Perm-3 and Week 12 for SRBR-1). Iron and Al contributed to the majority of metal (98.0-99.0%) and acidity (median 79.2% (66.8-81.3%)) loading to each system. Influent and effluent Fe and Al concentrations and treatment efficiency for each reactor are displayed in Fig. 13. Treatment efficiency was generally stable during the study for Fe and Al (with exception of SRBR-1). However, treatment effectiveness was better for Al. A decrease in Fe removal efficiency was more notable, especially during the final
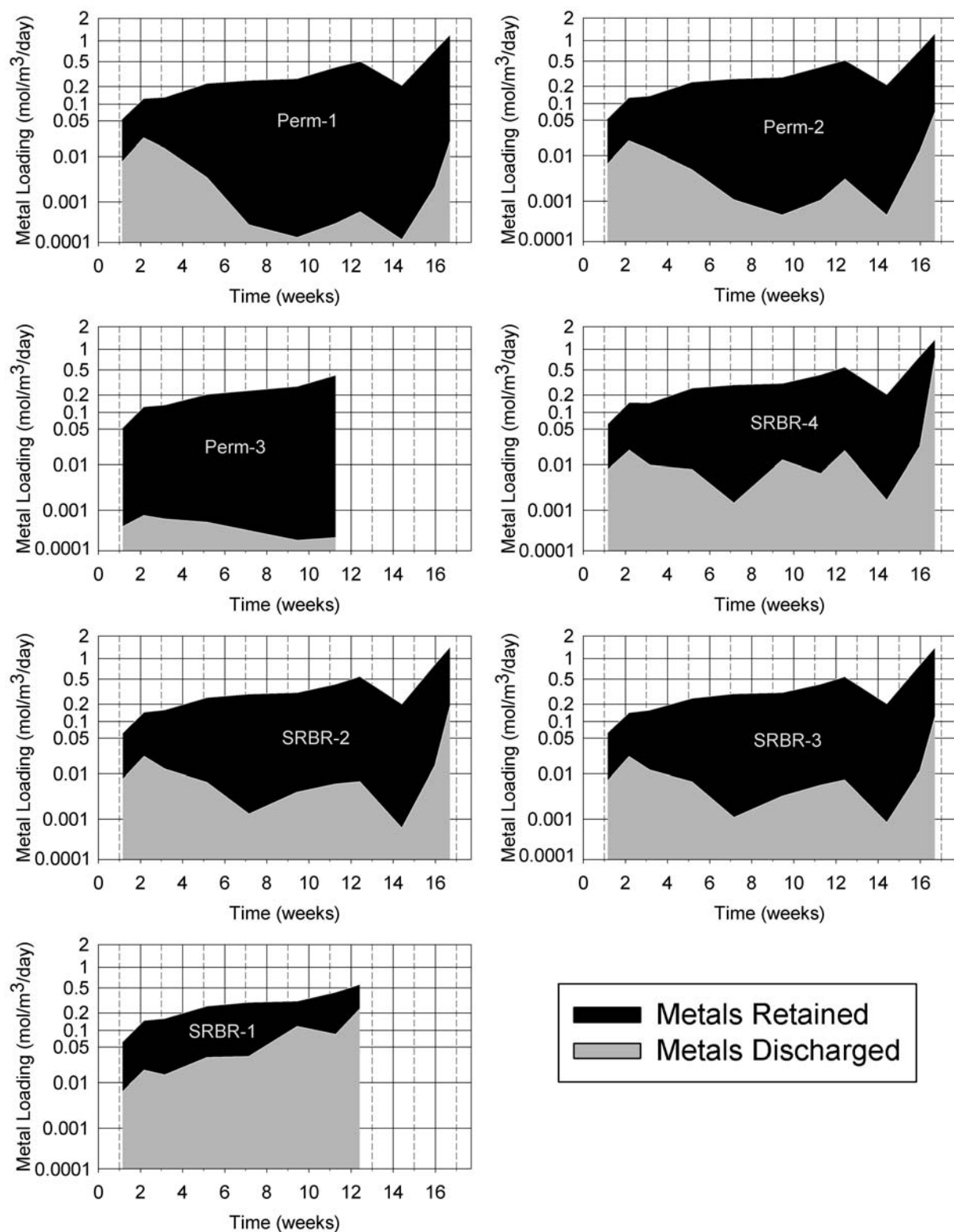
Figure 9. Influent and effluent molar volumetric metal loading during the mesocosm-scale SRBR treatability tests. Data presented on a probability scale. Metal loading measured on a moles of metals/m^3 substrate/day basis.
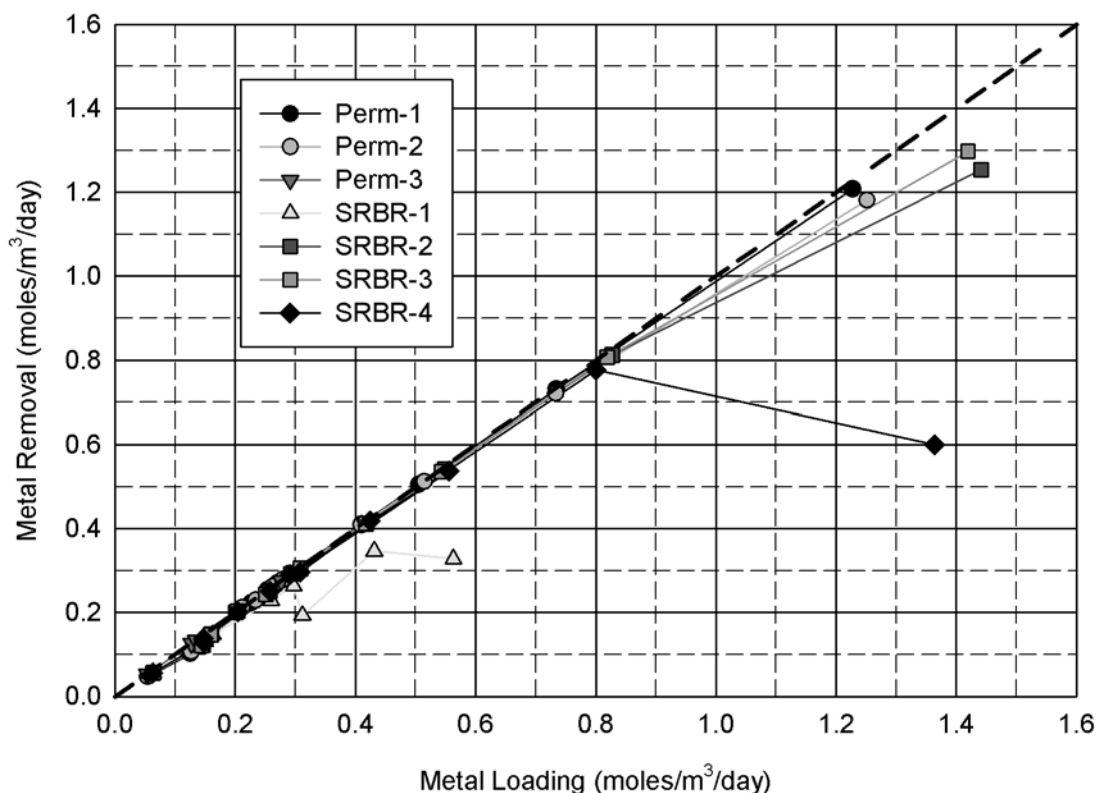
Figure 10. Molar volumetric influent metal loading and removal during the mesocosm-scale SRBR treatability tests. Dashed line represents equal loading and removal (no net export).

sampling event, for most systems (metal loading >0.8 moles/m^3/day) and throughout the operation of SRBR-1.

Discussion of Reactor Treatment Effectiveness – Metals and Acidity

All reactors exhibited good metal removal capabilities (Fig. 9-13). SRBR-1 was least effective at generating alkalinity and sequestering metals. Perm-3 showed the best metal removal efficiency, but effluent was caustic. Systems containing mussel shells as the primary alkalinity source displayed the best alkalinity generation and metal sequestration of all feasible substrate mixtures tested. The substrate mixture in Perm-1 showed the most promise. Perm-2, SRBR-2, SRBR-3 and SRBR-4 also displayed good treatment performance, but not as effective as Perm-1.

Overall, Al, Cu, Ni, Zn, Cd and Pb were easily removed in reactors containing mussel shells during stable operating conditions (weeks 5-16) as shown in Table 3. Iron was also successfully
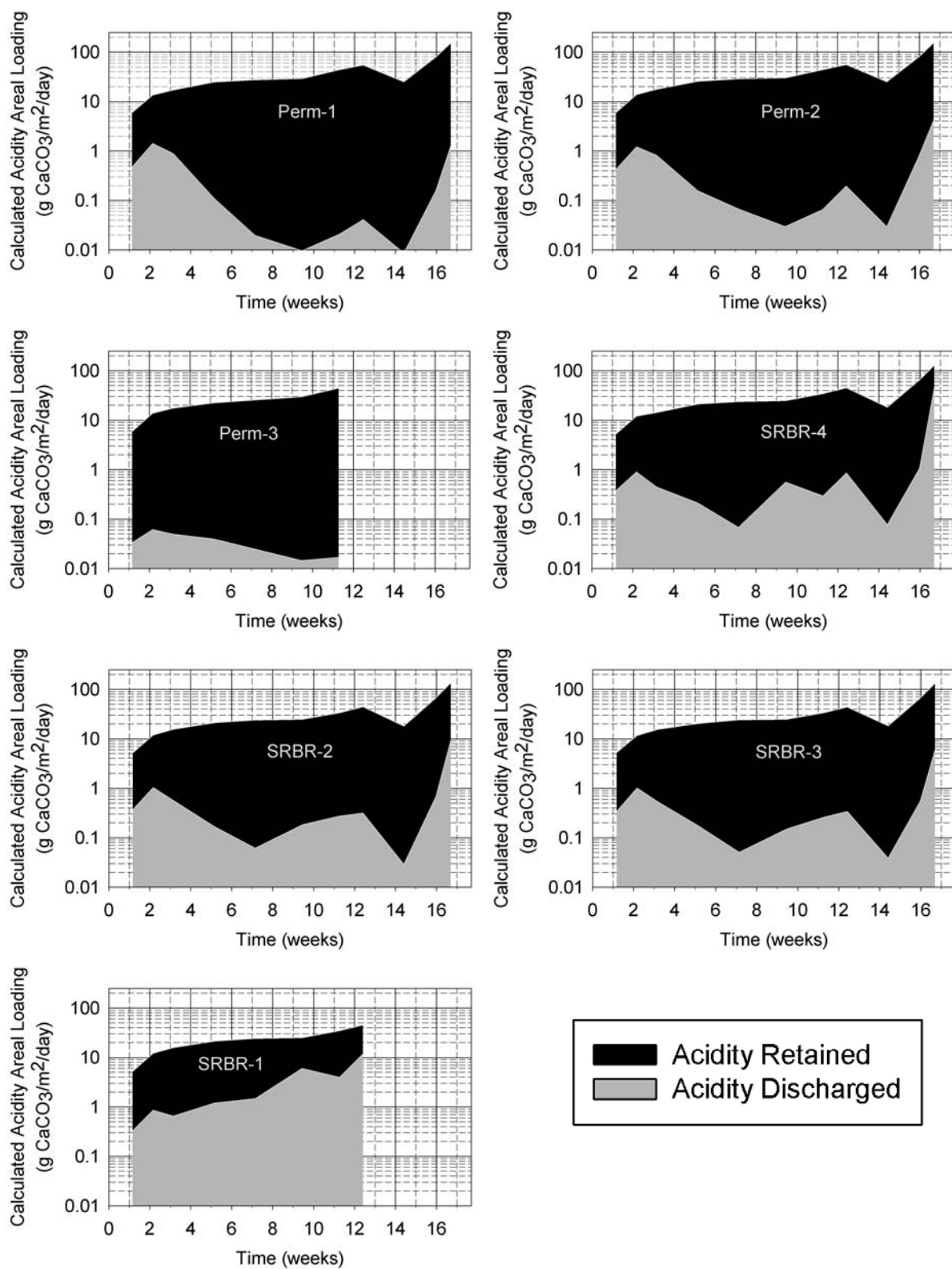
Figure 11. Influent and effluent acidity areal loading and discharge during the mesocosm-scale SRBR treatability tests. Acidity measured on a g $CaCO_3/m^2$ substrate surface area/day basis and presented on a log scale.
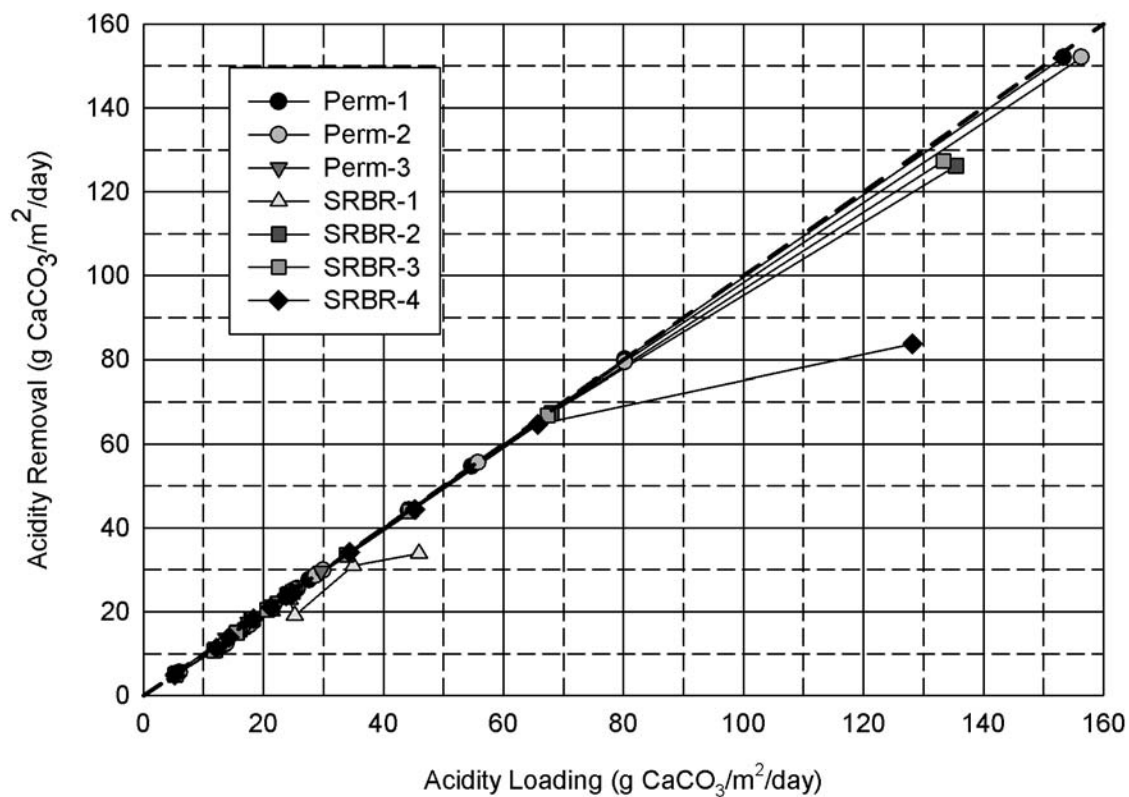
Figure 12. Acidity areal loading and removal during the mesocosm-scale treatability tests. Dashed line represents equal loading and removal (no net export).

Table 3. Bioreactor influent and effluent metal concentrations in units mg/L. Data represents samples collected between weeks 5-16 during stable operating conditions (metal loading rates 0.23-0.83 moles/m^3/day and acidity loading rates 21-80 g CaCO$_3$/m^2/day). Data presented excludes the first three and final sampling events (unstable operating conditions), except for Perm-3 and SRBR-1. Effluent data from Perm-3 and SRBR-1 includes samples collected from week 5 until bioreactor operation ceased (during week 11 for Perm-3 and week 12 for SRBR-1). Sample concentrations below laboratory practical quantitation limits (PQLs) were halved for statistical calculations.

	Mean	Median	Min	Max	Std. Dev.
	AMD Influent (n=7)				
Fe	78.4	70.7	54.8	106	20.7
Al	53.6	51.8	42.6	69.5	10.7
Cu	0.209	0.199	0.146	0.272	0.048
Ni	0.230	0.210	0.187	0.296	0.043
Zn	1.27	1.23	1.03	1.55	0.197
Cd	0.00186	0.00169	0.00155	0.00235	0.00031
Pb	0.0152	0.0150	0.0090	0.0284	0.0071
	Perm-1 (n=7)				
Fe	0.27	0.12	0.05	1.04	0.35
Al	0.044	0.026	0.017	0.122	0.038
Cu	<0.0005	<0.0005	<0.0005	<0.0005	0
Ni	0.0008	0.0005	<0.0005	0.0020	0.0006
Zn	0.002	0.002	0.001 (or <0.002)	0.003	0.0008
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	<0.0001	<0.0001	<0.0001	<0.0001	0
	Perm-2 (n=7)				
Fe	1.03	0.58	0.28	2.91	0.93
Al	0.066	0.029	0.025	0.246	0.080
Cu	<0.0005	<0.0005	<0.0005	<0.0005	0
Ni	0.0009	0.0005	<0.0005	0.0020	0.0006
Zn	0.001	0.001	<0.001	0.003	0.0009
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	<0.0001	<0.0001	<0.0001	<0.0001	0

Table 3 continued.

|	Mean	Median	Min	Max	Std. Dev.
	Perm-3 (n=3)				
Fe	0.05	0.04	0.04	0.06	0.01
Al	0.075	0.054	0.039	0.133	0.051
Cu		<0.0005	<0.0005	<0.001	
Ni	0.0058	0.0070	<0.001	0.010	0.0049
Zn	0.005	0.003	0.002	0.010	0.004
Cd	0.00008	<0.00005	<0.00005	0.00020	0.00010
Pb			<0.0001	<0.0002	
	SRBR-1 (n=5)				
Fe	38.1	41.7	15.7	64.3	21.4
Al	5.84	2.75	0.075	15.0	6.87
Cu	0.0012	<0.0005	<0.0005	0.0020	0.0012
Ni	0.036	0.0038	0.0013	0.125	0.053
Zn	0.021	0.004	0.002	0.071	0.030
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	<0.0001	<0.0001	<0.0001	<0.0001	0
	SRBR-2 (n=7)				
Fe	2.17	2.16	0.44	3.46	1.25
Al	0.062	0.039	0.023	0.194	0.061
Cu		<0.0005	<0.0005	<0.0010	
Ni	0.0010	0.0005	<0.00050	0.0020	0.0008
Zn	0.002	0.002	0.00075 (or <0.001)	0.004	0.001
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	<0.0001	<0.0001	<0.0001	<0.0001	0
	SRBR-3 (n=7)				
Fe	1.98	2.28	0.52	3.30	1.05
Al	0.070	0.031	0.021	0.256	0.084
Cu		<0.0005	<0.0005	<0.0010	
Ni	0.0010	0.0005	<0.0005	0.0020	0.0008
Zn	0.001	0.001	<0.001	0.003	0.0007
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	0.00005	<0.0001	0.00005	<0.0001	
	SRBR-4 (n=7)				
Fe	4.28	3.65	0.72	10.2	3.27
Al	0.063	0.031	0.027	0.230	0.074
Cu		<0.0005	<0.0005	<0.0010	
Ni	0.0007	0.0005	<0.0005	0.0014	0.0004
Zn	0.002	0.001	<0.001	0.003	0.0009
Cd	<0.00005	<0.00005	<0.00005	<0.00005	0
Pb	<0.0001	<0.0001	<0.0001	<0.0001	0
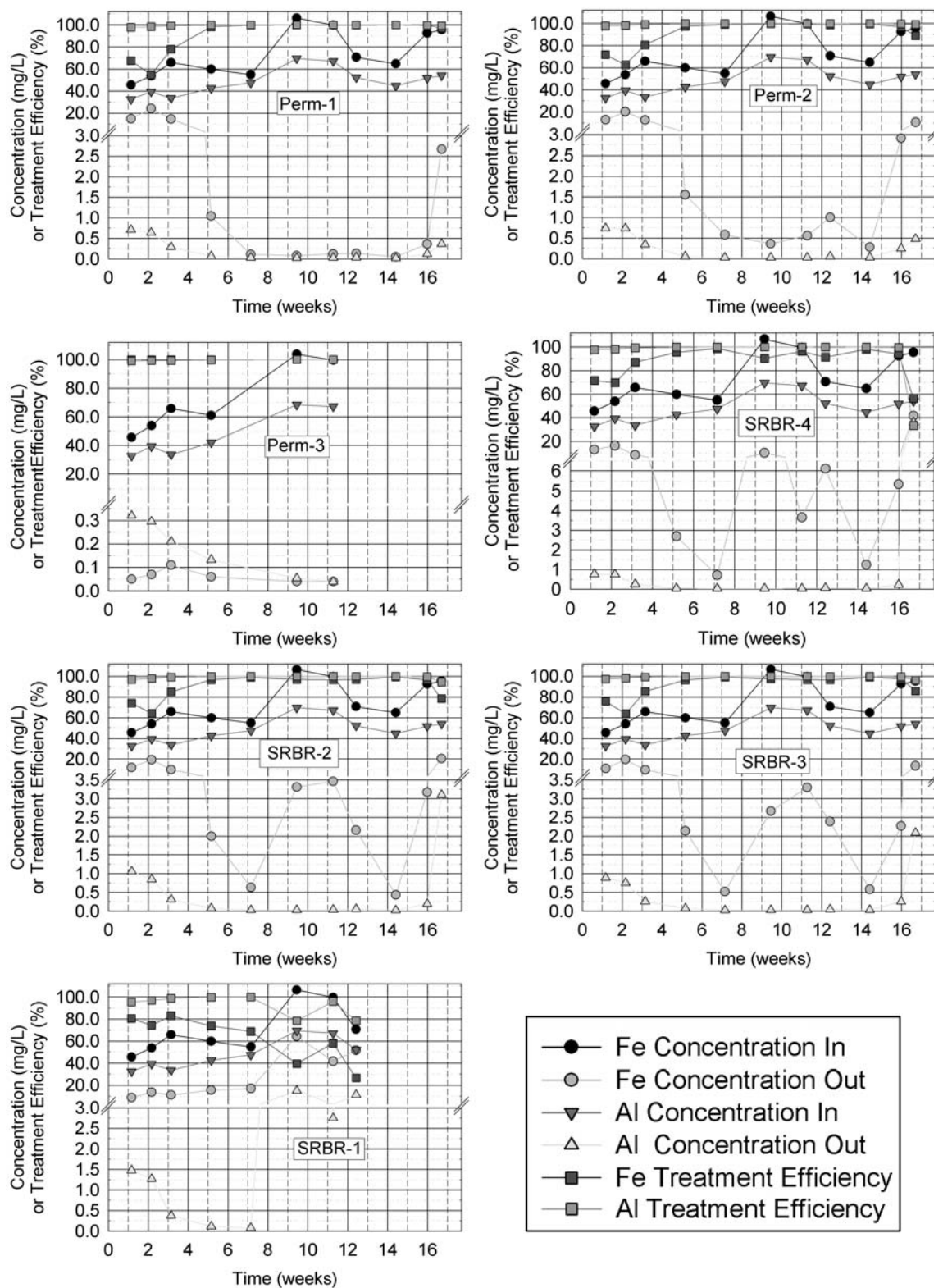
Figure 13. Influent and effluent Fe and Al concentrations during the mesocosm-scale treatability tests. Treatment efficiency based on reduction in concentrations.

removed, but effluent concentrations were greater than other metal concentrations indicating its removal was less effective. Higher effluent metal concentrations were typically exhibited at the highest metal (1.23-1.44 moles/m^3/day) and acidity (128-156 g $CaCO_3$/m^2/day) loading rates tested (week 17) as shown in Table 4. However, Cd and Pb effluent concentrations remained below practical quantization limits (PQLs) except for SRBR-4. Copper and Ni concentrations were below PQLs throughout the experiments for Perm-1 and Perm-2, but detectable at the highest metal loading rates tested for SRBR-2, SRBR-3 and SRBR-4. Effluent Zn concentrations were consistent throughout the experiments except at the highest loading rates tested for SRBR-2, SRBR-3 and SRBR-4. Zinc concentrations increased about an order of magnitude for SRBR-2 and SRBR-3 and about two orders of magnitude for SRBR-4. Effluent Al concentrations increased about an order of magnitude for all reactors at the second highest metal (0.73-0.83 moles/m^3/day) and acidity (66-80 g $CaCO_3$/m^2/day) loading rates compared with lower loading rates. Aluminum concentrations increased an additional order of magnitude at the highest metal loading rates evaluated for SRBR-2 and SRBR-3 and an additional two orders of magnitude for SRBR-4. Effluent Al concentrations for Perm-1 and Perm-2 were about two to three times greater at the highest metal loading rates compared with the second highest metal loading rates. All systems incorporating mussel shells showed a significant decline in Fe removal at the highest metal loading rates tested with effluent concentrations 3.7-7.8 times greater than at the second highest metal loading rates.

Table 4. Bioreactor effluent metal concentrations for SRBRs containing mussel shells at the highest metal (1.23-1.44 moles/m^3/day) and acidity (128-156 g $CaCO_3$/m^2/day) loading rates tested. Metal concentrations are in units mg/L.

	SRBR-2	SRBR-3	SRBR-4	Perm-1	Perm-2
% Mussel Shells	20	20	12	30	12
% Limestone	0	0	5	0	5
Fe	20.6	13.6	41.8	2.67	10.7
Al	3.10	2.09	36.1	0.363	0.481
Cu	0.0015	0.0007	0.0325	<0.0005	<0.0005
Ni	0.009	0.007	0.084	<0.001	<0.001
Zn	0.040	0.025	0.628	0.003	0.002
Cd	<0.00005	<0.00005	0.0007	<0.00005	<0.00005
Pb	<0.0001	<0.0001	0.0015	<0.0001	<0.0001

In SRBR-1, limestone was the only alkalinity generating material, excluding bicarbonate (HCO_3^-) generated by SO_4^{2-} reduction. Although SRBR-1 contained the least amount of alkalinity generating material on a volumetric basis, it actually contained more on a weight basis compared with all other reactors of equal volume. Limestone used in SRBR-1 was likely too large (20-70 mm diameter) to achieve optimal dissolution due to less surface area exposed to influent AMD compared with smaller diameter material. Gusek and Wildeman (2002) used crushed limestone in SRBRs that adequately removed Al (to concentrations <0.1 mg/L) from AMD. Thomas and Romanek (2002a and 2002b) reported alkalinity generation of 88 g $CaCO_3/m^2$ surface area/day in a VFW using a mixture of 75% compost amended with 25% fine-grained limestone (nominal grain size of 1.23 mm diameter) on a volumetric basis. Using a smaller diameter and larger percentage of limestone would have likely improved SRBR-1 treatment performance. SRBR-1 removed about two-thirds of metals at a metal loading of approximately 0.3 moles of metals/m^3 substrate/day (25 g $CaCO_3/m^2$/day).

Nodulated stack dust in Perm-3 was the primary media contributing to its ability to sequester metals better than all other reactors. It dissolved quicker than mussel shells and limestone when contacted with AMD. However, caustic effluent containing pH of 9.23-10.27 and an export of sulfur yielded the system unfeasible for field-scale implementation so operation was terminated after 11.3 weeks of operation. More than 99.9% of metals were removed, including Fe, at the highest metal and acidity loading rates tested in Perm-3 (0.414 moles/m^3/day and 44.6 g $CaCO_3/m^2$/day).

Perm-1 showed the best treatment performance overall after eliminating NSD as a suitable reactive media (Fig. 9-13). It also contained the largest percentage of mussel shells at 30 volumetric percent. Metal removal efficiency was 99.7% at a metal loading rate of 0.734 moles/m^3/day (80.2 g $CaCO_3/m^2$/day). Iron and Al concentrations were reduced from 92.5 to 0.36 mg/L (99.6% removal efficiency) and 51.8 to 0.122 mg/L (99.8% removal efficiency), respectively. At the maximum loading rates tested (1.23 moles of metals/m^3/day and 153 g $CaCO_3/m^2$/day), Fe concentration was reduced from 95.5 to 2.67 mg/L (97.2% removal efficiency). Aluminum concentration was reduced from 54.1 to 0.363 mg/L (99.3% removal efficiency).

Perm-2 displayed the next best treatment performance after Perm-1. However, results from SRBR-4, which contained the same substrate mixture as Perm-2, indicate that reactor shape and

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subsequently substrate depth influence treatment performance (Fig. 9-13). It is suspected that actual and theoretical hydraulic residence times better align in the 138 L drum reactors compared with the 337 L E4 trapezoidal prism reactors accounting for better treatment in Perm-2 than SRBR-4. Subsequent tracer studies are currently being undertaken to quantify flow hydraulics of Perm-2 and SRBR-4.

Perm-2 consistently exhibited better treatment performance compared with SRBR-4 throughout the experiments. Iron effluent concentrations were 2.91 mg/L for Perm-2 and 5.34 mg/L for SRBR-4 at metal loading rates of 0.734 and 0.800 moles/m^3/day, respectively. Aluminum effluent concentrations were comparable at about 0.24 mg/L. At the highest metal loading tested (1.25 moles/m^3/day for Perm-2 and 1.37 moles/m^3/day for SRBR-4), Perm-2 yielded 94.4% metal removal with effluent concentrations of 10.7 mg Fe/L and 0.481 mg Al/L. Metal removal for SRBR-4 was 44.0% with effluent concentrations of 41.8 mg Fe/L and Al 36.1 mg Al/L.

SRBR-2 and SRBR-3 outperformed SRBR-4 in terms of metal and acidity removal implying that reactors containing 20 volumetric percent mussel shells outperform the mixture of 5.0% limestone and 12% mussel shells used in SRBR-4 (Fig. 9-13). Treatment performance of SRBR-2 and SRBR-3 were similar throughout most of the experiment. However SRBR-3 outperformed SRBR-2 at the maximum metal loading tested (1.42 and 1.44 moles/m^3/day and 133 and 135 g CaCO$_3$/m^2/day). Metal removal rates for SRBR-3 and SRBR-2 were 1.30 moles/m^3/day (91.4%) and 1.25 (87.0%) (127 and 126 g CaCO$_3$/m^2/day), respectively. Substrate mixtures were similar for SRBR-2 and SRBR-3 except SRBR-2 contained 40% *Pinus radiata* bark and 25% post peel, while SRBR-3 contained 30% *Pinus radiata* bark and 35% post peel. Experimental results indicate better treatment performance when using a higher percentage of post peel than bark in the substrate mixture. Reasons are uncertain but may be due to material chemical composition or substrate shape and how they influence system hydraulics.

Discussion of Design Criteria - Metal and Acidity Loading

Design criteria for metal and acidity removal were established for future pilot-scale systems based on treatment performance of the mesocosm-scale SRBRs. Data points deviating from the 100% removal efficiency dashed line in Fig. 10 and 12 indicate points where SRBRs are stressed or system limitations are exceeded. Based on reactor configuration, it is appropriate to assume

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that a pilot or industrial-scale SRBR constructed on site would better mimic the 337 L trapezoidal container reactors (SRBR-1, 2, 3 and 4) rather than a cylindrical drum. Therefore, design criteria used for future pilot-scale research was based primarily on the maximum removal capabilities of SRBR-2 and 3 measured during stable operation. These criteria range between 0.807 and 1.25 moles of metals removed/m^3 substrate/day or acidity removal of 66.7-126 g $CaCO_3$/m^2/day. Therefore, conservative design criteria based on the performances of SRBR-2 and SRBR-3 are given at 0.80 moles of metals/m^3 substrate/day (32.3 g metals/m^3 substrate/day) or acidity removal of 66 g $CaCO_3$/m^2/day.

Overall, the treatment performance of the SRBRs in this study exceeded recommended design criteria used for similar systems including SRBRs and VFWs. However, most other systems incorporated limestone as the primary alkalinity material, not mussel shells. Wildeman et al. (2006) recommended design criteria of 0.3 moles of metal removal/m^3 of substrate/day for SRBRs with a mixture of organic materials and crushed limestone. Our study found metal removal >0.8 moles of metal removed/m^3 substrate/day. Watzlaf et al. (2003) recommend applying areal removal rates of 25-30 g acidity as $CaCO_3$/m^2 surface area/day in VFWs based on empirical results of full-scale systems. Skousen and Ziemkiewicz (2005) evaluated 16 VFWs and found acidity removal rates >200 g $CaCO_3$/m^2/day for two systems, five between 39 and 87 g/m^2/day, eight between 2 and 17 g $CaCO_3$/m^2/day and one system that did not reduce acidity. Rose and Dietz (2002) found acidity removal rates between 25 and 50 g $CaCO_3$/m^2/day during evaluation of 12 VFW systems with net-acid effluent. Their study also reported net-alkaline effluent when acidity loading was <40 g $CaCO_3$/m^2/day. Rose (2004) reevaluated their earlier study (Rose and Dietz 2002) and proposed a non-Mn acidity design criteria of about 35 g $CaCO_3$/m^2/day for VFWs. Systems incorporating fine limestone in the compost mixture yielded about twice this acidity removal. Thomas and Romanek (2002a) found average acidity removal of 87.8 g $CaCO_3$/m^2/day; however, average acidity feed rate for the experiments was 57.8 g $CaCO_3$/m^2/day. These results indicate higher alkalinity generation rates occur when influent acidity loading is high, which corresponds with findings by Rose and Dietz (2002) who showed positive correlations between retention time, pH, Fe concentrations and alkalinity generation. A comprehensive evaluation by Ziemkiewicz et al. (2003) showed average acidity removal of 62.3 g $CaCO_3$/m^2/day. Our studies showed acidity removal of >66 g $CaCO_3$/m^2/day.

Discussion of Additional Effluent Water Chemistry

This section summarizes effluent water chemistry (in addition to metals and acidity) for systems containing mussel shells (Perm-1, Perm-2, SRBR-2, SRBR-3 and SRBR-4) during stable operating conditions (weeks 5-16). Temperatures ranged from 13 to 17^oC. Conductivity was typically between 1100 and 1300 µS/cm and primarily attributed to Ca^{2+}. Specific conductance (conductivity standardized to 25^oC as KCl) ranged from 1300 to 1800 µS/cm. Dissolved oxygen was ≤ 1.0 mg/L, a substantial reduction from the AMD feed average of 9.64 mg/L or 95.5% saturation. Redox potential (as Eh) ranged from -20 to 80 mV, reduced from average AMD influent of 745 mV. Dissolved oxygen and Eh data support the fact that reducing conditions were prevalent in the SRBRs. Turbidity was less than 4 NTUs.

It was observed that when effluent pH remained stable above about 6.7, reactors operated most effectively. Treatment effectiveness was reduced with lower effluent pHs indicating the microorganisms contributing to the biogeochemical balance were potentially stressed. The pH in effluent from Perm-1 was >6.8 during optimal operating conditions and consequently showed the best treatment efficiency of all SRBRs. The pH in SRBR-1, the least effective SRBR, never exceeded 6.4.

Effluent from the SRBRs contained excess alkalinity primarily attributed to bicarbonate (HCO_3^-) generated from the dissolution of mussel shells and, to a lesser extent, SO_4^{2-} reduction. Alkalinity (pH 4.5) ranged from 276 to 619 mg/L as $CaCO_3$ with lower concentrations at higher metal and acidity loading rates. Calculated acidity in AMD influent averaged 605 mg/L as $CaCO_3$ (388 to 869 mg/L as $CaCO_3$). Acidity removal efficiencies were 98.2 to 99.9%.

Total S (or equivalent SO_4^{2-}) concentrations were reduced from the AMD during treatment with exception of Perm-3. Influent SO_4^{2-} concentrations averaged 657 mg/L (491-1007 mg/L). Effluent concentrations ranged from 145 to 656 mg/L. The highest effluent concentrations were measured at the highest loading rates, while the lowest effluent concentrations were typically measured at lowest flow rates. Overall, sulfur reduction ranged from -2.2% (2.2% export of sulfur) to 58%. Perm-3 exhibited a net export of sulfur throughout the experiments with effluent SO_4^{2-} (equivalent) concentration initially 4044 mg/L but reduced to 1025 mg/L after 11 weeks of operation. Sulfur is likely being retained within the SRBRs as amorphous monosulfide, metal sulfides, various minerals including carbonates and sulfates and through adsorption. Some sulfur also evolved as gaseous hydrogen sulfide formed during SO_4^{2-} reduction, as evident from

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olfactory detection. Release of H_2S pockets is likely influenced with changes in atmospheric pressure.

High concentrations of fecal coliforms and BOD_5 were measured initially in the effluent but were reduced to stable concentrations within nine weeks. Fecal coliform counts averaged 36,000 cfu/100 mL (6000-80,000 cfu/100 mL) after one week, 252 cfu/100 mL (10-700 cfu/100 mL) after five weeks and <10-15 cfu/100 mL after nine weeks. Concentrations of BOD_5 averaged 1500 mg/L (1070-2150 mg/L) after one week, 98.3 mg/L (76.9-116 mg/L) after five weeks and 19.3 mg/L (9.9-29.9 mg/L) after nine weeks. Therefore, it may be necessary to treat effluent for high fecal coliform and BOD_5 concentrations, depending on compliance, until concentrations stabilize to acceptable discharge levels.

Conclusions

Sulfate-reducing bioreactors containing mussel shells and forestry waste products offer a promising technology for mitigating acidity and sequestering metals associated with AMD at Stockton Mine in New Zealand. Mussel shells tend to dissolve more readily than limestone in the presence of AMD as indicated by alkalinity generation in the SRBRs evaluated in this study. Possible contributing factors include grain size, shape, reactive surface area, unique mineralogy (aragonite and calcite) or mineralogical dynamics and consequent structural change when dissolved. Therefore, SRBRs containing mussel shells and a diversity of carbon sources exhibit more efficient AMD treatment than systems utilizing limestone as the sole alkalinity source. Additionally, labile carbon attached to the mussel shells and nitrogen within the mussel shell matrix may potentially benefit the consortium of microorganisms which develop as systems reach stable treatment conditions (after 5 weeks in this study). Forestry waste products including *Pinus radiata* bark, post peel and composted wood provide sustainable short and long-term carbon sources for microorganisms. Substrate mixtures used in this study are considered low risk for plugging but are of potential concern if used on a long-term basis in a SRBR. Hydraulic conductivity rates measured on the substrate mixtures were on the order of magnitude of 1E-3 m/s. The hydraulic conductivity of compost alone used in this study was one to two orders of magnitude less indicating that system clogging is more likely if compost is used alone.

Based on results of the mesocosm-scale reactors, a preliminary design criteria greater than 0.8 moles of metals/m^3 of substrate/day (32.3 g of metals/m^3 of substrate/day) is appropriate for

pilot-scale treatment system designs. Applying an acidity areal loading design criteria is less certain although results indicate acidity removal greater than 66 g $CaCO_3/m^2$/day. Regardless, contaminant loading rates should be reevaluated or reduced to avoid potentially altering the biogeochemical system balance if effluent pH falls below 6.7. System hydraulics are also an important design consideration. Maximizing bioreactor substrate depth and minimizing surface area footprint should be considered to reduce treatment footprint and reduce discrepancies between actual hydraulic residence time and theoretical hydraulic residence time (tracer studies are currently being conducted to assess actual residence time and system hydraulics).

Although this research offers a promising passive-treatment solution for mitigating acidity and sequestering metals from AMD, system longevity is unknown and has yet to be demonstrated in a field application. The extreme rainfall quantities (>6000 mm/year (>236 in./year)) and intensities typical at Stockton Mine need to be considered when scaling the reactors up to pilot or industrial scale. Since land disturbances are typical at active mine sites, extreme care and planning is essential to ensure that chemistry and flow of AMD seeps is not exacerbated. Treatment effectiveness of SRBRs will be reduced, as demonstrated in this study, if metal and acidity loading exceeds system limitations (or design criteria). Implementation of an SRBR or VFW to treat Manchester Seep AMD should incorporate contingency overflow diversion to prevent system overloading and damage in the event of unexpected site disturbances.

While this study has demonstrated successful treatment of AMD at a mesocosm scale using waste products as the substrate media, there are further considerations required in up-scaling to operational sized systems. Ideally, an SRBR would comprise part of an overall treatment train which would be preceded with a sedimentation pond to capture diffuse sediment inputs upstream. Further downstream, aerobic wetlands, rock filters or ponds should be incorporated to increase DO from SRBR effluent and reduce fecal coliforms and BOD_5 concentrations. Overall, water quality discharging from a passive treatment technology should aim to improve biodiversity and ecological health of the receiving water body.

Acknowledgements

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