

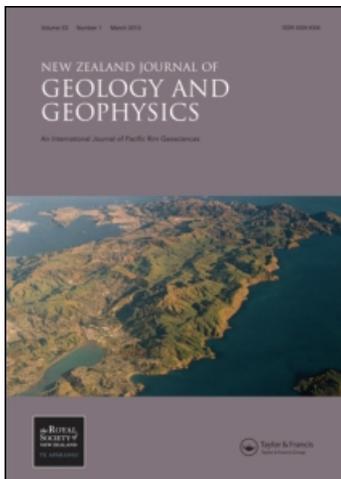
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## Results of small-scale passive system trials to treat acid mine drainage, West Coast Region, South Island, New Zealand

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Successful passive treatment of acid mine drainage can be improved through the use of small-scale pilot treatment systems to confirm appropriate system selection. Small-scale reducing and alkalinity producing systems were tested at two acid mine drainage sites in the West Coast Region, South Island, New Zealand: the Sullivan Mine and the Pike River Adit. A laboratory trial consisting of a limestone leaching column was conducted on the Blackball Mine acid mine drainage, West Coast Region. All three sites contain low pH (Sullivan Mine, 2.9; Pike River Adit, 3.2; Blackball Mine, 3.1), elevated Fe (Sullivan Mine, 47 mg/L; Pike River Adit, 34 mg/L; Blackball Mine, 10.6 mg/L), elevated Al (Sullivan Mine, 14 mg/L; Pike River Adit, 1.6 mg/L; Blackball Mine, 14.1 mg/L) and minor concentrations of Mn (0.35–0.51 mg/L), Ni (0.005–0.13 mg/L) and Zn (0.14–1.1 mg/L). The percentages of metals removed by the Sullivan Mine reducing and alkalinity producing system were: Fe (97%), Al (100%) and Ni (66%). The percentage metal removals at the Pike River Adit reducing and alkalinity producing system were: Fe (99%), Al (96%), Ni (95%) and Zn (99%). Percent metal removals for the Blackball Mine acid mine drainage were: Fe (87%), Al (91%), Mn (21%) and Zn (68%). Interpretation of data from these small-scale systems suggests that a reducing strategy may be successful at the Sullivan Mine and Pike River Adit and that an oxidising strategy may be appropriate for the Blackball Mine.

**Keywords:** acid mine drainage; AMD; passive treatment; coal; limestone; Pike River; Sullivan Mine; vertical flow wetlands; VFW; reducing and alkalinity producing systems; RAPS; successive alkalinity producing systems; SAPS; water treatment

### Introduction

Acid mine drainage (AMD) is an environmental problem that can be associated with coal mining in New Zealand (Black et al. 2005). AMD has been documented at both active and abandoned mines, both opencast and underground in various areas throughout New Zealand. However, most AMD occurs on the West Coast of the South Island, and it is estimated that 125 km of waterways are affected by AMD on the West Coast alone (James 2003).

Although there have been many studies in New Zealand on the effects of AMD from coal mines on the environment, and on the geochemistry of AMD (e.g. Alarcon 1997; deJoux 2003; Lindsay et al. 2003; Hughes et al. 2004; Black et al. 2005; Harding 2005; Pope et al. 2010), few studies have focused on treatment (Trumm et al. 2005; Weber et al. 2007; Trumm et al. 2008; Weber et al. 2008; McCauley et al. 2010). Neutralisation of AMD can be accomplished by either active or passive treatment systems. In the long term, passive treatment is typically more economic than active treatment. However, careful system choice and design are required to ensure that the system does not fail (Skousen et al. 2000; Skousen & Ziemkiewicz 2005). Potential problems with passive systems include underdesign for flow and/or acidity, short circuiting of flow, armouring of limestone and plugging with precipitates. Flow charts can be used to identify potential solutions based on water chemistry

and available land area and small-scale trials can be constructed on site to test potential systems before full-scale construction (Trumm 2010).

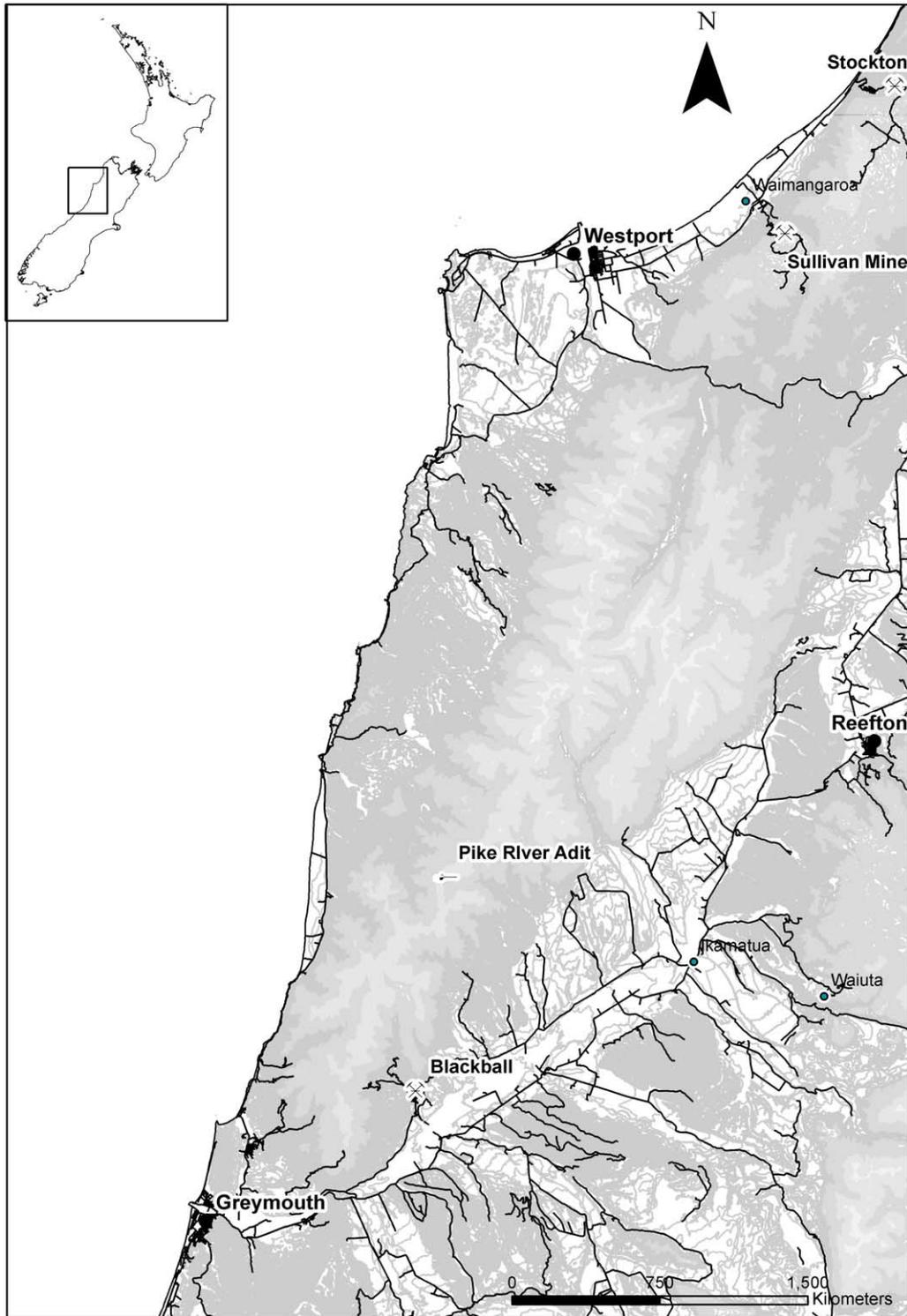
In this study, small-scale systems are used to test passive treatment of AMD from three sites in New Zealand, the Sullivan Mine, the Pike River Adit and the Blackball Mine. Each site is an abandoned mine in a remote setting with uncontrolled discharge of AMD. Active treatment is an unlikely option due to the remote setting and the cost of active treatment, therefore, passive treatment is a more attractive solution. Based on water chemistry and the land area available, potential solutions are selected and tested at each site. Similar results to those presented in this study have been obtained from small-scale passive system trials at Herbert Stream on Stockton Plateau (Trumm et al. 2008). The small-scale passive treatment systems installed at Herbert Stream provide a good basis for comparison to results presented in this study.

### Site backgrounds

#### *Sullivan Mine*

Sullivan Mine is an abandoned underground coal mine located on the Denniston Plateau, West Coast Region, New Zealand (Fig. 1). Coal deposits at Sullivan Mine are contained within the Brunner Coal Measures (BCM), which

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**Fig. 1** Location of study sites. Sullivan Mine is on the Denniston Plateau north of Westport. Sullivan Mine AMD flows into Rapid Stream which flows to the Tasman Sea. The Pike River Adit is at the upper reaches of the Paparoa Ranges between Greymouth and Westport. The AMD flows out of the adit into a small mountain stream which flows into the Pike River. Blackball Mine is near the township of Blackball north of Greymouth. The AMD flows from the mine into Ford Creek.

outcrop in uplifted blocks around the West Coast and Northern Westland area of New Zealand (Flores & Sykes 1996). The BCM are of Eocene age, are typically 30 to 100 m thick, and are composed of transgressive sandstone-dominated sequences that also contain carbonaceous mudstones, conglomerates and shales (Titheridge 1992).

In 1992, after 40 years of operation, Sullivan Mine ceased operating, with acidic, metal-rich mine waters discharging from two drives into nearby Rapid Stream (Table 1) (Trumm et al. 2003). Kinetic column and static acid generating tests showed that sulphide-rich mudstones are likely the source of the AMD (deJoux 2003). Previous work has shown that the variability in the AMD flow rate is much less than the nearby Rapid Stream (Trumm et al. 2005). The flow rate of Rapid Stream upstream of the Sullivan AMD input is highly variable, it averages 198 L/s and ranges between 0.04 L/s and 29000 L/s. In contrast, the mean flow rate of the AMD is 46 L/s with a SD of 9.8 L/s.

### Pike River Coal Field

The Pike River Coal Field is located in the Paparoa Range, West Coast Region, New Zealand (Fig. 1). Coal deposits are contained within the BCM (Paleocene to Eocene) and the underlying Paparoa Coal Measures (Late Cretaceous to Paleocene) (Wellman 1949). The BCM are well exposed in a west-facing escarpment. The typical succession comprises a single thick coal seam (3–12 m thick) which is underlain by Paparoa Coal Measures and overlain by the marginal marine Island Sandstone (Bates 1981). The Island Sandstone

**Table 1** Analytical results for water samples collected from untreated Sullivan Mine AMD, Pike River Adit AMD and Blackball Mine AMD. Results for metals express dissolved concentrations.

Parameter*	Sullivan Mine AMD	Pike River AMD	Blackball Mine AMD
pH	2.9	3.2	3.1
Acidity (mg/L as CaCO <sub>3</sub> )	214	113	216
DO (mg/L)	10	9	6
Al (mg/L)	14	1.6	14.1
Fe (mg/L)	47	34	10.6
Mn (mg/L)	0.51	0.35	0.39
Ni (mg/L)	0.13	0.12	0.005
Zn (mg/L)	0.72	1.1	0.14
Percentage of iron as Fe <sup>3+</sup>	96	93	60
Mean flow rate (L/s)	46	0.025	65

\*Analytical Methods

Acidity: Hot acidity procedure, APHA 2310B (modified) 20th ed. 1998.

Samples filtered using method APHA 3030B.

Al, Fe, Mn, Ni, Zn: ICP-MS, APHA 3125B.

Ferrous iron concentration: portable Merck Photometer SQ 300.

and the Brunner coals have locally elevated pyrite concentrations.

Exploration in the Pike River Coal Field began in the 1940s when coal was discovered in the Pike River. Exploration intensified in the 1980s and 1990s by the Pike River Coal Company and in the late 1980s a small adit was excavated into an outcrop of Brunner coal in the Paparoa Range. Subsequently, a small stream of AMD began flowing out of the adit with a mean flow rate of 1.5 L/min (0.025 L/s) with a SD of 0.7 L/min.

Compared to the chemistry of the Sullivan Mine AMD, the Pike River Adit AMD contains much lower acidity, slightly higher pH, and most significantly, much lower Al (Table 1). It is possible that these differences are due to different source rock lithologies. At the Sullivan Mine, the source of the Fe and sulphate in the AMD is mostly pyrite within mudstone that form the roof lithology over a significant portion of the mine and the Al is suspected as originating from feldspars within the sandstone units which are interbedded with the coal (Trumm et al. 2005). At the Pike River Adit, the walls, floor and ceiling of the adit are still located within the coal. It is likely that the source of the AMD is from oxidation of sulphides within the coal and the AMD flows out of the adit without contacting surrounding lithologies which could be a source of other elements such as Al.

### Blackball Mine

The underground Blackball Mine is located at the base of Paparoa Range, West Coast Region, New Zealand, not far from the Pike River Coal Field (Fig. 1). Coal deposits are contained within the BCM with coal thicknesses from 3 to 5 m, and pyrite is widely distributed as concretions in both the overlying Island Sandstone and the coal (Gage 1952).

The Blackball Mine operated from 1939 until it was abandoned in the mid 1960s. Currently, AMD with high concentrations of Fe and Al discharges from one of the lower entrances to the mine at an mean flow rate of 65 L/s with a SD of 33 L/s (Table 1) (Trumm & Gordon 2004). The AMD flows out onto a terrace approximately 12 m wide and 25 m long and 3 m above an adjacent creek (Ford Creek). During high flow, the entire terrace is inundated with AMD and three waterfalls mark the junction of the AMD with the creek.

### Remediation strategies

AMD is generated by oxidation of Fe sulphides present in coal and surrounding lithologies, which results in the dominant contaminant, Fe, being present in two oxidation states: ferrous iron (Fe<sup>2+</sup>) and ferric iron (Fe<sup>3+</sup>) (Singer & Stumm 1970; Caruccio et al. 1981). To remove Fe from AMD, this oxidation process can be encouraged to continue so that all Fe<sup>2+</sup> is oxidised to Fe<sup>3+</sup>, and as the pH is

increased during treatment, Fe is precipitated out of the AMD as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) or similar minerals. Alternatively, treatment can reverse the sulphide oxidation process, so that Fe and sulphate are reduced, forming the compounds  $\text{FeS}_2$ ,  $\text{FeS}$ , and  $\text{H}_2\text{S}$ , and this removes dissolved Fe and sulphate from the AMD (Rose & Cravotta 1998; Sexstone et al. 1999; Skousen et al. 2000). We refer to these two strategies as the oxidising and reducing remediation strategies, respectively (Trumm et al. 2003, 2005).

During AMD treatment by the oxidising remediation strategy, alkalinity is added by limestone dissolution, and dissolved oxygen (DO) is added by aeration of the AMD. Typical remediation systems that employ the oxidising strategy are open limestone channels (OLCs) (Ziemkiewicz et al. 1994), open limestone drains (Cravotta & Trahan 1999), limestone leaching beds (LLBs) (Black et al. 1999), slag leaching beds (SLB) (Simmons et al. 2002), and diversion wells (DWs) (Arnold 1991). OLCs and DWs typically require a steep topography in order to generate the necessary aeration and to prevent armouring of limestone by metal hydroxides, which can inhibit the dissolution of limestone (Ziemkiewicz et al. 1997).

During AMD treatment by the reducing remediation strategy, DO is stripped from the AMD using a system that creates an anaerobic environment, and alkalinity is added by limestone dissolution. After the pH is raised to neutral by the system, the water is aerated and any remaining Fe not already removed as sulphides precipitates as metal hydroxides. Typical remediation systems that employ the reducing strategy are anaerobic wetlands (Skousen et al. 2000; PIRAMID Consortium 2003; O'Sullivan 2005), anoxic limestone drains (ALDs) (Hedin & Watzlaf 1994), sulphate-reducing bioreactors (SRBRs) (Neculita et al. 2007), and successive alkalinity producing systems (SAPS) (Kepler & McCleary 1994), also known as vertical flow wetlands (VFWs) or reducing and alkalinity producing systems (RAPS) (Zipper & Jage 2001).

The choice of appropriate AMD treatment strategy and system type within the strategy is critical for treatment success. A comprehensive review of treatment system selection is provided by Trumm (2010). The choice between the two strategies is often based on the water chemistry (largely DO content and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio). For AMD which is highly oxidised (DO level at saturation and most Fe as  $\text{Fe}^{3+}$ ) the oxidising strategy is often most appropriate; for AMD with low DO and most Fe as  $\text{Fe}^{2+}$ , the reducing strategy is usually recommended. However, some reducing systems (such as RAPS and anaerobic wetlands) can be used to treat highly oxidised AMD under the right conditions (such as with longer residence times or constructed with thicker compost layers). Conversely, most oxidising systems can be used to treat highly reduced AMD if an oxidising component (such as a cascade) is added to the system. Therefore, if topography or available land area prevent use of the most appropriate strategy for a given AMD site, the

alternative strategy can sometimes be used if system parameters are modified.

To choose among the various systems within the oxidising and reducing categories, water chemistry should be considered. High concentrations of Fe ( $>10$  mg/L) can limit the use of some oxidising systems due to the armouring of limestone by precipitates that form during treatment. Similarly, high concentrations of Al ( $>25$  mg/L) can limit the use of some reducing systems due to plugging of pore spaces with precipitates.

At the Sullivan Mine AMD nearly all of the dissolved Fe is in the ferric state and the DO levels are near saturation. The surface topography near the AMD includes a large level area (approximately 1 ha) where a treatment system can be constructed. The AMD chemistry suggests that an oxidising strategy is appropriate (low  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios and high DO concentrations), however, given the land area available, and the relatively consistent flow rate, a reducing system may be more appropriate. The flow chart in Trumm (2010) suggests three potential systems for a site such as the Sullivan Mine AMD: a RAPS, an anaerobic wetland, or an SLB. In this study, we investigate the effectiveness of a RAPS in treating the Sullivan Mine AMD.

For the Pike River Adit AMD, with the exception of very low levels of Al and lower acidity, the chemistry is similar to the Sullivan Mine AMD. The flow rate is very low (about 2000 times less than that of the Sullivan Mine AMD) and surface area in the vicinity of the AMD is limited, with only the floor of the adit suitable for any treatment system. Similar to the Sullivan Mine AMD, high DO levels and low  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios suggest using an oxidising strategy, however flow rates and available land area suggest using a reducing strategy. The flow chart in Trumm (2010) suggests similar options for treatment as for the Sullivan Mine (RAPS, anaerobic wetlands, SLB). In this study, we investigate the effectiveness of a RAPS in treating the Pike River AMD.

The chemistry of the AMD from the Blackball Mine is similar to the Sullivan Mine AMD with the exception of Fe. The Blackball Mine Fe concentrations are only about one quarter of the Sullivan Mine concentrations. This is significant for determining appropriate treatment strategies. Iron typically hinders oxidising passive treatment systems by armouring limestone with Fe hydroxides which decreases dissolution rates (Ziemkiewicz et al. 1997), and by clogging passages in leaching beds which decreases permeability and, hence, decreases residence time (Watzlaf & Hyman 1995; Faulkner & Skousen 1996). Aluminium does not appear to armour limestone to the same degree and possibly can be effectively flushed from leaching beds (Hammarstrom et al. 2003; Hilton et al. 2003; Trumm et al. 2008). A second difference between Sullivan and Blackball Mine AMD is in the flow rate. At Blackball Mine, AMD flow rates vary from 36 to 101 L/s and appear to be influenced by precipitation events (Trumm & Gordon 2004). At Sullivan, a relatively

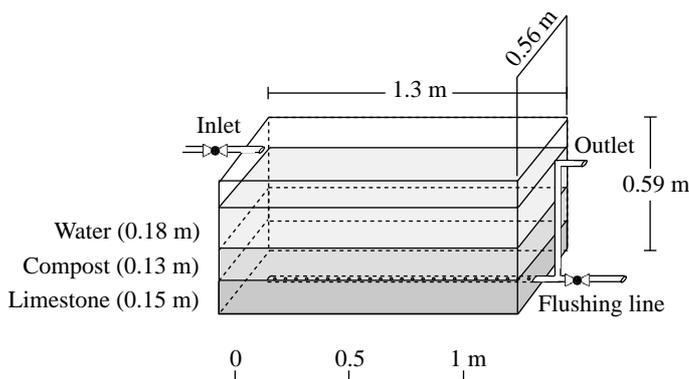
stable flow rate is easy to control in a reducing system such as a RAPS. At Blackball, a highly variable flow rate can be useful to help flush precipitates that have built up in an oxidising system.

The land area available for a treatment system at Blackball Mine includes a small flat area adjacent to the adit (25 m long by 15 m wide), a long narrow sloping strip of land along Ford Creek (500 m long by 2 m wide) and a large flat area about 0.5 km downstream (approximately 3 ha). With this land area and AMD chemistry, the flow chart in Trumm (2010) suggests treatment with OLCs, limestone sand dosing, LLBs, SLBs, VFWs or anaerobic wetlands. In this study, we investigate the effectiveness of an LLB in treating the Blackball Mine AMD by conducting a laboratory column leaching experiment.

## Methods

### *Sullivan Mine passive treatment system*

A small-scale RAPS was constructed at the Sullivan Mine site using a plastic tub 1.3 m long by 0.56 m wide and 0.59 m high. Limestone gravel (from Karamea, West Coast) was placed at the base at a thickness of 15 cm and covered by 13 cm of spent mushroom compost and 18 cm of water (Fig. 2). Typical RAPS are designed with 13–30 cm compost underlain by 0.5–1 m limestone (Kepler & McCleary 1994), although Watzlaf et al. (2003) suggest compost thicknesses between 15 and 60 cm and Demchak et al. (2001) suggest at least 50 cm of compost. As our tub was only 0.59 m high, we chose the minimum compost thickness and since the trial was only a short duration experiment, we did not need a thick layer of limestone. AMD entered the system through a PVC pipe placed on top of the RAPS and the flow rate was regulated with a ball valve. Treated water exited the system through a



**Fig. 2** Schematic of RAPS at Sullivan Mine and Pike River Adit. Water entered the unit at the top and flowed vertically downward to a perforated drain and exited the system through a standpipe to maintain the water level. A drain was at the base for vertical flushing capability. The flow rate was controlled by a ball valve at the inlet.

perforated PVC pipe buried in the limestone layer and connected to an external PVC pipe with the outlet near the level of the top of the tub. This method of discharge ensured that sufficient water was always above the compost layer for the RAPS to remain anaerobic.

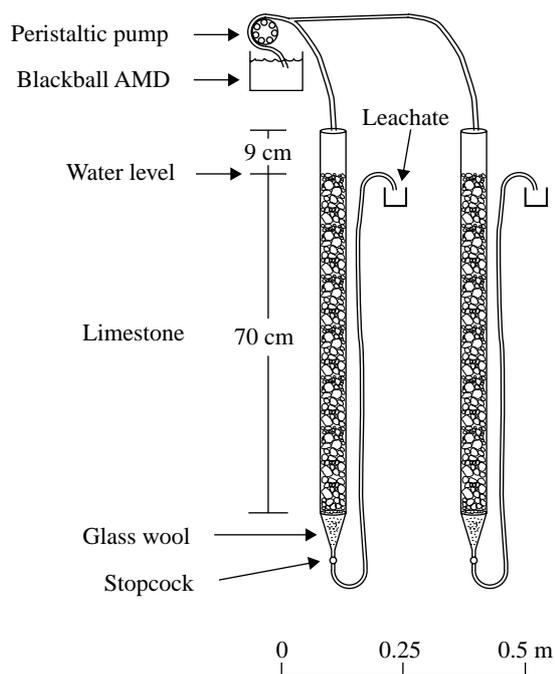
The trial was conducted over 38 days. Sampling events were conducted weekly from both the inlet and outlet to the system. As no controls were used in the trial, any improvement in water quality was assumed to be due to performance of the RAPS system. Flow rates were determined during each sampling event by measuring the volume of water collected in a calibrated container (100 mL, 500 mL, or 1000 mL) over 1 min. The measurement was repeated three times and averaged. Residence time of the AMD in the system was determined for each sampling event by dividing the capacity of the system by flow rate and assumed no short circuiting of flow. Only the residence time in the limestone layer was used for calculations (Watzlaf, et. al 2003). Due to slow build up of Fe deposits on the inlet valve during the duration of the trial, flow rate decreased over the 38 days, resulting in longer residence times.

### *Pike River Adit passive treatment system*

A small-scale RAPS was constructed at the Pike River Adit using the same design and dimensions as at the Sullivan Mine (Fig. 2). The system operated for a period of 151 days. Sampling events were conducted monthly from both the inlet and outlet to the system. Flow rates and residence times were determined as for the Sullivan Mine trials. As with the Sullivan RAPS unit, build up of Fe deposits on the inlet valve resulting in lower flow rates as the experiment progressed.

### *Blackball Mine laboratory experiments*

To test the effectiveness of treating the Blackball AMD with limestone, and to simulate a LLB oxidising treatment system, a column leaching experiment was conducted. In this experiment, the AMD water was passed through a glass column filled with limestone gravel and the collected leachate was monitored for treatment effectiveness (Fig. 3). The column was 79 cm long with a diameter of 5.2 cm and a tapered tap 10 cm long fitted with a glass stopcock. The column was filled to within 9 cm of the top with limestone ranging in size from 5 to 20 mm in diameter. This design was not modelled off any particular system but was derived by the authors. The limestone was sourced from Karamea on the West Coast and had been rinsed in distilled water to remove any contaminants. AMD was passed vertically downward through the column at a rate of 3.0 mL/min continuously for a period of nine days (216 h) using a peristaltic pump. Assuming a porosity of 0.5, the residence time of AMD within the column was approximately 4 h. The experiment was duplicated with a second



**Fig. 3** Schematic of Blackball AMD column experiment. The AMD was passed downward vertically through two duplicate columns filled with limestone at a rate of 3.0 mL/min over 9 days.

column. As no controls were used in the experiment, any improvement in water quality was assumed to be due to treatment from the limestone in the columns. The experiment was conducted in Greymouth, West Coast. Leachate samples were analysed daily for pH, conductivity, temperature, and DO and on days 1, 4, and 9, samples were submitted for laboratory analysis.

#### Analytical methods

For all three sites, field parameters pH, conductivity, temperature, and DO were determined using a WTW Multiline P4 probe. Ferrous iron was analysed immediately upon collection using Hach Method 8146 (1,10 Phenanthroline Method) and concentrations determined through absorbance using a Hach DR/2400 Portable Spectrophotometer or a Merck SQ300 Spectrophotometer. Samples collected from the untreated AMD and the outlet to each system were laboratory-analysed for hot acidity and dissolved Al, Fe, Mn, Ni and Zn using ICP-MS at Hill Laboratories according to American Public Health Association (APHA) Methods 2310B and 3125B (APHA 1998). For the Blackball column experiment samples were also analysed for sulphate and Ca according to APHA Methods 4500E and 3111B. Samples were filtered in the laboratory using a 0.45 µm filter (APHA Method 3030B).

Treatment system performance is evaluated by comparing total metal loading rates into each system with the metal load in effluent leaving each system. Metal load is expressed as moles of dissolved metals per m<sup>3</sup> of treatment

substrate per day and is calculated using the following formula:

$$\text{Metal load (mole/m}^3\text{/day)} = (C)(\text{amu})(Q)/V$$

where C is dissolved metal concentration in mg/L, amu is molecular weight in moles/mg, Q is the flow rate in L/day, and V is the volume of treatment system in m<sup>3</sup>.

## Results

### Sullivan Mine passive treatment system

The concentration of DO in the outlet to the RAPS decreased throughout the field trial and by day 22 of the experiment, over 90% of the Fe was in the reduced Fe<sup>2+</sup> state, indicating that reducing conditions were being achieved in the system (Fig. 4A). The pH in treated AMD reached 5.8 after the first week of operation at a residence time of 2 h, and at residence times of 4 h and above, the pH reached neutral (Fig. 4B).

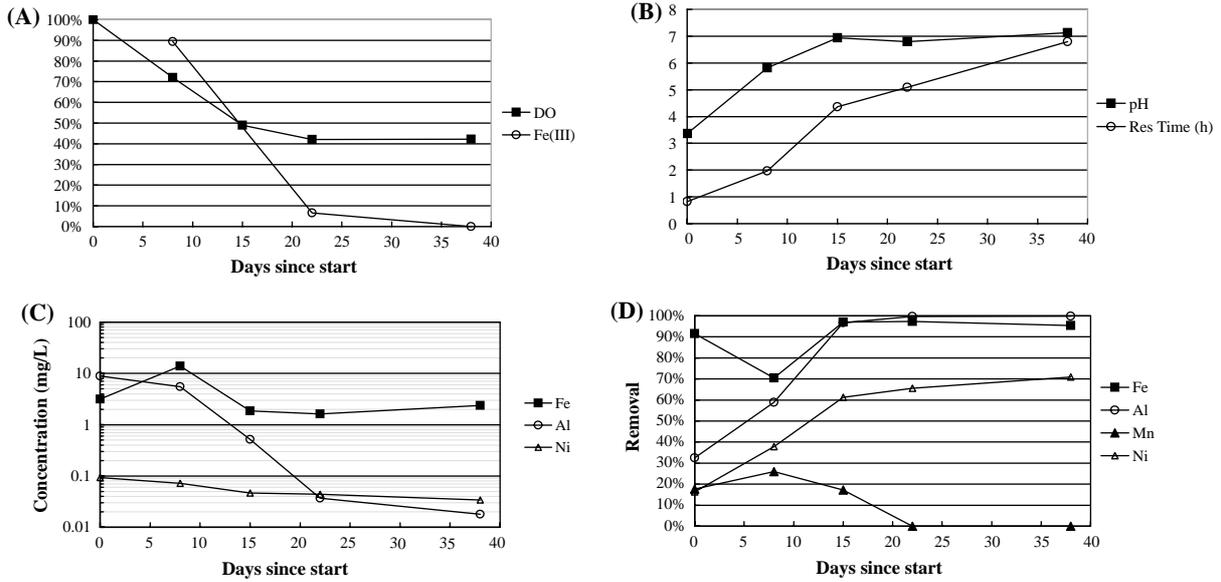
The concentrations of Fe and Al were significantly lower in the outlet from the RAPS throughout the duration of the field trial, and all contaminants, with the exception of Mn, were effectively removed by the RAPS (Fig. 4C, 4D). At a residence time of only 5 h in the limestone layer (day 22), the levels of Fe were reduced by 97%, Al by 100%, and Ni by 66%.

### Pike River Adit passive treatment system

Results from the field trial show that the concentration of DO was lowered by the RAPS and that the percent of Fe in the Fe<sup>3+</sup> state was less in treated water compared to the AMD, indicating that reducing conditions were present in the RAPS (Fig. 5A). The pH in treated AMD remained neutral throughout the duration of the trial at residence times as low as 5 h (Fig. 5B). Similar to the Sullivan Mine AMD trial, concentrations of Fe and Al were significantly lowered by the RAPS, and all contaminants, with the exception of Mn after 2 months, were removed (Fig. 5C, 5D). By day 58, at a residence time of 15 h in the limestone layer, the system was reducing the levels of Fe by 99%, Al by 96%, Ni by 95%, and Mn by 51% (although later there was a net export of Mn).

### Blackball Mine laboratory experiments

Successful neutralisation of acidity and removal of metals was achieved through treatment of the AMD with limestone in the laboratory column experiment. The pH of the leachate ranged from 7.18 to 7.65 in column 1, and from 7.18 to 7.60 in column 2 during the duration of the experiment. Acidity was replaced with net alkalinity (285–359 mg/L as CaCO<sub>3</sub> alkalinity generated) and Ca concentrations were elevated in the leachate, although effective neutralisation showed a decrease over the duration of the experiment (Fig. 6A). Iron, Al, Mn and Zn concentrations were reduced in the



**Fig. 4** Effluent data from the RAPS at Sullivan Mine. (A) Dissolved oxygen and percentage of Fe in the ferric state. (B) Residence time and pH. Longer residence times equate to better treatment performance. (C) Dissolved Fe, Al and Ni concentrations. (D) Percentage of metal removal from AMD by system. Performance was best after day 15 (above residence times of 4 h).

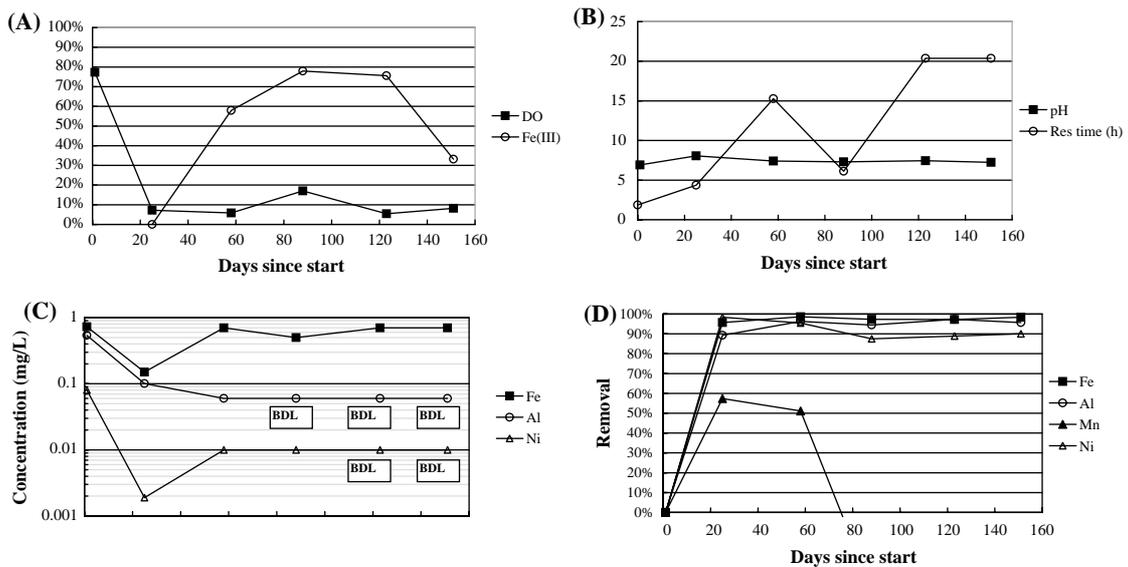
leachate relative to the AMD (Fe 87%, Al 91%, Mn 21% and Zn 68%), but Ni concentrations were slightly elevated in the leachate from both columns (Fig. 6B).

**Discussion**

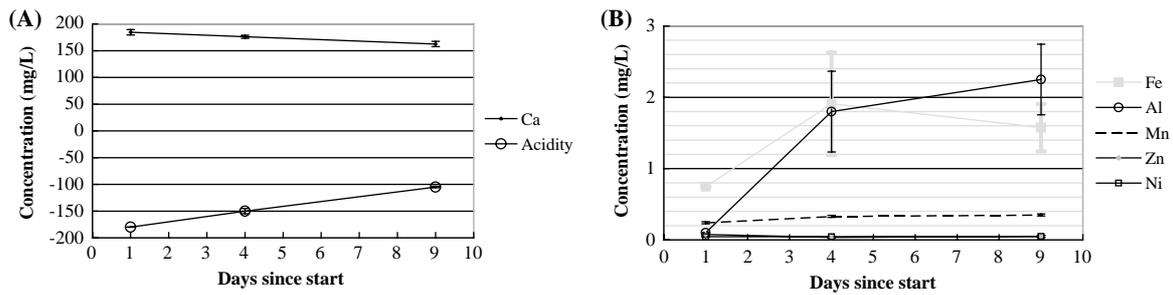
**Sullivan Mine and Pike River Adit RAPS**

The results of the Sullivan Mine and Pike River RAPS trials can be compared to a RAPS trial at the Herbert Stream

at the Stockton Mine, West Coast Region, New Zealand (Fig. 1) (Trumm et al. 2008). Three different evaluation methods can be used to compare the results: metal removal rate per unit volume of system, minimum residence time to achieve neutral pH, and net alkalinity generated versus residence time. The dominant method of metal removal in RAPS units is through sulphate and Fe reduction, similar to that of SRBRs. Wildeman et al. (2006) suggest designing SRBRs with a metal removal rate of 0.3 mole metals/m<sup>3</sup>



**Fig. 5** Effluent data from the RAPS at Pike River Adit. (A) Dissolved oxygen and percentage of Fe in the ferric state. (B) Residence time and pH. (C) Dissolved Fe, Al, and Ni concentrations. (D) Percentage of metal removal from AMD by system. The pH was raised to neutral and Fe, Al, and Ni were removed from the AMD throughout the trial.



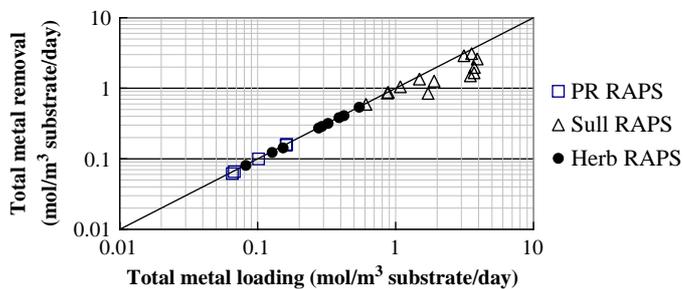
**Fig. 6** Effluent data from the Blackball laboratory column experiment. Means for 2 columns are shown with 1 SD error bars. **(A)** Acidity and Ca in the leachate. Acidity was replaced with net alkalinity and calcium was elevated in leachate due to dissolution of limestone. **(B)** Dissolved Fe, Al, Mn, Zn and Ni in the leachate.

substrate/day. Our results show that consistent removal can be achieved at rates of 1 mole metals/m<sup>3</sup> substrate/day (Fig. 7). Metal loading rates from AMD into the Pike River RAPS ranged from 0.07 to 0.16 mole metals/m<sup>3</sup>/day with 94% to 99% of these loads removed by the system. For the Herbert Stream, metal loading rates from AMD into the RAPS ranged from 0.08 to 0.55 mole metals/m<sup>3</sup>/day with removal of these loads ranging from 93% to 98% (Al 99%, Fe 91%, and Zn 70% at a residence time of 1.5 h in limestone layer). Maximum metal removal rate by the Herbert Stream RAPS was 0.54 mole metals/m<sup>3</sup>/day, nearly double the design recommendations of 0.3 mole metals/m<sup>3</sup>/day for SRBRs by Wildeman et al. (2006). At Sullivan Mine, metal loading rates from the AMD were much higher, ranging from 0.61 to 3.9 mole metals/m<sup>3</sup>/day with removal of these loads ranging from 43% to 99%. The maximum metal removal rate by the Sullivan Mine RAPS was 3.09 mole metals/m<sup>3</sup>/day, which was an order of magnitude greater than design recommendations. Greater than 90% removal of total metal loads was consistently achieved at loading rates below 1.49 mole metals/m<sup>3</sup>/day. McCauley et al. (2010) show sufficient removal in SRBRs in a laboratory trial at rates up to 0.8 mole metals/m<sup>3</sup>/day. The results from our trials suggest that the literature-recommended design rate

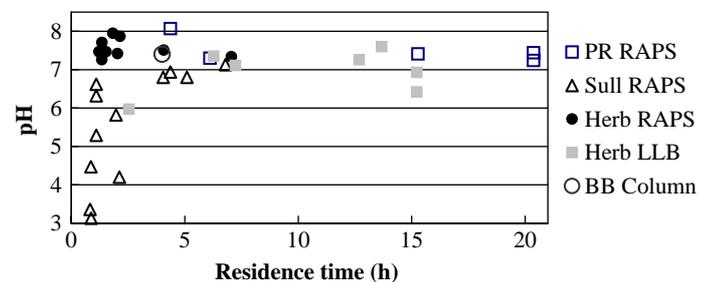
may be conservative and that rates of up to 1 mole total metals/m<sup>3</sup>/day can be achieved in RAPS cells.

A common suggested design criteria for RAPS units is 15 h of residence in the limestone layer to ensure dissolution of limestone is adequate to neutralise the pH (Watzlaf et al. 2003). In our second evaluation method, a comparison of residence times and resulting pH shows that residence times as low as 6 h in all three RAPS were sufficient to achieve a neutral pH (Fig. 8). At sites with low acidity such as Herbert Stream (90 mg/L, Trumm et al. 2008), residence times as low as 1.2 h achieved neutral pH. All RAPS units performed slightly better than an LLB at Herbert Stream, likely because some pH adjustment occurs in the compost layer of these units as metals are reduced, and residence within the compost layer is not included in this comparison. These data suggest that rather than using the conservative literature-recommended residence time of 15 h, a site-specific residence time can be determined through field trials, which may be significantly less. Lower residence times equate to smaller systems for a given flow rate, and hence, lower treatment cost. It is likely that differences in residence time relate to reactivity of limestone from different sources.

A third way to compare performance of the systems is to note net alkalinity generation as a function of residence time



**Fig. 7** Total metal loading rates (moles of dissolved metals/m<sup>3</sup> treatment substrate/day) in the influent to RAPS systems at three sites (Pike River Adit, Sullivan Mine, Herbert Stream) compared to metal load in effluent. Dashed line indicates 100% removal of total metal load. Near 100% removal was achieved in all three systems below about 1 mole of metals/m<sup>3</sup> treatment substrate/day. PR, Pike River Adit; Sull, Sullivan Mine; Herb, Herbert Stream.



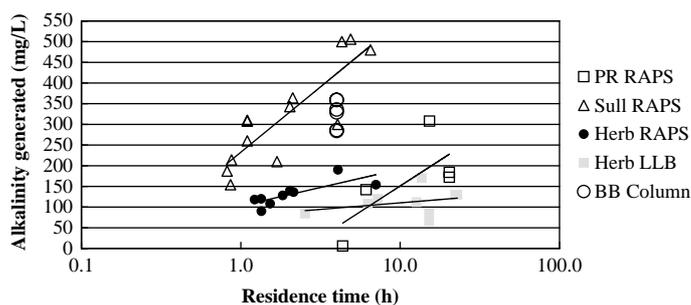
**Fig. 8** Effluent pH from the three RAPS systems (at Pike River Adit, Sullivan Mine, and Herbert Stream), from the Herbert Stream LLB and from the Blackball column experiment compared to residence time in each system. All five systems raised pH to neutral above residence times of 6 h. PR, Pike River Adit; Sull, Sullivan Mine; Herb, Herbert Stream; Herb LLB, Herbert Stream limestone leaching bed; BB Column, Blackball column experiment.

(Fig. 9). The relationship is logarithmic, indicating that the most rapid alkalinity generation occurs in the first few hours and that the rate of limestone dissolution slows with time likely as water reaches saturation with respect to calcite (Rose 1999). This relationship was also noted by Jage et al. (2001) in a review of five SAPS cells in West Virginia. Net alkalinity generation rates in our RAPS units were greatest at Sullivan Mine followed by Herbert Stream and Pike River. The slope of trend lines fitted to the data are much steeper for the Sullivan Mine and Pike River than for the Herbert Stream RAPS and LLB, showing that alkalinity generation is much more sensitive to residence time in these systems. This is likely due to the much higher acidity and lower pH at the Sullivan Mine and Pike River compared to the Herbert Stream, which can result in faster limestone dissolution rates, and therefore a strong response to increases in limestone contact residence times. Jage et al. (2001) noted a similar positive relationship between influent acidity and net alkalinity generation and attributed this in part to the higher solubility of calcite under acidic conditions.

Based on the promising results of the field trials and the land area available in the vicinity of the Sullivan Mine and Pike River Adit AMD sites, full-scale RAPS designs have been prepared. The system for the Pike River Adit has subsequently been installed and is operating well.

#### Blackball Mine Laboratory experiments

Restoration of pH in the Blackball experiment was similar to the Herbert Stream and Pike River RAPS and slightly better than the Sullivan Mine RAPS and an LLB which was trialled at the Herbert Stream site (Fig. 8) (Trumm et al. 2008). Alkalinity generation was very similar to the Sullivan Mine RAPS, exceeding all the other systems, because the acidity levels are nearly identical, and alkalinity generation



**Fig. 9** Net alkalinity generation according to residence time for the three RAPS systems (at Pike River Adit, Sullivan Mine, and Herbert Stream), from the Herbert Stream LLB and from the Blackball column experiment. Trend lines are shown for each data set. Sullivan Mine RAPS showed the highest alkalinity generation rates, followed by the Blackball experiment, the Herbert Stream RAPS, the Pike River RAPS and the Herbert Stream LLB. PR, Pike River Adit; Sull, Sullivan Mine; Herb, Herbert Stream; Herb LLB, Herbert Stream limestone leaching bed; BB Column, Blackball column experiment.

is related to influent acidity (Fig. 9) (Jage et al. 2001). As the experiment was only conducted over a nine day period, and alkalinity generation declined over the nine days, it is likely that long-term performance may more closely resemble that of the LLB. Iron and Al were likely removed as metal oxyhydroxide precipitates, Mn as Mn oxide precipitates or through adsorption onto reactive Fe oxyhydroxide surfaces (Rose & Cravotta 1998), and Zn through adsorption onto reactive Fe oxyhydroxide surfaces (Bostick et al. 2001).

The laboratory column leaching experiment suggests that a simple limestone-based treatment system utilising an oxidising strategy (such as an OLC or LLB) can be effective at removing acidity, reducing the concentration of metals, and producing net alkalinity. With the land area available, an LLB could be constructed on the terrace area near where the AMD originates, followed by an OLC along Ford Creek and finished with another LLB. However, as the experiment was only nine days long, we recommend that experiments with longer duration are conducted prior to scale-up design and construction.

#### Summary of recommended evaluation criteria for small-scale systems

This work provides insight into the usefulness of small-scale passive treatment systems prior to investment in full-scale passive treatment. During operation of small-scale systems, several different flow rates (and therefore, residence times) should be trialled. In evaluating systems, metal loading and removal rates per unit volume of treatment system can provide valuable information on system metal removal limits. Net alkalinity generation rates and pH attained compared to residence time is used to determine neutralisation effectiveness of treatment systems and is crucial information for full-scale design.

#### Conclusions

All three AMD sites (Sullivan Mine, Pike River Adit and Blackball Mine) contain elevated Fe (10.6–47 mg/L) and Al (1.6–14.1 mg/L) and minor concentrations of Mn, Ni and Zn. Each AMD is oxidised with the majority of Fe as  $\text{Fe}^{3+}$  and DO levels near saturation, suggesting an oxidising remediation strategy may be appropriate. Available land area for the Sullivan Mine and Pike River Adit, however is more amenable to a reducing-type system.

The results of RAPS small-scale trials at the Sullivan Mine and Pike River Adit show that this reducing system is effective at removing metals, generating alkalinity and raising pH and is an appropriate solution to the AMD at these sites. Metal removal rates at the Sullivan Mine RAPS (at a residence time of only 5 h) were: Fe (97%), Al (100%) and Ni (66%). Metal removal rates at the Pike River Adit RAPS (at a residence time of 15 h) were: Fe (99%), Al (96%) and Ni (95%). These results are comparable to previous

RAPS results from Herbert Stream (Fe 91%, Al 99% and Zn 70% at a residence time of 1.5 h in the limestone layer).

The results of a limestone column leaching experiment on the Blackball AMD suggest that an oxidising system such as an OLC or LLB may be appropriate for the site. Metal removal rates (at a residence time of 4 h) were: Fe 87%, Al 91%, Mn 21% and Zn 68%, similar to the previous LLB results from Herbert Stream. Net alkalinity was generated and the pH was restored to neutral.

Field trials should continue to be used to test the effectiveness of different treatment strategies to reduce the level of contaminants at AMD sites. The results of trials, in conjunction with an evaluation of AMD chemistry, flow rates, available land area and surface topography are useful when designing full-scale remediation systems.

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