

Using pilot trials to test geochemical treatment of acid mine drainage on Stockton Plateau

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Abstract Herbert Stream, a tributary of the Waimangaroa River on the Stockton Plateau, South Island, New Zealand, has elevated metal concentrations (Al 7.68 ppm, Fe 1.37 ppm, Mn 0.69 ppm, and Zn 0.12 ppm) and low pH (2.3–3.4) characteristic of acid mine drainage. Average flow rate is 5.3 L/s. To determine the effectiveness of different geochemical treatment strategies, small-scale trials consisting of a reducing and alkalinity producing system (RAPS), a limestone leaching bed (LLB), and an open limestone channel (OLC) were operated for 8 months. All three trial systems performed well, removing metals and raising pH. Maximum removal rates were: Al 99% (all three systems); Fe 97% (RAPS), 99% (LLB), and 95% (OLC); Mn 95% (RAPS), 92% (LLB), and 74% (OLC); and Zn 87% (RAPS) and 91% (LLB). The OLC was less effective than the other trial systems in raising pH, and the effectiveness of Al removal decreased with time, probably due to armouring of the limestone by hydroxide precipitates. Minimal armouring of the limestone in the RAPS and LLB occurred, and the RAPS was successful at reducing oxidised Fe to Fe monosulfides (most likely mackinawite). Based on monitoring of the trial AMD treatment systems, a full-scale LLB was designed to treat the entire flow of Herbert Stream.

Keywords acid mine drainage; vertical flow wetlands; limestone leaching beds; passive treatment; Stockton Plateau

INTRODUCTION

Oxidation of sulfide minerals in waste related to mining produces acid mine drainage (AMD), which can have large downstream environmental impacts (Eary 1999; Nordstrom & Alpers 1999; Ezpana et al. 2005). In New Zealand's South Island, West Coast coal measures can produce acidic drainage when disturbed by mining activities (Black et al. 2005).

AMD typically has low pH and high concentrations of Fe and sulfate. Other common constituents of West Coast AMD include the metals Al, Mn, Ni and Zn. The composition of AMD often reflects the mineralogical assemblage within the coal measures (Rose & Cravotta 1998).

The Brunner Coal Measures on the West Coast produce the greatest amount of AMD in New Zealand. Pope et al. (2006) hypothesise that this is likely due to the depositional and diagenetic history of the coal beds. The effects of AMD on the aquatic ecosystem in New Zealand can be severe, often resulting in an absence of fish, crayfish, and eels and the presence of only acid-tolerant algae and occasional invertebrate taxa (Winterbourn 1998; Harding & Boothryd 2004; Harding 2005).

Although there have been many studies in New Zealand on the effects of AMD on the environment, and on the geochemistry of AMD (e.g., Lindsay et al. 2003; Hughes et al. 2004; Pope et al. 2006), few studies have focused on treatment. In other parts of the world, research demonstrates that, in the long term, treatment of AMD using passive treatment systems is typically more economic than using active treatment systems (Skousen & Ziemkiewicz 2005), especially after mine closure. Passive systems typically rely on natural geochemical and biological processes to neutralise AMD and precipitate metals out of solution.

There are many types of passive treatment systems. Open limestone channels (OLCs) are systems in which limestone is placed along the sides and bottom of culverts, ditches, or stream channels (Ziemkiewicz et al. 1994). Diversion wells (DWs) are chambers filled with limestone chips (Arnold 1991). OLCs and DWs typically require a steep topography in order to prevent armouring of limestone by metal hydroxides that precipitate during AMD neutralisation and can inhibit dissolution (Ziemkiewicz et al. 1997). Anoxic limestone drains (ALDs) are buried trenches filled with limestone gravel (Hedin & Watzlaf 1994). Under anoxic (low dissolved oxygen) conditions, the limestone does not coat or armour with Fe hydroxides. Reducing and alkalinity producing systems (RAPS) are a combination of an ALD and an organic substrate, and are also known as vertical flow wetlands (Kepler & McCleary 1994; Zipper & Jage 2001). Sulfate reduction and metal sulfide precipitation can occur in the compost material while the underlying limestone adds alkalinity to the AMD. These systems require that the AMD remain in the system long enough for reduction reactions to occur. In anaerobic wetlands, water is passed through organic-rich substrates, and dissolved metals are reduced (Skousen et al. 2000; O'Sullivan 2005). Some wetlands may have a layer of limestone at the base to increase pH.

In this study, pilot trials were constructed at Herbert Stream, an AMD site on the Stockton Plateau, West Coast, to test the effectiveness of passive geochemical treatment. Site parameters were first evaluated to determine which systems to trial, and the results of the trials have been used to design a full-scale passive treatment system for the site.

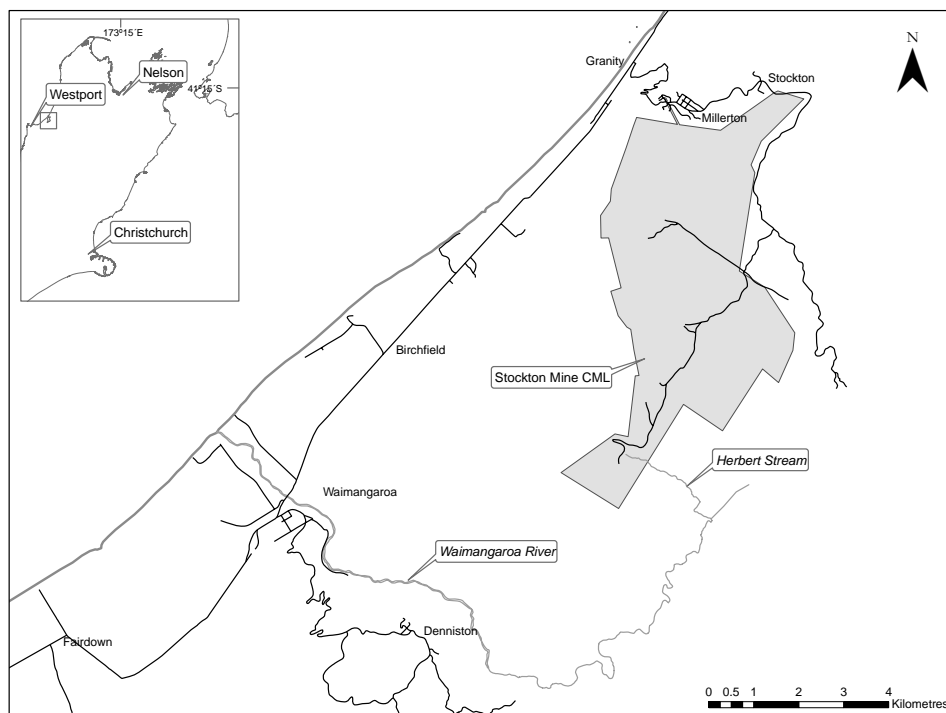


Fig. 1 Location of study site. Herbert Stream flows southeast c. 1.8 km from the Stockton opencast coal mine to join the Waimangaroa River, which flows south and west to the Tasman Sea. CLM, coal mining license.

Site description

The study site, Herbert Stream, is located at New Zealand Map Grid E2415196 and N5944126 (41.704086 lat., 171.861035 long.) at an elevation of 920 m near the Mt Frederick block of the Solid Energy opencast Stockton Mine, Stockton Plateau, West Coast (Fig. 1). Economic coal in this area is associated with the Eocene Brunner Coal Measures, which are dominated by sandstones interlayered with siltstones, mudstones, carbonaceous mudstones, and coal seams. The Brunner Coal Measures unconformably overlie the Paleozoic–Cretaceous Greenland Group, a greywacke and argillite turbidite sequence, and are overlain by and interfinger with the Eocene Kaiata Mudstone Formation (Flores & Sykes 1996; Nathan 1996). The sequence is locally intruded by granite and porphyry. The Brunner Coal Measures contain a variable percentage of sulfur (<1–7%) and average 1.37% for the Stockton Mine. Pyritic sulfur is typically 95% of total sulfur, and pyrite morphology includes both euhedral and framboidal forms, although larger nodules and dendritic pyrite also occur (Weber et al. 2008). Due to the lack of carbonate minerals in the Brunner Coal Measures, the acid neutralising capacity is <1 kg H₂SO₄/t and drainage through discarded overburden material from mining is typically acidic.

The headwaters valley for Herbert Stream was buried with overburden from opencast mining at Stockton (Fig. 2). The stream now emerges from the base of the overburden dump and flows c. 1.8 km southeast to the Waimangaroa River, which flows south and west c. 20 km to join the Tasman Sea.

Site evaluation and remediation goals

Before construction and during operation of trial remediation systems, data were collected from the site to determine flow rates and general water chemistry. The flow rate in Herbert Stream ranged from 2.3 to 26.6 L/s and averaged 5.3 L/s (Fig. 3). High flow rates occurred over very brief time periods, likely correlated with rainfall. For example, the flow rate only

Table 1 Analytical results for Herbert Stream. Values are averages of nine analyses over an 8-month period.

Parameter	Units	Herbert Stream
pH		2.8–3.4
Dissolved oxygen	mg/L	9.4
Acidity	mg CaCO ₃ /L	90.5
Sulfate	g/m ³	133.5
Dissolved Al	g/m ³	7.68
Dissolved Fe	g/m ³	1.37
Dissolved Mn	g/m ³	0.69
Dissolved Zn	g/m ³	0.119

exceeded 6 L/s 10.2% of the time, 7 L/s 3.8% of the time, 8 L/s 2.2% of the time, 9 L/s 1.1% of the time, and 10 L/s 0.4% of the time. The dominant contaminants in the Herbert Stream AMD are Fe and Al, with Al concentration being more than three times the Fe concentration (Table 1).

The majority of surface water impacted from mining on the Stockton Plateau flows into the Ngakawau River (Lindsay et al. 2003). However, some impacted water, such as the Herbert Stream, flows into the Waimangaroa River. Solid Energy have committed to maintaining the water quality of the Ngakawau River at a pH ≥ 4.7 with dissolved Al concentrations no greater than 1 mg/L 99% of the time by 2010 (Weber et al. 2007). By default, these same goals have been applied to the Herbert Stream. It is anticipated that this water quality will enable restoration of the aquatic macro-invertebrate community.

MATERIALS AND METHODS

A flow chart specific to New Zealand for selecting treatment systems based on water chemistry and available land area (Trumm 2007) was used to identify systems to trial based on initial water quality results for Herbert Stream. Three trial

Fig. 2 Photo of the headwaters of Herbert Stream, taken from helicopter looking to the southwest. Scale approximate. Overburden from opencast mining was placed in the headwaters valley and Herbert Stream now emerges from the base of the overburden dump. The small-scale trials are visible in the photo.

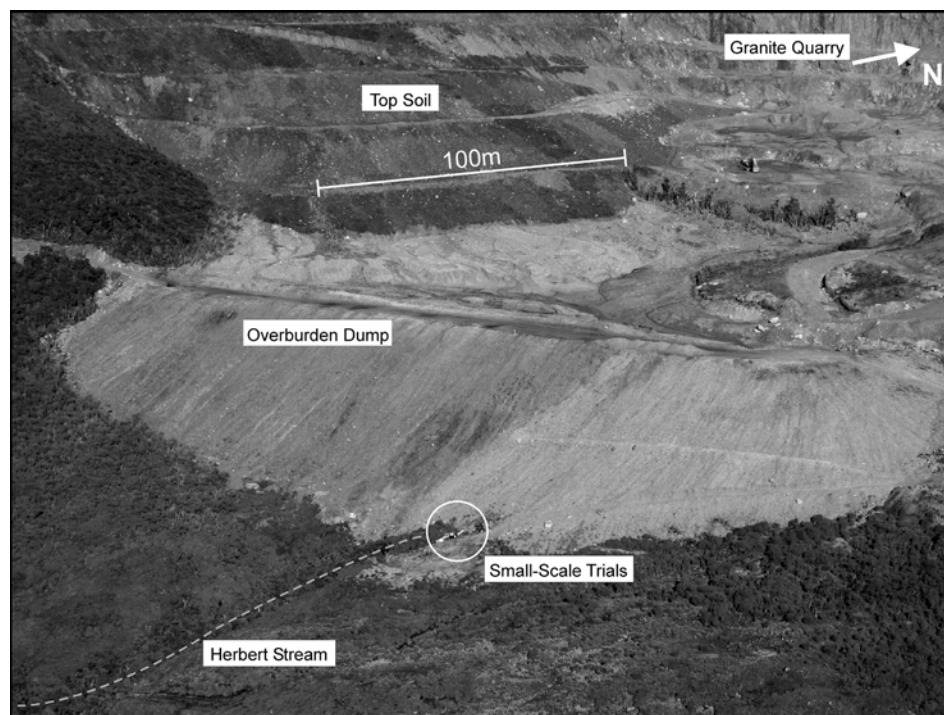
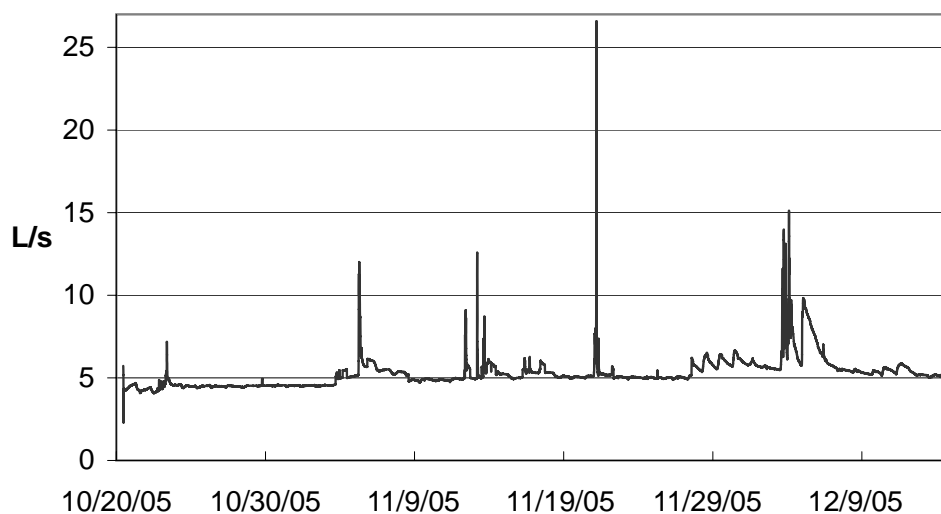


Fig. 3 Flow rate in Herbert Stream. High flow rates occur only over brief time periods and likely correlate with precipitation events.



systems were constructed: an OLC, a RAPS, and a limestone leaching bed (LLB). The OLC and RAPS were designed based on previous successes with small-scale systems (Trumm et al. 2005, 2006). The LLB was based on a design by Hellier (2000) for a similar system in the eastern USA.

The systems were constructed out of low-budget materials such as PVC piping, plastic tubs, valves, and tarpaulins. The OLC and LLB contained only limestone as the treatment media; the RAPS contained both limestone and compost. The limestone was sourced from Karama Lime, in Karama, West Coast, and the compost was obtained from a local garden centre. The limestone is moderately well recrystallised and therefore of very low permeability, and consists of approximately 90% CaCO_3 (Paul Weber, Solid Energy, pers. comm.). For particle size, in the RAPS and LLB, 76.2% of the limestone passed the 26.5 mm sieve and not the 12.7 mm

sieve, and in the OLC the average size of the limestone was 80 mm diameter. The compost was spent mushroom compost, residual compost waste generated by mushroom production, and consisted of chicken manure and straw.

The OLC was 2.7 m long, 0.5 m wide, with a thickness of 15–20 cm of limestone rocks (Fig. 4). The RAPS container was 1.2 m long, 0.73 m wide, and 0.54 m high. A limestone layer was placed at the base of the RAPS at a thickness of 12 cm, overlain by mushroom compost at a thickness of 30 cm and standing water of 8 cm. Although scaled down, this RAPS differed significantly from the recommended full-scale design of 1 m of standing water over 0.15–0.30 m of organic compost, underlain by 0.5–1.0 m of limestone (Kepler & McCleary 1994). The LLB container was 1.2 m long, 0.73 m wide, and 0.54 m high and was filled with limestone to a thickness of 45 cm. Piping and valves were placed to ensure

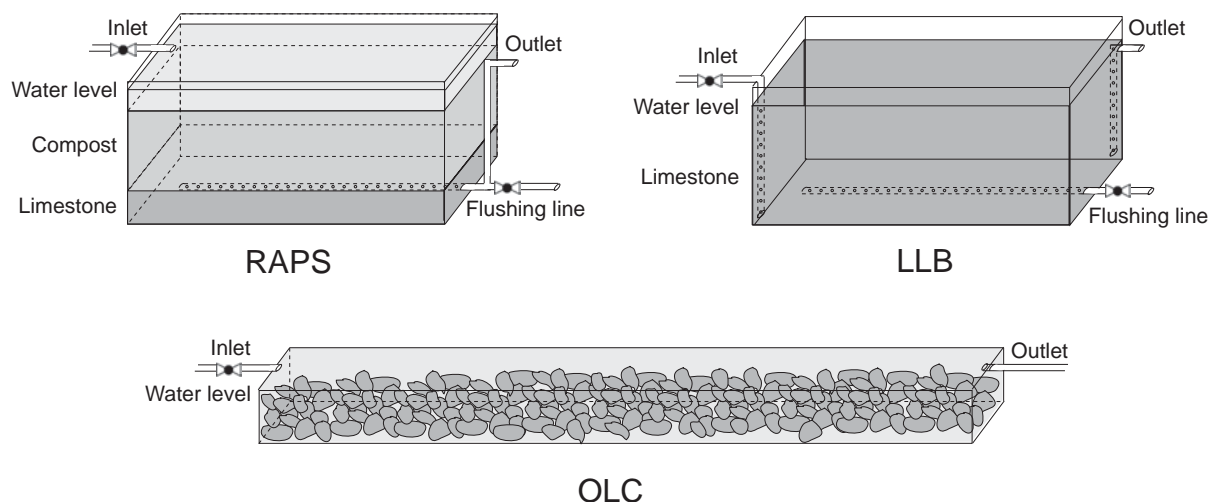


Fig. 4 Schematic of experimental setup. The RAPS consisted of a layer of limestone overlain by spent mushroom compost. Water entered the unit and flowed vertically downward to a drain. The LLB consisted of a bed of limestone. Water entered the unit on one side through a perforated pipe and flowed horizontally to a perforated pipe on the other side of the unit. Both the RAPS and LLB had a drain at the base for vertical flushing capability. The OLC consisted of a channel filled with limestone cobbles. The flow rate to each system was controlled by a ball valve at the inlet. OLC, Open limestone channel; LLB, limestone leaching bed; RAPS, reducing and alkalinity producing system.

evenly distributed horizontal flow of AMD through both the OLC and the LLB and vertical downward flow through the RAPS.

Flow rate in Herbert Stream was determined using a datalogger (type WT-HR 64K), which measured water height behind a V-notch weir on a 15 min basis. Piping was placed in the AMD where the water emanates from the overburden dump to convey water to the trial systems. Flow to the systems was regulated using ball valves. On several occasions during operation, suspended sediment in the AMD partially blocked the valves and reduced the flow rates, necessitating readjustment. To minimise this problem, we suggest that future trials should include a header pond to allow suspended sediment to settle out of solution before passing AMD through the ball valves. Flow rates were determined for each system during each sampling event by measuring the volume of water collected in a calibrated container (100, 500, or 1000 ml) over 1 min. The measurement was repeated three times for each system and averaged. Residence time of the AMD in each system was determined for each sampling event by dividing the capacity of the system by flow rate and assuming no short circuiting of flow. System capacities for the LLB and RAPS were measured by filling each system to capacity and flushing the water to a holding tank for measurement. Capacity for the OLC was estimated by measuring the dimensions of the water-filled channel and assuming a porosity of 50%.

The systems were operated over an 8-month period. Water samples from the inlet and outlet of the LLB and RAPS were collected on nine occasions and from the outlet of the OLC were collected on five occasions and laboratory analysed for hot acidity, alkalinity, sulfate, and total and dissolved Ca, Al, Fe, Mn, As, and Zn according to APHA Methods 2310B, 2320B, 4500-SO₄-G, 3030E, and 3125B (APHA 1998). Samples for dissolved metal analyses were filtered in the laboratory (APHA Method 3030B). Samples were single samples for each event from each system. For the LLB and RAPS the

first seven samples were collected approximately weekly (3, 10, 17, 39, 45, 52, and 66 days after startup), the eighth sample 3 months after start-up, and the final sample at the end of the trial at 8 months. Samples were collected less frequently from the OLC due to problems with leaking from the liner early in the experiment. Instead of seven weekly samples following startup, only three samples were collected (3, 10, and 52 days after startup), followed by a sample 3 months after startup and the final sample at the end of the 8 months. Field parameters pH, conductivity, temperature, and dissolved oxygen were determined using a WTW Multiline P4 probe. The oxidation/reduction potential was measured using a YSI Model 100 pH meter equipped with an ORP probe (SN JC01426). Ferrous iron was analysed in the field immediately upon collection using Hach Method 8146 (1,10 Phenanthroline Method) and concentrations determined through absorbance using a Hach DR/2400 Portable Spectrophotometer and a Merck SQ300 Spectrophotometer.

One of the goals of the pilot trials was to determine the effectiveness of each of the remediation systems in raising pH and removing metals at various residence times. Residence time of AMD in passive treatment systems is typically correlated with dissolution of the limestone and, therefore, treatment effectiveness of systems (Skousen et al. 2000; Watzlaf et al. 2004). A model of treatment effectiveness in OLCs using first order rate kinetics suggests that 15 h residence time for Herbert Stream AMD should be sufficient for adequate treatment (Zeimkiewicz et al. 1994, 1997). Black et al. (1999) recommend a residence time of 15 h for LLBs. Sizing for constructed wetlands, such as RAPS units, is based on estimated removal rates per surface area of wetland. Watzlaf et al. (2004) recommend sizing based on an acid removal rate of 25–30 g/m² per day, with a minimum residence time of 15 h in the limestone layer. Therefore, for all three systems, a residence time in the limestone of c. 15 h is recommended for treatment of AMD in Herbert Stream.

Fig. 5 Residence time of acid mine drainage (AMD) in each system during pilot trials. Residence times were mostly between 5 and 25 h. Longer residence times generally equate to better treatment performance. OLC, Open limestone channel; LLB, limestone leaching bed; RAPS, reducing and alkalinity producing system.

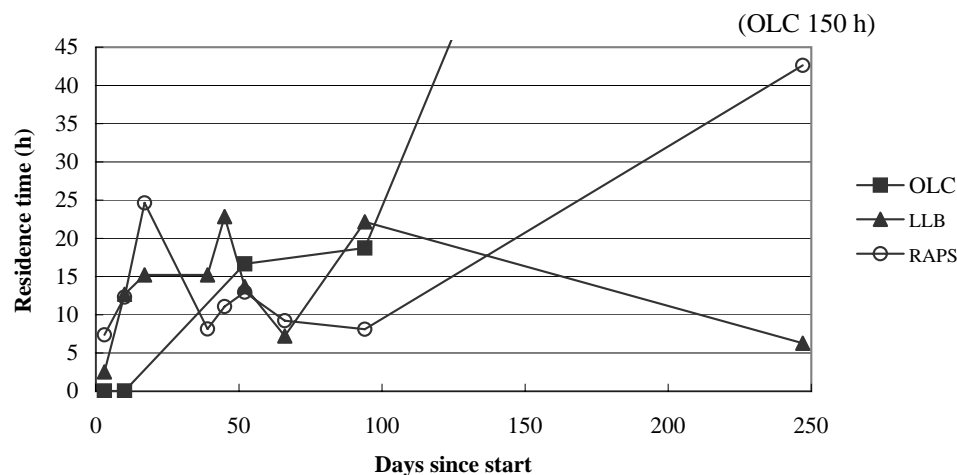
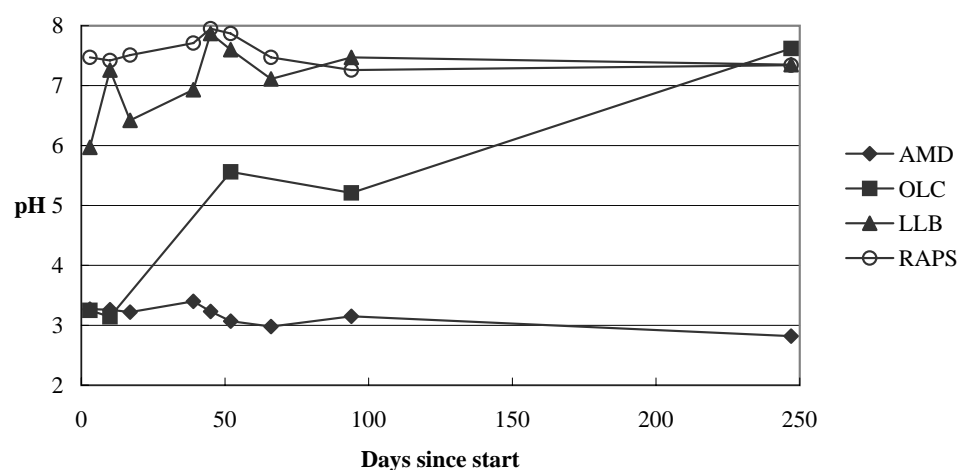


Fig. 6 The pH of effluent from systems during pilot trials compared to untreated AMD. The RAPS raised pH to above neutral throughout the experiment. The LLB raised pH to circum-neutral at residence times above 8 h (cf. Fig. 5). The OLC achieved neutral pH only at a long residence time at the end of the trial. AMD, Acid mine drainage; OLC, open limestone channel; LLB, limestone leaching bed; RAPS, reducing and alkalinity producing system.



A second goal of the pilot trials was to determine if effectiveness of each system changed with time over the duration of the trial. Effectiveness can drop due to problems such as plugging of pore spaces in RAPS and LLBs with precipitates, which can reduce capacity of treatment systems, or armouring of limestone with hydroxide precipitates, which can reduce limestone dissolution rates (Ziemkiewicz et al. 1997; Watzlaf et al. 2000a,b). These systems are typically built with flushing mechanisms to remove accumulated precipitates to a holding pond (Danehy et al. 2002). The RAPS and the LLB were constructed with a vertical-flushing capability, and each system was flushed at least once during the trials and water samples were collected to determine the effectiveness of flushing in removing accumulated precipitates. The compost in the RAPS unit was analysed for total recoverable metals to determine the amount of metals retained in the compost. At the end of the trials, autopsies were performed on each system to quantify the degree of armouring of limestone by Fe hydroxides. The percentage of surface area coated in hydroxides was estimated for each system and the colour of the hydroxide coating was documented using the Munsell Colour Chart.

RESULTS

Open limestone channel

Flow rate of the AMD through the OLC ranged from 0.00013 to 0.75 L/s with residence times ranging from <1 to 150 h (Fig. 5). The pH was raised from c. 3 to between 5 and 6 at residence times of 15–20 h, and only reached neutral at a residence time of 150 h at the end of the trial (Fig. 6). Aluminium removal in the OLC was sufficient initially but ineffective at the end of the trial, indicating potential decrease in Al treatment effectiveness with time (Fig. 7). Iron and Mn removal were effective throughout the trial with sufficient removal occurring even after 8 months of operation (Fig. 7). The highest removal rates documented were 99% for Al (day 52; residence time 17 h), 95% for Fe, and 74% for Mn (both on day 247, residence time 150 h).

Limestone leaching bed

Flow rates of the AMD through the LLB ranged from 0.0017 to 0.015 L/s, with residence times ranging from 3 to 23 h (Fig. 5). The pH was raised to between 6.5 and 8 at residence

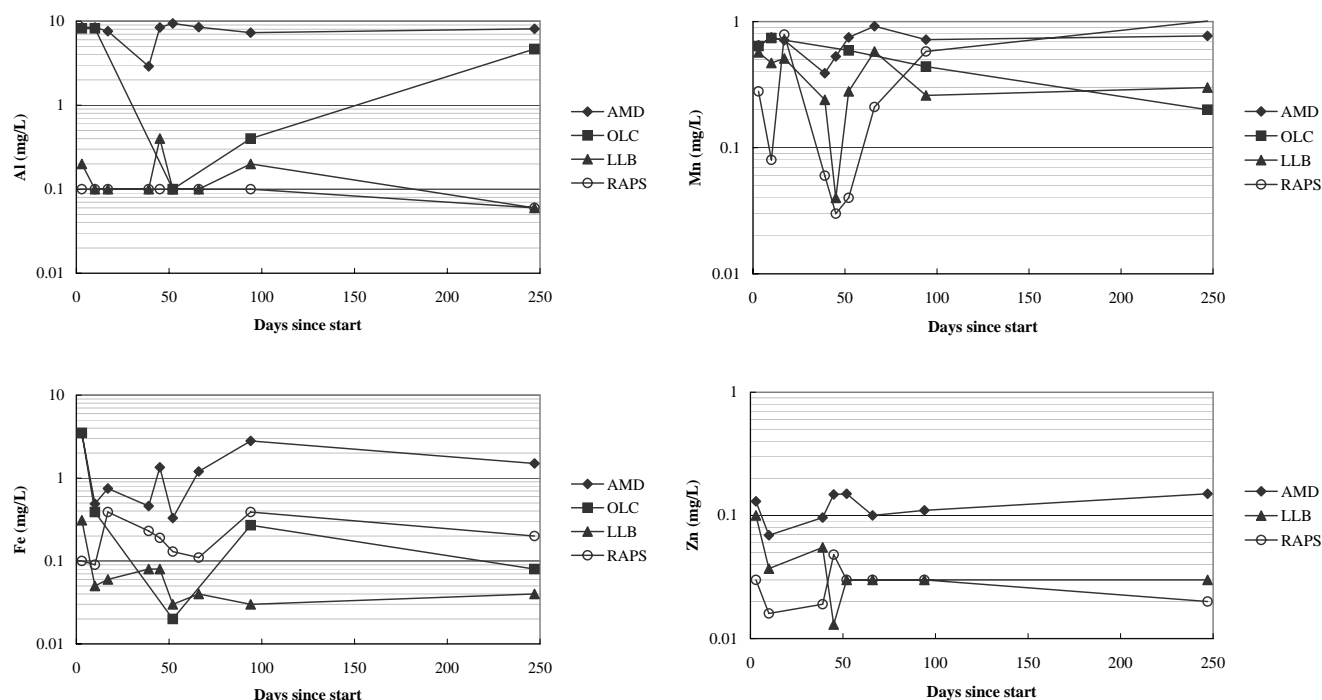


Fig. 7 Dissolved metal concentrations in effluent from systems during pilot trials compared to untreated AMD. The OLC was effective at lowering the concentrations of Fe and Mn throughout the experiment but lowered Al only initially. No Zn data were available for the OLC. The RAPS consistently lowered the concentrations of Al, Fe, and Zn throughout the experiment but was a net exporter of Mn at the end of the experiment. The LLB consistently lowered the concentrations of all metals throughout the experiment. AMD, Acid mine drainage; OLC, open limestone channel; LLB, limestone leaching bed; RAPS, reducing and alkalinity producing system.

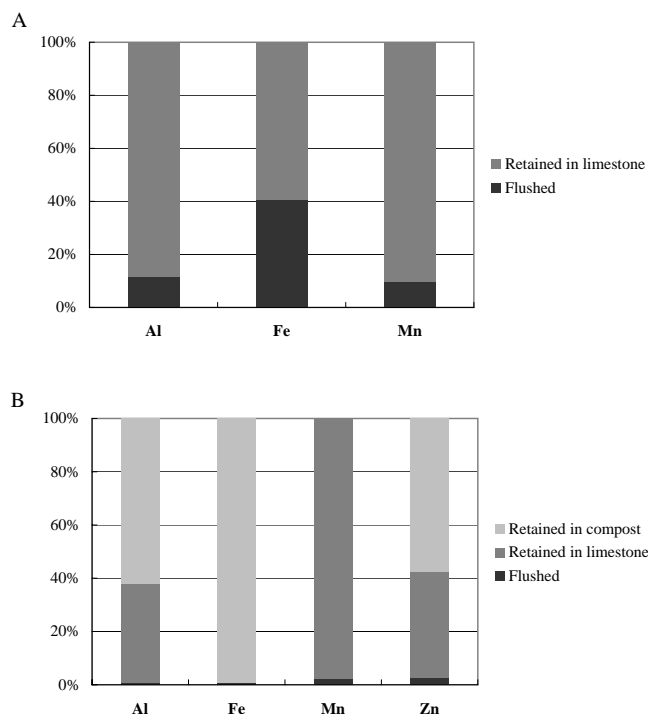


Fig. 8 Effectiveness of flushing systems in limestone leaching bed and reducing and alkalinity producing systems. Mass balance of metals removed from the acid mine drainage by each system is shown according to percent flushed and percent retained in the system. **A**, Limestone leaching bed. The majority of Al, Fe, and Mn was retained in the limestone. **B**, Reducing and alkalinity producing system. The compost retained the majority of Al and Zn and all of the Fe, while the limestone retained Mn.

times ranging from 6 to 23 h, with pH at or above neutral at residence times of more than 8 h (Fig. 5, 6). Aluminium, Fe, Mn, and Zn concentrations were reduced consistently at residence times above 8 h and treatment performance had not decreased by the end of the trial (Fig. 7). The highest removal rates were 99% for Al (day 247, residence time 6 h), 99% for Fe (day 94, residence time 22 h), 92% for Mn, and 91% for Zn (both on day 45, residence time 23 h).

Reducing and alkalinity producing system

Flow rates of the AMD through the RAPS ranged from 0.000876 to 0.005 L/s, with residence times ranging from 7 to 43 h (Fig. 5). The pH was raised to between 7.3 and 8 consistently throughout the trial with most residence times between 7 and 13 h (Fig. 5, 6). Dissolved oxygen was consistently lowered to below 1 mg/L, the oxidation/reduction potential was lowered from 536 mV for the untreated AMD to -286 mV, and all remaining Fe in the effluent was in the ferrous state, indicating that reducing conditions were achieved by the RAPS. Aluminium, Fe, and Zn concentrations were decreased consistently at residence times above 8 h, and treatment performance had not diminished by the end of the trial (Fig. 7). Manganese removal was initially good, but at the end of the trial the concentration in the effluent from the system was greater than the influent. The highest removal rates were 99% for Al (day 247, residence time 43 h), 97% for Fe (day 3, residence time 7 h), 95% for Mn (day 52, residence time 13 h), and 87% for Zn (day 247, residence time 43 h). Acid removal rates ranged from 13 to 58 g/m² per day, with the highest removal rates occurring at the lowest residence times (high flow rates). Alkalinity generation in a RAPS unit is at first rapid but decreases over time, with the response of

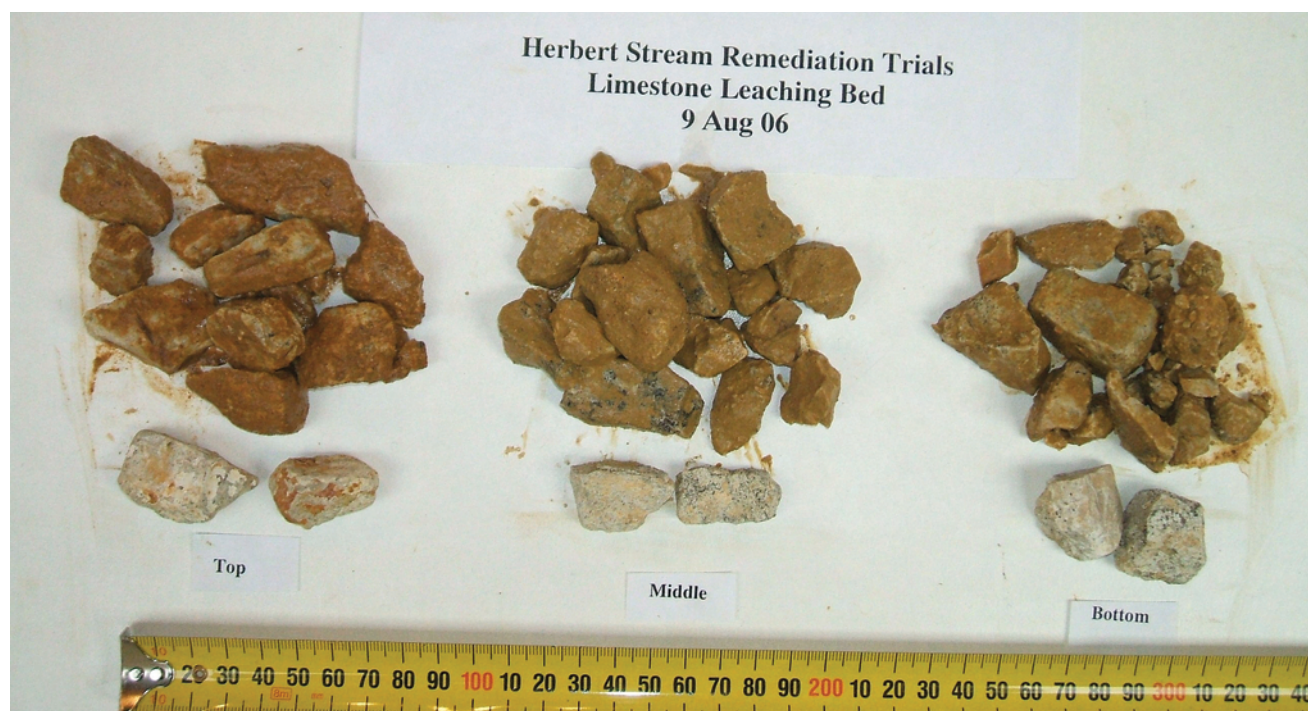


Fig. 9 Limestone from the limestone leaching bed post-pilot trials showing extent of armouring by Fe hydroxides. Top, Middle, Bottom designates location in the system. Rocks along the top of the photo are unwashed; rocks along the bottom were rinsed briefly. Unwashed rocks exhibit a marked decrease in redness and increase in yellowness with depth. Washed rocks show a marked decrease in percent covering with reddish precipitates.

Table 2 Colour and minerals of precipitates in slurry surrounding limestone rocks in LLB and RAPS noted during autopsies. LLB, Limestone leaching bed; RAPS, reducing and alkalinity producing system. Top, Middle, Bottom designates location in system. For comparison purposes, unused limestone is light grey (5Y 7/2).

Stage in system	LLB	RAPS
Top	5YR 5/6 (yellowish red) some 10R 4/6 (red), Fe hydroxides	N4 (medium dark grey), Fe monosulfides
Middle	10YR 6/6 (brownish yellow), Al hydroxides	
Bottom	10YR 6/6 (brownish yellow), Al hydroxides	10YR 6/6 (brownish yellow), Al hydroxides

alkalinity generation to residence time logarithmic (Jage et al. 2001). In our RAPS, high alkalinity was generated even at the lowest residence times and this equates to a rapid acid neutralisation rate.

System autopsies

Before autopsies, the LLB and RAPS were flushed to determine the effectiveness of the flushing systems in removing accumulated precipitates. For the LLB, flushing removed 12% of the Al, 40% of the Fe, and 10% of the Mn which had been retained by the system (Fig. 8). In the RAPS, <5% of each metal was flushed from the system (Fig. 8). The compost retained the majority of the Al and Zn and all of the Fe. A more effective flushing system with larger diameter holes and more frequent flushing may remove more of the accumulated precipitates. Full-scale system design of the LLB incorporates a more extensive flushing network.

To determine if the precipitates remaining within the limestone layers of the LLB and RAPS post-flushing were armouring the limestone, or remained as sludge which could be removed with more vigorous flushing, we inspected

unwashed and washed rocks from three levels of the LLB and two levels of the RAPS and compared these to the Munsell Colour Chart (Fig. 9, 10). For comparison purposes, unused limestone is light grey (5Y 7/2).

Unwashed rocks from the LLB top layer were mostly yellowish red (5YR 5/6) with some red (10R 4/6), and from the middle and bottom layers were brownish yellow (10YR 6/6; Fig. 9; Table 2). The cleaned rocks from all three layers were light grey (5Y 7/2) with decreasing percentage of covering with precipitates with depth. The top layer had an average of 5% coating with reddish yellow (7.5YR 6/8), the middle layer had an average of 4% coating with brownish yellow (10YR 6/8) and rarely strong brown (7.5YR 5/6), and the bottom layer had a 1–2% coating with yellowish red (5YR 5/8; Table 3).

Unwashed rocks from the RAPS top layer were mostly medium dark grey (N4) and from the bottom layer were brownish yellow (10YR 6/6; Fig. 10; Table 2). The cleaned rocks from all three layers were light grey (5Y 7/2) with decreasing percentage of coating with precipitates with depth. The top layer had an average of 10% coating with



Fig. 10 Limestone from the reducing and alkalinity producing system post-pilot trials showing extent of armouring by Fe monosulfides and hydroxides. Top, Bottom designates location in the system. Rocks along the top of the photo are unwashed; rocks along the bottom were rinsed briefly. Unwashed rocks are associated with black deposits at the top of the limestone layer and brownish yellow deposits at the base. Washed rocks show minimal covering with reddish precipitates in both layers.



Fig. 11 Limestone from the open limestone channel post-pilot trials showing extent of armouring by Fe hydroxides. Start, Middle, End designates location in the system. The rocks exhibit a marked decrease in percent covering with precipitates and a change in colour from reddish to yellowish down the channel.

black (N1) and 2% coating with red (10R 4/6) and yellowish red (5YR 5/6; Table 3). The bottom layer had an average of <1% coating with red (10R 4/6) and brownish yellow (10YR 6/6).

For the OLC, random rocks from the start, middle, and end of the channel were selected to quantify the degree and colour of precipitates armouring the rocks. Uncoated portions of each

rock were light grey (5Y 7/2) and the percentage coating with precipitate decreased down the channel (Fig. 11). The rock at the start of the channel had 20% coating with yellowish red (5YR 5/8) in a 4 cm wide band, the rock from the middle of the channel had 15% coating with reddish yellow (7.5YR 6/8), and the rock from the end of the channel had a 5% coating with yellow brown (10YR 5/8; Table 3).

Fig. 12 Alkalinity generation by each system at different residence times. Alkalinity generation was consistently greater in the LLB and RAPS compared to the OLC. OLC, Open limestone channel; LLB, limestone leaching bed; RAPS, reducing and alkalinity producing system.

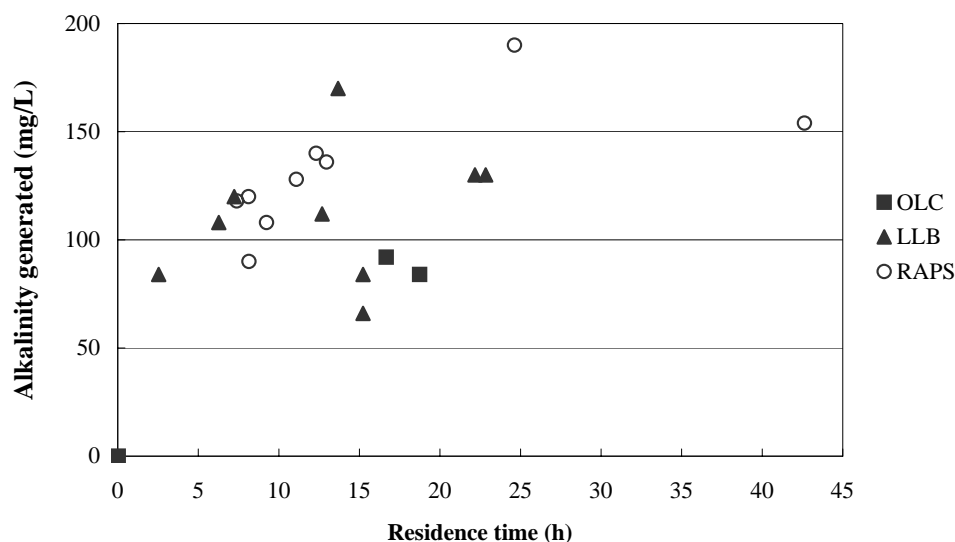


Table 3 Colour and minerals of precipitates armouring washed limestone rocks in LLB, RAPS, and OLC noted during autopsies. LLB, Limestone leaching bed; RAPS, reducing and alkalinity producing system; OLC, open limestone channel. Top, Middle, Bottom designates location in system. For comparison purposes, unused limestone is light grey (5Y 7/2).

Stage in system	LLB	RAPS	OLC
Top	5% 7.5YR 6/8 (reddish yellow), Fe hydroxides	10% N1 (black), Fe monosulphides 2% 10R 4/6 to 5YR 5/6 (red to yellowish red), Fe hydroxides	20% 5YR 5/8 (yellowish red), Fe hydroxides
Middle	rare 7.5YR 5/6 (strong brown) 4% 10YR 6/8 (brownish yellow), Al hydroxides		15% 7.5YR 6/8 (reddish yellow), Fe hydroxides
Bottom	1-2% 5YR 5/8 (yellowish red), Fe hydroxides	<1% 10R 4/6 to 10YR 6/6 (red to brownish yellow), Fe, Al hydroxides	5% 10YR 5/8 (yellowish brown), Al hydroxides

DISCUSSION

The results for the OLC suggest that adequate metal removal can be achieved at the recommended residence time of 15 h (Zeimkiewicz et al. 1994, 1997) but that performance of the system may decrease with time. Aluminium and Fe removal effectiveness decreased from day 52 to day 94 even though residence time had increased 2 h. We note that at the end of the trial, although sufficient alkalinity was generated at a residence time of 150 h to raise the pH to 7.6 and adequately remove Fe and Mn, Al removal had decreased markedly. Normally, as the pH is raised to above 5, Al concentrations rapidly decrease. It is possible that laboratory error may account for this anomalous result.

For the LLB, the results suggest that a residence time lower than the recommended 15 h (Black et al. 1999) may be adequate for treatment of Herbert Stream AMD and that long-term performance may be maintained. Aluminium, Fe, Mn, and Zn were removed at a residence time as low as 8 h at the end of the trial after 8 months of operation.

Aluminium and Zn removal effectiveness by the RAPS were comparable to the LLB, and Fe removal effectiveness was similar to the OLC. The results suggest that acid removal rates for Herbert Stream AMD up to 58 g/m² per day

can be achieved in a RAPS unit with residence times as low as 8 h, much less than the recommended 15 h (Watzlf et al. 2004). Since the rate of alkalinity generation in a RAPS unit decreases logarithmically and the most rapid gain in alkalinity occurs within the first several hours of AMD-limestone contact (Jage et al. 2001), the highest acid removal rates were at the lowest residence times. The residence times in our calculations (Fig. 5) are for the entire RAPS system, not just the limestone layer, which was much thinner than typical RAPS units. The residence times in the limestone layer of our RAPS ranged from 1 to 7 h, suggesting that the dominant treatment media in our system may have been the compost rather than the limestone. Aside from Mn, the data suggest that long-term performance may be maintained. Other workers have documented the ineffectiveness of RAPS in removing Mn (Kepler & McCleary 1994), and due to low concentrations of Mn at this site, it is not considered a contaminant of concern.

Overall alkalinity generation rates were greater in the LLB and the RAPS compared to the OLC (Fig. 12). This may be due to the larger size of the limestone in the OLC and therefore a lower reactive surface area. The low effective residence times in the LLB and RAPS (8 h) compared to literature-recommended residence times (15 h) may be due to the relatively small size and therefore high reactive surface

area of the limestone in these systems. Danehy et al. (2002) recommend using AASHTO #1 size limestone (88% between 37.5 and 90 mm), whereas the majority of our limestone (76.2%) ranged between 12.7 and 26.5 mm.

Metal removal mechanisms

Aluminium and Fe are removed in OLCs and LLBs during neutralisation of AMD by formation of metal hydroxide, oxyhydroxide, or hydroxy-sulfate precipitates as the pH is raised (Nordstrom & Alpers 1999; Skousen et al. 2000). Zinc and Mn are likely removed in these systems by adsorption onto reactive Fe hydroxide surfaces (Stumm & Morgan 1981; Bostick et al. 2001). The decreased redness with depth and increase in light colour in the unwashed rocks of the LLB and decreased redness and increase in light colour in the precipitates in the OLC down the channel noted during the autopsies, likely reflect precipitation of Fe hydroxides at lower pH near the inlet to these systems, and precipitation of Al hydroxides at high pH near the middle and outlet from these systems (Hammarstrom et al. 2003; Table 2, 3). Minimal armouring of the limestone in the LLB suggests the majority of the retained metals remained as a sludge rather than an armour coating on the limestone; however, significant armouring was noted in the OLC. OLCs are prone to armouring unless constructed at gradients of >20%, where turbulence within the channel limits coating of the limestone cobbles (Ziemkiewicz et al. 1997).

In RAPS, reducing conditions in the compost layer reduce ferric iron to ferrous iron and reduce sulfate to hydrogen sulfide, generating bicarbonate alkalinity (Hedin et al. 1994; Jage et al. 2001). The ferrous iron, hydrogen sulfide, and bicarbonate react to form Fe monosulfides. Laboratory studies demonstrate that under reducing conditions the pathway to pyrite involves the formation of mackinawite (FeS), followed by reaction with sulfide to form greigite (Fe_3S_4), which then reacts with sulfide to form pyrite (FeS_2) (Hunger & Benning 2007). Zinc removal in RAPS is likely through formation of Zn sulfide or as impurities in FeS (likely to be sphalerite). The very limited amount of reddish colour in the unwashed rocks and the very limited amount of coating with reddish precipitates noted during the autopsy suggests that the majority of the Fe treated by the RAPS remained in the compost layer, as shown quantitatively through the flushing exercise. When the black precipitates in the upper layer were exposed to air, the colour quickly faded and within 8 h was completely gone. This suggests that the black precipitates are dominantly an Fe monosulfide (such as mackinawite), as these are extremely oxygen sensitive (Hunger & Benning 2007). The lighter colour in the unwashed rocks from the lower layer likely reflects precipitation of Al hydroxides at high pH (Hammarstrom et al. 2003).

Net export of Mn from the RAPS at the end of the trial was possibly caused by precipitation of Fe hydroxide early in the trial before reducing conditions were present. If Mn was removed by adsorption onto the hydroxide surfaces, once reducing conditions were established and the Fe hydroxides were transformed to Fe monosulfides (Burton et al. 2006), Mn could be released.

Proposed full-scale system

Based on the field trial results, each of the three systems (OLC, LLB, and RAPS) is capable of removing Fe and Al and raising pH to nearly neutral, although the effectiveness of an OLC may be compromised with time due to armouring of the limestone with hydroxide precipitates. In addition to

this, an OLC would likely not be appropriate as a full-scale system for the site due to the disturbance that would occur to the natural stream channel during construction. To achieve a residence time of 15 h in the channel, the length of the channel would be c. 5 km, and would significantly disturb the riparian strip of native vegetation currently along the channel. We recommend that an LLB be constructed as a full-scale system for the Herbert Stream AMD because it is simple and effective.

SUMMARY AND CONCLUSIONS

1. The Herbert Stream, a tributary of the Waimangaroa located on the Stockton Plateau, contains Al (7.68 ppm), Fe (1.37 ppm), Mn (0.69 ppm), and Zn (0.12 ppm) and low pH (2.3–3.4), chemistry typical of acid mine drainage.
2. Potential geochemical treatment options identified to remove metals from Herbert Stream and restore pH included a reducing and alkalinity producing system (RAPS), a limestone leaching bed (LLB), and an open limestone channel (OLC). Each of these systems was constructed and operated for 8 months as a pilot trial on site to test effectiveness in treating the drainage.
3. All three systems were effective in removing metals and restoring pH, although the OLC was less effective at Al removal near the end of the trial. Maximum removal rates were: Al 99% (all three systems); Fe 97% (RAPS), 99% (LLB), and 95% (OLC); Mn 95% (RAPS), 92% (LLB), and 74% (OLC); and Zn 87% (RAPS) and 91% (LLB).
4. A residence time for water through the RAPS and LLB of only 8 h attained effective treatment, which is much lower than the literature-recommended residence time of 15 h. This is likely due to the small-size limestone (12.7–26.5 mm) and therefore higher reactive surface areas in our systems compared to literature-recommended limestone size (37.5–90 mm).
5. System autopsies showed that insignificant armouring of limestone with hydroxides occurred in the RAPS and LLB, and that significant amounts of Fe monosulfides had precipitated in the RAPS unit, suggesting that the units were operating as designed.
6. Because of the simplicity and effectiveness of the LLB, and considering the available land area for a remediation system, we proposed the LLB be constructed to full-scale size to treat the entire Herbert Stream.

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