

# AMD Treatment in New Zealand – Use of Small-scale Passive Systems<sup>1</sup>

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**Abstract.** The general goal of passive AMD treatment is to reduce levels of acidity and metals to acceptable levels. Most treatment systems use either an oxidizing or a reducing strategy. In oxidizing systems, alkalinity is added along with dissolved oxygen; in reducing systems, dissolved oxygen is removed (if present) and then alkalinity is added. To test the applicability of oxidizing and reducing strategies to treat AMD, small-scale passive treatment systems have been constructed and tested successfully at two sites on the west coast of the South Island, New Zealand. At the Sullivan Mine, a reducing system consisting of a vertical-flow wetland reduced the levels of acidity by 100%, iron by 97%, aluminum by 100%, and nickel by 66%. The Pike River Coal Company has shown foresight by using the same system to treat AMD at a small adit within the Pike River Coal Field. The system reduced acidity by 100%, iron by 99%, aluminum by 96%, nickel by 95%, manganese by 51%, and zinc by 99%. At a third AMD site, the Blackball Mine, a laboratory-based experiment was used to test the applicability of an oxidizing system for AMD treatment. In the experiment, AMD was passed through a limestone leaching column over a nine-day period. Acidity was reduced by 100%, iron by 83%, aluminum by 82%, manganese by 8%, and zinc by 64%. To determine if this treatment method reduces the toxicity of the AMD to aquatic invertebrates, a 96-hour ecotoxicity experiment was conducted. The results show a significant decrease in mortality in the treated AMD compared to untreated. These small-scale systems and laboratory-based experiments suggest that a full-scale treatment system using a reducing strategy may be successful at the Sullivan and Pike River Mines and that a system using an oxidizing strategy may be appropriate for the Blackball Mine.

**Additional Key Words:** AMD, acid rock drainage (ARD), Pike River, Sullivan Mine, vertical flow wetlands, successive alkalinity producing systems (SAPS), water treatment

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## **Introduction**

Acid mine drainage (AMD) is an environmental problem that can be associated with coal mining in New Zealand (Alarcon, 1997; de Joux, 2003; James, 2003; Black et al., 2005, Trumm 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).

Research has been completed on the source, magnitude, and effects of AMD on the ecosystem in New Zealand (Lindsay et al., 2003; Bradley 2003; Brown et al., 2003; Hughes et al., 2004; Black et al., 2005), but few attempts have been made to remediate AMD in New Zealand. In this paper, we discuss strategies to treat AMD and the usefulness of small-scale pilot systems at AMD sites in New Zealand to test treatment effectiveness prior to design of full-scale systems.

## **Background of Sites**

### **Sullivan Mine**

The Sullivan Mine is an underground coal mine on the Denniston Plateau which operated from 1952 until 1992. Early mining utilized a room and pillar extraction technique followed later by hydro mining which allowed for extraction of virtually 100 per cent of the coal (Brazil and Yardley, 1986; Todd, 1989; Barry and Caffyn, 1988). In 1992, Sullivan Mine ceased operating, with acidic, metal-rich mine waters discharging from two drives into nearby Rapid Stream (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 AMD flow rates vary between approximately 20 and 35 L/s, and that recovery of pH to near background levels may require between 30 and 100 years of oxidation (Trumm et al., 2005).

### **Pike River Coal Field**

Exploration in the Pike River Coal Field began in the 1940s when coal was discovered in the Pike River (Wellman, 1949). 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 the coal in the Paparoa Range. Subsequently, a small stream of AMD began flowing out of the adit.

### **Blackball Mine**

The underground Blackball Mine operated from 1939 to the mid 1960s (Gage, 1952; Pers. Comm., Nigel Newman). Records indicate that recovery of coal was poor due to weak roof conditions, which required that the top coal be left behind to reduce infiltration of water. Approximately 800,000 gallons of water was removed from the mine during each shift and the water was noted as being highly corrosive due to the presence of sulfuric acid (Gage, 1952). The lithology in the area is similar to that in the Sullivan Mine area, suggesting that sulfidic mudstones, may be a dominant source for the AMD. The coal from the Blackball Mine was noted as being high in sulfur, and since much of the coal remained as roof rock, this may also be a significant source of AMD (Gage, 1952).

## **Remediation Strategies**

AMD is generated by oxidation of sulfides present in coal and surrounding lithologies, which results in the dominant contaminant, iron, being present in two oxidation states, ferrous iron ( $\text{Fe}^{+2}$ ) and ferric iron ( $\text{Fe}^{+3}$ ) (Singer and Stumm, 1970; Caruccio et al., 1981). To remove Fe from AMD, this oxidation process can be encouraged to continue so that all  $\text{Fe}^{+2}$  is oxidized to  $\text{Fe}^{+3}$ , and once the pH has been increased sufficiently, Fe is precipitated out of the AMD as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ). Alternatively, the process can be reversed, so that oxidized Fe is reduced and precipitates as  $\text{FeS}_2$  and  $\text{FeS}$  (Rose and Cravotta, 1998; Sexstone et al., 1999; Skousen et al., 2000). We refer to these two strategies as the oxidizing and reducing remediation strategies, respectively (Trumm et al., 2005).

During treatment by the oxidizing remediation strategy, alkalinity is added by limestone dissolution, and dissolved oxygen (DO) is added by aerating the AMD. Typical remedial systems that employ the oxidizing strategy are open limestone channels (OLCs) and diversion wells (Anonymous, 2001). During 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 pH is raised, any remaining Fe not already removed as sulfides precipitate as metal hydroxides upon aeration. Typical remediation systems that employ a reducing strategy are anaerobic wetlands (Anonymous, 2001), vertical flow wetlands (VFWs) (Zipper and Jage, 2001), and if the AMD is already low in DO, anoxic limestone drains (ALDs) (Hedin and Watzlaf, 1994). Selection between oxidizing and reducing strategies is typically based on the water chemistry, flow rates, surface topography, and available land area.

## **Methods**

### **Sullivan Mine Passive Treatment Systems**

At the Sullivan Mine AMD, small-scale remediation systems consisting of an OLC, a VFW and an ALD were constructed on site out of low-budget materials such as pressure PVC piping, plastic tubs, valves and tarps. The trials were conducted over 38 days. Field parameters DO,  $\text{Fe}^{+2}$  concentration, pH, conductivity, temperature and flow rate were measured on a weekly basis and samples from the untreated AMD and the outlet to the system were laboratory-analyzed for acidity and dissolved Fe, Al, Mn, Ni and Ca. Details of the construction and performance of these systems are presented in Trumm et al. (2005). In the current paper, we compare the results of the VFW to the results of a small-scale system at the Pike River adit AMD.

### **Pike River Adit Passive Treatment System**

A small-scale VFW was constructed at the Pike River adit site using a plastic tub 1.3 m long by 0.56 m wide. Fifteen cm of limestone gravel at the base was covered by 13 cm of spent mushroom compost. AMD entered the system through a PVC pipe placed on top of the VFW and the flow rate was regulated with a valve. Treated water exited the system through a 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 a sufficient head of water was always above the compost layer for the VFW to remain anaerobic.

The system operated for a period of 151 days. During the trial, DO,  $\text{Fe}^{+2}$  concentration, pH, conductivity, temperature and flow rate were measured on a monthly basis. Samples were

collected from the untreated AMD and the outlet to the system on a monthly basis and laboratory-analyzed for acidity and dissolved Fe, Al, Mn, Ni, Ca, and  $\text{SO}_4^{-2}$ .

#### Blackball Mine AMD Laboratory Experiments

To test the effectiveness of treating the Blackball AMD with limestone, 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. 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 nine cm of the top with limestone ranging in size from five to 20 mm in diameter. The limestone was sourced from Karamea on the West Coast and had been rinsed in distilled water to remove any contaminants. AMD was passed through the column at a rate of 3.0 ml/min continuously for a period of nine days (216 hours). Assuming a porosity of 0.5, the residence time of AMD within the column was approximately 4 hours. The experiment was duplicated with a second column.

Leachate samples were analyzed daily for pH, temperature, DO, conductivity, and  $\text{Fe}^{+2}$  concentration using field instruments, and on day one, four, and nine, samples were analyzed in a laboratory for acidity,  $\text{SO}_4^{-2}$ , Ca and dissolved metals (Fe, Al, Zn, Mn, and Ni).

To test the efficiency of limestone treatment in reducing the toxicity of the Blackball AMD, a laboratory-based toxicity test was conducted. Aquatic invertebrates were collected from an unaffected stream (Bray Creek coordinates 2378295E 5866075N sheet K31 NZMG) approximately three kilometers south of Blackball and transported to Landcare Research (Christchurch) on ice in 500-ml containers containing stream water, rocks and leaves. The test proper required 150 freshly-caught healthy common mayfly larvae (*Deleatidium* spp.) Less than 60 organisms were in a suitable state for testing, and positive identification of mayfly larvae was uncertain. Therefore limited tests were conducted on the animals available, with the primary objective to determine if mortality was significantly reduced in the AMD water that had been subjected to limestone treatment. There were insufficient animals to conduct a control to ascertain mortality due to the stress of transport and handling procedure. Two liters of AMD and two liters of AMD treated through limestone column number one collected on day nine were used for the experiment.

The temperature of the water samples was allowed to warm up to the required exposure temperature (10°C). Forty ml of each treatment were placed into triplicate 50-ml containers. Each container was supplied with continuous air. Eight to 10 animals were randomly assigned to each of the six containers. Exposures were conducted under 'autumn' conditions of light (10 hrs light, 14 hrs dark). Treatment pH was checked at the initiation and conclusion of the experiment. Mortality was recorded at 24-hour intervals over 96 hours.

### Results

#### Sullivan Mine AMD

The dominant contaminants in the AMD from each site are Fe and Al with minor concentrations of Mn, Ni, and Zn (Table 1). In the Sullivan Mine AMD nearly all of the dissolved Fe is in the  $\text{Fe}^{+3}$  state and the DO levels are near saturation. This suggests that an oxidizing strategy may be more appropriate than a reducing strategy to treat the AMD, however, long residence times in reducing systems may be sufficient to reduce  $\text{Fe}^{+3}$  iron to  $\text{Fe}^{+2}$  iron and to form  $\text{FeS}_2$ . Both the oxidizing and reducing strategy were tested in the field trials (an OLC and a

VFW). The results of the OLC show that pH was restored to background levels and Fe and Al concentrations were lowered at residence times greater than two hours, however, effectiveness dropped after 50 days of operation likely due to armoring of the limestone with  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  precipitates (results are presented in Trumm et al., 2005).

Table 1. Analytical results for water samples collected from Sullivan Mine AMD, Blackball Mine AMD, and the Pike River Adit AMD.

| Parameter*                          | Sullivan Mine AMD | Pike River AMD | Blackball Mine AMD |
|-------------------------------------|-------------------|----------------|--------------------|
| pH                                  | 2.9               | 3.2            | 3.1                |
| Acidity (mg/L)                      | 214               | 113            | 216                |
| Dissolved oxygen (mg/L)             | 10                | 9              | 6                  |
| Aluminium (mg/L)                    | 14                | 1.6            | 14.1               |
| Iron (mg/L)                         | 47                | 34             | 10.6               |
| Manganese (mg/L)                    | 0.51              | 0.35           | 0.39               |
| Nickel (mg/L)                       | 0.13              | 0.12           | 0.005              |
| Zinc (mg/L)                         | 0.72              | 1.1            | 0.14               |
| Percent of iron as $\text{Fe}^{3+}$ | 96%               | 93%            | 60%                |

\* - Analytical Methods

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

Samples filtered using method APHA 3030B

Aluminium, Iron, Manganese, Nickel, Zinc: ICP-MS, APHA 3125B

Ferrous iron concentration: portable Merck Photometer SQ 300

The results of the VFW at the Sullivan Mine AMD are reproduced in the current paper to allow comparison with the results of the VFW at the Pike River adit AMD. The concentration of DO in the outlet to the VFW dropped throughout the field trial and by day 22 of the experiment, over 90% of the Fe was in the reduced  $\text{Fe}^{+2}$  state, indicating that reducing conditions were being achieved in the system (Fig. 1A, 1B). The pH in treated AMD reached 5.8 after the first week of operation at a residence time of 2 hours, and at residence times of 4 hours and above, the pH reached neutral (Fig. 1C, 1D).

The concentrations of Fe and Al were significantly lower in the outlet from the VFW throughout the duration of the field trial, and all contaminants, with the exception of Mn, were effectively removed by the VFW (Fig. 2A, 2B, 2C). At a residence time of only 5 hours (by day 22), the levels of acidity were reduced by 100 %, Fe by 97 %, Al by 100 %, and Ni by 66 %.

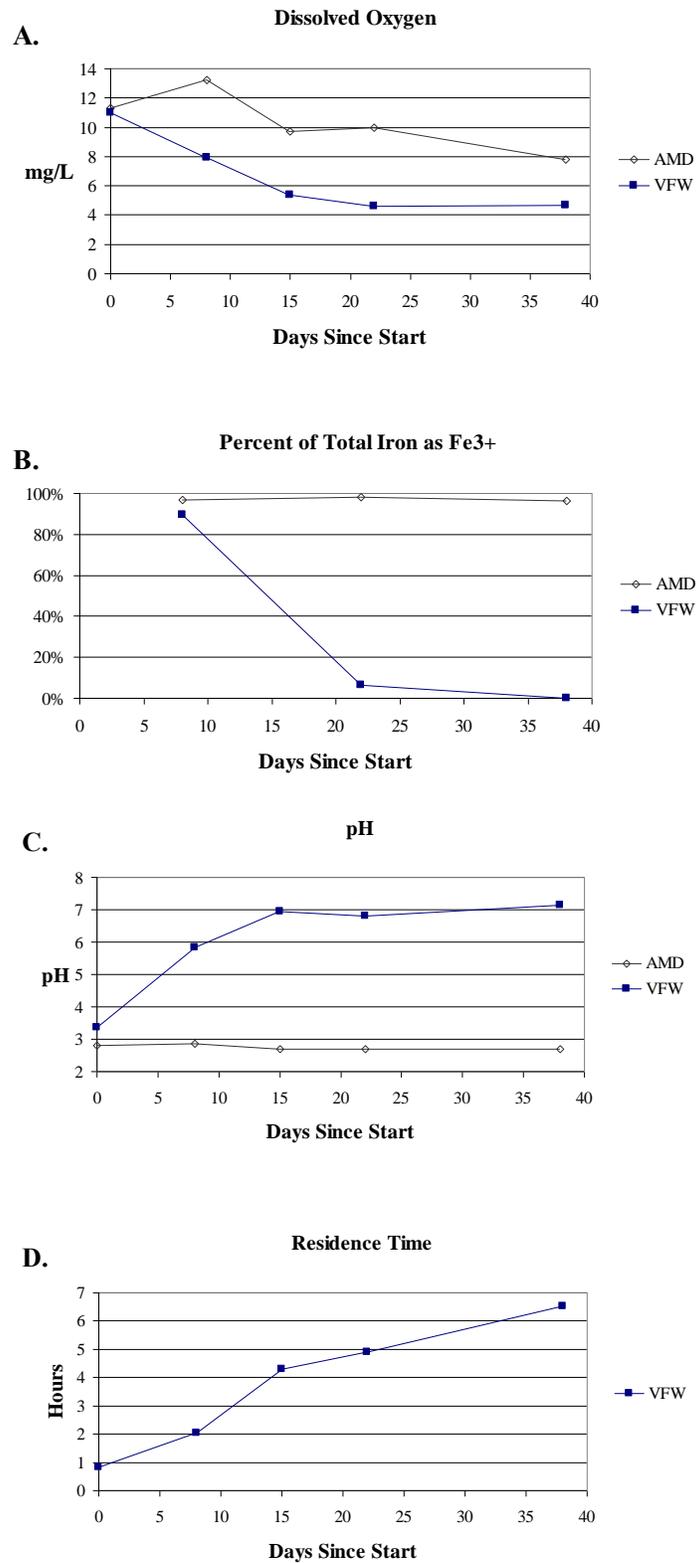


Figure 1. Field parameters measured from VFW at Sullivan Mine. (A) Dissolved Oxygen. (B) Percent of Iron in Ferric State (Fe<sup>3+</sup>). (C) pH. (D) Residence Time.

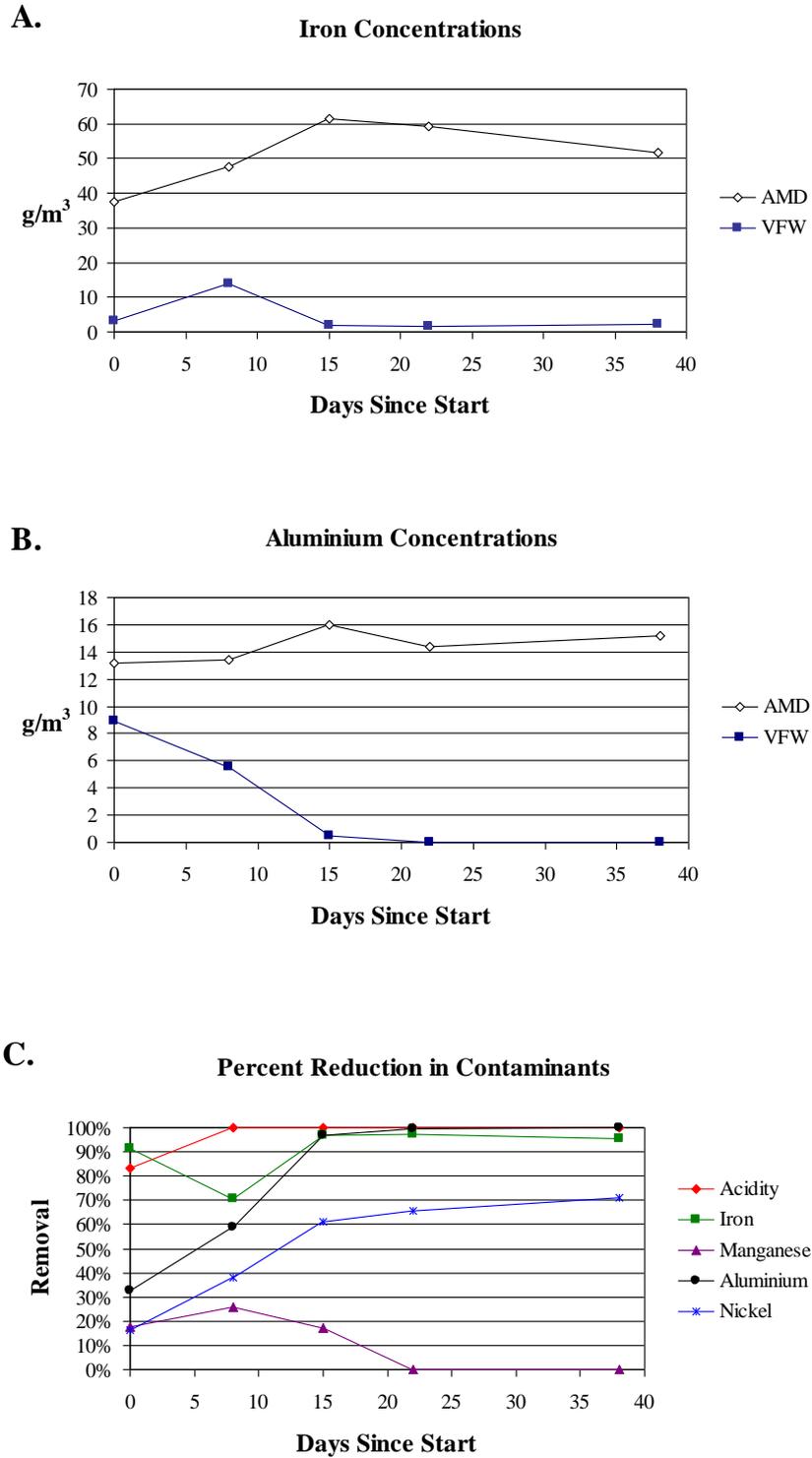


Figure 2. Analytical results from VFW at Sullivan Mine. (A) Iron concentrations. (B) Aluminum concentrations. (C) Percent removal of acidity and metals.

### Pike River Adit AMD

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  $\text{SO}_4^{2-}$  in the AMD is mostly mudstones 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 sulfides 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. The flow rate from the adit was relatively consistent at about 8 L/min throughout the trial.

Following the successful trial of the VFW at the Sullivan Mine, the Pike River Coal Company decided to treat the drainage from the Pike River adit using the same system. Results from the field trial show that the concentration of DO was lowered by the VFW; and that the percent of Fe in the  $\text{Fe}^{+3}$  state was less in treated water compared to the AMD, indicating that reducing conditions were present in the VFW (Fig. 3A, 3B). The pH in treated AMD remained neutral throughout the duration of the trial (Fig. 3C). Residence time of the AMD in the VFW averaged about 23 hours through the duration of the trial (Fig. 3D). Similar to the Sullivan Mine AMD trial, concentrations of Fe and Al were significantly lowered by the VFW, and all contaminants, with the exception of Mn after two months, were removed (Fig. 4A, 4B, 4C). By day 58 the system was reducing the levels of acidity by 100%, Fe by 99%, Al by 96%, Nil by 95%, Mn by 51%, and Zn by 99%.

### Blackball Mine AMD

The Blackball Mine AMD contains much higher concentrations of aluminum relative to iron compared to the Pike River and Sullivan Mine AMD (Table 1). In addition, DO levels are below saturation and up to 40% of the Fe is in the  $\text{Fe}^{+2}$  state. As at the Pike River site, these differences are likely due to different source rock lithologies.

Successful neutralization 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 and Ca concentrations were elevated in the leachate, although effective neutralization showed a decrease over the duration of the experiment (Fig. 5). Iron, Al, Mn, and Zn concentrations were reduced in the leachate relative to the AMD, but nickel concentrations were elevated, albeit slightly, in the leachate from both columns (Fig. 6, 7). Iron and Al were likely removed as metal hydroxide precipitates, Mn as manganese oxide precipitates (Rose and Cravotta, 1998), and Zn through adsorption onto reactive Fe or Mn oxide surfaces (Bostick et al., 2001). The elevated Ni concentrations suggest that Ni was present in the limestone and was released upon dissolution of the limestone gravel.

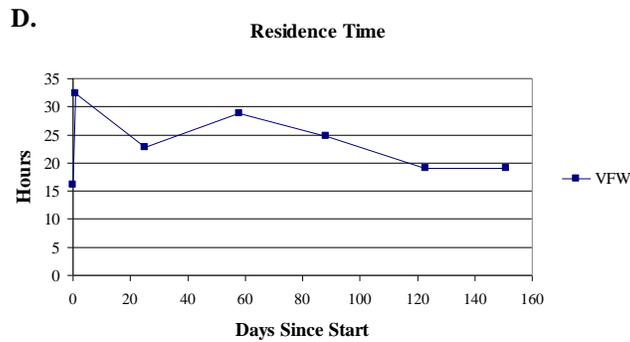
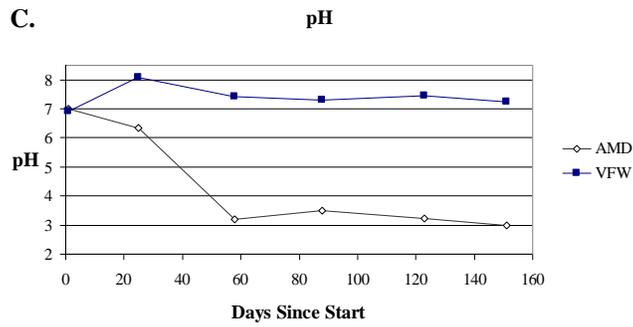
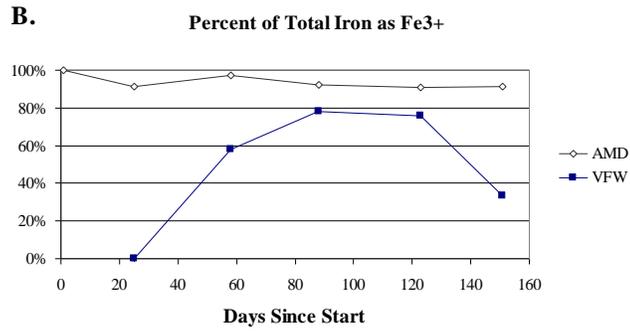
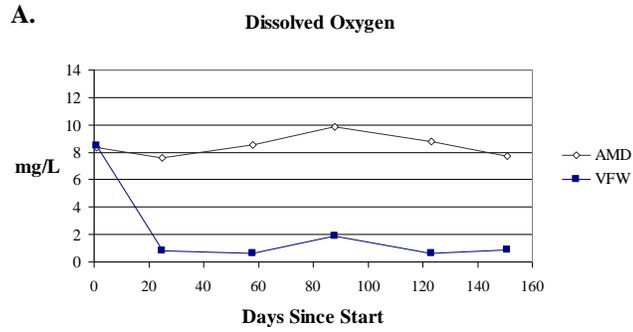


Figure 3. Field parameters measured from VFW at Pike River Adit. (A) Dissolved Oxygen. (B) Percent of Iron in Ferric State (Fe<sup>3+</sup>). (C) pH. (D) Residence Time.

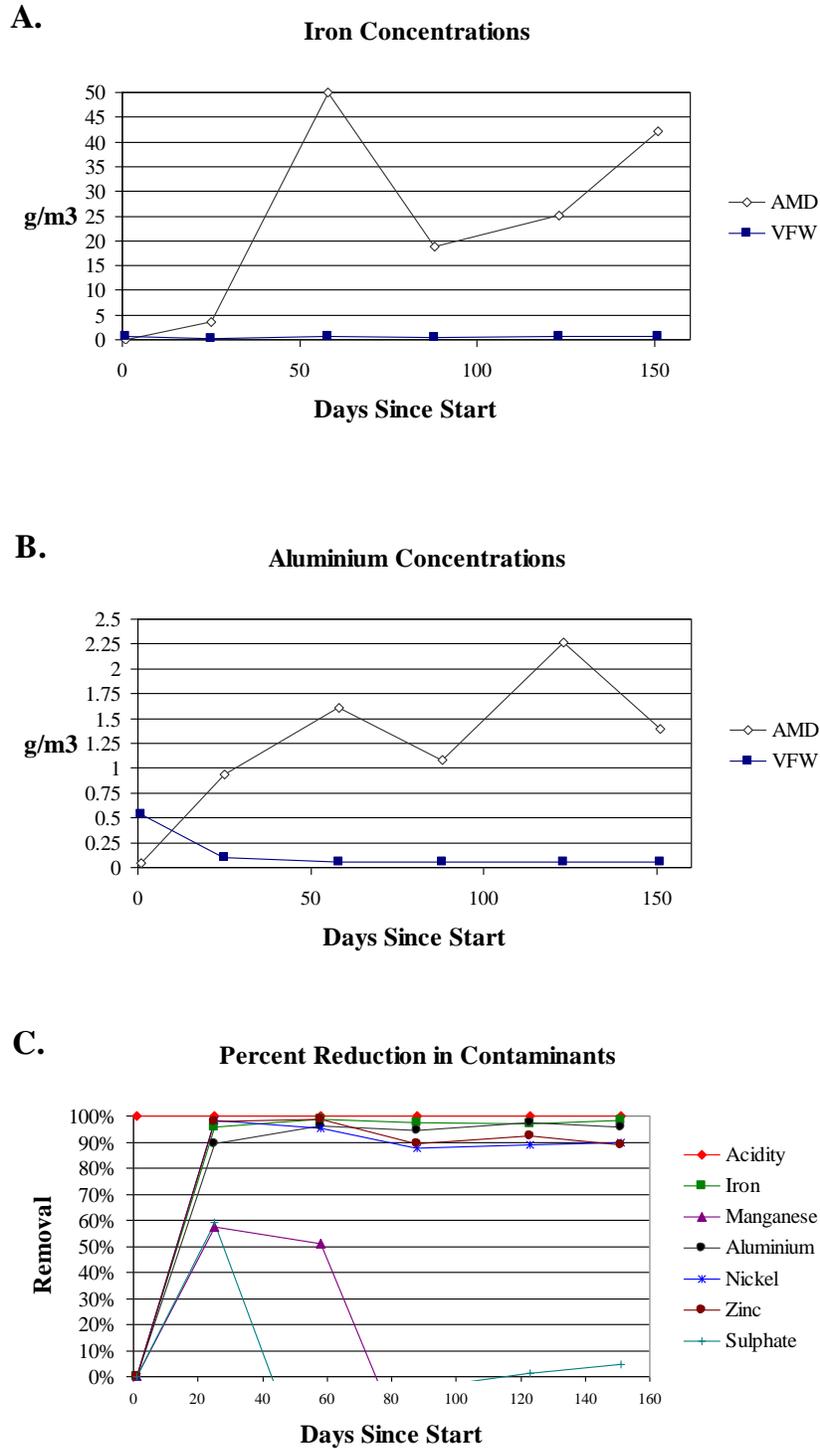


Figure 4. Analytical results from VFW at Pike River Adit. (A) Iron concentrations. (B) Aluminum concentrations. (C) Percent removal of acidity and metals.

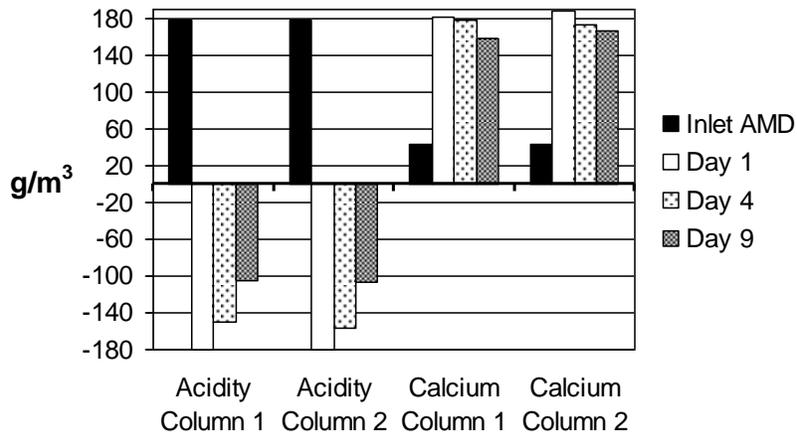


Figure 5. Levels of acidity and calcium in the leachate from the Blackball AMD column experiment compared to untreated AMD.

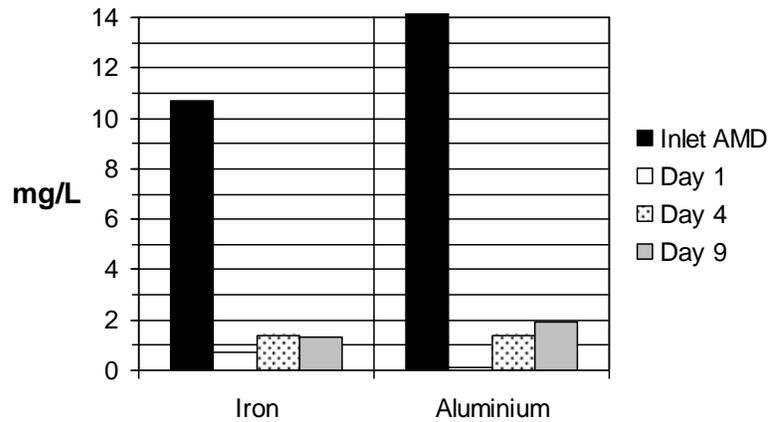
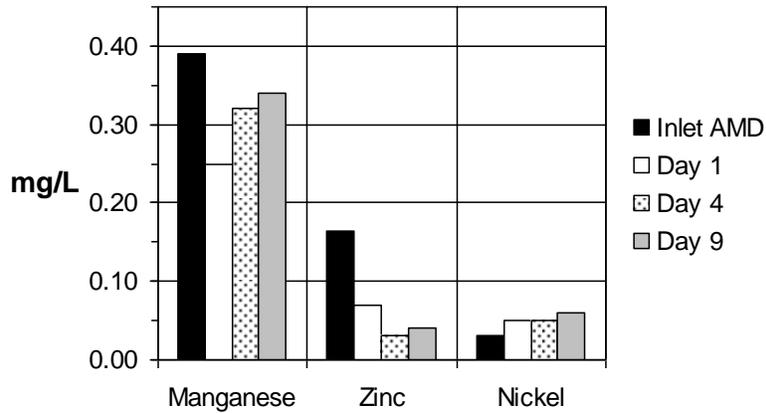


Figure 6. Concentration of Fe, Al, Mn, Zn and Ni in the leachate from the Blackball AMD column experiment for column number one compared to untreated AMD.

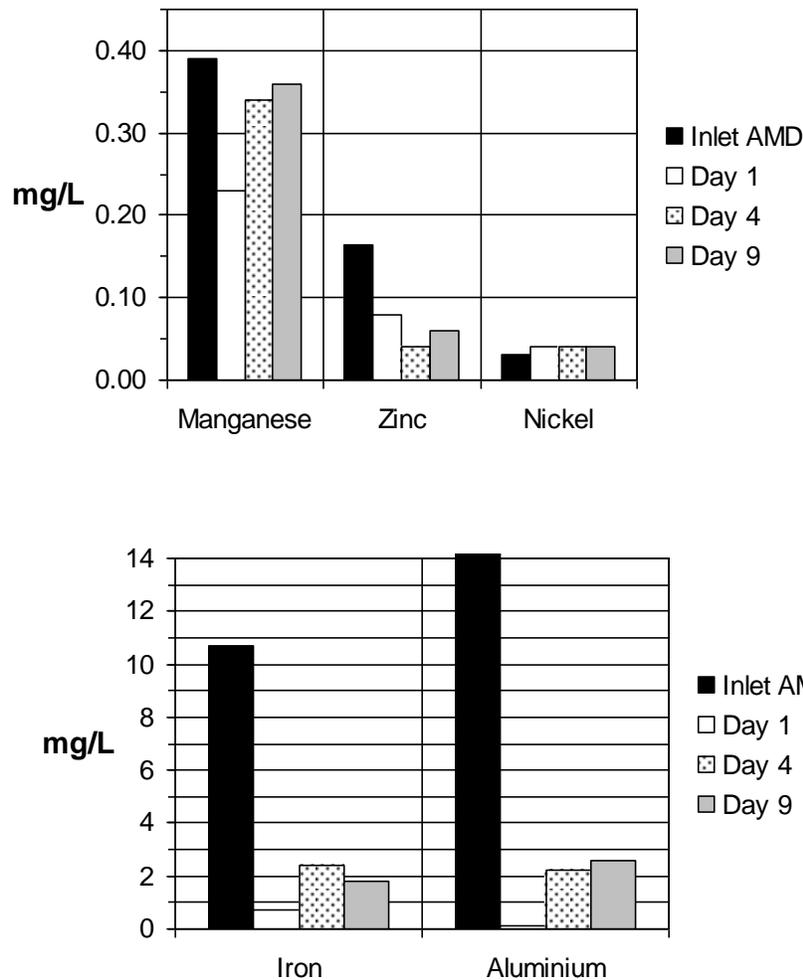


Figure 7. Concentration of Fe, Al, Mn, Zn and Ni in the leachate from the Blackball AMD column experiment for column number two compared to untreated AMD.

Mortality of aquatic invertebrates, although highly variable, was reduced in the treated AMD samples compared to the untreated samples (1-tailed T-test,  $p = 0.029$ ) (Fig. 8). This result was also reflected in the different pH of the treatments. Initial mortality (at 24 hours) in the treated water was quite high, which may have been due to transport and handling stress. Although the animals were randomly assigned to exposure vessels, one of the replicates for the treated samples had an unexpected high mortality that has skewed the results.

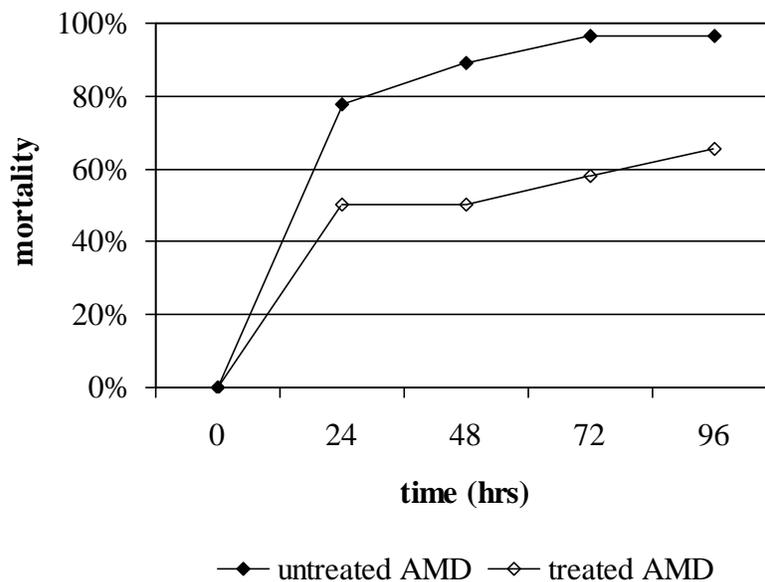


Figure 8. Mortality of aquatic invertebrates exposed over a 96-hour period to Blackball AMD and Blackball AMD treated through limestone column one.

### Discussion and Conclusions

AMD has been studied extensively in New Zealand, however there are few examples of passive or active treatment systems to remediate AMD. This project aimed to determine potential treatment strategies for three AMD sites in New Zealand, and to test these strategies with field and laboratory trials.

At the Sullivan Mine and Pike River Adit AMD sites, a VFW utilizing a reducing strategy was effective at restoring pH to neutrality and removing dissolved metals. For the Blackball Mine AMD site, a laboratory column leaching experiment showed that a simple limestone-based treatment system utilizing an oxidizing strategy may be effective at removing acidity, reducing the concentration of metals, and producing net alkalinity.

Full-scale passive AMD treatment systems should be based on AMD chemistry, flow rates, available land area, surface topography, and the results of small-scale field trials and laboratory experiments. For the Sullivan Mine AMD, Trumm et al. (2005) document that the flow rates is relatively constant and hypothesize that it is not markedly influenced by precipitation events. The surface topography near the AMD includes a large level area where a treatment system can be constructed. Although the AMD chemistry suggests using an oxidizing strategy (low  $Fe^{+2}/Fe^{+3}$  iron ratios and high DO concentrations), flow rates, the available land area, and the results of the field trials suggest that a reducing system may be more appropriate. Preliminary calculations for sizing VFWs to treat the full volume of the AMD were made using the program AMD Treat, Version 3.1 (Anonymous, 2002), along with the results of the field trials as indications of potential treatment effectiveness. Seven VFW cells, each with a dimension 30 m

long by 10 m wide and thickness of 2.7 m should be adequate to treat the AMD for 20 years (Trumm et al., 2005).

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 (only 1/250<sup>th</sup> that of the Sullivan Mine AMD) and surface area in the vicinity of the AMD is limited, with only the floor of the adit and a small area outside suitable for any treatment system. Similar to the Sullivan Mine AMD, high DO levels suggest using an oxidizing strategy; however flow rates, available land area and a successful field trial suggest using a reducing strategy. Preliminary calculations for full-scale treatment of the AMD using the program AMD Treat show that a VFW unit 6 m long by 0.5 m wide and 1.5 m deep should be sufficient to treat the full volume of the AMD for 20 years.

The chemistry of the AMD from the Blackball Mine is similar to the Sullivan Mine AMD with the exception of iron. At the Sullivan Mine, iron concentrations are more than three times that of Al, whereas for the Blackball Mine, the Fe and Al levels are nearly the same and are at a low level, close to that of Al at Sullivan Mine. This is significant for determining appropriate treatment strategies. Iron typically hinders oxidizing passive treatment systems by armoring 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 (Faulkner and Skousen, 1996; Watzlaf and Hyman 1995). Aluminum, however, does not appear to armor limestone to the same degree and possibly can be effectively flushed from leaching beds (vertical flow ponds referenced in Hellier, 1999). 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 and Gordon, 2004). At Sullivan, a relatively stable flow rate is easy to control in a reducing system such as a VFW. At Blackball, a highly variable flow rate can be useful to help flush precipitates that have built up in an oxidizing system.

The chemistry of the Blackball Mine AMD, along with the flow rate and the results of the column experiment and ecotoxicity work, suggest that a passive system using an oxidizing system such as a limestone leaching bed and an open limestone channel may be effective at treating the AMD. The land available in the vicinity of the AMD for construction of treatment systems includes a small terrace (25 m long by 15 m wide), a 500-m long sloping strip of land, and a very large flat area. Preliminary calculations using the program AMD Treat show that a system comprised of the following can treat the full volume of AMD for a period of 20 years: a limestone leaching bed 20 m long by 10 m wide and 1 m deep constructed on the terrace, followed by an open limestone channel 2 m wide and 500 m long, followed by a limestone leaching bed 30 m wide by 100 m long and 2 m thick.

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

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