Passive Treatment of AMD Using a Full-Scale Up-Flow Mussel Shell Reactor, Bellvue Coal Mine, New Zealand

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Abstract

This work presents the results of the first full-scale up-flow mussel shell reactor to treat AMD reported in the literature. In an up-flow configuration, the theory suggests that reducing conditions would be prevalent throughout the reactor, resulting in sulfate reduction and formation of sulfides rather than hydroxides which can reduce permeability with time in downflow reactors. The system raises the pH of the AMD from a median of 2.74 to a median of 6.94 and lowers metal concentrations by 97.2% (Fe), 99.8% (Al), 98.2% (Zn) and 97.0% (Ni). The benefits and challenges of up-flow reactors are discussed.

Keywords: Acid Mine Drainage, Passive Treatment, Mussel Shell Reactor, Bioreactor, Sulfides

Introduction

Incorporation of waste products is used whenever possible in passive treatment systems to minimise the cost of acid mine drainage (AMD) treatment (Gusek 2002, Younger *et al*. 2002, Watzlaf *et al*. 2004). Native to New Zealand, the Greenshell Mussel (*Perna canaliculus*) is the largest seafood export from New Zealand, which produces over 97,000 t per year at a revenue of over $380 m (Aquaculture New Zealand 2020, Stenton-Dozey *et al*. 2020). Much of the export is fully shelled mussels, producing approximately 68,000 t of shell waste annually (approximately 30% of the shellfish weight is meat). Although some of the waste is used as a lime amendment by the agricultural industry, much of it ends up in landfills. Research in New Zealand has shown that this waste product is useful in the treatment of AMD.

Since 2007, waste mussel shells have been used as alkalinity amendments in numerous experiments with bioreactors (McCauley *et al*. 2009, Mackenzie 2010, Mackenzie *et al*. 2011, Uster *et al*. 2015), and were used in full-scale construction of a mussel shell reactor with no organic amendments at the Stockton Coal Mine (Weber *et al*. 2015, Diloreto *et al*. 2016). Two additional full-scale reactors were constructed at other mines in New Zealand (unpublished). All the reactors were constructed with a downflow configuration. Research at the Stockton Coal Mine showed that metals are removed in distinct zones and in distinct forms within the reactor, with the upper layers dominated by Fe hydroxide and Al hydroxide precipitates and the lower regions dominated by Zn and Ni sulfides (Weber 2015, Weisener *et al*. 2015). It was concluded that the waste mussel meat in the shells and other sea life (about 10% by mass) provide organic material for sulfate-reducing bacteria, and lower oxygen concentrations at depth result in the formation of metal sulfides.

The lifespan of mussel shell reactors is likely controlled by reduced permeability as the hydroxides accumulate in the upper layers of the reactor, and it is likely that precipitated sulfides may be oxidised and released as the oxidation front migrates downwards. Trumm *et al*. (2015) used a small-scale trial to show that if these reactors are constructed with an up-flow configuration, the incoming water encounters a highly reduced environment populated with iron reducing and sulfate reducing bacteria (FRB and SRB). The FRB reduce oxidised Fe in the water to reduced Fe and the SRB reduce the sulfate to hydrogen sulphide. The hydrogen sulphide then combines with the divalent metals to form insoluble metal sulfides. Dissolution of the shells results in pH increase and an increase in Ca concentration, which results in removal of Al through the precipitation of Al hydroxide and some removal of Mn through the precipitation of Mn carbonate. Based on the results of Trumm *et al*. (2015) and Trumm *et al*. (2017), a full-scale up-flow mussel shell reactor was constructed at the abandoned Bellvue Coal Mine in New Zealand.

Methods

The abandoned underground Bellvue Coal Mine is in a relatively remote area of native forest with steep hillsides and deep gullies on the West Coast of New Zealand. The mine adit is on a steep slope (33° angle) approximately 25 m above nearby Cannel Creek. Prior to treatment, AMD discharged from the adit and cascaded down the slope, traversing a platform approximately 25 m by 15 m before joining Cannel Creek. Due to the limited area for a treatment system, it was decided to construct the reactor in tanks. The system consists of five 30,000 L plastic water tanks (3.7 m diameter, 2.5 m high), with associated alkathene piping and plastic valves to convey the AMD from the adit and distribute it equally to the base of each of the five tanks. The water enters each tank through perforated PVC and flows upwards through the treatment media, discharging through perforated PVC at the top of the tank and alkathene piping to Cannel Creek. Each tank is filled with approximately 24 m^3 of fresh mussel shells, broken into pieces approximately 5 cm long. The discharge piping is approximately 22 cm above the top of the shells, thereby maintaining a free water surface above the shells to ensure the reactor remains under reducing conditions.

The tanks were filled with AMD and left static for 10 weeks prior to operation to allow reducing conditions to establish and for FRB and SRB to populate the tanks. After start-up, site visits were conducted on 17 occasions over an 11-month period. During each visit, field parameters were measured, and water samples were collected from the inlet and the outlet of the system and from Cannel Creek upstream and downstream of the confluence with the treated AMD. Field parameters included temperature, pH, dissolved oxygen, conductivity, total dissolved solids, salinity, and oxidation-reduction potential. The water samples were submitted for laboratory analysis of total alkalinity, total ammoniacal nitrogen, nitrite nitrogen, nitrate nitrogen, dissolved reactive phosphorus, sulfate, dissolved organic carbon and dissolved metals (Ca, Fe, Al, Mg, Na, K, Mn, Zn, Sr, Ni, Co, Cr, Ba, Cu, As, Cd, V, Pb, Hg). For the first nine visits, the water samples were submitted from each individual tank; for the last eight visits, a single water sample was composited from the five tanks and submitted to reduce analysis costs.

Results

Mussel shell reactor

The flow rate through the system ranged from 0.16 to 1.23 L/s with an average of 0.62 L/s. The hydraulic residence time (HRT) in the system ranged from 19 to 152 h with an average of 39 h and a median of 34 h. The pH of the inlet water ranged from 2.54 to 2.94, sulfate concentrations ranged from 490 to 740 mg/L, and the average inlet dissolved metal concentrations were 46 mg/L Fe, 27 mg/L Al, 0.28 mg/L Zn, and 0.10 mg/L Ni. The treated water had a pH between 5.30 and 7.23 (median of 6.94) and had an average total alkalinity of 321 mg/L as $CaCO_3$. The treated water average dissolved metal concentrations were 1.5 mg/L Fe, 0.047 mg/L Al, 0.010 mg/L Zn, and 0.0063 mg/L Ni (fig. 1). Regulatory discharge limits in New Zealand are determined on a site-specific basis by risk analysis; they have not been determined for this site. The system removed an average of 97.2% of the Fe, 99.8% of the Al, 98.2% of the Zn, and 97.0% of the Ni and is correlated with HRT (fig. 2). Sulfate concentrations decreased an average of 116 mg/L through the reactor.

Ammonia concentrations in the inlet water ranged from 0.27 to 0.50 mg/L (0.35 mg/L average) and in the outlet ranged from 1.2 to 54 mg/L (10 mg/L average). The highest concentration was detected on the day the system was started and the concentration had declined to 1.25 mg/L seven days later. An unexplained increase in concentration occurred 11 months later (to 32 mg/L). Nitrate plus nitrite concentrations in the inlet water ranged from below detection limits to 0.10 mg/L, and in the outlet water they ranged from below detection limit to

0.30 mg/L. As with the ammonia, the highest concentrations were detected on the day the system was started.

Cannel Creek

The pH of Cannel Creek was raised from a previous median level of 3.1 to a median of 4.8 (ranging from 3.8 to 6.7). Alkalinity in the creek increased from a previous level of below detection limits to 15 mg/L as $CaCO_3$ (upstream alkalinity averages 12 mg/L as $CaCO_3$). Prior to installation of the treatment system the average dissolved metal concentrations in Cannel Creek were 6.98 mg/L Fe, 6.68 mg/L Al, 0.052 mg/L Zn, and 0.028 mg/L Ni (West 2014). After the system was started, the average dissolved metal concentrations in Cannel Creek were 0.82 mg/L Fe, 0.84 mg/L Al, 0.020 mg/L Zn, and 0.012 mg/L Ni. Average dissolved metal concentrations in Cannel Creek upstream of the confluence are 0.39 mg/L Fe, 0.14 mg/L Al, 0.0050 mg/L Zn, and 0.0012 mg/L Ni. Ammonia in Cannel Creek increased from an upstream average concentration of 0.30 mg/L (ranging from 0.010 to 1.0 mg/L) to a

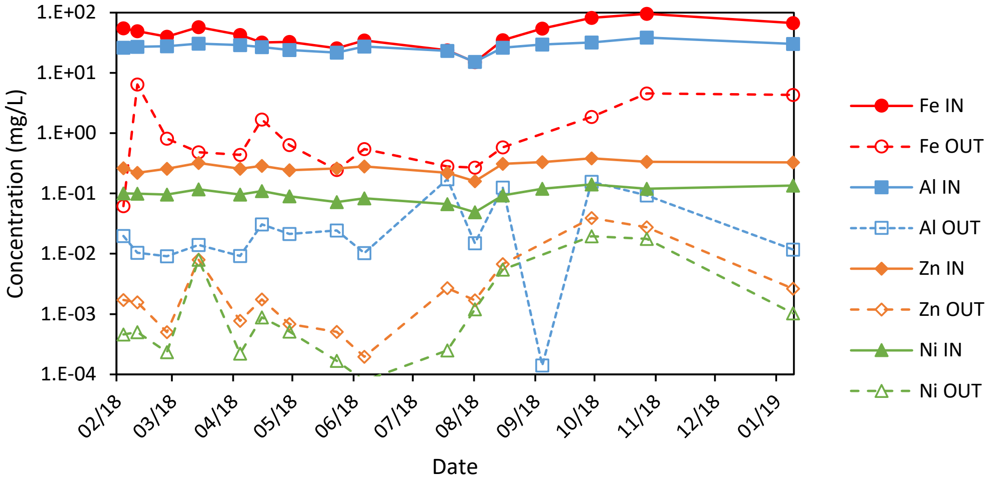

__Figure 1__ Dissolved metal concentrations for mussel shell reactor. IN, inlet concentrations; OUT, outlet concentrations.

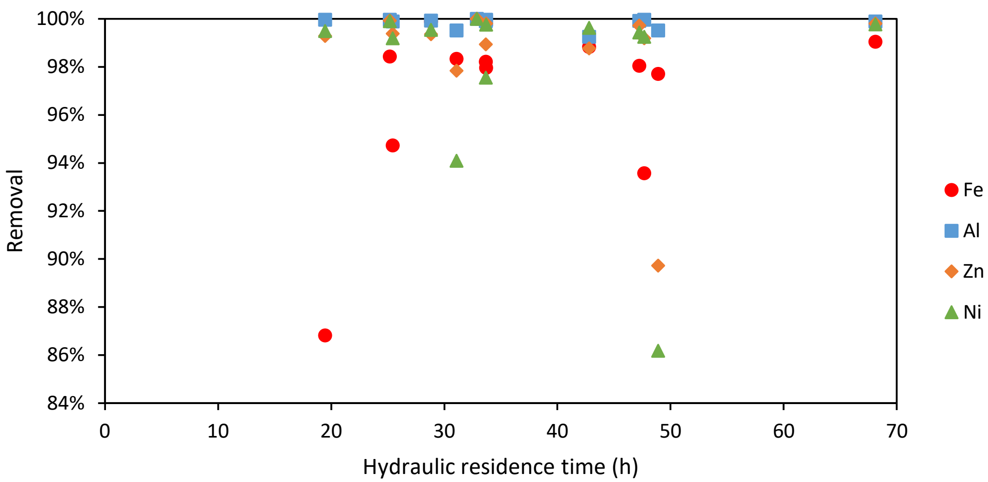

__Figure 2__ Percent removal of dissolved metal concentrations in mussel shell reactor.

downstream average concentration of 0.49 mg/L (ranging from 0.13 to 1.8 mg/L). Nitrate plus nitrite increased from an upstream average concentration of 0.0014 mg/L (ranging from below detection limits to 0.0090 mg/L) to a downstream average concentration of 0.037 mg/L (ranging from below detection limits to 0.16 mg/L).

Discussion

Mussel shell reactor

The treatment system at the Bellvue Coal Mine is the first full-scale up-flow mussel shell reactor in New Zealand (and in the published literature). The results of the Bellvue reactor suggest that an up-flow configuration can be successful at sulfate reduction and removal of metals through the formation of metal sulfides. Treatment effectiveness was similar to the up-flow mussel shell reactor documented for the small-scale trials in Trumm *et al.* (2015). In that system, metal removal percentages, compared to the Bellvue Mine treatment system, were 96-99% Fe (97.2% for Bellvue), >99% Al (99.8% for Bellvue), 98-99% Zn (98.2% for Bellvue) and 95-99% Ni (97.0% for Bellvue). Furthermore, the HRT at Bellvue (19-152 h) was less than that at the other system (40-675 h), suggesting better overall treatment effectiveness at the Bellvue reactor.

Although analysis of metal precipitates has not yet been completed for the reactor, observations during sampling suggest that Fe and divalent trace elements such as Zn and Ni are likely being removed as sulfides. During sampling events, there is a noticeable odour of hydrogen sulfide and a hand-carried hydrogen sulfide gas detector records elevated levels of hydrogen sulfide (often triggering the alarm for dangerously high levels). In addition to this, when drain valves at the base of the reactor tanks are opened briefly, the colour of the water and sediment is black and a noticeable hydrogen sulfide smell is evident. The results of sulfate analyses also support the contention that sulfate reduction is occurring. Future analyses will include XRD and SEM/EDS techniques to determine if sulfides are formed in the reactor.

Aluminium will likely form hydroxides in the reactor, which, along with the accumulation of metal sulfides, may limit permeability with time. The system has been operating for three years as of the date of this publication, and it now requires additional head pressure to maintain flow through the reactor, suggesting that accumulated of precipitate is reducing permeability. Each tank is equipped with a flushing valve at the base. Plans are underway to conduct the first flush of the system through these valves to remove the precipitates.

Cannel Creek

Data show that there has been an improvement in the water chemistry in Cannel Creek since installation of the system. Previously low pH levels, absence of alkalinity, and elevated dissolved metal concentrations are now replaced with pH levels, alkalinity, and dissolved metal concentrations more similar to background levels upstream of the confluence with the AMD. Compared to pre-treatment conditions, the Fe concentration is two times greater than background (previously it was 18 times greater), Al is six times greater (previously it was 48 times greater), Zn is four times greater (previously it was 10 times greater), and Ni is 10 times greater (previously it was 23 times greater).

Although the pH levels ranged from 3.8 to 6.7 in Cannel Creek post treatment, all the low pH levels occurred when flow rate through the system was hampered by build-up of sticks and leaves in the inlet piping. If those data points are removed, the pH level in Cannel Creek ranged from 4.7 to 6.7. Geochemical modelling work by Trumm *et al.* (2017) predicted the pH in Cannel Creek may range from 4.2 to 6.0 post treatment (related to asymmetric response of flow rates in the AMD vs. the creek during precipitation events), which is similar to the documented results to date. Future work to prevent blockages will ensure that pH levels remain elevated in Cannel Creek compared to pre-treatment levels.

Prior to installation of the system, there was concern about potential discharge of ammonia from the system. Since treatment in up-flow mussel shell reactors is primarily through sulfate reduction and formation and sequestration of metal sulfides, the discharge water from these systems is largely anoxic. During the early stages of operation, significant ammonia may be discharged from the system under these anaerobic conditions. Small-scale up-flow mussel shell reactor trials by West (2014) found initial concentrations of total ammoniacal nitrogen exiting the systems were at concentrations of up to 100 mg/L; however, these concentrations decreased to approximately 50 mg/L within two months of operation and to approximately 5 mg/L three months after start-up. Within four months after start-up, concentrations had decreased to between 1 and 3 mg/L. The New Zealand guidelines for protection of freshwater and marine ecosystems specify ammonia trigger level concentrations according to pH (ANZG 2018). For the expected maximum discharge pH of 7 from the mussel shell reactors, the specified ammonia trigger level for protection of 95% of species of the freshwater ecosystem is 2.18 mg/L. The data for the full-scale Bellvue treatment system shows that although the ammonia concentration in the reactor outlet occasionally exceeds this level, once diluted in Cannel Creek, concentrations are below the threshold. Oxidation of the water occurs as it flows down a channel to Cannel Creek.

As a result of the success of the small-scale trials documented in Trumm *et al.* (2015) and the success of the treatment system at the Bellvue Mine, two additional full-scale up-flow mussel shell reactors have been installed in New Zealand, both at active coal mines. One of the systems is a 1,000 m^3 up-flow reactor and the other is a 3,000 m^3 up-flow reactor. Data to date show both reactors are effectively treating AMD through sulfate reduction and formation of metal sulfides.

Conclusions

The first full-scale mussel shell reactor with an up-flow configuration was installed at the abandoned Bellvue Coal Mine on the West Coast of New Zealand. In an up-flow configuration, the theory suggests that reducing conditions would be prevalent throughout the reactor, resulting in sulfate reduction and formation of Fe sulfides rather than Fe hydroxides which can reduce permeability with time in downflow reactors. Furthermore, the reactors can be constructed with a flushing mechanism so that accumulated Al hydroxides and the metal sulfides can be removed periodically.

The inlet water chemistry to the system had a pH of 2.54 to 2.94, sulfate concentrations of 490 to 740 mg/L (average of 643 mg/L), and average dissolved metal concentrations as follows: Fe (46 mg/L), Al (27 mg/L), Zn (0.28 mg/L), and Ni (0.10 mg/L). Residence time in the system ranged from 19 to 152 h (an average of 39 h). The pH increased through the reactor to a level between 5.30 and 7.23 (median of 6.94) and the alkalinity increased by an average of 321 mg/L as $CaCO_3$. Average metal removal percentages through the reactor were as follows: Fe (97.2%), Al (99.8%), Zn (98.2%), and Ni (97.0%). Sulfate concentrations were reduced by an average of 116 mg/L. Reduction of sulfate concentrations through the reactor, the presence of hydrogen sulfide at the outlet and base of the reactor, and the lack of red iron oxide precipitates in the outlet and base of the reactor suggest that sulfate reduction and metal sulfide precipitation are the dominant treatment mechanisms.

The water chemistry of the receiving stream, Cannel Creek, improved post treatment. A previous median pH of 3.1 was raised to a median of 4.8, alkalinity was increased to an average of 15 mg/L of $CaCO_3$, and dissolved metal concentrations were reduced as follows: Fe (by 88%), Al (by 87%), Zn (by 62%) and Ni (by 52%). Low pH events in the creek correspond to times when the inlet piping to the reactor were blocked by sticks and leaves. Better management of the system is now preventing this occurrence. As a result of the successful system at the Bellvue Coal Mine, two additional full-scale up-flow mussel shell reactors have been constructed at two active coal mines in New Zealand.

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