Passive Treatment of AMD Using a Full-Scale Upflow Mussel Shell Reactor, Echo Coal Mine, New Zealand

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Abstract

This work presents the results of the first full-scale up-flow mussel shell reactor at an active mine 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 3.3 to a median of 7.2 and lowers metal concentrations by an average of 91.4% (Fe), 97.6% (Al), 83.3% (Zn), 85.6% (Cd), 85.2% (Co), 85.6% (Cu), and 87.0% (Ni). The benefits of up-flow reactors are discussed.

Keywords: Acid mine drainage, Passive treatment, Mussel shell reactor, Bioreactor, Sulfides

Introduction

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. Work 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 small-scale experiments with bioreactors (McCauley *et al*. 2009, Mackenzie 2010, Mackenzie *et al*. 2011, West 2014, Uster *et al*. 2015), and later were used in full-scale construction of mussel shell reactors with no organic amendments at three active coal mines. In a downflow configuration, Fe and Al are removed as hydroxides in the upper regions and trace elements (such as Zn and Ni) are removed as sulfides in the lower regions (Weber 2015, Weisener *et al*. 2015, Diloreto *et al*. 2016). The waste mussel meat in the shells and other sea life (about 10% by mass) provide enough organic material for sulfate-reducing bacteria, and lower oxygen concentrations at depth result in the formation of metal sulfides.

Further experiments have shown that when constructed with upflow configurations, the incoming water encounters a highly reduced environment populated with iron reducing and sulfate reducing bacteria (FRB and SRB), resulting in the formation of metal sulfides throughout the reactor and the removal of divalent metals (West 2014, Trumm *et al*. 2015). Dissolution of the shells results in pH increase, and the sulfate reduction reaction increases alkalinity. The first full-scale application of this technology was the installation of an upflow mussel shell reactor at the abandoned Bellvue Coal Mine in New Zealand (Trumm *et al*. 2017, Trumm *et al*. 2021). Based on the results at Bellvue, and the results of a small-scale trial at the active Echo Coal Mine (Trumm *et al*. 2015), the largest full-scale upflow reactor to date in New Zealand has now been installed.

Methods

Echo Coal Mine is located in an area of native forest with steep hillsides and deep gullies on the West Coast of New Zealand, near the town of Reefton. Historically, the area was mined through underground methods but is now an open-cast mine, operated by Francis Mining Co. Ltd a subsidiary of New Zealand Coal & Carbon Ltd, producing low ash, semi-soft coking coal exported for use in metallurgy and in the production of steel and silicon metal in locations around the globe including Japan, Saudia Arabia, China, Australia, Canada, and India.

AMD discharges from the mine into Wellman Creek which joins Garvey Creek and then flows down to the Inangahua River. Garvey Creek is impacted by AMD from other mines nearby. Geochemical modelling shows that AMD treatment using an upflow mussel shell reactor should prevent impact to Wellman Creek and the Inangahua River (unpublished data).

Approximately 3,000 m3 of fresh mussel shells were placed in a channel approximately 130 m long, 8 m wide, and 3 m deep, which was the original flow path of the AMD. Fresh shells ensured the maximum organic content with the shells. A sample of the shells was submitted to a laboratory to determine organic content. Two perforated alkathene pipes (100 mm) run the length of the reactor at the base of the shells, with one exiting at the start and the other at the end of the reactor. Both pipelines run uphill to a heading pond feeding the reactor. The pipeline that exits at the end of the reactor has a tee-junction and valves for flushing precipitates out of the reactor. The water flows upward through the shells and discharges through a culvert at the downstream end of the reactor. Approximately 0.7 m of free water is above the shells to ensure that the reactor remains under reducing conditions.

The system was installed in May, 2019 and flow through the system began on 16 May 2019. Sampling is conducted on a fortnightly basis. During each visit, field parameters are measured, and water samples are collected from the inlet and the outlet of the system, from Wellman Creek upstream and downstream of the confluence with the treated AMD, from Garvey Creek upstream and downstream of the confluence with Wellman Creek, and from the Inangahua River upstream and downstream of the confluence with Garvey Creek (eight locations). Field parameters include temperature, pH, dissolved oxygen, conductivity, total dissolved solids, salinity, and oxidation-reduction potential. The water samples are submitted for laboratory analysis of total alkalinity, total acidity, total hardness, sulfate, and dissolved metals (Al, Ca, Fe, Mg, Mn, Zn). The samples from the inlet and the outlet of the system are also analysed for total ammoniacal nitrogen, nitrite nitrogen, nitrate nitrogen, dissolved reactive phosphorus, and dissolved organic carbon. On a quarterly basis the inlet and outlet of the system are also analysed for the dissolved metals Sb, As, Ba, B, Cd, Cs, Cr, Co, Cu, La, Pb, Li, Mo, Ni, K, Rb, Se, Ag, Na, Sr, Tl, Sn, U, and V. The first three years worth of data is presented in this paper.

Results

The analysis of the mussel shells showed that 9.7% by mass of the shells was organic matter. The flow rate through the system ranged from 0.6 to 8.6 L/s, averaging 3.7 L/s. The hydraulic residence time (HRT) in the system ranged from 3 to 42 d with an average of 11 d and a median of 8 d.

The median pH of the inlet water was 3.3, the average sulfate concentrations was 1185 mg/L, and the average inlet dissolved metal concentrations were 14.3 mg/L Fe, 5.3 mg/L Al, 1.12 mg/L Zn, 0.41 mg/L Ni, and 0.27 mg/L Co. Remaining trace elements were all below 0.05 mg/L.

The treated water had a median pH of 7.2 and had an average total alkalinity of 140 mg/L as $CaCO_3$ (but a maximum of 300 mg/L). The treated water average dissolved metal concentrations were 0.54 mg/L Fe, 0.084 mg/L Al, 0.14 mg/L Zn, 0.0547 mg/L Ni, and 0.0366 mg/L Co (figs. 1, 2). The system removed an average of 91.4% of the Fe, 97.6% of the Al, 83.3% of the Zn, 87.0% of the Ni, and 84.3% of the Co and is correlated with HRT (fig. 3). Other trace elements which showed high average removal included La (97.8%), Cu (96.2%), Cs (96.1%), Tl (95.6%), Cd (94.9%), Pb (92.9%), Rb (82.0%), and U (73.8%). The average decrease in sulfate concentrations through the reactor was 451 mg/L (47.2% reduction).

Ammonia concentrations in the inlet water ranged from 0.010 to 0.75 mg/L and in the outlet ranged from 0.010 to 5.4 mg/L (0.810 mg/L average). The highest concentrations were during the first 10 months of operation. For the last two years the concentration has been below 1 mg/L and the average increase in concentration for the duration of operation is 0.81 mg/L.

Nitrate concentrations in the inlet water ranged from below detection limits to 2.1 mg/L, and in the outlet water they ranged from below detection limit to 17.7 mg/L. The highest concentration was detected on the day the system was started. Over the last year of operation, the outlet nitrate concentration has been less than the inlet concentration.

Discussion

The treatment system at the Echo Coal Mine is the largest full-scale up-flow mussel shell reactor in New Zealand (and in the published literature). The results of the Echo 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 for Fe and Al was similar to the up-flow mussel shell reactor documented for the small-scale trials in Trumm *et al.* (2015) and for the full-scale up-flow reactor installed at the Bellvue Coal Mine (Trumm *et al.* 2021), however removal of the trace elements Zn and Ni were slightly less. In those systems, metal removal percentages, compared to the Echo Mine treatment system, were 96-97% Fe (91.4% for Echo), >99% Al (97.6% for Echo), 98–99% Zn (83.3% for Echo) and 95–99% Ni (87.0% for Echo).

Although the treatment system treats only a portion of the total flow of the AMD, downstream of the confluence of the untreated AMD with the reactor discharge, the resulting pH in Wellman Creek has averaged 6.7 for the last year of operation. It is likely that this is due to the elevated alkalinity from the reactor.

Although analysis of metal precipitates has not been undertaken, 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. In addition to this, when

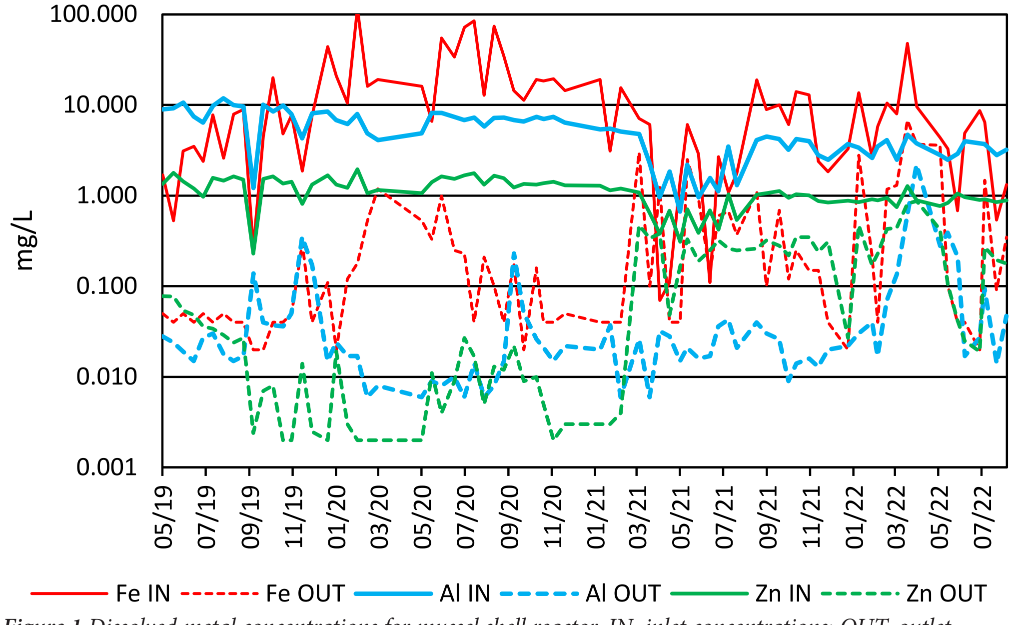

Figure 1 *Dissolved metal concentrations for mussel shell reactor. IN, inlet concentrations; OUT, outlet concentrations.*

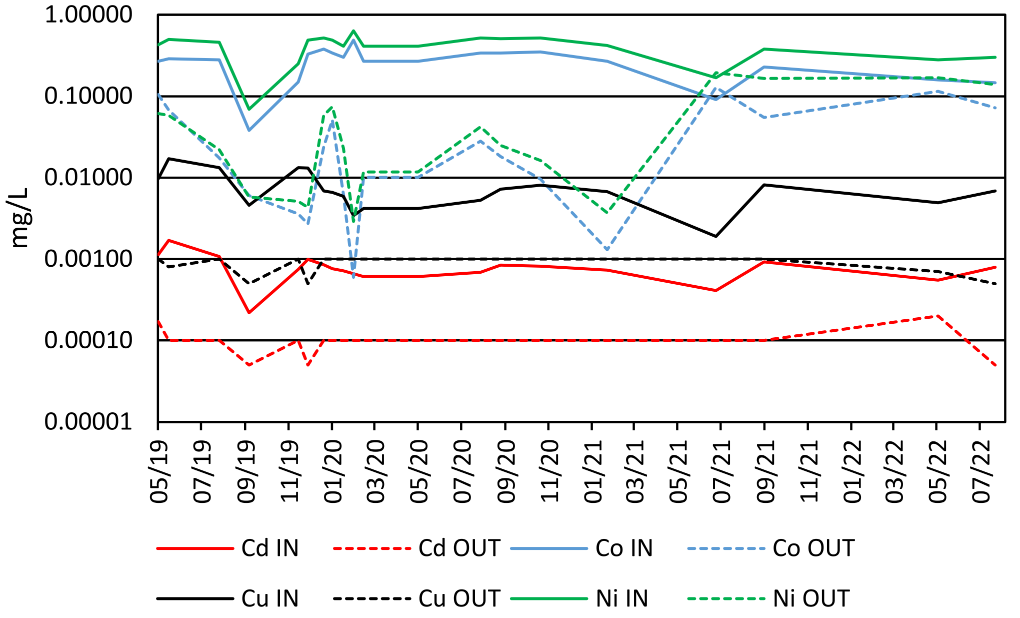

Figure 2 *Dissolved metal concentrations for mussel shell reactor. IN, inlet concentrations; OUT, outlet concentrations.*

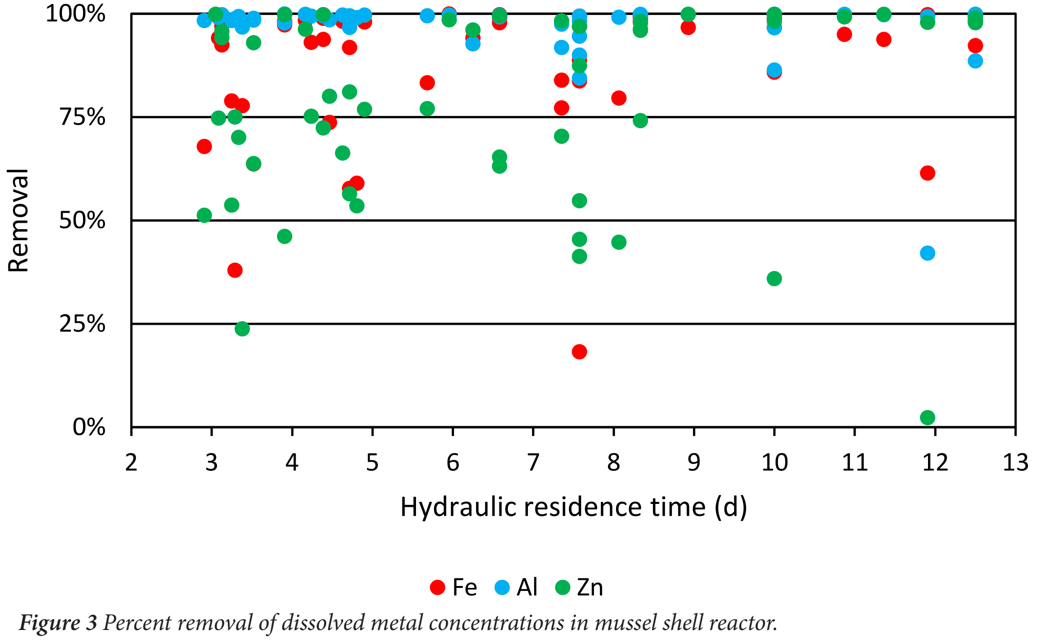

Figure 3 *Percent removal of dissolved metal concentrations in mussel shell reactor.*

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. Reduction in sulfate concentrations, ammonia discharge and low DO levels support the contention that sulfide reduction is occurring.

Alkalinity is generated in mussel shell reactors by both CaCO3 dissolution and by SRB neutralisation. Following the methods in Uster *et al.* (2015), microbial contribution to alkalinity generation was calculated using the sulfate concentration mass balances by assuming that the only sulfate removal mechanism was microbial reduction, and that no gypsum was precipitating in the substrate. CaCO3 contribution to alkalinity was then obtained by subtracting the sulfate-reduction contribution from the total alkalinity generated, and these results were compared to net Ca export from the system. The results show that SRB neutralisation generated substantially more alkalinity than shell dissolution (between 60 and 70%). At times, however, all of the alkalinity was generated through CaCO3 dissolution, and these events generally correlate with lower HRT in the system (fig. 4). A similar correlation was found in Uster *et al.* (2015).

Conclusions

The largest full-scale up-flow mussel shell reactor in New Zealand and in the published literature was installed at the active Echo Coal Mine. The reactor is comprised of approximately 3,000 m3 of fresh mussel shells and treats AMD through sulfate reduction and dissolution of shells. Organic substrate associated with the shells and inlet DOC in the AMD provide nutrients for bacteria to reduce ferric iron and sulfate. Trace elements are removed through the formation of metal sulfides in the reactor. Metal concentrations are lowered by an average of 91.4% (Fe), 97.6% (Al), 83.3% (Zn), 85.6% (Cd), 85.2% (Co), 85.6% (Cu), and 87.0% (Ni). Other trace elements which showed high average removal included La (97.8%), Cu (96.2%), Cs (96.1%), Tl (95.6%), Cd (94.9%), Pb (92.9%), Rb (82.0%), and U (73.8%). The average decrease in sulfate concentrations through the reactor was 451 mg/L (47.2% reduction).

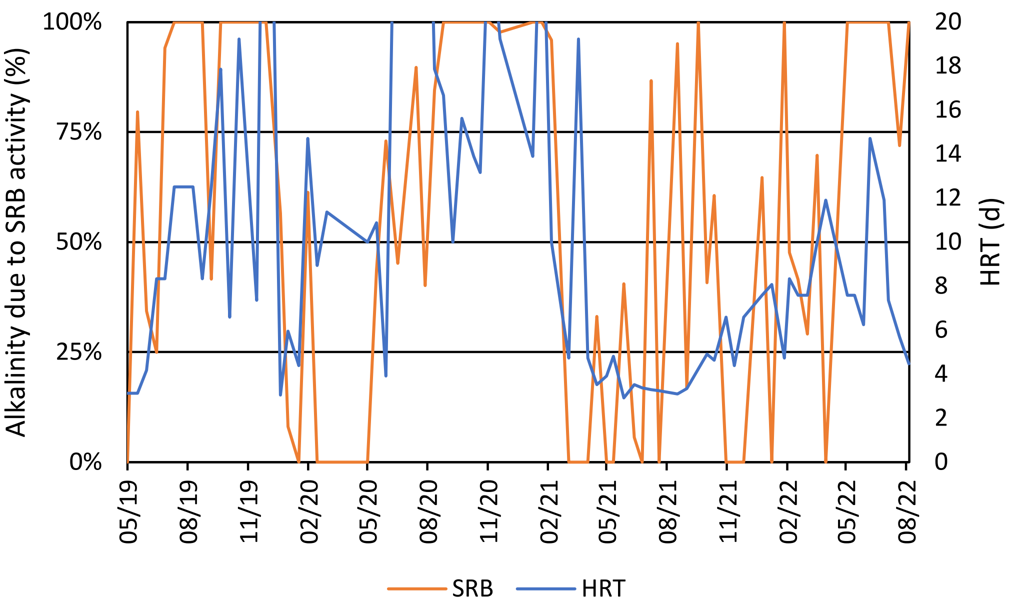

***Figure 4** Alkalinity generation due to SRB activity over time compared to HRT.*

Acknowledgements

We thank New Zealand Coal & Carbon Ltd for the opportunity to present these results. The research supporting the theory of treatment through up-flow mussel shell reactors was originally financed by the Ministry for Business, Innovation and Employment, contract CRLE 1403 and the Coal Association of New Zealand. We thank Ngati Hako, Ngatiwai, Ngai Tahu, West Coast Regional Council (WCRC), Waikato Regional Council, Northland Regional Council, Department of Conservation (DOC), Straterra, Minerals West Coast, OceanaGold, Solid Energy of New Zealand, Francis Mining Co. Ltd, New Zealand Coal & Carbon Ltd and Bathurst Resources for their involvement and support for the research programme. More information on the Centre for Minerals Environmental Research (CMER) is available at: https://www.cmer.nz.

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