Passive Treatment of ARD Using Mussel Shells – Part I: System Development and Geochemical Processes

Paul Weber[1], Chris Weisener[2], Zach DiLoreto[2] and Mark Pizey[3]

1. *O'Kane Consultants Ltd., New Zealand*
2. *Great Lakes Institute for Environmental Science, University of Windsor, Canada*
3. *Solid Energy New Zealand Ltd.*

ABSTRACT

The passive treatment of acid rock drainage (ARD) impacted waters using waste mussel shells utilises vertical flow successive alkalinity producing system (SAP) technology, with considerable industry acceptance in New Zealand. This paper discusses the seven year R&D pathway for this technology. The process is attractive to the mining industry as the shells are free-to-site in some instances, and the installation process is relatively straightforward.

Sulfate Reducing Bioreactors (SRB's) and oxic and anoxic treatment of ARD impacted waters are common passive treatment technologies employed by the mining industry. Mussel shells have significant advantages over these systems, being negative value (and thus free-to site, or even delivered for profit), having a high acid neutralisation capacity (> 80 wt% $CaCO_3$ equivalent), good hydraulic conductivity (~$1x10^{-3}$ m/s), and sufficient organics to support sulfate reducing bacteria catalysts for metal removal. This means that processing costs are reduced and the shells can be placed directly into the reactor.

Down-flow bioreactors using shells have been investigated to encourage the calcium carbonate induced neutralisation of ARD followed by SRB alkalinity generation and trace metal removal. Details are presented of two systems (fresh and weathered shells) that were established at the Solid Energy Stockton Coal Mine, West Coast, New Zealand. Results show the formation of an upper zone dominated by sediment transitioning into underlying Fe then Al precipitate zones that is eventually replaced by a deeper sulfate reducing zone. Metal removal efficiencies range from 96 – 99% for Fe, Al, Ni, and Zn. The longevity of the system is linked to permeability, which is controlled by layers of sludge that develop during treatment.

INTRODUCTION

Acid Rock Drainage (ARD) is typically, the greatest long-term environmental and financial liability for the mining industry where acid-forming waste rock is disturbed. It can result in a project 'hangover' after closure that requires water treatment in perpetuity. Hence other projects and new mines are required to support the cost of legacy treatment. The goal for many companies at closure is to implement passive treatment as a final, lower cost ARD treatment option compared to active treatment.

For remote locations, the use of convention media (compost, bark, sawdust, limestone, etc) for passive treatment is expensive and transport costs can be significant. In New Zealand, research into passive treatment of ARD has been ongoing for a number of years (e.g., Trumm et al., 2008; McCauley et al., 2009; Trumm, 2010; Mackenzie et al., 2011). More recently, since 2007 research investigating the benefits of waste mussel shells for passive treatment of ARD impacted waters has been completed in New Zealand (e.g., Weber et al., 2008; Crombie et al., 2011., Uster et al., 2014; Weisener et al., 2015; Trumm et al., 2015)

BACKGROUND

The green-lipped mussel (*Perna canalicuta*), known as the New Zealand Mussel is an endemic shellfish occurring along most New Zealand coast lines. More than 95,000 tonnes of mussels were harvested from farms in 2011 and greater than 80% of these mussels were exported as half-shells generating considerable shell waste (Uster et al., 2014). Significant cost are associated with the disposal of these shells, which means that any beneficial reuse option becomes a win-win outcome for both suppliers and end-users.

In 2007, a trial was conducted at the Stockton Coal Mine to determine the benefits of the addition of a 300 mm layer of shells beneath 5 m of potentially acid forming (PAF) waste rock (Weber et al., 2008). The trial involved 10 tonnes of mussel shells in a 4 m by 10 m lysimeter that was then covered with 3 m of PAF. A control lysimeter containing only acid-forming overburden was set up adjacent in the same manner. Leachate from the lysimeter treated with mussel shells had a pH of 6.7; acidity of 2 mg/L $CaCO_3$; 0.5 mg/L Fe and 0.2 mg/L Al versus pH 3.3 for the control; acidity of 350 mg/L $CaCO_3$, 8.5 Fe mg/L and 54.7 mg/L Al.

Subsequent work investigated the use of mussel shells as an alternative ARD neutralisation source in vertical flow sulfate reducing bioreactors (SRB) (e.g., McCauley et al., 2009; McCauley, 2011). Laboratory trials indicated that the shells provided significant alkalinity compared to limestone (McCauley, 2011; Uster et al., 2014) confirming the use of shells as an alkalinity source in a SRB type systems.

Key components of any material blend to be used within an SRB are a source of alkalinity, a source of organic matter suitable for bacteria, bacteria, and good porosity. Generally for SRBs this requires the use of materials such as sawdust, bark, compost, limestone, etc, which can be expensive. Mussel shells, as provided from the processing factory, have been chipped to reduce particle size and have a porosity of 0.72 (McCauley, 2011); an acid neutralisation capacity (ANC) or carbonate content of 786 - 894 kg $CaCO_3$/tonne as determined by the ANC test; and an organic (meat) content for fresh shells of 5 – 12 wt% (Crombie et al., 2011). In addition to this 'meat' the shells contain significant protein and chitin.

MANCHESTOR STREET PILOT SCALE MUSSEL SHELL BIOREACTOR

The Manchester Street Mussel Shell Bioreactor, a pilot scale trial, was constructed in June 2009 to treat the Manchester Street Seep (pH 2.8; 422 mg $CaCO_3$/L Acidity; 29 mg/L Fe; 51 mg/L Al) derived from acid forming waste coal overburden. Fresh shells were chipped to < 30 mm in diameter to enable full-weight loads for transport and were typically delivered within 24 hrs. Odour associated with the decomposing meat residue present in the shells was a key issue along the transport route and for onsite stockpiling.

A simple system was planned to minimise costs, which involved a downwards flow reactor design (Figure 1). Manchester Seep influent entered the bioreactor and formed a pond over the shells. This was created by having a riser on the outflow pipe that created a 200 mm water cover over the shells to control odour and ensure saturation of the shells. Water then flowed from this pond down through the shells into a drainage network, which then discharged to Ford Creek, a stream impacted by ARD. A total of 160 t of shells was placed in the reactor to produce a layer 2 m deep and 35 m by ~ 5m wide (range 2.7 -10.2 m).

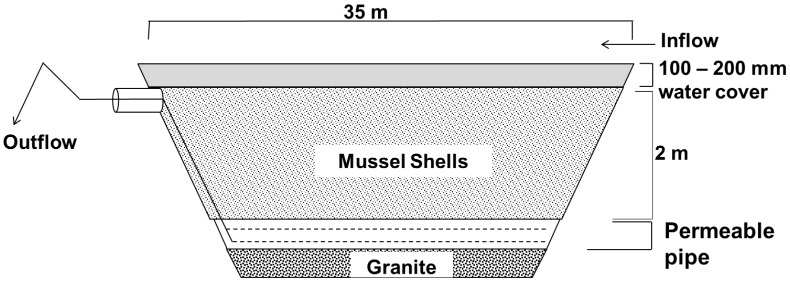

Figure 1 Manchester Street mussel shell bioreactor design.

Water samples from the influent and effluent were collected daily for 28 days and thereafter weekly. Field-based analysis included temperature, pH, EC, DO, odour, and flow. Laboratory analysis included acidity (mg $CaCO_3$/L), ammoniacal nitrogen, and dissolved Al, Fe, Ni, and Zn (Ni and Zn were selected to due being elevated in ARD impacted waters at site). Typical flows for the system were 0.04 – 0.59 L/s with a mean of 0.3 L/s. Often during higher flow (> ~1L/sec) the capacity of the mussel shell reactor was exceeded.

Monitoring results indicated that the mean pH (based on [H+]) of the seep increased from pH 2.8 to pH 6.9 after treatment, and for 59 out of 84 days the effluent pH was ≥7. The mean acidity recorded in the influent was 422 mg $CaCO_3$/L, which is significantly above the mean effluent of 0.3 mg $CaCO_3$/L. Metal removal efficiency was 96-99% for Al, Fe, Ni, and Zn (Crombie et al., 2011). Ammoniacal nitrogen and carbonaceous biochemical oxygen demand ($CBOD_5$) were initially elevated at 46 mg/L and 200 g O_2/m^3 respectively on day 16 before, decreasing steadily to a mean of 3.4 mg/L and 58.44 g O_2/m^3 respectively.

An autopsy of the mussel shell bioreactor was completed by draining the pond (and diverting the inflow) and digging several 300 mm square holes through the sludge layer into the shells (Figure 2). It was observed that the reactor had an upper sludge-sediment layer, a lower thinner orange layer, a white precipitate layer beneath that changed into a lower layer of black shells, which continued to the base of the reactor. It was expected these zones reflected a change from a low pH, high DO, high acidity, high metal ARD to a circum-neutral pH, low DO, low acidity, low metal environment. Samples were sent for laboratory analysis.

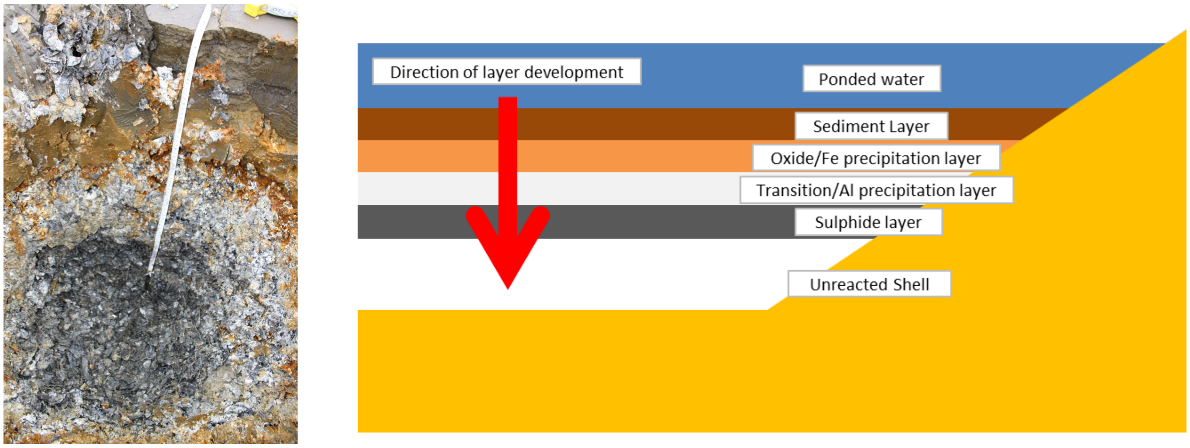

Figure 2 Manchester Street Mussel Shell Bioreactor (photo and schematic). Autopsy test pit (photo) showing sediment (TSS) sludge layer; Fe precipitate layer; Al precipitate layer; and at depth black unreacted shells. The tape measure is 800 mm from the surface to the base of the hole.

The red-brown sludge layer (~200 mm deep) forming on top of the mussel shells is likely to be a combination of road dust, sediment (TSS) transported into the reactor from the seep, and mineral precipitates derived from the AMD. Based on the depth of the sludge and pond dimensions 5 m^3 of sludge was calculated to have accumulated after one year. The median TSS for the seep that drains into the reactor is 18.8 mg/L, although intensive events can range up to 2,960 mg/L (McCauley et al., 2009). Analysis indicated that the Fe layer contained predominantly Fe (24,000 mg/kg) with minor Al (1,620 mg/kg) and less Si (32 mg/kg). Analysis of the white precipitate on the shells below the Fe layer confirmed it was a precipitate high in Al (~70% of the sample or 14,000 – 28,000 mg/kg).

Testing indicated that the neutralization capacity of the shells in the upper white precipitate layer had decreased compared to the black underlying shells. This was determined by flooding shells from the different layers with influent AMD in a sealed container and measuring the time to reach pH 7.0. Results (Crombie et al., 2011) indicated that significant buffering occurred at pH 4 - 5, most likely due to $Al(OH)_3$ precipitation (and acidity buffering). Acidity was neutralized in 1 day for the black shells and 3 days for the white Al layer shells suggesting its neutralization capacity was diminished. ANC testing of the shell from different layers showed that ANC increased with depth and the upper layers are providing significant carbonate neutralization as indicated by reduced ANC (Table 1). Weathered shells have a higher ANC again (956 kg $CaCO_3$/t), which is likely to be a function of less organics due to decomposition.

Table 1 Manchester Street mussel shell bioreactor autopsy results.

Layer	Mean Depth (mm)	ANC (Diloreto, 2013)	Rinse pH	Dominant region of metal removal	Metal removal mechanism
Sediment Sludge Layer	160	8.76	3.01		
Orange Fe Layer	340	288	6.86	Fe, As, Cr	As – Adsorbed Cr- co-precipitated
White Al layer	420	499	6.84	Al (peak), Cu	Cu - sorbed

White Al Layer	550	825	7.54	Al, Zn, Ni	Ni- Co-precipitated with Al Zn - sulfides
Black Shell Zone	1050	846	8.64		Sulfides: wurtzite
Weathered shell from stockpile	Stockpile	956	8.77	-	-

Table 1 indicates that rinse pH increases with depth with a significant increase in pH from the sediment sludge layer to the orange Fe oxide layer. This suggests that the dominant zone of carbonate neutralization is within the orange Fe oxide layer raising the pH to > 6. The system can be divided into five layers if the Al-rich layer is divided into two zones based on the redox gradient and that together with pH this controls the metal removal mechanisms. Key observations from selective extractions (Table 1) indicate a variety of removal processes as shown in Table 1 (Diloreto, 2013).

The longevity of the bioreactor is compromised by the low permeability ferruginous-sediment rich sludge. The autopsy pits that were dug allowed ponded water to drain quickly indicating the higher permeability of the underlying shell layers. Therefore sludge management will be an important component of successful operation of down flow reactors using mussel shells.

Results indicated that ~0.035 tonnes of acidity were neutralised by the mussel shell bioreactor per day. The cost of water treatment for the site in 2011 was ~$320 per tonne of acidity. The cost of installing the mussel shell reactor was approximately $5,300, thus if the system neutralised ~17 tonnes of acidity, the payback of the capex to construct the mussel shell reactor had been achieved. Based on a neutralisation rate of 0.035 tonnes of acidity per day the reactor would achieve pay back after 480 days. This initial trial suggested that the technology had merit and a larger operational trial was planned.

WHIRLWIND STREAM OPERATIONAL MUSSEL SHELL BIOREACTOR

The Whirlwind Stream, towards the southern end of the Stockton Coal Mine and impacted by ARD was selected as a site for the construction of an operational mussel shell bioreactor capable of treating up to 6 L/sec flow, although expected flow rate for the site was ~1 L/s. Results indicated that the seep has less concentrated ARD chemistry compared to the Manchester Seep having pH = ~3.3; dissolved Al = 7.3 mg/L; dissolved Fe = 1.1 mg/L; acidity = 71.5 mg $CaCO_3$/L. In this system the Whirlwind seep flows into an upstream settling pond prior to entering the mussel shell bioreactor (see Weisener et al., 2015 this volume for schematics of the system). It was expected this would reduce the suspended sediment load significantly. Design data is provided in Table 2.

Table 2 Whirlwind Mussel Shell Bioreactor design specifications. Calculations are based on a shell density of 990 kg/m3 and a mussel shell ANC of 800 kg/t.

Parameter	**Rough size**
Average Plan Dimensions (m) (Shell layer)	14.0 x 21.5
Average Plan Area (m^2) (Shell layer)	302
Average Shell depth (m)	1.2
Ponding depth (m)	0.2 - 0.6
Freeboard (m)	0.8 - 0.4

Volume of shells (m^3)	366
Mass of Shells (T)	362
Pore volume (m^3)	192
Residence time (days) (@ 1 - 6 L/s)	2.2 - 0.44
Total ANC (T $CaCO_3$)	290

The pond height in the Whirlwind bioreactor was controlled by a riser from an underdrainage network providing 200 mm ponding depth above the shells. An overflow spillway was constructed at 600 mm above the shells. This provided 400 mm of storm water buffer until overflow to the spillway occurred. Based on the average plan dimensions (Table 2) this provided 120,400 L of capacity. Often after larger rainfall events the spillway was running and the discharge pipe from the mussel shell bioreactor was running at full capacity (6 L/s being the capacity of the drainage network).

One different aspect of this mussel shell bioreactor compared to Manchester Street was that weathered shells were used. As shown in Table 1 the ANC was higher, and the organic content was lower. It was the expectation of the authors that sufficient organic matter remained and little carbon was needed for the sulfate reducing bacteria. Results (Weisener et al., 2015) indicate that a similar geochemical gradient has occurred after 18 months although the thickness of the layers is smaller due to the lower ARD loadings per square meter. Carbon longevity still needs to be considered for this system and trials are in progress.

The treated water from the Whirlwind bioreactor was typically pH 7 and then entered the Whirlwind tributary at compliance water monitoring point S4 together with additional AMD impacted drainage. A significant increase in pH was observed at the S4 monitoring point within the Whirlwind stream after the mussel shell bioreactor was installed (Figure 3).

A key limitation for the longevity of down-flow passive treatment systems using mussel shells is the formation of a low permeability sludge layer. In June 2014, 18 months after the Whirlwind bioreactor was started a double ring infiltrometer was used to measure infiltration rates through the sludge layer that had formed on top of the reactor (22 mm thick). Results indicates that infiltration was in the order of 1.87×10^{-5} m/s, which based on the average plan area (Table 2) generated a flow of 5.7 L/sec for the system. This is within the design specifications of the system and ongoing monitoring will be undertaken every 6 months to measure any further decrease. It is proposed that the system has failed when permeability reduces such that treated flow is < 1 L/sec, or an infiltration rate of $<3.3 \times 10^{-6}$ m/s. At this point the sludge layer would be removed and additional mussel shells placed back in the bioreactor.

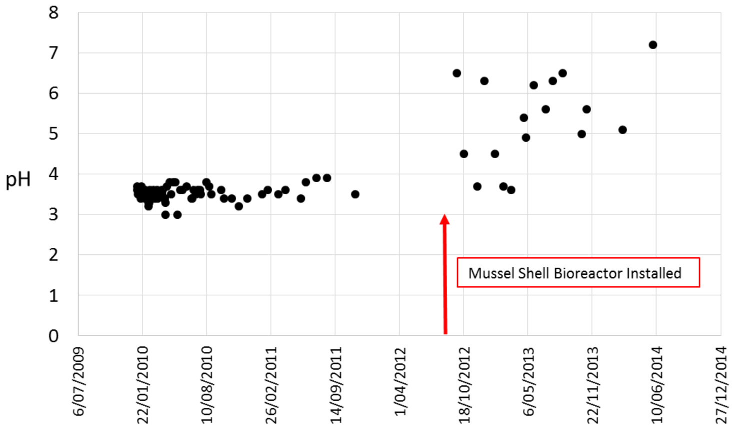

Figure 3 pH versus time profile for the S4 compliance monitoring point (affected by additional AMD impacted mine water) in the Whirlwind Tributary downstream of the Whirlwind Mussel Shell Bioreactor.

The Whirlwind bioreactor has been operating since September 2012. Ongoing research continues to investigate the bio-geochemical reactions occurring within the reactor (e.g., Diloreto, 2014; Weisener et al., 2015) and other research groups are considering other options for the use of mussel shells for passive treatment of AMD impacted waters (e.g., Trumm et al., 2015). A number of issues such as longevity; changing redox fronts, waste management, etc for mussel shell bioreactors still require consideration.

SUMMARY

A significant issue for passive treatment systems is longevity and surety that upfront capex costs will be a favourable use of resources for the treatment of AMD impacted waters in the long term. The short term performance of passive treatment systems are often well quantified, however, their long-term effectiveness is still poorly understood. Carbon exhaustion and hydraulic malfunctions are often amongst the most frequent reasons reported for system failure. As a summary, a risk analysis is presented for mussel shell bioreactors as a passive treatment technology for AMD impacted waters, based on the experience obtained from Stockton Coal Mine. The observations and approach developed is likely to transfer directly to other calcium carbonate shell waste from aquiculture (oyster shells, abalone, cockles, scallops, etc) as their physicochemical attributes are likely to be similar.

Table 3 Summary of key issues for down-flow mussel shell bioreactors. Traffic light classification is green for positive benefits or the process is understood and can be managed; red is negative aspects; and orange components are either indeterminate or need further investigations.

Component	**Comment**	**Traffic Light**
Material Characteristics		
Supply	• Limited by location of shells and reasonable transport distance. • Other shells may also be suitable (e.g., oyster, zebra mussels).	🟧
Cost	• Low- or no-cost dependant on transport distance and commercial negotiations.	🟩
Preparation	• No preparation costs as suppliers generally chip shells to increase density for transport to landfill.	🟩
Blending	• No blending of shell with other materials required as it is a stand-alone product.	🟩
Carbonate Neutralisation	• ANC values of > 800 kg CaCO$_3$/tonne expected with high surface area. • Carbonate alkalinity better than limestone based products on a weight basis.	🟩
Organic Matter	• Greater organic matter content in fresh shells; unweathered shells contain less. • Longevity of organic matter unknown, although bacterial recycling may provide additional carbon. **Further investigations are underway.**	🟧
Porosity	• Measured hydraulic conductivities of 1 x 10^{-3} m/s for fresh shells. • Porosity better than limestone for the same quantity of ANC / surface area	🟩
Odour	• Can be a key issue for community and workforce. • Burial under a water cover removes the issue of odour; fine limestone application to the stockpile can also reduce the odour.	🟥

Component	**Comment**	**Traffic Light**
Lifecycle Analysis	• Mussel shells are a waste stream and beneficial reuse of such materials provides a win-win for both the supplier and end-user. • $CaCO_3$ is not fossil CO_2 and can be considered renewable.	🟩
Operational Performance		
Construction	• Shells can be placed directly into the reactor without further processing. • The system should be constructed such that excavators can access the site and remove any sludge as required.	🟩
Start-up	• AMD impacted waters were fed in directly (no need to equilibrate system) • Sulfate reducing bacteria quickly populate the low DO high pH zones.	🟩
Permeability	• Measured infiltration rates of 1.87 x 10^{-5} m/s determined; although this may decrease with time. **Further investigations are underway.**	🟧
Longevity	• Such systems are expected to last 10-20 years and will be a function of cycling organic C, acidity and metal load. **Further investigations are underway.**	🟧
Transitional pH, Eh profiles	• With maturity the defined geochemical layers may change resulting in the release of metals. Monitoring effluent discharge will provide early warning signs of such changes and system failure. **Further investigations are underway.**	🟧
Maintenance	• It is expected regular maintenance is required to remove the formation of sludge on the surface of the reactor. Timeframes for this will be site specific. • Removal of the sediment sludge and Fe-oxide sludge in down-flow reactors could provide additional space in the reactor for upper shell layer replenishment.	🟩
Sludge Disposal	• Oxidised materials from the upper layers can be disposed of in a "high and dry' environment. • Reduced materials need to be disposed in a structure that prevents oxidation of any sulfide minerals formed (e.g., permanently submerged, disused underground workings, etc)	🟩
Health and Safety Concerns	• Potential for bacteria associated with rotting shellfish. • SRB reactors can produce H_2S and CO_2 and risks should be managed appropriately. • H_2S can create odour issues.	🟧

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