

PASSIVE TREATMENT OF ACID MINE DRAINAGE USING WASTE MUSSEL SHELL, STOCKTON COAL MINE, NEW ZEALAND

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ABSTRACT

Acid Mine Drainage (AMD), a result of historical and current coal mining, and the associated oxidation of pyrite within the coal measures, is a significant environmental liability for Stockton Opencast Mine, located on the West Coast of the South Island, New Zealand. This liability is likely to persist for at least 100 years. With up to 6,000 mm of rainfall per year, often in intensive events (some up to 100 mm/hr), water management is critical for the control of adverse effects that include low pH, dissolved metals (including aluminium), and high suspended solids in drainage waterways. Traditionally, neutralisation of AMD at Stockton coal mine has been carried out by direct dosing of ultra-fine limestone (UFL) to affected waterways.

An alternative passive treatment system utilising mussel shell, generally considered a waste stream and dumped at landfill, offers a cheaper, less labour-intensive method of reducing the acid load reporting to the primary waterways on site.

An operational field trial was conducted on the Manchester Street Seep and indicated a payback period of 1,027 days (up to March 2012) when compared to the cost of UFL treatment. The bioreactor has been treating water with an initial pH of <3 to a pH >7; and achieving a metal removal efficiency of 96-99% for Al, Fe, Ni, Tl, and Zn. Low DO and initial high concentrations of CBOD₅ and ammonia nitrogen in the discharge due to remnant mussel flesh had negligible effect on the receiving waterway. The removal of sediment and sludge build-up on the surface of the system is required approximately every two years to increase the system's porosity and treatment capacity.

KEYWORDS

KEYWORDS: Acid mine drainage, Stockton coal mine, mussel shell, passive treatment system, *Perna Canaliculus*, water treatment.

1 INTRODUCTION

Stockton Opencast Mine, owned by Solid Energy New Zealand Ltd, and located on the West Coast of the South Island, 35 km north of Westport and 700 – 1,100 m above sea level (Fig. 1 inset), is the largest opencast coal mine in New Zealand, with an active mining area of ~900 ha; ~200 ha of which is rehabilitated. Annual precipitation at the coast near Stockton mine is ~ 3,000 mm/a, increasing to ~6,000 mm/a at the mine site (Davies et al., 2011). Frequent rain events with daily rainfall exceeding 200 mm can occur at any time throughout the year; mean annual temperature is ~9°C (Davies et al., 2011). Coal mining has been a feature at Stockton since 1896, within the Eocene Brunner Coal Measures (BCM) that formed in a marginal marine setting. The BCM are overlain by marine sediments, mainly mudstones, with some marginal marine sandstone near the contact with the coal measures. Pyrite is abundant (up to 5 wt.%) in the upper portions of the coal measures and the lower parts of the overlying marine sediments. The Brunner Coal Measures have very unreactive alumino-silicate minerals (K-feldspar, kaolinite, muscovite) that provide little silicate neutralisation of acidity such that the oxidation of pyrite typically leads to the formation of acid mine drainage (AMD).

Pyrite is the most common sulfide mineral in the BCM and when it is exposed to water and atmospheric oxygen during the mining process; acidity is generated resulting in AMD, a significant environmental liability for the mine, which is likely to persist for at least 100 years. The low pH associated with AMD leads to the acid dissolution from the surrounding rock of metals such as aluminium from the aluminosilicate minerals present. Traditionally, acid neutralisation of waterways at the mine has been carried out by direct dosing of ultra-fine limestone (UFL) to affected waterways which raises the pH and precipitates out metals such as Fe and Al. Further details on AMD at Stockton are provided in Elder et al. (2011).

Mussel shell, primarily made up of calcium carbonate (CaCO_3), protein, chitin, and small amounts of lipid and phosphate, are increasingly being investigated as a means to treat contaminated water. The use of mussel shell to treat AMD has received limited attention in literature, although several comparable studies are available (e.g., Mackenzie 2010; McCauley 2010a,b). Biogenic aragonite has been investigated for Cd removal and other metals to the order of $0.5 \mu\text{M}$, and mussel and oyster shell was used to treat waters containing Cd, Fe, Pb, and Zn (Kohler et al. 2007). Laboratory scale bioreactors containing organic materials and mussel shell have shown promising results in their ability to sequester metals, increase the pH, and decrease the acidity of AMD (McCauley et al., 2008; MacKenzie, 2010; McCauley et al., 2010b). >99.8% - 99.9% of Al, Fe, Cd, Cu, Ni, Pb, and Zn was removed from three laboratory bioreactors containing organic materials and mussel shell (McCauley 2008; McCauley, 2010b). Metal removal efficiencies of 47% for Cu, 80% for Zn, and 89% for Pb were seen in rain gardens that used mussel shell to treat storm water runoff (Good, 2011).

Seafood is New Zealand's fifth largest export by value. International sales have grown from \$500 million to more than \$1.35 billion over the past 20 years, and mussels have the greatest market share at approximately \$202 million (32,724 tonnes in 2009) (NZTE, 2010). The major mussel-growing areas in New Zealand are the Coromandel, the Marlborough Sounds, and Stewart Island (FAO, 2012). Seasonal variation and subsequent harvest season means mussel shell is not available during part of the year (June to September). The South Island of New Zealand has close to 4,000 tonnes of mussel shell that could be used for AMD treatment and this paper looks at the opportunity that this presents.

This paper documents the improvement in quality of AMD through the use of 100% green lipped-mussel (*Perna canaliculus*) shell (a waste stream generally dumped at landfill), and compares the cost of this water treatment strategy to dosing waterways with UFL.

2 MATERIALS AND METHODS

2.1 MATERIALS

Perna canaliculus shell, commonly known as the green lipped-mussel, was used in this field trial to treat AMD. *Perna canaliculus* shell is composed of a hard inner layer (nacreous layer) made of CaCO_3 , a middle chalky layer (prismatic layer) composed of inorganic CaCO_3 (90%) in a crystalline structure of either calcite and/or aragonite, mixed with a small amount of protein (conchiolin), and a thin outer protective layer composed predominantly of organic protein (SITO, 2006; Kohler et al., 2007).

Shell for this operational trial was obtained after the mussel flesh had been removed as part of the food processing. The shell was crushed to approximately 30 mm to compact its volume for transport, volume being the limiting factor to bulk transport rather than weight in a truck. Crushing also provides a large reactive surface area for neutralisation reactions to occur on, and significant porosity in the bioreactor due to poor packing of crushed shells. Mussel shell supplied for this trial typically contained between 5 and 12 wt.% meat (determined by scraping the meat from samples of the supplied shell and weighing the two components). The acid neutralisation capacity (ANC) of the shell (containing meat) ranged from 786 – 894 kg CaCO_3/t equivalent (mean 850 kg CaCO_3/t) as determined by the ANC test (Smart et al., 2002).

2.2 MUSSEL SHELL BIOREACTOR

The mussel shell bioreactor was designed as a passive treatment system for the neutralisation of acidity and the removal of dissolved metals contained in the AMD. From a cost-benefit perspective, a simple system was required, to make the process less expensive compared to conventional treatment by UFL. A seep day lighting below Manchester Street (Fig. 1) and next to the main 2-5 Haul Road at Stockton coal mine was selected to be treated.

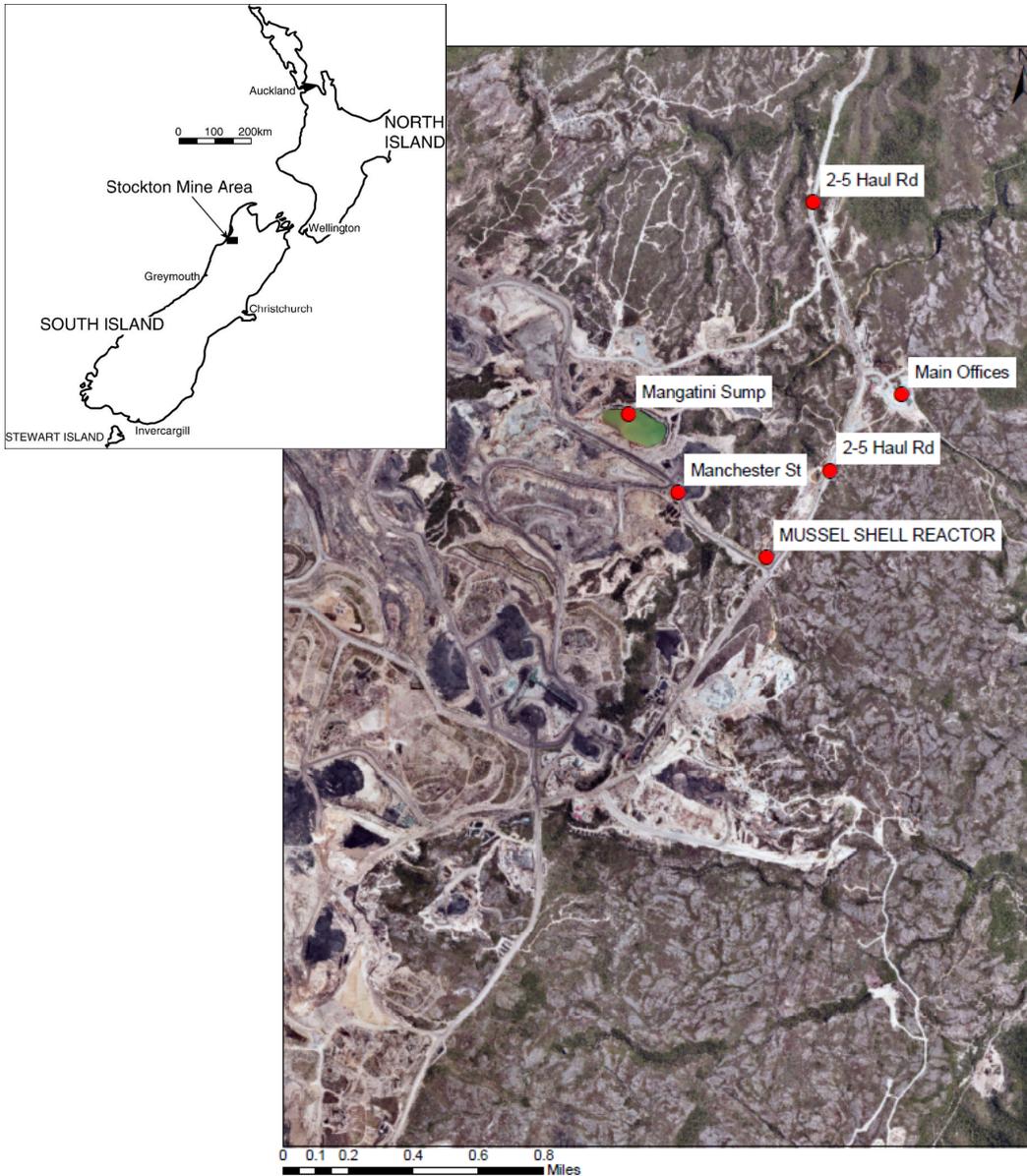


Figure 1. Location of Stockton coal mine on the West Coast of the South Island of New Zealand (inset) and location of the mussel shell bioreactor at Stockton coal mine. The mussel shell bioreactor is located below Manchester Street and next to the 2-5 Haul Rd.

A sedimentation pond located beneath the AMD seep was excavated to form a bioreactor 2 m deep, 35 m long, and between 2.7 and 10.2 m wide. The bioreactor, with 60° angle sides, had permeable pipe (2 lengths of 25 mm x 50 m) placed in the bottom. Each length of this permeable pipe was then attached to a length of alkathene pipe (25 mm diameter) which was feed through the culvert (sealed with bentonite) down to the discharge channel where the treated water would be released onto rocks before being discharged into the receiving waterway. The alkathene pipe was used as a riser to control the pond height and 100-200 mm of water was kept above the shells to control odour and oxygen ingress into the bioreactor (to maintain anaerobic conditions). 160 tonnes (236 m³) of shells were placed in the bioreactor on top of the permeable pipe and levelled (Fig. 2). This set-up

allowed the influent to flow horizontally across the pond before moving vertically through the shells into the permeable and out through the alkathene pipe.

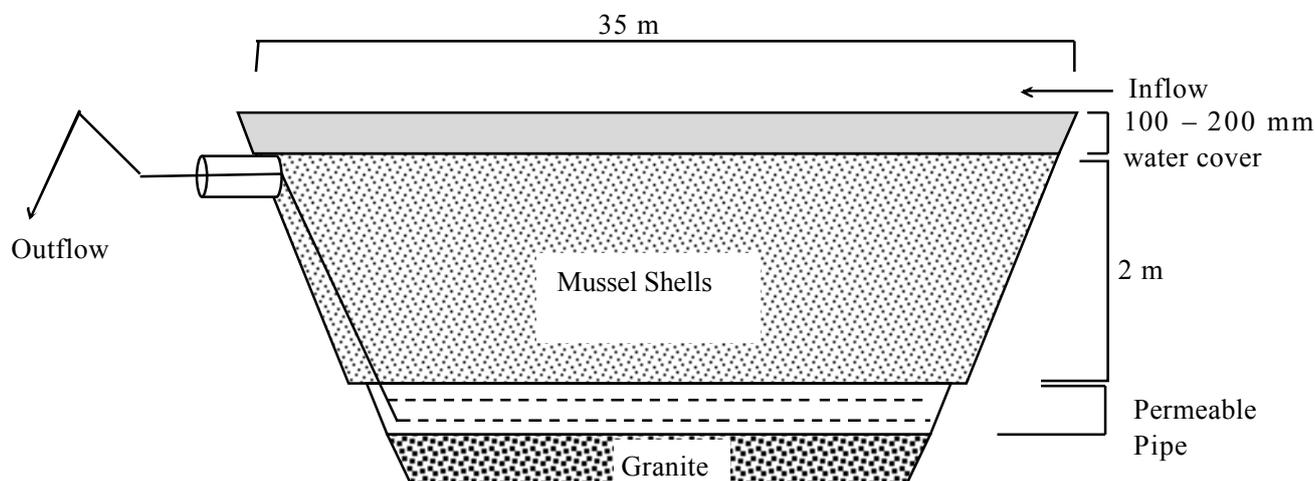


Figure 2. Schematic of the mussel shell bioreactor installed at Stockton coal mine

2.3 WATER SAMPLING AND ANALYSIS

Daily water samples from the influent and effluent were collected from June 2009 for 28 days and, thereafter weekly in accordance with the Australian/New Zealand Standard for Water Quality - Sampling (AS/NZS 5667.1:1998). Routine *in-situ* analysis included temperature, pH, EC, odour, and flow.

Water samples were analysed in the field for DO in accordance with the 4500-OG Dissolved Oxygen Membrane Electrode Method, while the pH, EC, and temperature were determined using a TPS WP 81 pH, Cond, Salinity meter using a TPS pH and conductivity probe, pH electrode double junction with porous Teflon BNC Plug. The meter was calibrated at pH 4, and 7 using TPS or BDH branded buffers weekly. Odour was recorded by staff using a basic assessment scale - no odour, odour, strong odour, and persistent odour (>50m away).

Acidity ($\text{mg L}^{-1} \text{CaCO}_3$) was measured by back-titration of a 50 mL aliquot to pH 4, 5, and 7 with 0.1 M NaOH; acidity was then calculated as per the American Public Health Association (APHA 2005). An unacidified sample was filtered through a 0.45 μm membrane filter to remove suspended particulate matter and then sent to R J Hill Laboratory for ammonia nitrogen (phenol/hypochlorite colorimetry using a discrete analyser APHA 4500-NH₃ F (modified from manual analysis) 21st ed. 2005); CBOD₅ (APHA 5 Day BOD Test, 5210 B, 21st edition 2005); and dissolved Al, Fe, Ni, and Zn by ICP-MS using the APHA 3125 B 21st ed. 2005 standard method.

Three inflow and outflow water samples were collected (11/12/09, 15/01/10, 29/01/10) for complete water analysis and subsequent geochemical modelling using PHREEQC. The full mass balance was carried out by R J Hill Laboratory and involved nitric acid digestion as a pre-treatment prior to analysis (APHA 3030 E 21st ed. 2005). Mean pH for the three samples was determined from the $-\log(\text{H}^+)$.

A Sensus flow meter was used to monitor the effluent flow and determine the quantity of water treated by the system. The meter was cleaned every six weeks to prevent build-up of a grey-white precipitate which would block the impeller and consequently not record the flow. The influent flow was recorded when possible using a 150-300 mL container and a stopwatch. At times during high flow the bioreactor capacity was exceeded, resulting in untreated water overflowing and running directly into the receiving waterway. Water passing

through the bioreactor, however, was still treated to a comparable standard to that during low-flow periods. The residence time for the mussel shell bioreactor was calculated as per Equation 1. The void space within the bioreactor was determined from a dry bulk density of 0.698 t/m^3 and a saturated bulk density of $1,420 \text{ t/m}^3$ as determined by McCauley et al. (2010b).

Residence Time:

$$(\text{Void volume (m}^3\text{)/Flow rate (L/s)}) \times (1,000 \text{ L/1 m}^3) \times (60\text{s/1 min}) \times (60 \text{ min/hr}) \times (24 \text{ hr/1 day}) \quad (1)$$

Where;

$$\text{Void volume} = \text{mussel shell volume (m}^3\text{)} / \text{void space (m}^3\text{/m}^3 \text{ mussel shell)}$$

$$\text{Void space} = \text{saturated mussel shell bulk density (kg/m}^3\text{)} - \text{dry mussel shell bulk density (kg/m}^3\text{)}$$

$$\text{Mussel shell volume} = \text{mussel shell weight (kg)} / \text{dry mussel shell bulk density (kg/m}^3\text{)}$$

$$\text{Void space} = \text{mussel shell volume} - (\text{mass of mussel shells (kg)} / \text{dry mussel shell bulk density (kg/m}^3\text{)})$$

$$\text{Mussel shell volume} = \text{mass mussel shells (kg)} / \text{dry mussel shell bulk density (kg/m}^3\text{)}$$

2.4 PRECIPITATE ANALYSIS

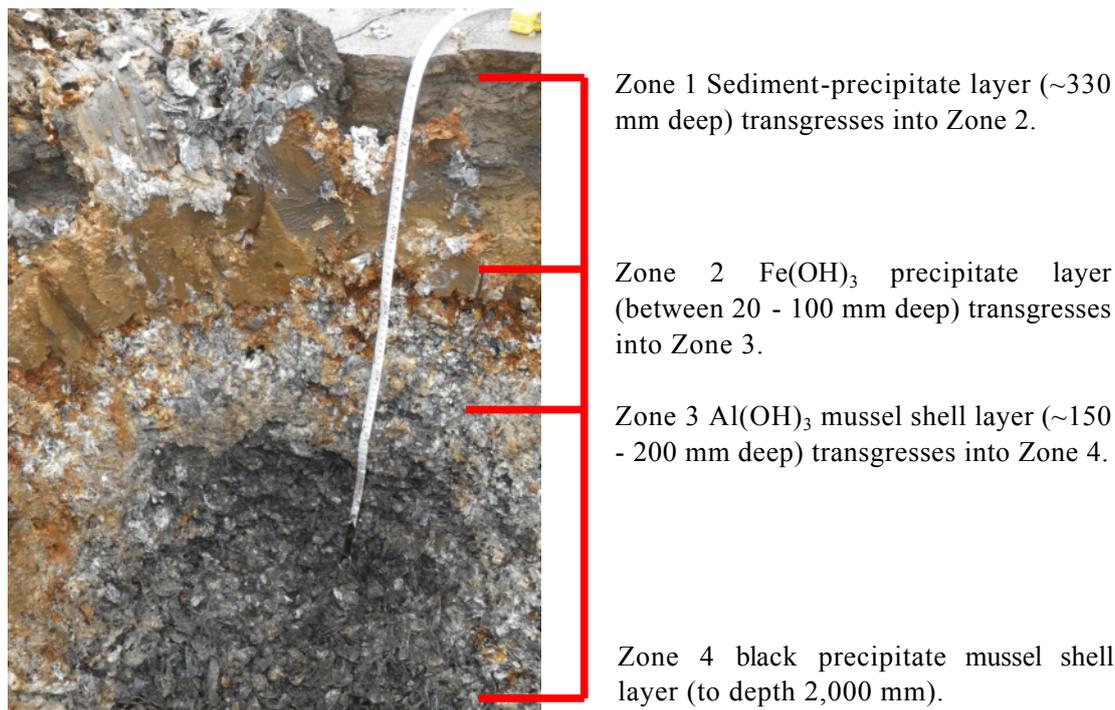
A black and grey-white precipitate was observed forming below the discharge point of the mussel shell bioreactor (Photograph 1.). Several rock samples coated in the precipitates were sent to CRL Energy Limited and R J Hills Laboratory for XRD and ICP-MS analysis of an acid digestate (APHA 3125 B 21st ed. 2005, US EPA 200.8).



Photograph 1. Black precipitate at the effluent discharge point for the Manchester Street seep mussel shell bioreactor at Stockton coal mine.

After 320 days the mussel shell bioreactor was drained and a number of 400 mm (width) x 400 mm (length) x 1,000 mm (depth) holes dug through the top sludge and sediment-precipitate layers into the layer of shell as part of the autopsy process. A number of distinct zones were identified, including an upper sediment-precipitate sludge layer (Zone 1) above the mussel shell that graduated into Zone 2 an orange Fe(OH)_3 precipitate zone; Zone 2 was gradational down into a white Al(OH)_3 precipitate zone (Zone 3) within the shells; and a black precipitate zone within the shells and beneath the Zone 3 shells (Zone 4) to depth (Photograph 2). A white precipitate accumulating on the outside of the Zone 3 shell was extracted during the leach test and sent to CRL Energy for XRD analysis, while a sample of the black precipitate within Zone 4 was also extracted during the

leach tests and sent to CRL Energy for XRD and XRF analysis. PHREEQC, a computer programme for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, was also used to predict potential precipitates that were likely to be forming in the bioreactor.



Photograph 2. Cross section through the mussel shell bioreactor at Stockton coal mine on day 933. Four distinct zones are shown (sediment-precipitate sludge layer, $\text{Fe}(\text{OH})_3$ layer, mussel shell with $\text{Al}(\text{OH})_3$, and black precipitate mussel shell layer) and the depth of each layer.

2.5 LEACH TEST

Three samples of shells from the $\text{Al}(\text{OH})_3$ layer (Zone 3) and the underlying black precipitate zone (Zone 4) were collected in 1 L containers and flooded with influent AMD to create zero headspace, and thence transported back to the laboratory where the samples were stored in a fridge until test work was undertaken. The AMD was removed from the containers in the laboratory using a pipette and then the remaining sample was weighed. 500 mL of fresh influent AMD was poured into the container and then a pH meter connected to a data logger was placed into the container and the pH recorded over 4 days to look at neutralisation profiles.

A pipette was used to collect the white precipitate that had loosely adhered to the shells in the Zone 3 sample. The precipitate was filtered through 11 μm filter paper and the retentates sent to R J Hill's Laboratories where the sample was placed through a modified aqua regia digestion procedure followed by ICP-MS (in-house method 7303 based on NIOSH, issue 1 (modified)) to obtain results for total and dissolved metals.

2.6 COST DETERMINATION

The cost to neutralise one tonne of acidity by means of the mussel shell bioreactor was compared to the cost to neutralise one tonne of acidity using UFL. The amount of acid neutralised per day by the mussel shell bioreactor was determined from the flow of water discharged over 23 days multiplied by the tonnes of acidity per m^3 of water treated converted to a daily acidity neutralisation rate. ~0.035 tonnes of acidity was neutralised by the mussel shell bioreactor per day.

The current cost of direct dosing UFL at Stockton coal mine is ~\$320 per tonne of acidity (based on 60% efficiency). The cost of installing the mussel shell bioreactor was approximately \$11,000, including equipment,

on-site labour and machinery. Thus, payback of the capital cost of construction is achieved if ~36 tonnes of acidity is neutralised by the mussel shell bioreactor. Based on a neutralisation rate of 0.035 tonnes of acidity per day, payback therefore occurs after 1,027 days. This is equivalent to ~36 tonnes of acidity. The calculation does not include the savings to suppliers of shell that do not have to pay to dispose of the waste shell in the likes of landfills, which are constantly increasing their disposal fees.

3 RESULTS

3.1 WATER CHEMISTRY

The mean pH (as determined from the hydrogen ion concentration) of the seep increased from pH 2.8 (initial) to pH 6.9, while for 59 out of 84 days the effluent pH was ≥ 7 (Fig. 3). The mean level of acidity recorded in the mussel shell bioreactor influent was 422 mg CaCO₃ L⁻¹ eq., which is significantly higher than the mean effluent acidity of 0.3 mg CaCO₃ L⁻¹ eq. (Fig. 4). The temperature of the influent and effluent was relatively constant with a mean influent and effluent temperature of 11°C, while the average effluent hardness (275 mg/L) was five times greater than the influent hardness (55 mg/L). The flow rate for the discharge effluent varied dependant on pond head (which would rise during storm events as discharge capacity from the alkathene pipe was exceeded) and ranged from 0.04 L s⁻¹ to 0.59 L s⁻¹. The latest results indicate a mean flow from the mussel shell bioreactor of 0.3 L s⁻¹. The residence time was calculated as ~6 days.

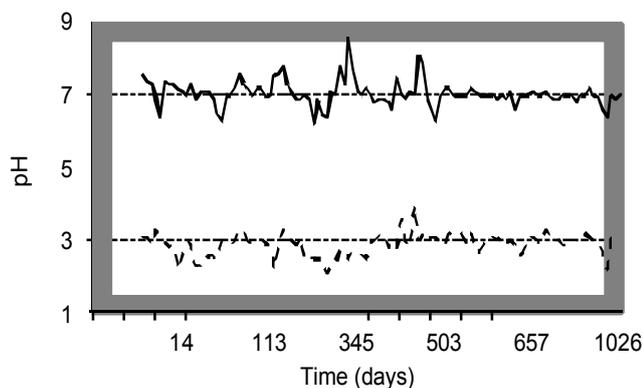


Figure 3. pH results. pH of effluent (____) and influent (---) for the mussel shell bioreactor installed at Stockton coal mine.

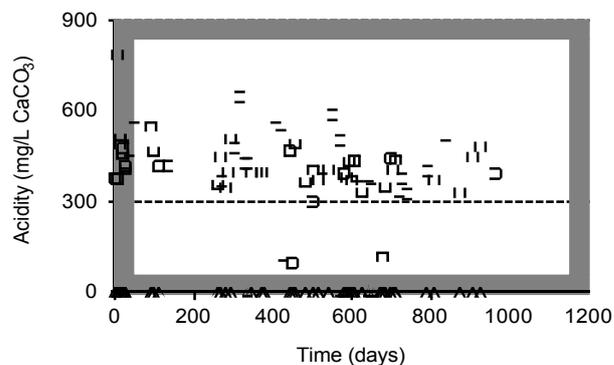


Figure 4. Acidity results. Concentration of acidity (mg/L CaCO₃) in the influent (□ squares) prior to passing through the mussel shell bioreactor and after (Δ triangles) passing through the bioreactor.

Ammonia nitrogen and carbonaceous biochemical oxygen demand (CBOD₅) were initially elevated (Fig. 5) peaking at 46 mg L⁻¹ and 200 g.O₂ m⁻³ respectively on day 16 before, decreasing steadily to a mean of 3.4 mg L⁻¹ for the last 20 (out of 25) samples for ammonia nitrogen and, to a mean of 58.44 g.O₂ m⁻³ over the last six samples for CBOD₅. Downstream monitoring in the receiving waterway (Ford Creek) indicated that DO, CBOD₅, and ammonia nitrogen were comparable to baseline values, indicating discharging the effluent into the creek did not have a negative effect on the creek's water quality.

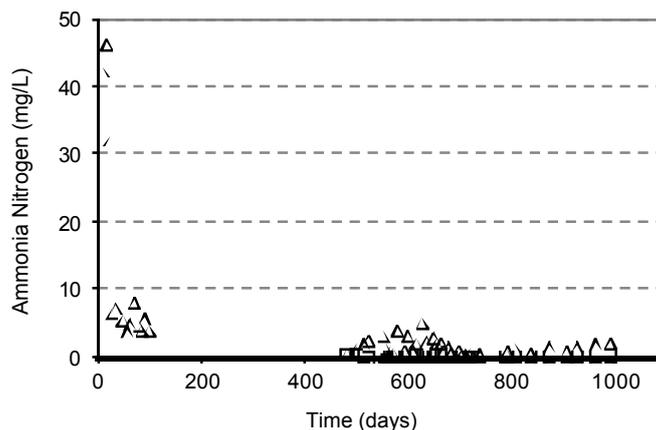


Figure 5. Ammonia nitrogen. Concentration of ammonia nitrogen (mg/L) in the influent (□ squares) prior to passing through the mussel shell bioreactor and after (Δ triangles) passing through the mussel shell reactor over time (days).

3.2 METAL REMOVAL EFFICIENCY

Metal removal efficiency was 96-99% for Al, Fe, Ni, Tl, and Zn (Fig. 6a-e and Table 1). Fe was two to three orders of magnitude lower (99% reduction) post treatment. Dissolved Al in the effluent from the mussel shell bioreactor was reduced to below the detection limit >50% of the time, whereas the influent was typically four orders of magnitude higher. The mean Ni in the influent and effluent results decreased one order of magnitude. The mean metal load of Zn was reduced four orders of magnitude in the effluent. 97.8 – 99.1% of Tl was removed from a mean concentration of 0.0046 in the influent to 0.00007 mg/L CaCO₃ in the effluent. The concentration of dissolved Zn in the influent fluctuated directly with the concentration of dissolved Fe. Similar trends of Zn removal coincident with Fe removal from solution have previously been identified at Stockton for the Mangatini Stream following UFL treatment of AMD (Davies et al. in prep). Three sampling runs were analysed for total anions and cations (days 184, 219, and 233) with results indicating that B, Br, Ca, Cs, Mg, Na, and Sr increased in concentration, a supposed result from the dissolution of the shells, although they were not at significant levels.

Table 1. Influent and effluent water chemistry (Al, Fe, Ni, Zn, pH, EC, acidity, DO and ammonia nitrogen) for the mussel shell bioreactor installed at Stockton coal mine after operating for 1040 days. Mean pH determined from hydrogen ion concentration.

	Al (mg L ⁻¹)	Fe (mg L ⁻¹)	Ni (mg L ⁻¹)	Zn (mg L ⁻¹)	pH	EC (μS cm ⁻¹)	Acidity (mg L ⁻¹ CaCO ₃ eq.)	DO (mg L ⁻¹)	Ammonia Nitrogen (mg L ⁻¹)
Influent									
Min	<0.003	0.81	0.10	0.5	2.1	332	240	2.1	0.037
Mean	51	29	0.27	1.18	2.8	1246	422	8.5	0.15
Max	80	140	0.5	2.2	4.0	1621	790	10.2	0.32
Effluent									
Min	<0.003	<0.02	<0.0005	<0.001	6.2	943	0	0.5	0.06
Mean	0.013	0.17	0.028	0.008	6.9	1445	0.3	2.8	7.81
Max	0.21	0.92	0.038	0.045	8.6	2110	9.9	6.1	46

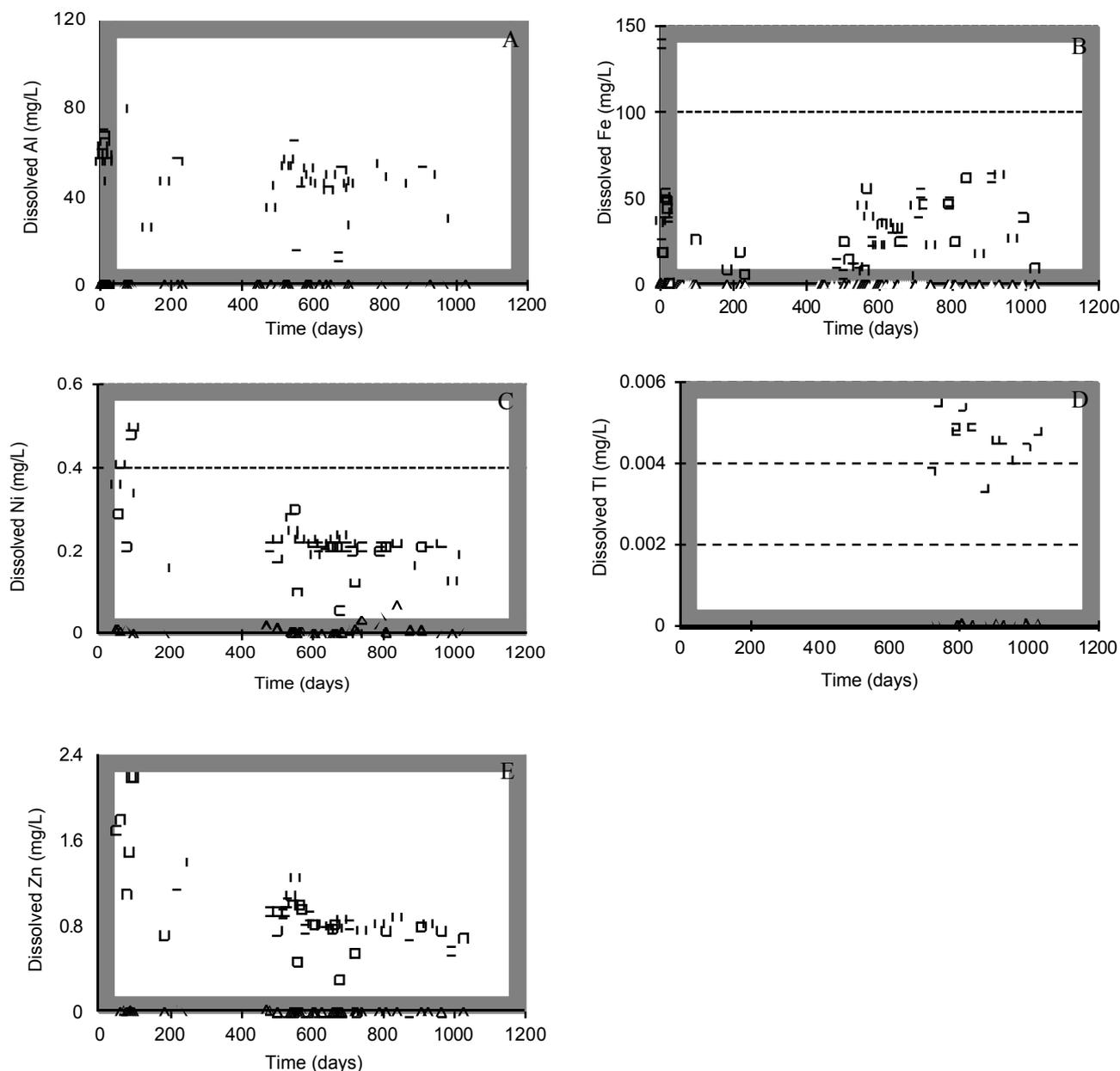


Figure 6(a – e). Dissolved metals results. Concentration of dissolved Al (a), Fe (b), Ni (c), Tl (d), and Zn (e) (mg/L) in the influent (\square squares) prior to passing through the mussel shell bioreactor and after (Δ triangles) passing through the mussel shell bioreactor.

3.3 PRECIPITATE CHARACTERISATION

A number of distinct zones were identified upon conducting the autopsy including an upper sediment-sludge precipitate layer (Zone 1) above the mussel shell; an orange $\text{Fe}(\text{OH})_3$ precipitate zone (Zone 2) immediately at the top of the mussel shell; a white $\text{Al}(\text{OH})_3$ precipitate zone (Zone 3) beneath the orange layer; and a black precipitate zone beneath these layers (Zone 4) to depth (Photograph. 2).

The red-brown sediment-precipitate layer (Zone 1) that accumulated on top of the bioreactor was likely to be a combination of road dust, sediment transported into the bioreactor from the seep, erosion of the sides of the bioreactor and chemical precipitate derived from the AMD. The median total suspended solids (TSS) for the seep which drains into the bioreactor was reported to be 18.8 mg L^{-1} , although intensive events can range up to $2,960 \text{ mg L}^{-1}$ (McCauley et al., 2009). Using a mean flow rate of 0.3 L s^{-1} and a mean TSS of 18.8 mg L^{-1} ~ 290 kg of sediment could have been deposited in the pond over 600 days, although frequent high-flow events (~ 10 - 20 per year) could also deposit up to ~ 70 kg each event over a 24-hour period. Thus, it is reasonable to assume up to one tonne of sediment could be deposited on top of the system annually.

Zone was analysed and determined to be predominantly of Fe origin ($24,000 \text{ mg kg}^{-1}$), with minor Al ($1,620 \text{ mg kg}^{-1}$) and less Si (32 mg kg^{-1}). After 320 days Zone 2 was ~ 200 mm deep, after 933 days it was ~ 330 mm deep. This $\text{Fe}(\text{OH})_3$ precipitate zone extends down into the mussel shell (Zone 3), and after 320 days was observed to a depth of 100 mm into the shells, however, was typically 20 mm. From the depth of Zone 1 and 2 (~ 200 mm deep) and pond dimensions $\sim 5 \text{ m}^3$ of sludge and sediment accumulated over one year. Based on the flow rate (0.3 L s^{-1}) and mean concentration of Fe in the influent (29 mg L^{-1}), 0.55 tonnes of Fe would be deposited over two years or $\sim 1,000 \text{ kg Fe}(\text{OH})_3$.

ICP-MS analysis of the white precipitate confirmed Zone 3 was high in Al ($\sim 70\%$ of the sample or $14,000 - 28,000 \text{ mg kg}^{-1}$). PHREEQC analysis indicated that this could be in the form of the hydrated mineral alunite (aluminium potassium sulfate, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) or gibbsite ($\text{Al}(\text{OH})_3$). To date the concentration of metals in the effluent has been consistently 96–100% lower than the influent, suggesting no re-dissolution of the metals (Al, Fe, Ni, Tl, and Zn) has occurred. XRD and XRF analysis of the black precipitate in Zone 4 indicates sulfur was the major mineral element detected respectively (92.5% S by XRF). Magnetite (Fe_3O_4) was also picked up as a trace mineral on the XRD, while XRF reported Fe as 3.48% and total carbon as 5.75 wt.%. It is likely this material is a mono-sulfide. These results suggest that although a significant amount of Fe is precipitating higher up in zones 1 and 2 due to carbonate neutralisation raising the pH to a point that allows $\text{Fe}(\text{OH})_3$ precipitation, below Zone 2, the system becomes anaerobic and the Fe is maintained in solution until it precipitates as a sulphide.

Leach test results for Zone 3 and 4 (Fig. 7) indicate Zone 3 is significantly slower at neutralising acidity than Zone 4. Zone 4 samples neutralised (pH 7) AMD within 1 day, whereas Zone 3 required 3 - 4 days, suggesting the presence of the aluminium coating caused decreased neutralisation rates. For both layers the increase to \sim pH 4 was rapid, however, buffering then occurs as Lewis acidity associated with Al is slowly neutralised between pH 4 – 5. The period of buffering is longer for Zone 3 at 49 hours compared to 14 hours for Zone 4, due to a combination of the Al coating and possibly equilibrium reactions (Al starts to dissolve below \sim pH 4.5).

If, as detected in the leach test, the neutralisation capacity of shells in Zone 3 is mostly exhausted and therefore limits the performance of the mussel shell bioreactor, then the forecast life of the mussel shell bioreactor determined from the growth rate of Zone 3 (150 – 200 mm over 320 days), depth of the reactor (2,000 mm) and exhausting the full depth of the bioreactor at is 8 – 10 years, at which point the mussel shell would need to be replaced. The ANC of the shell in each layer is currently being determined.

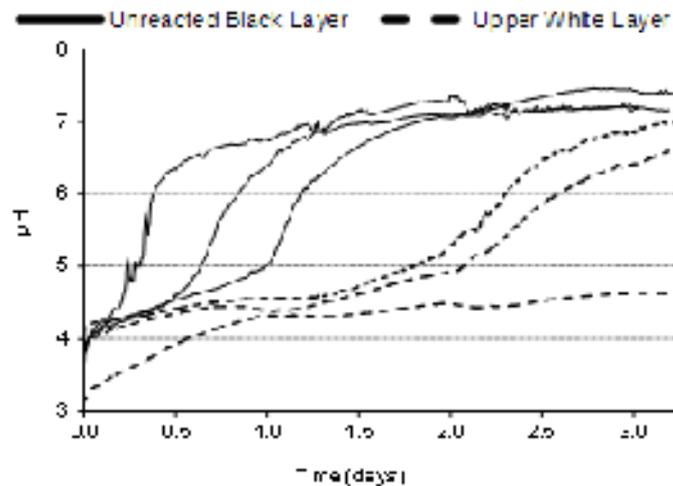


Figure 7. Leach test results. pH against time for the unreacted black layer and the upper white aluminium precipitate layer. The buffering zone between pH 4 and 5 is extended for the shells with the white precipitate layer compared to shells without a layer of armouring, extending the required residence time from 1-2 days to 3-4 days.

3.4 DISCHARGE PRECIPITATES CHARACTERISATION

Two precipitates observed at the effluent discharge (Photograph. 1), one black and the other grey-white. XRD detected gypsum as the major mineral in the grey-white precipitate; minor quantities of quartz, sulfur, and potassium magnesium aluminium fluoride silicate were also detected. ICP-MS analysis detected iron (92,000 mg/kg dry wt.) to be the largest component of the black precipitate (~9 wt.%), followed by sulphate (4,500 mg/kg dry wt.) and aluminium (1,330 mg/kg dry wt.). It was also high in trace elements Mg (510 mg/kg dry wt.), Ni (260 mg/kg dry wt.), and Zn (530 mg/kg dry wt.). The elevated Fe determined in the effluent stream is comparable to the Fe content of the precipitate observed in Zone 4 (~3.5 wt.%). A slight sulfur smell (H_2S) could be detected within five metres of the bioreactor effluent discharge point. 50 m down-gradient in the rock drain the black precipitate was absent and the only observable effect was iron staining, which is likely to be a function of Fe(II) oxidation and subsequent precipitation. No significant environmental effects other than aesthetic are expected from this precipitate.

4 DISCUSSION

The bioreactor has been operating for 1,027 days and, at March 2012, remains in operation. The results presented show significant improvement in water chemistry of the seep. pH increased to >7, and ~36 tonnes of acidity was neutralised by the bioreactor during this time (based on recorded effluent flow and influent acidity). 96-100% of Al, Fe, Ni, Tl, and Zn were removed from the influent. Based on a mean flow and metal load for dissolved Al, Fe, Ni, and Zn, 432 kg of metals are estimated to be removed from the AMD seep per year by the bioreactor. Effluent metal concentrations from the bioreactor for Al, Fe, Ni, and Zn are in accordance with the 99% protection level recommended in the ANZECC guidelines (2000). The presence of DO in the influent likely promotes the oxidation of Fe^{2+} to Fe^{3+} where it is precipitated as $Fe(OH)_3$ following an increase in pH derived by neutralisation of the acid load by the $CaCO_3$ present in the mussel shells.

The mussel shell bioreactor has greater metal removal efficiency in AMD-impacted waterways than active ultra-fine limestone (UFL) ($90\% < 100 \mu m$). Direct dosing of UFL to an AMD-impacted waterway at Stockton mine lead to metal removal efficiencies of 96%, 99%, 45%, and 71% for Al, Fe, Ni, and Zn respectively, which is significantly less than the mussel shell bioreactor. The field-based mussel shell reactor also outperformed limestone and mixtures of limestone and mussel shell in laboratory based bioreactors (McCauley et al., 2009). The residence time was calculated as ~6 days, however, as the reactor is not lined water is likely to be leaking out

the base of the bioreactor thus the reported flow may be lower than the actual flow. Nevertheless, water seeping out the base will have been treated and its quality improved.

A decrease in SO_4^{2-} between the influent and effluent, presence of H_2S at the discharge point, anaerobic conditions (low DO), degradation of mussel shell meat, supply of organic carbon (mussel shells), consistent supply of sulfate in the influent and circum-neutral pH between 5 – 8 indicates the presence of sulfate-reducing bacteria. Gas bubbles released during the autopsy of the bioreactor had no noticeable odour and could be CH_4 , CO_2 or a combination of both and derived from anaerobic conditions and the dissolution of carbonate. This gas was likely to be captured in pockets created by shells and also retained by the lower permeability sediment and sludge layers (Zone 1 and 2 respectively).

The bacterial decomposition of remnant mussel flesh and degradation of protein from the shell initially causes low DO and high ammonia nitrogen and CBOD_5 levels in the effluent. However, as DO continues to be low after day 16 when reactive organic material appears to be exhausted (decreased ammonia nitrogen and CBOD_5 levels), SRB are likely to be established and retaining the bioreactor in an anaerobic-reductive state. Low DO and high CBOD_5 and ammonia nitrogen in the effluent had no effect on the receiving waterway.

The Zone 2 $\text{Fe}(\text{OH})_3$ sludge could affect the longevity of the bioreactor by creating a low permeability layer, thus preventing the ingress of influent AMD and potentially reducing treatment capacity. As part of the autopsy the bioreactor was drained and test pits dug to expose the Zone 4 black unreacted shell (Photograph 2). Upon digging the holes the remaining pooled surface water on the surface of the bioreactor quickly drained and flow rates increased, suggesting water infiltration is being inhibited by Zone 1 and Zone 2 (sediment sludge layer). Therefore, to prevent the system from losing its efficiency, Zone 1 and 2 may need to be removed periodically as part of any maintenance programme.

A second bioreactor to be built at Stockton coal mine using 500 tonnes of weathered mussel shell, to eliminate any associated odour, has been designed to include a sedimentation pond in front of the mussel shell bioreactor to significantly reduce the mean TSS of 12.7 mg/L. The second bioreactor will treat a slightly higher flow (0.62 L/s), lower mean acidity (165 mg CaCO_3/L eq.) and a lower total acid load (8.78 kg CaCO_3/day eq.).

The only other maintenance required would be if remobilisation of metals is observed due to the pH in the mussel bioreactor dropping; Ni and Zn would be released first, followed by Al (Kohler et al., 2007) and thence Fe, as has been demonstrated by laboratory based sludge stability trials (McDonald and Webb, 2006). The black and grey-white precipitates discharged from the bioreactor were the only downstream issues, and those only aesthetic. Stockpiling of mussel shell generated a small number of odour complaints, however, once flooded by AMD there were no odour issues except within 5 m of the discharge point.

The system has been operating for 1,027 days and has treated a calculated 36 tonnes of acidity and remains in operation. Payback of the mussel shell bioreactor occurs after 1,027 days and thus provides a good argument for installing further systems.

5 CONCLUSIONS

The use of mussel shell in a field-scale bioreactor to treat AMD in New Zealand is not only a first in New Zealand, but in the world. The mussel shell bioreactor successfully treated an AMD seep high in acidity and removed 96 - 99% of Al, Fe, Ni, Tl, and Zn. pH increased to ~ 7 , and acidity reduced to 0.5 mg/L CaCO_3 . The bioreactor has operated for over 1,027 days thereby achieving payback compared to treating with UFL. A low-permeable sludge composed predominantly of an acid mine drainage precipitate $\text{Fe}(\text{OH})_3$ accumulated on top of the shells reducing the infiltration of water into the bioreactor. As AMD progressed down through the mussel shell bioreactor aluminium was precipitated out onto the outer layer of Zone 3 shells, which reduced the performance of these shells and therefore the system. Based on the rate of growth of this layer the mussel shell bioreactor is expected to continue to provide treatment for another 8 – 10 years. Passive on-site treatment of AMD using mussel shells is simple and cost-effective, and has been shown to successfully treat AMD.

ACKNOWLEDGEMENTS

The authors would like to thank James Pope for his assistance with the computer programme PHREEQC, Phyllis Shi for her laboratory assistance, and the Environmental Team at Stockton Coal Mine.

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