Enhanced Passive Treatment of Sulfate and Nitrate Enriched Mine Water: Laboratory Optimisation Experiments

Hana Christenson[1], Rachel Skews[1], Dave Trumm[1], James Pope[1], Nigel Newman[1], Gavin Lee[2], Duncan Ross[2]

[1]*Verum Group Ltd, 97 Nazareth Ave, Christchurch, New Zealand*
h.christenson@verumgroup.co.nz

[2]*OceanaGold (NewZealand) Ltd, Golden Point Rd, Macraes Flat, New Zealand.*

Abstract

Enhanced passive treatment systems (EPTS) are bioreactors dosed with nutrients to improve water treatment rates relative to traditional passive treatment systems.This paper presents laboratory trials of enhanced passive treatment systems to treat waste rock stack seep water from Macreas Mine. Nutrient addition to influent water occurred for lab scale bioreactors, to test contaminant removal rates with varying substrates, temperatures, hydraulic residence time (HRT) and nutrient addition rates, in order to optimise parameter selection for field trials.

Successful removal of sulfate was observed in most reactors, and the best sulfate removal rate achieved was 15 mol/m^3/day, with consistent rates above 7 mol/m^3/day maintained. Dissolved organic carbon consumption showed a linear correlation with sulfate removal. Near-complete nitrate removal occurred in all bioreactors (17 mg/L influent to <0.5 mg/L effluent NO_3-N) independent of substrate, temperature or HRT. Ammoniacal nitrogen and hydrogen sulfide were generated in reactors where nitrate and sulfate reduction occured.

The treatment rates measured in lab trials represent a >25-fold increase on standard passive bioreactors, which typically remove 0.3 mol/m^3/day of sulfate from mine water. This paper shows that nutrient dosing can vastly improve the treatment rates of traditional passive treatment systems , and highlights controls of habitat, temperature and reactor chemistry on treatment success and secondary contaminant generation.

Keywords: Enhanced passive treatment, Sulfate, Nitrate, Nutrient, Bioreactor

Introduction

Seep water from waste rock stacks at Macraes Mine can contain elevated concentrations of sulfate and nitrate (Craw and Pope, 2017). These ions are of environmental relevance, and are regulated in some waterways that receive water from the mine site. EPTS offer a potential water management tool to reduce concentrations of these contaminant through the use of microbial reduction pathways, which can convert the sulfur and nitrogen into solid and gaseous forms.

Sulfate and nitrate are both oxidized species that are able to be utilized as electron acceptors in the metabolism of anaerobic microorganisms (Equations 1 and 2, Hao *et al* 2014). Passive bioreactor treatment systems often rely on these metabolic reactions to convert dissolved contaminants into a gaseous or solid phase. The reactions require dissolved organic carbon that is provided by the breakdown of organic matrix materials in the passive bioreactor (Trumm *et al* 2017, Macauley *et al* 2009, Dilorreto *et al* 2016). Enhanced passive treatment systems provide additional labile nutrients to facilitate the desired reduction reactions.

Equation 1: $SO_4^{2-} + 2CH_2O \xrightarrow{SRB} H_2S + 2HCO_3^-$

Equation 2: $4\,NO_3^- + 4H^+ + 5\,CH_2O \xrightarrow{NRB} 2N_2 + 7H_2O + 5CO_2$

Previous trials of batch fed enhanced passive treatment of sulfate- and nitrate-rich waters (Christenson *et al*, 2017, Christenson *et al*, 2018) demonstrated that under lab

conditions, direct nutrient supply increased sulfate removal rates by up to fifteen times the rate of the undosed control. Trials utilizing direct nutrient supply decreased sulfate concentrations from 1,300 mg/L to between 400 and 1,000 mg/L, depending on hydraulic residence times (HRT) and carbon amendment ratios (Christenson *et al*, 2017). Near complete nitrate removal from agricultural water was achieved in woodchip matrix bioreactors with additional nutrient supply (Christenson *et al*, 2018).

This paper investigates controls on treatment rates for nitrate and sulfate removal from mine water in continuous flow EPTS bioreactors under a range of physical and chemical conditions. These trials have led to the design and commissioning of a field trial EPTS.

Methods

Mine water was collected from a seep into 1000 L polyethylene containers and stored at ambient temperature prior to use. A sample of reduced black mud with H2S odour was also collected from the seep area and was stored at 16 °C prior to its use as an inoculant for the various EPTS matrices. The mine water had ≈ 3,000 mg/L sulfate and ≈20 mg/L nitrate, and slight variations were observed over time and between the three sampling events.

Seven bioreactors were built in an upflow configuration which were continuously fed nutrient dosed mine water by a peristaltic pump. The experiment design tested habitat substrates, temperature, nutrient dose rate and nitrogen sparging to remove gaseous metabolic products (Table 1).

At the start of the experiment, the reactors were filled with a mixture of 50 % mine water and 50 % municipal drinking water, and left for 48 hours. Continuous flow of minewater then commenced with all reactors at a one day hydraulic retention time. Flow through bioreactor 1 was doubled after 220 days of operation to test treatment capacity at a higher contaminant load. Influent and effluent water was sampled weekly and analysed for pH, temperature, conductivity, dissolved oxygen, sulfate, nitrate and nitrite nitrogen, ammoniacal nitrogen, dissolved organic carbon and sulfide.

Results

Concentrations of sulfate decreased in all reactors except for the reactor with the broom matrix (Figure 1). Performance was best in the standard dose bioreactor and the nitrogen purged bioreactor, with effluent sulfate concentrations below 1500 mg/L achieved consistently after 110 days of system operation. The low carbon dose and low temperature reactors initially performed poorly, with improvements observed after the dose rate and temperature were increased at day 128 of operation. The schist, fresh pine and broom substrates were inferior to the mixture of mulch, bark and compost.

Table 1 *Experimental bioreactor descriptions*

Bioreactor	Name	Variable	Explanation
1	Standard dose bioreactor	Control	Mulch, bark and compost mixture substrate matrix. Nutrient dose rate 0.7 of equation 1 stoichiometric ratio.
2	Fresh pine	Habitat 1	A fresh pine chip substrate matrix. Nutrient dose rate 0.7 of equation 1 stoichiometric ratio.
3	Schist	Habitat 2	A crushed schist substrate matrix. Nutrient dose rate 0.7 of equation 1 stoichiometric ratio.
4	Nitrogen sparged	Sulfide removal	Mulch, bark and compost mixture substrate matrix. Nutrient dose rate 0.7 of equation 1 stoichiometric ratio. Periodic sparging with nitrogen gas, changing to continuous sparging after 230 days.
5	Low temp	Low temperature	Mulch, bark and compost mixture substrate matrix. Nutrient dose rate 0.7 of equation 1 stoichiometric ratio. Temperature held at 2-6 °C changing to ambient after 128 days.
6	Low C	Low carbon dose	Mulch, bark and compost mixture substrate matrix. Nutrient dose rate 0.35 of equation 1 stoichiometric ratio, changing to 0.7 after 128 days.
7	Broom	Habitat 3	A reactor set up on day 205. Broom and silage substrate. Nutrient dosed at the same rate as the control.

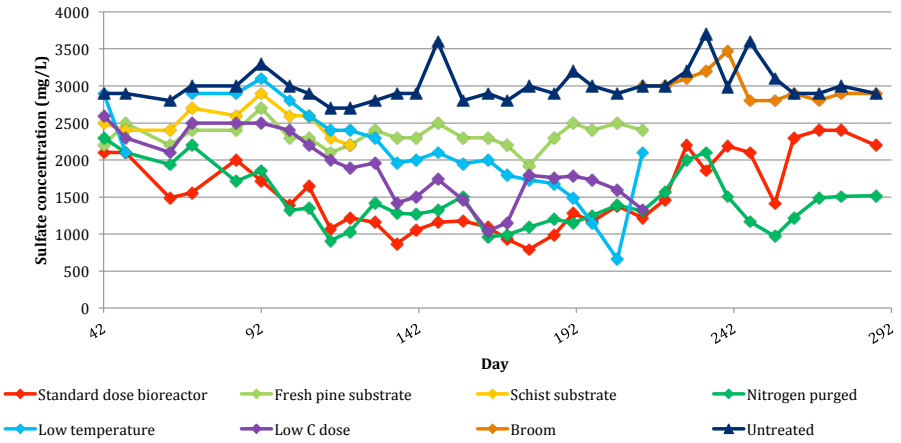

Figure 1 *EPTS bioreactor effluent sulfate concentrations. The untreated water sulfate concentration is also displayed.*

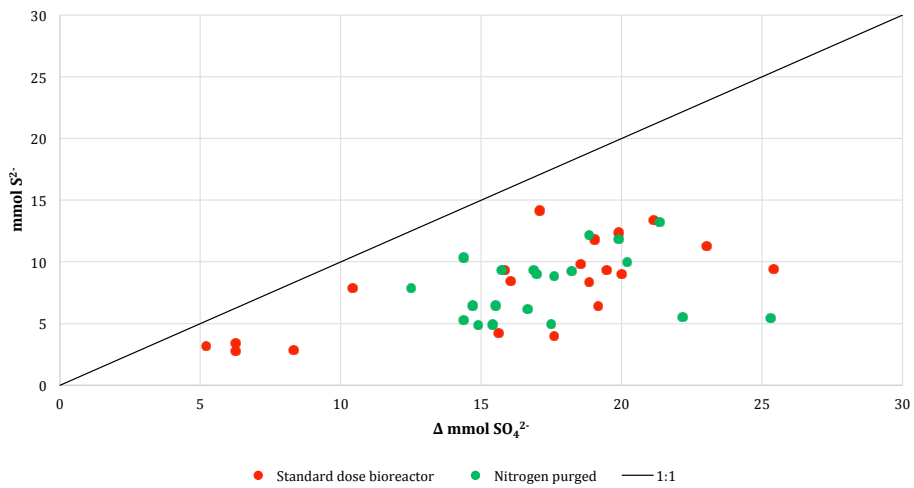

Figure 2 *Concentration of sulphide in the bioreactor effluents versus the change in sulfate concentration for that bioreactor.*

Low temperature and low nutrient dose rate result in poorer sulfate removal. Periodic and continuous nitrogen sparging did not increase sulfate removal above the standard dose bioreactor.

Sulfide is generated during microbial sulfate reduction (Equation 1), and sulfide concentrations exceeding New Zealand water quality guidelines (ANZG, 2018) occurred in most of the reactor effleunts. Concentrations were highest in the standard dose bioreactor and the nitrogen purged bioreactor, however the concentrations generated did not strongly correlate with the change in sulfate concentration (Figure 2). Elemental sulfur precipitate was observed at the surface of many of the reactors.

Nitrate and nitrite nitrogen were removed to below detection (0.02 mg/L) in all reactors for the majority of the experiment (Figure 3). The maximum effluent combined nitrate and nitrite concentration was 0.3 mg/L

In reducing conditions, ammoniacal nitrogen can be generated from redox reactions involving nitrogen species. Ammoniacal nitrogen was not detected

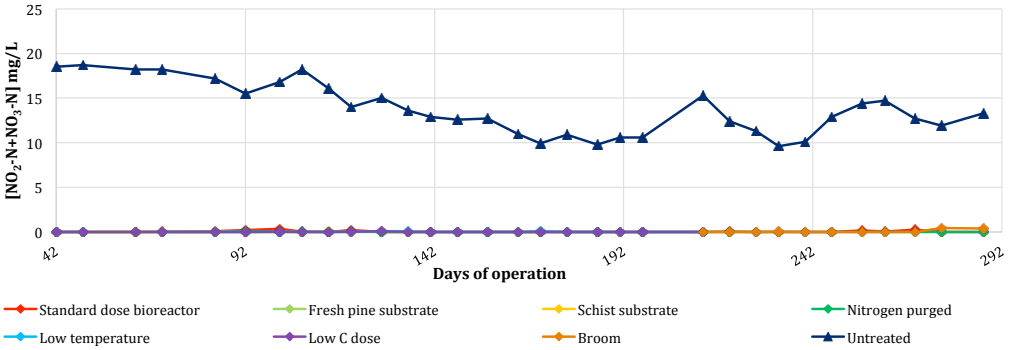

Figure 3 Nitrate+nitrite nitrogen concentration in the bioreactor effluents, shown from day 42 of operation.

in the untreated minewater. Effluent from the bioreactors contained ammoniacal nitrogen concentrations ranging from below detection to concentrations above the New Zealand 2.3 mg/L guideline value to protect 80% of aquatic organisms (ANZG 2018). The schist substrate reactor had the lowest concentrations of ammoniacal nitrogen in the reactor effluent, typically <0.1 mg/L and a maximum concentration of 0.43 mg/L.

Discussion

Sulfate and nitrate reduction were measured in all bioreactors, and the standard dose bioreactor consistently delivered the highest rate of sulfate removal with concentrations decreasing from ~ 3,000 mg/L SO4 to at times <1000 mg/L SO4. The chemical reduction of SO4 resulted in elevated H2S in the discharge water. Variable amounts of sulfate removal were observed, and generally, a greater change in sulfate concentration correlated to a greater effluent sulfide concentration. However, removed sulfate was not entirely converted to sulfide (Figure 2) Elemental sulfur was identified and factors controlling its formation have been investigated with geochemical models. Formation of this phase, and minimising effluent sulfide concentrations will be prioritised in field trials. Nitrate was removed from solution concentrations of ~17 to ≤0.5 mg/L in all reactors throughout the experiment; however, variable concentrations of ammoniacal nitrogen were generated. The more reducing conditions that are required for sulfate reduction than nitrate reduction

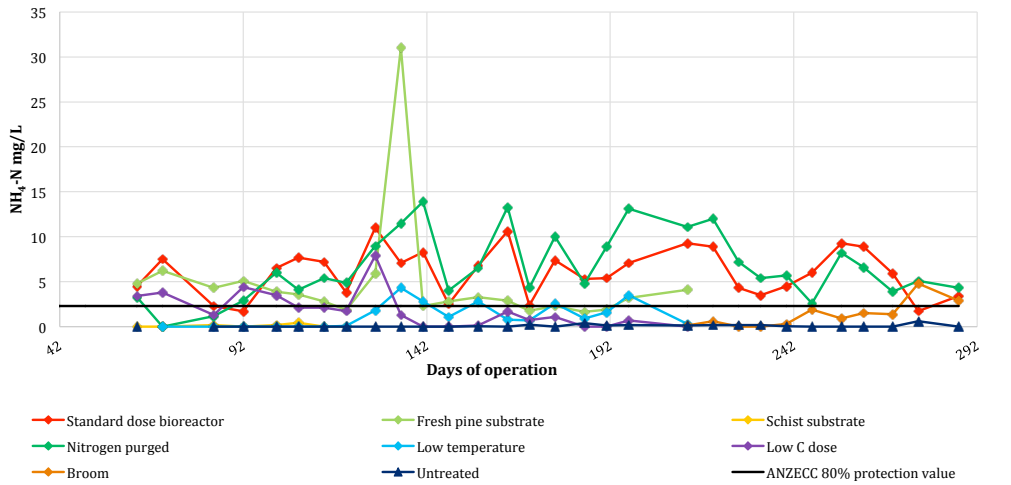

Figure 4 Ammoniacal nitrogen concentration in bioreactor effluents, shown from day 42 of operation

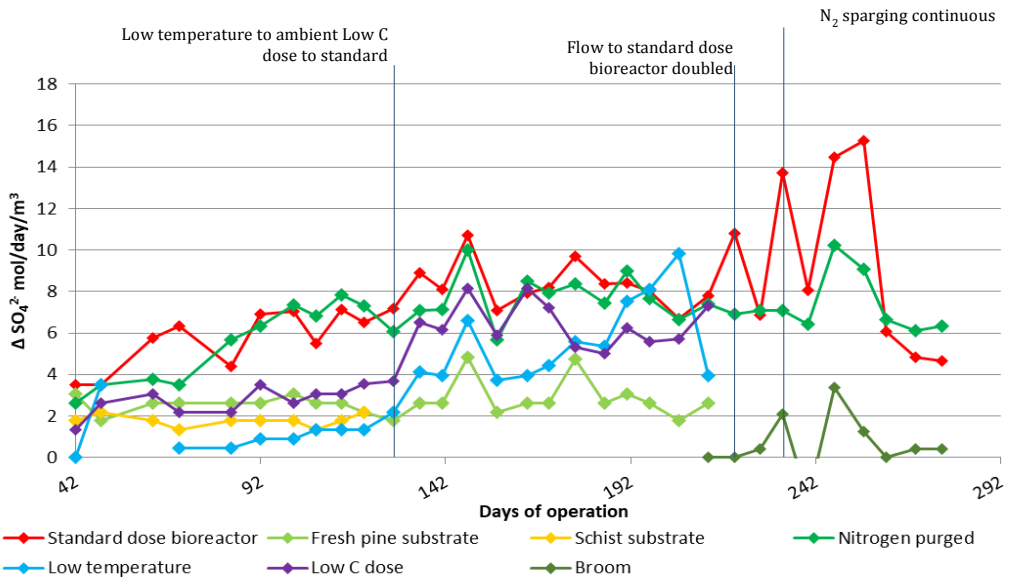

Figure 5 Sulfate removal rate for all bioreactors

likely promote ammoniacal nitrogen formation, and the reactors that performed less well for sulfate removal typically had lower ammoniacal nitrogen concentrations in their effluents.

The sulfate removal rate is the standard method of comparing bioreactor performance and is calculated as the amount of sulfate reduced per cubic meter of reactor volume per day. Traditional passive treatment systems are often designed for a 0.3 mol/m^3/day removal rate. The standard dose bioreactor had the best removal rate of ~8 mol/day/m^3 at a one day HRT (Figure 5). The standard dose bioreactor also had a peak of 15.3 mol/day/m^3 at a 12 hour HRT. In the nitrogen purged bioreactor, sulfate removal rates remained stable at around 7 mol/day/m^3 after 92 days of operation and remained stable even after the nitrogen sparging was made continuous. This removal was maintained even when effluent sulfate concentrations increased due to an increase in flow rate during this period. Purging the bioreactor with N2 did not improve the sulfate removal rate.

The mulch, bark and compost mixture was the best performing substraten for sulfate removal. The nutrient dose rate and temperature impacted sulfate removal, however when these variables were removed sulfate removal increased to levels similar to the standard dosed bioreactor. Consumption of organic carbon correlated with the load of sulfate that was removed for all bioreactors (Figure 6), at a ratio consistent with Equation 1.

These trials highlight differences in treatment efficiency and contaminant generation which have been used to design a field trial system. Management of various microbial processes through a multi-component EPTS system has been proposed to optimise contaminant removal while limiting generation of secondary contaminants.

Conclusions

The laboratory trials indicated that nitrate and sulfate are able to be removed from Macraes Mine seep water. Near-complete nitrate removal was achieved in all bioreactor configurations tested. The carbon dosed schist bioreactor had the best performance in terms of nitrate removal and ammoniacal nitrogen generation and will be tested as a nitrate removing step for field trials. Sulfate removal was measured at rates up to 15 mol/m3/day, and rates above 7 mol/m3/day were achieved consistently in the standard dosed bioreactor for three months. Elevated effluent sulfide concentrations from the bioreactors

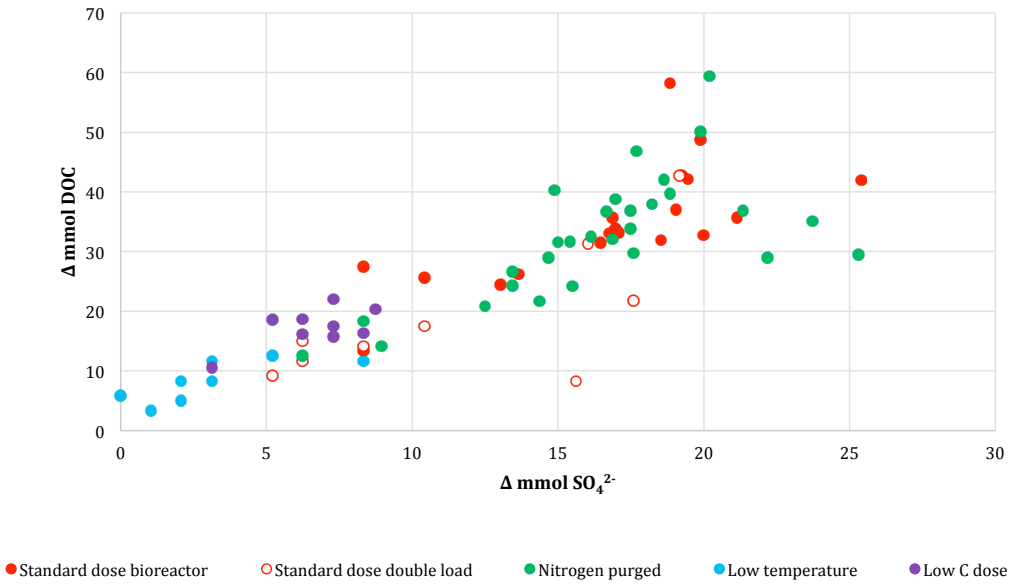

Figure 6 Change in sulfate concentration as a function of change in DOC concentration

is a concern, and sulfur precipitation methodologies will be tested in field trials.

A full-scale EPTS is likely to require a multiple stage approach to water treatment, as a complete treatment within one bioreactor results in elevated ammoniacal nitrogen and sulfide as secondary contaminants in the bioreactor effluent. A staged approach to treatment in field trials will test nitrate removal without ammoniacal nitrogen formation, sulfate reduction in an SRB bioreactor, then sulfide oxidation to elemental sulfur.

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