Start-Up of a Passive Remediation Bioreactor for Sulfate and Selenium Removal from Mine Tailings Water

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ABSTRACT

Before tailings pond water can be discharged to the environment it must meet the very stringent local water quality requirements. In British Columbia, selenium must be below 1µg/L and sulfate, depending on the hardness of the receiving water, must be as low as 100mg/L. To meet this challenge, in anticipation of future mine expansion, Mount Polley Mine commissioned a pilot-scale passive treatment system to remove selenium and sulfate from their tailings pond water. The design was based on laboratory column tests with wood chips and hay that verified removal of selenium and sulfate to the required levels. This paper describes the design and construction of a sub-surface flow wetland and its evolution over several years into a passive remediation system. Regular monitoring and troubleshooting led to upgrades and modifications that improved performance. The subsurface layer of woodchips, hay and manure provides microorganisms with carbon sources. As part of a genomics project, material from this layer was shown to contain many different species of sulfate-reducing bacteria. Additional carbon inputs come from plants and filamentous algae that are beginning to populate the periphery and surface of the wetland. The genomics work also showed that planktonic algae were plentiful in the water column. This pilot-scale process shows that passive remediation can be used to improve the water quality of mine tailings pond water.

Keywords: Biochemical reactors, metals, mining, bioremediation, microbial ecology, selenium, sulfate

INTRODUCTION

The mining industry in British Columbia was valued at C$8.3billion in 2012 (The Mining Association of Canada, 2012) and is therefore a great contributor to employment and prosperity in the Province. Almost every mine has a tailings storage facility into which process effluents consisting of finely ground rock and water are placed. These are very large (squares of kilometers in size). Mount Polley had been investigating several ways of treating their tailings pond water so that they could discharge some of it so as to ease the demand for additional storage capacity. One of the approaches under consideration included a passive treatment process for metal and sulfate removal.

Passive treatment means that natural biological and geochemical processes are harnessed in specially constructed sub-surface and/or surface flow wetlands. The purpose of each cell in the process is to provide the best environmental conditions to encourage the growth of biological organisms that promote metal immobilization and, in cases where needed, sulfate reduction. Since some engineering is usually required they are more accurately referred to as biochemical reactors (BCRs), and a variety of configurations have been used at mine sites to successfully remediate metal-contaminated water (Khoshnoodi et al., 2013; Mattes et al., 2011; Blumenstein and Gusek, 2008; Gusek, 2008).

The main constituents of interest that needed to be reduced in the Mount Polley tailings water in order to meet discharge requirements were sulfate, selenium, copper, molybdenum, phosphorus and nitrate. Sulfate can be reduced by sulfate-reducing bacteria, which are anaerobic organisms that grow in most natural terrestrial and oceanic sediments devoid of oxygen. Sulfate replaces oxygen as an electron acceptor in respiration of these organisms thereby producing the product sulfide. Metal removal occurs concomitantly as metal ions such as Cu^{2+} combine with S^{2-} to make sparingly soluble metal sulfide precipitates (Jalali, 2000). Metalloids such as selenate and selenite can be reduced directly by bacteria to produce elemental forms that precipitate and are immobilized (Stolz et al., 2006;Baldwin and Hodaly, 2003). To achieve metal and sulfate removal the microbes involved are encouraged to grow by being provided with nutrients and anoxic conditions. In BCRs this is achieved through using organic materials obtained from forestry, agricultural and other wastes available nearby the mine site. Within close proximity of the Mount Polley Mine, wood chips, hay and cattle feed lot manure were obtained and shown to support growth of sulfate-reducing bacteria in proof-of-concept laboratory reactors that successfully removed sulfate and selenium to below the required concentrations. Based on these results, a pilot-scale BCR was constructed at the mine site in 2009. This paper describes the configuration of this BCR, the results of water quality and microbial community monitoring carried out over the ensuing years and subsequent modifications that were made to improve performance.

METHODOLOGY

Proof of concept laboratory experiments

Plexiglas columns (I.D.: 11.43 cm, Length: 50.8 cm) with a mixture of 50%dw hay, 20%dw woodchips and 30%dw cow manure were used as up-flow BCRs. These organic materials were pre-soaked in water overnight and adjusted to pH 8.0 before being added to the columns together with laboratory cultures of sulfate-reducing and cellulose-degrading bacteria as inocula as well as

crushed limestone for pH control. For the first few weeks, the columns were fed with a Postgate-B growth medium (Postgate, 1983) to allow a healthy sulfate-reducing bacteria population to build up. Thereafter, simulated tailings water containing 600mg/L sulfate and 15μg/L selenium, plus 52mg/L Iron (Fe) and sources of nitrogen (N), phosphorus (P) and potassium (K) was fed to the BCRs. Iron was required as a source for excess sulfide precipitation. Accumulation of sulfide in the BCR would have inhibited the bacteria from growing, and therefore it had to be removed. The columns were set up so as to prevent any oxygen from getting in (since sulfate-reducers are obligate anaerobes). Over the period of operation, concentrations of sulfate and selenium were measured in the effluent using the turbidimetric barium sulfate American Water Work Association method 4500-SO_4^{2-}, and inductively coupled plasma mass spectroscopy (ICP-MS), respectively. Dissolved oxygen, pH and oxidation-reduction potential were monitored regularly so as to check that optimal conditions were being maintained in the BCRs.

Construction of the field-based pilot-scale BCR

A field-based pilot-scale BCR was constructed at the mine site in December 2009. After experimenting with smaller scale systems, a 100 gallon per minute sub-surface flow BCR with a water cover was constructed using the same organic material mixture composition as was used in the laboratory column experiments. The Figures below show the BCR during construction and immediately after commissioning.

Figure 1 Construction of the field-based BCR showing the perforated feed pipes, organics (brown) and rock (right-hand side) layers.

Figure 2 View of the completed BCR looking down from the top of the tailings storage facility.

Water from the tailings storage facility toe drain flows into the bottom of the BCR through a series of parallel, perforated pipes, percolates upwards through the organic material and then flows out. A layer of rocks on top of the organics keeps them in place. A 3-4m deep water cover acts as an oxygen barrier. The treatment area is approximately 50m by 70m. An island was included in the centre of the pond for aesthetics.

BCR monitoring

Water quality data were collected regularly from the influent and effluent to determine the effectiveness of metal and sulfate removal. The inside of the BCR was sampled once a year by the University of British Columbia team. Since samples from within the organic matrix could not be accessed easily due to the rock layer covering them, water samples from just above the

sediment/water interface were taken. If the BCR was performing as expected then the water percolating out of the sediments into the water column would be anaerobic with evidence of sulfide as an indication of active sulfate-reducing bacteria in the sediments. The microbiology of the water just above the sediments was assessed to see if any sulfate-reducing bacteria were entrained by the water flowing out of the sediments, and to see what other microbes were colonizing the water column. Microbiological analysis was done by extracting DNA and subjecting it to sequencing of the small subunit ribosomal ribonucleic acid (SSU rRNA) gene, which is a barcode that is used to identify microbes. In 2012, the BCR was shut down and drained. At this time, solid samples were taken from within the organic matrix and frozen to preserve the microbial community for later analysis. The BCR was modified based on monitoring results, adding a berm to increase hydraulic retention time and replenishing with fresh organics. Further modifications in 2013 included installation of booms to reduce wind mixing so that anaerobic conditions could be better maintained. One year after reconstruction (August 2013), samples taken from the sediment layer were used for metagenomics, which is a new technique for measuring both the microbes present as well as their function.

RESULTS AND DISCUSSION

Proof of concept laboratory experiments

Even though the pH was adjusted to 8.0 before starting the BCRs, additional NaOH needed to be added to maintain the pH above 6.5. Organic acids leaching from the wood, or produced due to fermentation of organic matter, contributed to pH decrease. Since the desired bacteria require a circum-neutral pH in which to grow, pH adjustment was needed. The pH of the laboratory BCR feed was 8.0, similar to that of the Mount Polley effluent. After 114 days, the pH stabilized above 6.0 and it was only necessary to add NaOH sporadically thereafter. Throughout their operation, conditions remained optimal for sulfate-reducers with dissolved oxygen below 1mg/L except until day 374, when it suddenly increased to 4.7-5.7mg/L. The ORP was below -300mV and the pH was steady between 6.0 and 7.0. Sulfide levels inside the BCR were always below 100mg/L, which is much lower than those known to cause inhibition of sulfate-reduction (Utgikar et al., 2002).
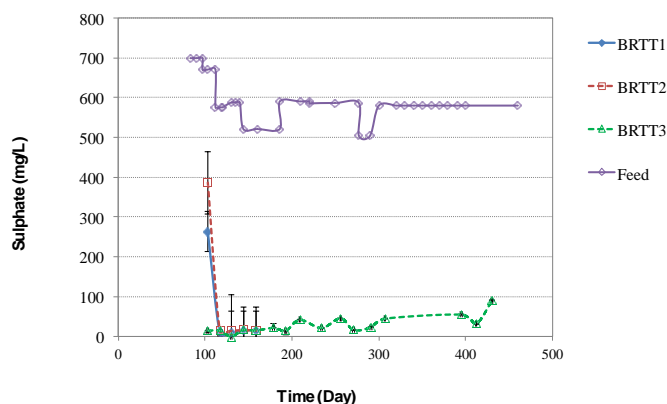
Figure 3 Plot of sulfate concentration versus time for the influent and effluents from all three of the laboratory BCRs. BRTT1, BRTT2 and BRTT3 are triplicate columns run under identical conditions. Sulfate concentration measurements were performed in triplicate with the average values plotted and the whiskers representing the standard deviation.

Two of the BCRs were stopped after approximately 100 days after starting feed of the simulated tailings pond water so as to examine the nature of the microbial population associated with successful performance. The third BCR was run for a total of 430 days to see if and when it would fail. Performance was consistently successful for the entire period (Figure 3). For all BCRs the sulfate concentrations in the effluent were below 100mg/L, the level desired for discharge. The selenium concentrations in the effluent were below the detection limit (< 0.0001mg/L). The proof-of-concept experiment demonstrated that sulfate and selenium can be removed from the Mount Polley tailings water to the required levels using these organic materials in a BCR, provided that the pH is maintained near neutral, no oxygen is allowed to enter the bioreactor and that enough metal ions be present to keep sulfide levels low.

Initial performance of the field-based pilot-scale BCR

Initially, the field-based BCR successfully removed nitrite- plus nitrate-N and selenium to below detection levels (Table 1). Twenty three percent of the sulfate coming in was removed, but the final sulfate concentration was still well above the desired concentration of 100mg/L. Molybdenum concentrations decreased slightly and copper concentrations increased a little. During the 17 June 2010 field trip, 1-3mg/L sulfide was found at the sediment water interface of the BCR at all of the four locations sampled. This indicated that sulfate-reducing bacteria were active in the sediments as expected. Over the course of the following year, performance of the BCR was similar with the exception that sulfate-reduction was less. During the second University field trip in August 2011, no sulfide was detected at three of the sampling locations in the BCR. Some, 4.3mg/L, was measured at only one of the locations, indicating that only parts of the BCR were active for sulfate-reduction. Also, at that time, the sulfate concentrations at the sediment/water interface (464-599mg/L) were not significantly different from those in the influent.

Table 1 Water quality parameters for the field-based pilot-scale BCR

| Sampling date	Nitrite + Nitrate-N		Sulfate		Cu (dissolved)		Mo (dissolved)		Se (dissolved)	
	In	Out	In	Out	In	Out	In	Out	In	Out
04/15/2010	3.98	<0.0050	499	384	0.00317	0.00454	0.185	0.121	0.0239	<0.0020
04/15/2010-05/31/2011 *	1.901	0.037	478	416	0.0031	0.0038	0.1650	0.1185	0.0031	0.000917
06/9/2011-07/5/2012 *	1.114	0.123	434	452	0.0030	0.0011	0.1786	0.1237	0.0025	0.0009
09/15/2012-08/8/2013 *	1.613	0.075	498	406	0.0030	<0.0006	0.203	0.081	0.0053	0.00064
09/5/2013-08/8/2014 *	1.975	0.0725	518	475	0.0030	0.0011	0.208	0.109	0.0066	0.0020

* average values

Microbial community analysis from 2010 to 2012

Samples taken during the first two field trips in 2010 and 2011 from the sediment/water interface were analysed for microbial community composition, and in particular the types of sulfate-reducers present was determined (Figure 4). Sulfate-reducers were detected in the BCR in 2010 consistent with presence of sulfide, but they were absent from the sediment/water interface in 2011. Even though sulfate-reducers were not detected just above the sediment surface, they may still have been present inside the organic matrix. Nevertheless, the lack of detection of sulfate reducers coincided with declining performance of the treatment system (Table 1). In 2012, the BCR was drained and it became possible to take samples directly from the organic matrix. When these samples were analysed for microbial community composition, many sulfate reducers were found (Figure 4). The presence of sulfate-reducers suggested that the organic matrix and conditions inside the BCR were suitable for hosting these organisms. But, contrary to expectations, sulfate-reduction rates through the BCR were low. One possible explanation was that sulfate may be reducing to sulfide within the organics, but low metal ion concentrations were not enough to precipitate all soluble sulfide and it was re-oxidized to sulfate upon contact with oxygen diffusing down through the water column. Such a phenomenon was observed in the laboratory bioreactors before Fe^{2+} was added to the column bioreactor feed (Mirjafari et al., 2011).

Performance since 2012 modifications

Recharging of the BCR organics and increasing of the retention time resulted in improved performance (Table 1). The BCR was again visited in August 2013 and sampled for microbial community analysis.
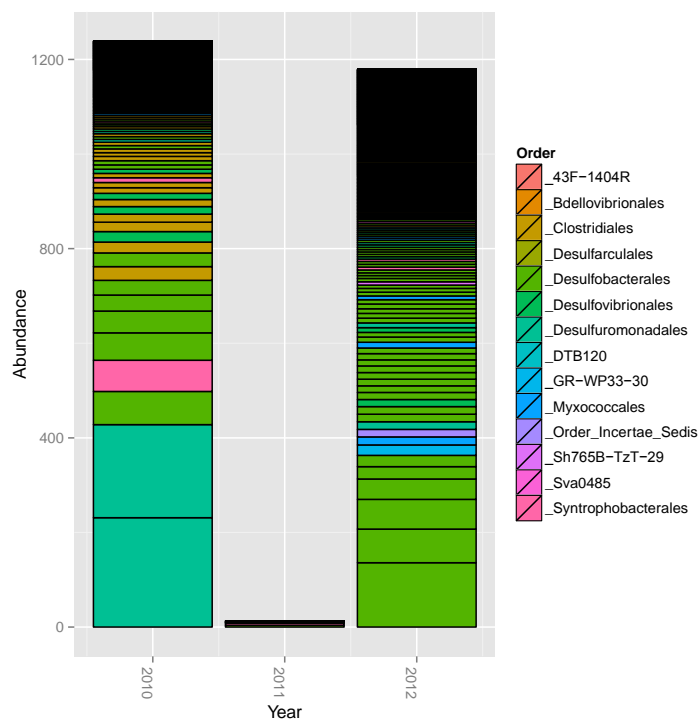
Figure 4 Sulfate-reducing micro-organisms detected in the BCR. Each bar on the plot represents one type of microbe. They are colored according to the Order in which they are classified. Bacteria are classified in taxonomic groups at different levels: Phylum;Class;Order;Family;Genus;Species. Abundance refers to the number of sequences out of a total of 12000, 8000 and 12000 for samples taken in 2010, 2011 and 2012, respectively.

*Microbial community composition in 2013*

A new technique was used called metagenomics. Instead of amplifying the SSU rRNA gene, which introduces possible biases, whole DNA was sequenced. From this we identified genes involved in sulfate metabolism, such as sulfate-reduction, and the types of bacteria that they came from, thus tying function to taxonomy. The results revealed that a psychrophilic organism, *Desulfotalea psychrophilia*, was the most prevalent sulfate-reducer in the BCR. Interestingly, this type of sulfate-reducer was first found in permanently cold Arctic marine sediments (Rabus et al., 2004), and even can survive at temperatures below 0°C. As before, the *Desulfobacterales*, *Desulfovibrionales* and *Desulfuromonadales* were sulfate-reducing bacteria taxa that were present in the BCR sediments. Presence of a healthy population of sulfate-reducers and detection of sulfide at the sediment/water interface (Table 2) coincided with active sulfate reduction and metal removal; although final sulfate concentrations were not meeting the 100mg/L discharge requirement.

A very interesting phenomenon was noted by the operators during the colder months of 2013, when the BCR was covered with ice and snow. Higher concentrations of sulfide and lower concentrations of BCR effluent sulfate were measured in Spring than in Summer (Table 2). This suggested that sulfate-reduction was active even though temperatures of the BCR water were between 2.1 and 7.7°C. The cover of ice and snow on the surface of the BCR prevented oxygen from getting into the water layer as dissolved oxygen profiles with depth revealed (Figure 5). Improved anaerobic conditions correlated with improved sulfate-reduction. The average BCR influent sulfate

concentration in 2013 was 498mg/L. Sulfate-reduction was highest (35%) in April. Metal removal was also greatly improved in the Spring compared with the rest of the year (percent removal: Se (86%); Cu(56%); Mo(44%)). Presence of cold-adapted sulfate-reducers in the BCR, and active sulfate-reduction and metal removal supports the use of biological treatment in cold climates

Table 2 Sulfate and sulfide concentrations measured in the BCR effluent over 2013

Parameter	14-Mar-13	4-Apr-13	1-May-13	6-Jun-13	10-Jul-13	8-Aug-13	5-Sep-13	3-Oct-13	5-Nov-13	3-Dec-13
Sulphate (SO_4) (mg/L)	383	323	365	434	446	486	488	469	481	493
Sulfides (mg/L) - Preserved with Zn-Acetate	31.6	14.5	0.71	1.23	0.085	0.01			0.106	5.1
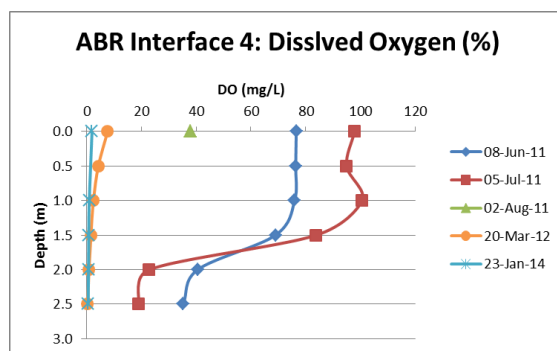
Figure 5 Dissolved oxygen concentrations versus depth below the BCR water surface during winter and summer months.

The BCR in 2014

During the most recent (26 August 2014) sampling of the sediment-water interface in the BCR, sulfide concentrations were higher than were measured in 2013 (August) (Table 2). The locations with higher sulfide concentrations coincided with lower sulfate concentrations. The North East side of the BCR (locations 3 and 4) was more active in terms of sulfate-reduction. Influent sulfate concentrations were 509mg/L. An extimated 15.6% sulfate is being reduced by the system.

Table 2 Concentrations of sulfate and sulfide in the Mount Polley BCR in 2013 and 2014.

Location	2013		2014	
	SO_4^{2-} (mg/L)	S^{2-} (mg/L)	SO_4^{2-} (mg/L)	S^{2-} (mg/L)
1	458	5	471	0
2	458	5	451	60
3	395	9	400	180
4	453	9	426	40-50
Average:	441		437	

Plants (*Typha latifolia*) and filamentus algae successfully colonized the sides and surface of the BCR (Figure 5). At other sites algae have been found to host many microbes, such as sulfate-reducers, and their presence adds organic carbon to the BCR plus they can directly improve water quality (Das et al., 2009;Larratt et al., 2007). Sequencing revealed many types of unicellular algae, such as *Dunaliella*, in the water column. Sub-aqueous plants could be seen growing on the bottom near the edges (Figure 6).
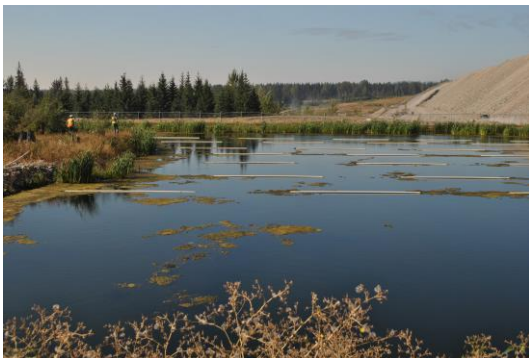
Figure 5 Photograph of the BCR looking South West.

Figure 6 Growth of aquatic plants

CONCLUSION

A laboratory proof-of-concept test demonstrated that removal of sulfate and selenium to below the required levels for discharge was possible. The field-based BCR constructed at Mount Polley Mine using a woodchip, hay and manure organic mixture was found to successfully support an active sulfate-reducing microbial community and some removal of nitrite/nitrate, metals and sulfate was occurring. The system worked best immediately after the addition of fresh organics but thereafter appeared to decline in performance. Rapid depletion of readily available organic material may be a limiting issue for passive treatment and is it recommended that an upstream surge pond be included in future designs into which fresh organics can be added. The BCR was more successful in the colder months when ice and snow covered the water and improved anaerobic conditions inside the BCR. Thus, addition of a more impermeable cover may improve performance throughout the year.

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