Closed loop for AMD treatment waste

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Abstract At the abandoned Leviathan copper mine, acid mine water is treated with an alcohol-based bioreactor. The bioreactor system has been successfully operating since 2003, treating 11.4 to 15.1 million liters of AMD annually. Biodiesel, produced at a nearby agricultural farm, has a manufacturing waste product rich in alcohols. This biodiesel waste can feed the mine bioreactor, and the waste sludge from mine water treatment could be used as a soil supplement at the farm.

Key words: acid drainage, biodiesel, bioreactor, glycerol, micronutrients, soil supplement, SRB

Introduction

The products left over from manufacturing biodiesel fuel and, entirely unrelated, the sludge from acid mine drainage treatment are both waste products. Biodiesel is manufactured by adding methanol and sodium- or potassium-hydroxide to vegetable oil, including waste cooking oil, resulting in trans-esterification of fatty acids to form biodiesel. The waste fraction contains glycerol and methanol, carbons that sulfate-reducing bacteria (SRB) can utilize, and hydroxides that raise pH. In laboratory columns, SRB were able to treat simulated acid mine drainage (AMD) by utilizing biodiesel waste (Zamzow et al. 2006). AMD treatment with SRB results in a metal-sulfide sludge waste. The loop of sharing waste products is discussed here.

Site location

Leviathan is a former copper and sulfur mine in the Sierra Nevada mountains (US). Underground mining was conducted from 1863 to 1872 for copper sulfate. From 1954-1962 open pit mining generated 20 million tonnes of waste rock. Aspen Creek runs through waste rock piles and forms the acid seep that is treated by the bioreactors. The site is at an elevation of 2135 m. Heavy snow can be expected from October to May, with significant variability. Electricity is provided by a diesel generator and solar panel arrays. Snow-melt generally occurs from April through July, significantly increasing flow into the bioreactor from an average of 20 L/min to 90 L/min (US EPA 2006).

Bioreactors

Compost-free bioreactors provide a carbon source SRB can directly utilize, such as ethanol, methanol, or ethylene glycol (Tsukamoto and Miller 1999; Luo 2004). Compost-free bioreactors at Leviathan were constructed as four open ponds. The first two (Pond 1, Pond 2) are the location of microbial activity and contain rock substrate for SRB attachment (Fig. 1). Downstream ponds (Pond 3, Pond 4) contain no rock and are for the precipitation of sulfide sludge. Influent into bioreactors is acidic (pH 2.5 to 3.2) and contains elevated metals, with average concentrations of 115 mg/L iron, 30 mg/L aluminum, 0.9 mg/L zinc, 0.8 mg/L copper, and 0.6 mg/L nickel (US EPA 2006).

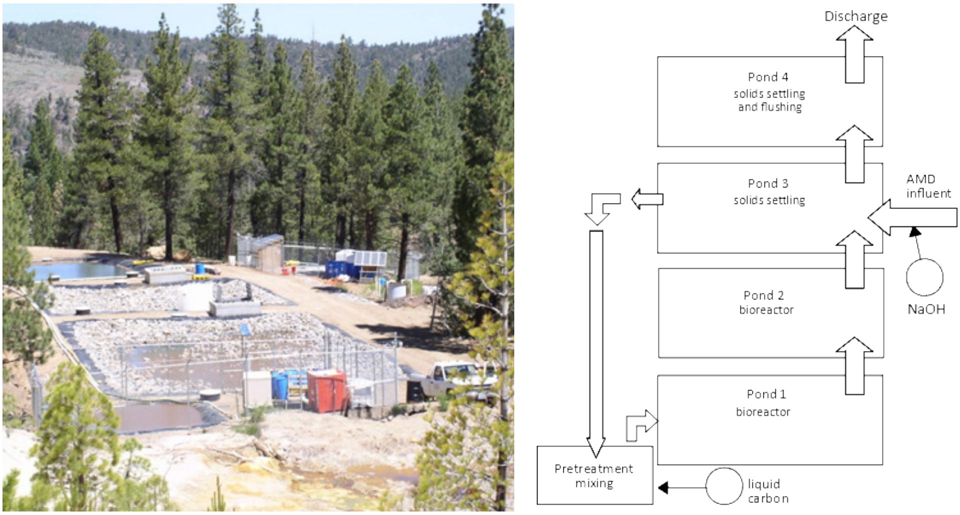

***Figure 1**. Compost-free pond reactor. (Photo) Ponds have approximate dimensions of 10m x 3.5m x 3.5m deep; the two bioreactors and one settling pond can be seen. The orange-colored acid seep (foreground) is directed to Pond 3, a sludge precipitation pond. (Schematic) Metal precipitation occurs in Pond 3, with Pond 4 as a backup for precipitation and sludge storage. About one-third of the water from Pond 3 is r ecirculated back to the small pre-treatment pond and on into the microbially-active Ponds 1 and 2. Photo: GC Miller.*

The acid influent does not flow directly into the bioreactor. The re-circulation system directs acid influent to enter sludge settling ponds below the microbial ponds. Metals precipitate in Pond 3 as they encounter Pond 2 effluent rich in SRB-produced sulfide, and acid is neutralized by SRB-produced alkalinity and a small amount of base added with a peristaltic pump. Overlying water, low in metals, rich in sulfate with neutral pH, is circulated to a mixing pond where a liquid carbon source is added, delivering an optimal environment to SRB in Pond 1. The system is designed to treat 114 L/min.

SRB consist are a heterogenous group of archaea and bacteria. Although there are acidophilic and thermophilic species, environments that favor SRB over other microbes are generally 25 °C to 35 °C, low in oxygen, with oxidation-reduction (ORP) potential of -150 to -400 mV, pH 4.5 to 8 (Barton 1995). Leviathan bioreactor ponds are maintained at pH 6 to 8, ORP of -100 to -300 mV, and water temperatures 0 °C to 21 °C. SRB activity reduced in winter but influent flows also reduced, with the result that good sulfate reduction occurred even with low temperatures.

Bioreactor waste sludge

Metal sulfide sludge produced by SRB bioreactors is denser than the hydroxide sludge that precipitates with lime treatment, resulting in lower volumes. In 2005, about one-third of the sludge in Pond 3 (5,000 kg) was pumped out of the pond and into filter bags (3 m x 4.6 m). From November 2003 to July 2005, an estimated 12,900 kg dry weight of sludge was produced (3,900 kg per million liters of AMD treated) with moisture content of 80% in filter bag solids. Sludge samples were collected from the pre-treatment pond, Pond 3, Pond 4, and the filter bags for analysis.

Biodiesel waste source

Bently Agrodynamics in Minden, Nevada, 20 miles from the mine site, is an agricultural operation that produces biodiesel for their farm vehicles and provides limited biodiesel fuel to the community. Employees collect used oil from restaurants and react it with potassium hydroxide in heated stainless steel tanks. Biodiesel waste (BD waste) fluid was supplied to us in 208 L drums.

Methods

Raw water samples (500 ml) were collected from the AMD influent, pond effluents, and from the final discharge and analyzed weekly or biweekly for sulfate, alcohols, and total and dissolved metals. Duplicate samples (125 ml) were acidified with nitric acid to pH < 1.5 for total metals and alcohol concentrations. Biodiesel waste varies in composition between batches. Fourteen samples taken from the Minden, Nevada plant showed glycerol at 8% to 30% and methanol 10% to 20%. During the field experiment, samples of BD waste were analyzed on a regular basis. Drums of methanol were occasionally added to the tote containing BD waste providing additional variability (Zamzow 2007).

Biodiesel waste feed

At the mine site, BD waste was pumped from drums to a 1,100 liter tote. From November 2005-June 2006, BD waste supplemented the ethanol feed to acclimate the microbial population. Feed was through a gravity drip system which, due to the glycerol and fat content, was highly temperature dependent. In June 2006, a solar-powered peristaltic pump was installed for more consistent BD waste feed control. In August 2006 the ethanol feed was stopped and the bioreactor operated solely on BD waste until October 2006. Based on the assumption that BD waste averaged 20% glycerol and 15% methanol, the goal was to provide a flow of 130-140 ml/min in order to reduce 100% of the sulfate, with sulfate at 1900-2000 mg/L (Zamzow 2007).

Analysis of bioreactor water

Sulfate removal and metal removal were indicators of bioreactor treatment effectiveness. Concentrations of Fe, Ni, and Zn were analyzed regularly with occasionally analysis of Cu and Mn. Analysis was conducted on a Perkin-Elmer 5000 flame atomic absorption spectrophotometer. Sulfate concentration was determined by standard gravimetric analysis using barium sulfate precipitation (Clesceri et al. 1998). Alcohols were analyzed by HPLC (HP 1050) equipped with an Aminex HPX-87H column heated to 60 °C, using 0.001M H_2SO_4 eluent. Refractive index and UV detectors were run in sequence. A Waters 510 HPLC was used to pump the eluent through the RID reference cell. The limits of detection were 15 mg/L (glycerol) and 20 mg/L (methanol) (Zamzow et al. 2006).

Sludge analysis

Grab samples of solids were collected from the pre-treatment pond, Pond 3, Pond 4, and the filter bags in 2005. Bioreactors were operating on a mix of ethanol and BD waste; no sludge from the period of operation solely on BD waste was collected, due to the short time of the pilot test. However, the sulfide sludge composition should be the same regardless of the carbon source provided. Samples were analyzed by Applied P & CH Laboratories, Chino, California for total metals and leachable metals for comparison to California and federal hazardous waste classification (EPA Methods 1311, 6010B, 7470, 7471). The following tests were conducted: California Total Threshold Limit Concentration (TTLC), Soluble Threshold Limit Concentration (STLC), Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP)

In a separate experiment, air dry sludge was added to low organic agricultural soils in Nevada to determine if the sulfides present in the soils would result in acidification of those soils. The pH of the soils was 7- 8, and the air dried sludge was added in percentages of 1-10%. Soils were allowed to equilibrate for three weeks.

Results

The bioreactor ran on BD waste for a 55-day pilot test. Acid seep influent flows averaged 54-60 L/min, pond recirculation 106-147 L/min, BD waste was supplied at 65-75 mL/min, and NaOH was supplied at about 72 mL/min for 4 weeks, then adjusted down to about 45 mL/min. Biodiesel feed provided to the bioreactors was tested in the months before the switch to full BD waste operation. June-August 2006 samples averaged 15%-22% glycerol and 13%-21% methanol. Free fatty acid content of the biodiesel wastes was not characterized, but was expected to be within 3-6%. The remaining fluid was primarily water with residual hydroxide. During the pilot test there were upsets and the bioreactor operated under normal conditions – with ponds full of water and consistent carbon and sodium hydroxide flows – only for the first two weeks. This made direct comparison of bioreactor operation on ethanol and BD waste difficult; however, the sludge composition under either carbon would be expected to be the same.

Sulfate and alcohol consumption

When operated on ethanol August-October 2005, sulfate reduction was 16-21% (mean 19%). When operated on ethanol February-July 2006, sulfate reduction was lower at 6-17% (mean 11%). While operated on BD waste, sulfate reduction was 7-12% (mean 10%). Sulfate reduction was higher in microbially-active Pond 2 (Table 1) and lower in Ponds 3 and 4 due to introduction of acid influent into Pond 3 in the bioreactor re-circulation configuration.

Glycerol was not utilized as well as ethanol, showing 20% to 30% reduction in concentration between the bioreactor system influent and effluent, compared to 35% to 65% utilization of ethanol.

***Table 1**. Sulfate, iron and trace element removal. A selection of samples is shown. The bioreactor ran on BD waste feed August 18-October 13, 2006. Remedial action discharge target concentrations were exceeded several times (bold) for iron. Concentrations are for unfiltered metals. Due to the recirculation design, the best sulfate removal was at Pond 2.*

Date	Sample	Fe (mM)	Zn (mM)	Ni (mM)	Sulfate (mM)	% sulfate reduction
Aug 21 2006	Influent	2.33	0.014	0.012	20.4	
	Pond 2	0.57	0.003	0.005	17.2	16%
	Discharge	**0.07**	0.002	0.002	18.9	8%
Sept 6 2006	Influent	2.26	0.015	0.013	19.9	
	Pond 2	0.23	0.002	0.004	15.3	23%
	Discharge	**0.17**	0.002	0.001	18.5	7%
Sept 20 2006	Influent	2.27	0.013	0.012	20.2	
	Pond 2	0.23	0.003	0.005	16.9	16%
	Discharge	**0.20**	0.002	**0.005**	18.0	12%
Oct 13 2006	Influent	2.89	0.020	0.011	19.8	
	Pond 2	0.03	0.003	0.001	16.8	15%
	Discharge	**0.07**	0.002	0.002	17.7	12%
Remedial action target	single sample	0.036	0.003	0.002		
	average	0.018	0.003	0.001		

Iron and trace metal removal

The bioreactor removed metals to lower concentrations when operated on ethanol than it did when operated on BD waste (Zamzow 2007). This was due primarily to disruptions of normal bioreactor operations during the test period, as all metals were removed below remedial action targets when the system had normal hydraulic retention time. Copper was removed below remedial action targets in all samples (not shown), zinc and nickel nearly always met removal targets, but iron did not meet removal targets when the bioreactor operated on BD waste (Table 1).

Iron makes up most of the concentration of metals in the bioreactors. On a molar basis, iron removal between influent and discharge points was within 0.7 mM of sulfate removal (Table 1).

Sludge composition

Bioreactor solids captured in filter bags met al.l state and federal leachate tests, indicating they would not leach toxic concentrations of metals (Table 2). Sludge in ponds was 86-99% moisture; sludge in filter bags was 80-82% moisture (EPA 2006).

***Table 2** Characterization of solids. Sludge from ponds and filter bags was analyzed for a suite of 17 trace element. Only the four primary metals of concern are shown, and only for Pond 4 (settling and flushing pond) and filter bag sludge. For all tests conducted on all analyst, sludge was determined to be non-hazardous. DI WET = waste extraction test using deionized water TCLP = toxicity characteristic leaching procedure SPLP = synthetic precipitation leaching procedure Adapted from Table 2-19 in US EPA 2006*

Parameter		Total Metals (mg/kg dry wt)	DI WET metals (mg/L)	TCLP metals (mg/L)	SPLP metals (mg/L)
Copper	Pond 4	707	0.035	0.026	0.61
	Filter bag	2030	0.021	0.015	0.0082
Lead	Pond 4	<26	<0.007	<0.0026	0.0018
	Filter bag	8.9	0.057	0.013	0.0025
Nickel	Pond 4	627	0.104	0.027	0.0384
	Filter bag	561	2.91	0.278	0.0025
Zinc	Pond 4	850	0.0546	0.0163	0.0086
	Filter bag	1400	0.58	0.137	0.0071

When sludge was mixed with soil, the saturated paste pH did not drop to less than 7 on any of the soils, indicating soils were well buffered, and were not acidified by addition of the bioreactor sludge. Since the sludge contained copper, nickel and zinc, the additions of these elements would need to be monitored over time. However, one application of the sludge, even at 10% of the weight of the soil did not alter the metal content of the soil in a substantial manner, and those metals could be considered micronutrients (Glenn Miller, personal communication).

Discussion

Consistent delivery of BD waste was a challenge. While ethanol was delivered via a gravity drip system, the viscosity of BD waste required delivery through a peristaltic pump and the caustic BD waste required tubing to be replaced every 7-10 days.

Low sulfate reduction averaging 8% in mid-June to mid-August 2006, when reactor was fed both ethanol and BD waste was due to unusually high influent flows experienced: 65-75 L/min compared to normal flows of 50-60 L/min in 2005. This reduced the hydraulic residence time in the bioreactor. Hydraulic residence time was also reduced when operating on BD waste, as Pond 3 was entirely drained for some weeks during maintenance unrelated to the pilot project. The low hydraulic residence time and the low utilization of the glycerol and methanol carbon source contributed to lower sulfate reduction. Sulfate reduction was highest in Pond 2 (15-23%), where microbial activity occurred, and lower at the treatment system discharge point, due to acid influent addition in Pond 3.

Laboratory (Luo 2004; Zamzow et al. 2006) and field experiments (Tsukamoto and Miller 1999) are evidence that compost-free bioreactors can be supplied with a variety of alcohols for a carbon source. This allows operators the flexibility to take advantage of lower cost material to adapt to different sources and fluctuating prices.

Regardless of the alcohol source, the precipitated metal-sulfide sludge may become an asset as a soil nutrient supplement, providing trace metals such as copper and zinc. Adding this sludge to soils appears to be a partial solution to bioreactor sludge management and should be investigated further, particularly where the amount of land available for sludge additions is large. However, the sludge at Leviathan contained appreciable amounts of sodium, due to the addition of sodium hydroxide base into Pond 3, which ultimately would be problematic for soils. Substitution of potassium hydroxide, although more expensive, may, in total, provide a primary nutrient to the soil. It would need to be monitored to protect the agronomic quality of the soil, but could reduce the overall cost of sludge management, and should be studied further.

Conclusions and Summary

The Leviathan mine bioreactor successfully transitioned from ethanol to BD waste. Sulfate reduction was not as high as previous years, but most metals were removed below effluent discharge requirements, particularly when appropriate hydraulic residence time was achieved. Difficulties with providing consistent BD waste deliver from storage tank to bioreactor may make it less suitable than other alcohols when used in cold climates. Analysis of metal leaching in waste sludge and preliminary tests of soil mixed with sludge indicate the bioreactor metal sulfide sludge waste could be provided as a soil supplement for trace minerals.

We suggest that compost-free bioreactors and resulting sludge be further tested under different conditions, considering local opportunities. In particular testing should determine efficiency under different alcohols and different ways in which to apply the sludge as an asset, rather than a cost.

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