Passive Treatment of Coal-mine Drainage by a Sulfate-reducing Bioreactor: A Case Study from the Illinois Coal Basin, USA

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ABSTRACT

The purpose of the study was to identify and monitor the geochemical and biogeochemical mechanisms that control the attenuation of coal-mine drainage during the first four years of treatment by an anaerobic sulfate-reducing bioreactor and associated oxidation ponds. This information is needed to investigate bioreactor design parameters, performance and longevity. The acid-mine drainage (AMD) at the case example site, the Tab-Simco Mine, had been highly acidic with an average pH of 2.9, a net acidity of 1,665 mg/L calcium carbonate equivalent-CCE, and high levels of dissolved SO_4^{2-}, Al, Fe, and Mn. The severity of the AMD at this site may be considered as beyond the treatment capabilities of conventional passive treatment techniques. Nevertheless, the treatment system has increased the pH of the acid mine drainage (AMD) to ~6.0 and decreased the median acidity from 1,647 to 64.6 mg/L CCE, SO_4^{2-} from 2,995 to 1,691 mg/L, Fe from 443.3 to 4.6 mg/l, Al from 116.5 to 0.69 mg/L, and Mn from 36.5 to 23.5 mg/L. Geochemical modeling indicates that the bioreactor discharge is saturated with respect to the minerals alunite, gibbsite, siderite, rhodochrosite, jarosite, and iron hydroxide precipitates. The $\delta^{34}S$ value of SO_4^{2-} increased in the bioreactor from an average of +6.9‰ to +9.2‰, suggesting the presence of bacterial sulfate reduction. Preliminary results of a bacterial community analysis show that DNA sequences corresponding to bacteria capable of sulfate reduction were present in the bioreactor outflow discharge, but were outnumbered by sequences similar to bacteria capable of re-oxidizing reduced sulfur species. The temporal trends include seasonal variation in SO_4^{2-} and metal concentration and a general decline in the amount of alkalinity. Recently, these declines have reduced the ability of the receiving stream to buffer the system discharge during dry seasons. Overall, this study illustrates the dynamic biogeochemical nature of the passive treatment systems.

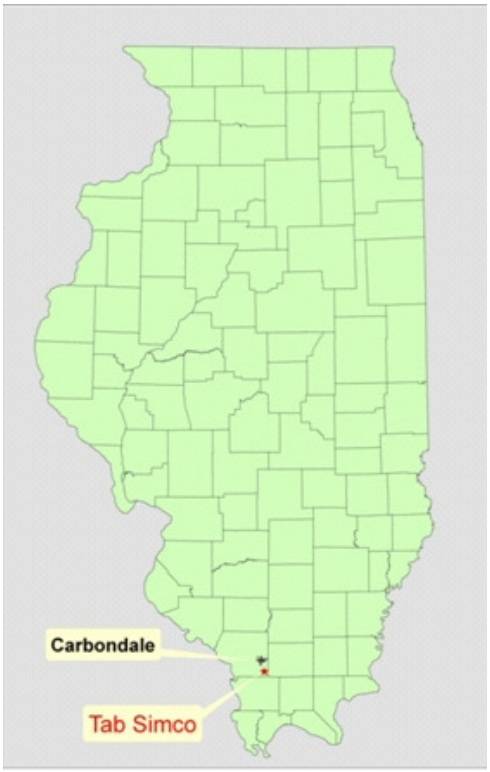
Keywords: Acid mine drainage, Tab-Simco, geochemical modeling, surface flow wetlands bacterial community analysis, low pH iron oxidation.

This information does not necessarily reflect the current policies of the Office of Surface Mining Reclamation and Enforcement. It is being provided to meet the need for timely "best science" information and to build upon the understanding of geochemical conditions inside a passive treatment system for AMD.

Introduction

Untreated AMD from some coal mining activities conducted prior to the enactment of environmental regulations are known to have a significant negative impact on the surrounding environment (Smith, 2002; Cravotta, 2008a and 2008b). Acid mine drainage (AMD) is produced by biochemical weathering of pyrite and other sulfides found in coal, overburden, and coal mine waste piles (Evangelou, 1995; Younger *et al*., 2002; Chugh *et al.*, 2007). Weathering results in the release of oxyanions (SO_4^{2-}) and cations such as Fe, Al, Mn, Ni, Co and Zn (Hyman and Watzlaf, 1996; Bigham and Nordstrom, 2000; Blowes *et al*., 2007; Cravotta, 2008a and 2008b). Extensive studies have been dedicated to understanding the biogeochemistry of coal mine drainage (pH < 6) and associated water-quality degradation (Bigham and Nordstrom, 2000; Cravotta, 2008a). The Illinois Basin contains some of the most important coal resources in the United States, with about 20 coal seams mined to date (USGS, 2002; Korose and Elrick, 2010). The Illinois coals have relatively high ash and mineral matter content, with total S content values between 0.5% and 7%, averaging 3.5%. Passive treatment, a technology pioneered to treat coal mine drainage in Appalachia (Hedin et al 1994), has also been used to mediate environmental impacts of abandoned coal mine drainage in Illinois and other Midwestern states (Behum *et al*., 2002, 2008 and 2010; Lewis, 2008; Lefticariu *et al*, 2008). One of these passive technologies, sulfate-reducing bioreactors, are similar to a successive alkalinity producing systems (SAPS), which has been widely used in remediation of coal mine AMD in Appalachia (Kepler and McCleary, 1994; Watzlaf, 1997). Bioreactors provide an environment in which organic carbon, as represented by CH_2O, is oxidized to bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}) is reduced to hydrogen sulfide $H_2S_{(aq)}$, by the following overall reactions:

$$2\ CH_2O + SO_4^{2-} \Rightarrow 2\ HCO_3^- + H_2S_{(aq)} \qquad (R1)$$



Bicarbonate is available to react with H^+, decreasing the acidity in the system. Hydrogen sulfide readily dissolves in water and combines with divalent metals (Me), such as Fe, Ni, and Zn, to form sulfide mineral precipitates MeS according to the following reaction:

$$H_2S_{(aq)} + Me^{2+} \rightleftharpoons MeS_{(s)} + 2\ H^+ \qquad (R2)$$

Additional metal removal can occur (1) during biologically-mediated precipitation of metal oxyhydroxide in the oxidized zone (at a pH where abiotic precipitation is unlikely; Thomas and Romanek, 2002; Burgos *et al*., 2008), and (2) by adsorption onto clay minerals and organic matter (Hong et al, 1995; Evangelou, 1998). A major shortfall of the passive remediation technologies is the inability of providing long-term (> 10 year) treatment of drainage with high metal and Al (>20 mg/L) contents. Operational problems arise from plugging by precipitates, dissolution of available carbonate minerals, and exhaustion of the organic carbon source (Thomas and Romanek, 2002; Neculita *et al*., 2008a and 2008b).

Figure 1. The location of Tab-Simco Project.

Site description

Tab-Simco is an abandoned coal mine located southeast of Carbondale in Jackson County, Illinois (Fig.1). Underground mining of the Murphysboro and Mt. Rorah coal beds of the Pennsylvanian age Spoon Formation occurred between 1890 and 1955; surface coal mining affected the area in the 1960's and 1970's. A series of exploratory drill holes have delineated an acidic mine pool within the abandoned underground mine workings. AMD seeps from this mine pool at a rate of about 35,000 gallons per day, which resulted in a significant aquatic impact on nearby Sycamore Creek.

Prior to treatment the largest, a 1.2 LPS (19 GPM) discharge, had a pH = 2.4, dissolved Fe = 422 mg/L, dissolved Al = 147 mg/L, dissolved Mn = 31.4 mg/L, SO_4^{2-} = 2,370 mg/L, and total acidity = 1,816 mg/L CCE (all median values). This discharge flowed across small floodplain and created a 3.65-ha (9-acre) area "kill zone" devoid of vegetation (Fig. 2; Smith, 2002). Natural processes within this "kill zone" resulted in attenuation of metals and sulfate. For example, Fe was lowered to 196.3 mg/L, which represents a 53.5%reduction; Al was reduced to 124.4 mg/L, a 15.4% reduction; and sulfate was reduced to 1,834 mg/L, a 22.6%reduction (Table 1). Geochemical modeling indicates that this seep was supersaturated with respect to the hydrous sulfate mineral jarosite and the iron oxyhydrate goethite. However, the mechanisms responsible for lowering metal and sulfate levels when the AMD traversed the "kill zone" were not investigated. Nevertheless, a large quantity of low pH (2.48) metal laden water remained and impacted the receiving stream, Sycamore Creek. This waterway downstream of the "kill zone" discharge was characterized by a pH = 2.92 mg/L, total Fe = 10.0 mg/L, total Al = 18.4 mg/L and total Mn = 33.8 mg/L (median values) in measurements prior to treatment system construction. To abate the large seep a passive-type treatment system was constructed in 2007 by the Illinois Department of Natural Resources, Office of Mines and Minerals (Lewis, 2008).

Methodology

A research team composed of the Illinois Department of Natural Resources (IDNR), the Office of Surface Mining Reclamation and Enforcement (OSMRE) and Southern Illinois University Carbondale (SIUC; Smith, 2002; Lewis, 2008; Lefticariu *et al*., 2009; Segid, 2010; Segid *et al*. 2010; Behum *et al*, 2011) has been conducting quarterly water quality measurements and sample collection since 2005 (Fig. 3).

Field parameter measured include pH, temperature, specific conductance, oxidation-reduction potential (ORP), and dissolved oxygen by electrochemical methods. Field laboratory tests include total and dissolved ferrous Fe by colorimetric methods (Hach Company, 2002) and field alkalinity for samples with a pH more than 4.5 using the Hach micropipette method (Hach Company, 2002).

All analytical tests have been performed at IDNR, OSMRE and SIUC laboratories (Table 1). Metals analyses are by a combination of ion couple plasma (ICP) and Hitachi (Schaumburg, IL) Z-2000 Polarized Zeeman atomic absorption (AA) mass spectrometry and colorimetric methods following Standard Methods; major anions have been determined by ion chromatography (IC), colorimetric, and gravimetric methods (American Public Health Association *et al*., 2005; Hach Company, 2002). The stable isotope ratios of sulfur of the dissolved SO_4^{2-} were measured at Indiana University using a Finnigan MAT 252 mass spectrometer equipped with an elemental analyzer.

Figure 2. The Tab-Simco "kill zone" prior to treatment system construction.

Passive Treatment System Construction

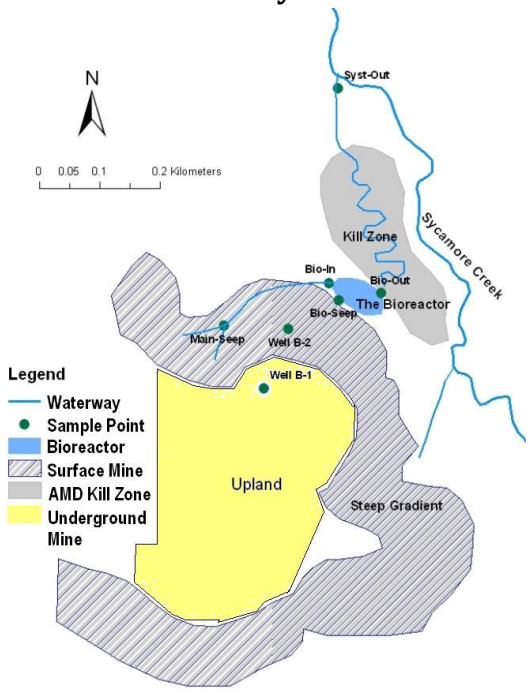


Figure 3. Overview of the Tab-Simco Treatment System, Illinois.

The Illinois Department of Natural Resources, Office of Mines and Minerals constructed a passive-type treatment system in 2007 to abate the pollution caused by AMD seeps (Main Seep, Fig. 3; Lewis, 2008; Segid, 2010; Segid *et al*, 2010; Behum *et al.*, 2011). The principle technology employed was a 0.3-ha (0.75-acre) sulfate-reducing bioreactor, which was one of the first full scale bioreactor employed for the treatment of acidic, coal mine drainage in the US (Fig. 4). This bioreactor was constructed in three layers: a shallow (0.3 m deep) acid impoundment (Fig. 4), an underlying thick (1.8 m) layer of compost, a geotextile fabric, and finally a 0.3 m-thick limestone layer with embedded drain pipes (Figs. 5 and 6). A series of oxidation cells/surface-flow wetlands follow the bioreactor unit constructed to allow for the precipitation of the remaining metals before the treated water discharges into Sycamore Creek (Fig. 4).

Currently, the Tab-Simco passive treatment system abates a collected 1.35 LPS (21.5 GPM) coal mine discharge with a high Fe and Al content (Table 1; Smith, 2002; Lewis, 2008; Segid, 2010; Segid *et al*, 2010; Lefticariu *et al*, 2009; Behum *et al*, 2011). The bioreactor input is the sum of AMD collected from major seeps (Bioreactor In) and seepage directly into the cell as characterized by well B-2 data (Table 1).

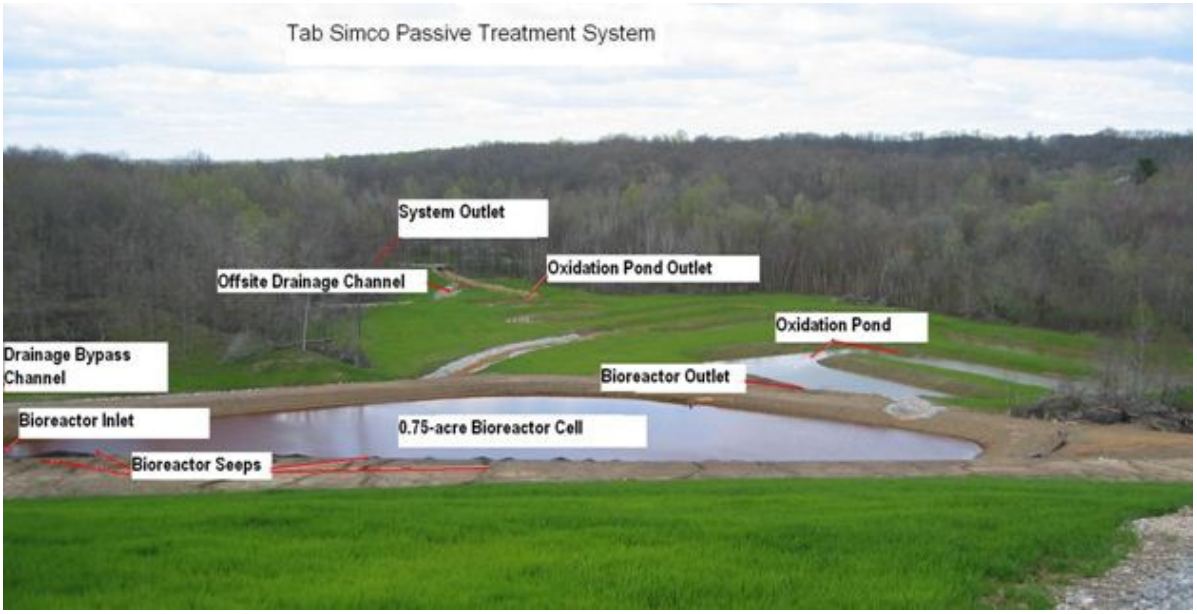


Figure 4. Overview looking north of the Tab-Simco passive treatment system.

The Tab-Simco bioreactor's organic substrate is composed of approximately 5,887 m^3 (7,700 cubic yards) of "compost," a blend of (by volume): 53% wood chips, 27% straw, 11% seasoned municipal (yard waste) compost and 9% agricultural ground limestone (*aglime*; Lewis, 2008; Fig. 6). Limited observations indicate that this design has may offer a solution to the treatment of poor quality AMD (Thomas and Romanek, 2002; Gusek, 2002, 2005; Behum *et al*, 2011). Gusek (2002, 2005) suggests a design goal a SO_4 loading of 0.30 moles/m^3/day. Reaction 2 suggests that for optimal conditions, the divalent metal flux of the inlet AMD must be equal or less than the rate of sulfate reduction for complete metal removal. However, URS (2003) recommends a lower cumulative heavy metal flux value of only 0.15 moles/m^3/day.

Table 1 – Geochemical Data for the Tab-Simco Treatment System, Illinois (Median Values)*

Site ID	pH	D. Fe	D. Mn	D. Al	D. Ni	D. Zn	Acidity	Alk.	SO_4
Main Seep	2.84	692.5	38.7	178.7	2.33	2.99	2,590	0	4,167
Well B-2	2.87	294.0	34.6	89.0	1.32	1.87	962	0	2,407
Bioreactor seep	3.14	268.8	35.2	80.4	1.57	2.08	997	0	2,688
Bioreactor In	2.93	595.0	39.9	146.3	2.40	2.66	2,321	0	3,703
Bioreactor in/ Well B-2 mix	2.90	444.5	36.9	117.6	1.87	2.27	1,647	0	3,055
Bioreactor Out	6.27	128.0	31.7	0.83	0.07	0.12	182.8	283	2,074
System Out	5.79	5.33	23.8	0.96	0.16	0.23	64.6	22.5	1,750

*All values except pH are in mg/L; acidity and alkalinity (Alk.) are calcium carbonate equivalent values; acidity = calculated acidity.

Due to the geotechnical constraints of the site (Lewis, 2008) the Tab-Simco system is smaller than optimum for an AMD discharge with a high SO_4 loading of 0.66 moles/m^3/day and a high

cumulative metal loading (excluding Mn) of 0.260 moles/m^3/day (Table 2). This design shortcoming may potentially impact the longevity of the Tab-Simco bioreactor.

Figure 5. Construction of the Tab-Simco bioreactor cell: limestone-bedded underdrain.

Figure 6. Construction of the Tab-Simco Bioreactor Cell: placement of the compost layer.

Results: Geochemistry of Tab-Simco Mine Drainage

Bioreactor Inlet AMD

Water quality data for mine water discharges along the Sycamore Creek are summarized in Table 1. The majority of seeps had a pH values in the 2.4 to 3.2 range, specific conductance (SC) in the 1,960 to 5,640 µS/cm range, with extremely high concentrations of SO_4^{2-} (up to 7,000 mg/L), Fe (up to

920 mg/L), Al (up to 260.5 mg/L) and Mn (up to 58.5 mg/L). Similar water quality have been reported for more severe AMD cases documented from Appalachian coal mine discharges (Hyman and Watzlaf, 1996; Cravotta, 2008a and 2008b). Following the 2007 construction about 50% of the AMD was captured by a collection ditch (Bioreactor In) with the remainder seeping directly into the cell from a series of small seeps (Bioreactor Seep); more extensive data collected for nearby monitoring well B-2 are used as a proxy for chemistry of Bioreactor Seeps (Figs. 3 and 4, Table 1).

Bioreactor AMD Treatment

Between January 2007 and October 2011, acidity of the AMD has dropped from a median of 1,647 in the bioreactor inlet to 208.9 mg/L CCE in the cell's discharge, an 82.1% reduction (Fig. 7); SO_4^{2-} has decreased by 32.1% at the bioreactor outlet to 2,074 mg/L (Fig. 8). During this period metal removal by the Tab-Simco bioreactor cell has averaged 71.2% for Fe, 99.3% for Al, 96.2% for Ni and 94.7% for Zn (Table 1). To enhance metal precipitation in the follow-up oxidation pond and surface flow wetland cells the Tab-Simco bioreactor discharge has a median pH of 5.8 and a net alkalinity of 0 mg/L CCE (Table 1, Fig 7). In bench studies, McCauley *et al*. (2009) reported an average sulfate removal rate of 0.308 moles/m^3/day. Gusek (2002, 2005) suggested a removal rate of 0.30 moles/m^3/day as a design criterion. The removal rate measured at the Tab-Simco system is 0.20 moles/m^3/day, a value slightly lower than the optimal rates (Table 2). This may be due to the fact that the system is undersized and that bacterial sulfate reduction at this site is undermined by the elevated levels of nitrate which favor the nitrate reduction over sulfate reduction (Reaction 1; Lefticariu *et al*, 2009).

Oxidation Pond and Wetland Treatment

A series of oxidation cells follow the bioreactor unit designed to induce the precipitation of the remaining sulfate and metals before discharge into Sycamore Creek. To monitor these improvements additional measurements were taken at the

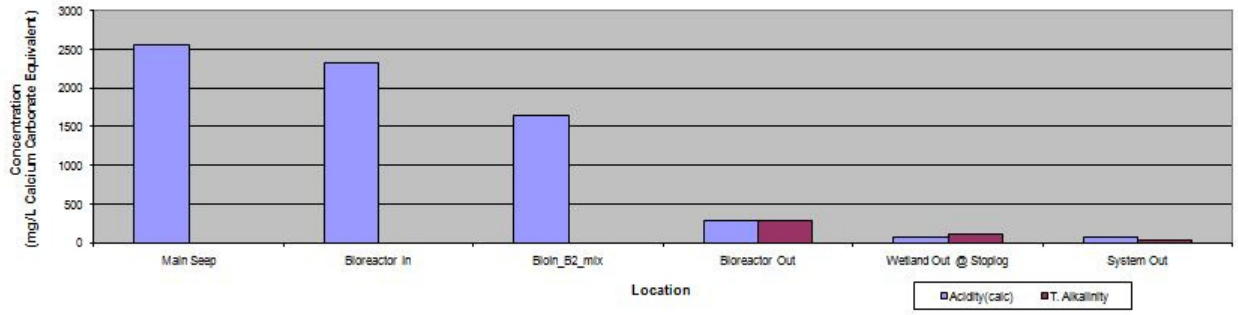


Figure 7. Changes in acidity and alkalinity values within the Tab-Simco Passive Treatment System.

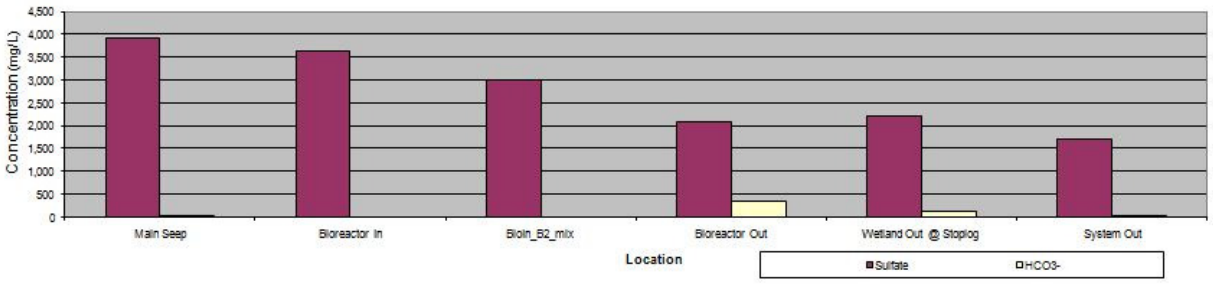


Figure 8. Changes in Sulfate and Bicarbonate values within the Tab-Simco Passive Treatment System.

System Outlet (Fig. 4, Table 2). The discharge from the bioreactor cell contains a median dissolved Fe concentration of 120.2 mg/L. However, subsequent Fe precipitation occurs as ferrihydrate in follow up oxidation cells (Fig. 4) with median Fe in the system discharge of 4.6 mg/L, a 99% removal rate. The following water quality improvements have been recorded from the inlet AMD to the system outlet: (1) acidity has dropped from a median 1,647 to 64.6 mg/L CCE, a 96.1% improvement, and (2) SO_4^{2-} has decreased by 43.4% (from a median of 2,995 to 1,691 mg/L). The overall cumulative dissolved metal removal by the Tab-Simco system of 99.7% (Table 2).

Table 2 - Median Loading and Removal Rates: Tab-Simco Passive Treatment System, Illinois*

Site ID	D. Fe	D. Al	D. Mn	D. Ni	D. Zn	Cumulative Metals	SO_4
Bioreactor Loading* Rate(moles/m^3/day)	0.160	0.091	0.0140	0.0005	0.0006	0.260	0.658
Bioreactor Removal Rate(moles/m^3/day)	0.122	0.090	0.0018	0.0005	0.0006	0.214	0.202
Removal (%)	72.9	99.3	13.2	98.6	96.2	82.3	30.7
Wetland Cell Load Rate(moles/m^2/day)	0.1477	0.0833	0.0127	0.0005	0.0006	0.2321	0.6139
Wet. Cell Removal Rate(moles/m^2/day)	0.1208	0.0832	0.0018	0.0005	0.0006	0.2051	0.1868
Cum. Removal (%)	99.9	99.4	36.1	89.8	90.8	99.7	43.4

*Bioreactor inlet channel and B2 mix; All values except pH are in mg/L; acidity and alkalinity are calcium carbonate equivalent values; acidity = calculated non-manganese acidity.

Microbial Community Analysis

To analyze the bacterial community associated with the site, molecular analysis of DNA extracted from the surface of the bioreactor cell, the bioreactor outlet, and the oxidation pond was performed by amplification and cloning of the 16S rRNA gene (present in all bacteria) and the dissimilatory sulfite reductase genes (only found in sulfate-reducing bacteria; Burns *et al*, 2011). Results from the surface of the bioreactor cell indicated that iron-oxidizing bacteria dominated the microbial community in the pretreated AMD, while sulfur-oxidizing bacteria and microbes capable of degrading complex carbon sources such as cellulose dominated the water directly from the bioreactor outlet. While this finding was expected due to the presence of compost in the bioreactor, it suggests that bacteria essential for breaking down compost into simple dissolved organic carbon sources often utilized by sulfate reducers, such as lactate and acetate are present to a certain extent. DNA sequences corresponding to bacteria capable of sulfate reduction were only detected in the bioreactor outflow and the oxidation pond. However, the sequences were of low diversity with the predominant sequence most closely related to the *Desulfobacca*

acetoxidans, a slow growing sulfate reducer that utilizes acetate as a carbon source. Thus, the relatively high level of sulfate detected in the post-treated AMD is likely due to a combination of the low diversity and slow growth of the sulfate reducing community stimulated by the bioreactor as well as the presence of sulfur-oxidizing bacteria. Sulfur-oxidizing bacteria yield sulfate and H^+ through the generation of sulfuric acid (H_2SO_4) and thus reverse the desired bioreactor process.

Discussion

The longevity of typical reducing and alkalinity producing (RAPS)-type vertical flow systems when treating high Al (> 20 mg/L) drainage is limited (Gusek, 2002). The limitation is due to increase in pH > 4.5 within the RAP's limestone layer. At this pH a prodigious amount of Al hydroxide can accumulate and normally clog the system, according to the reaction:

$$Al^{3+} + 3H_20 \rightleftharpoons \underset{\text{(Gibbsite)}}{Al(OH)_{3(s)}} + 3H^+ \qquad \text{(R3)}$$

Regular flushing of RAPS under drains is a common procedure to extend system life (Hedin Environmental, 2008: Weaver *et al*, 2004). However, unlike a RAPS-type system, Gusek and Wildeman (2002) suggest that Al precipitates within compost of the bioreactors are composed of relatively insoluble Al sulfate minerals such as alunite, which precipitates according to the following reaction:

$$3Al^{3+} + K^+ + 6H_2O + 2SO_4{}^{2-} \rightleftharpoons \underset{\text{(alunite)}}{KAl_3(OH)_6(SO_4)_2} + 6H^+ \quad \text{(R4)}$$

Alunite deposits are more compact than the bulky, amorphous gibbsite deposits. Additional research by Thomas and Romanek (2002) and McCauley et al. (2009) confirmed the presence of Al oxyhydrosulfates in deeper substrate zones of bench-scale bioreactor microcosms. For the Tab-Simco system, additional research is needed to characterize the fate of Al precipitates within the bioreactors. Iron can be removed as Fe hydroxides and oxyhydroxides in the upper oxidized zone, whereas the lower sulfidic zone Fe is removed as sulfide mineral precipitates. In general, divalent metals such as ferrous Fe, Ni, Zn and Co are mostly retained as sulfides. Because of the higher solubility of MnS and the moderate pH (<7.0) most Mn passes though the bioreactor cell (Table 2).

Limited performance data is available for pilot-and full-scale bioreactors treating coal mine drainage (Gusek, 2000; Gusek and Wildeman, 2002; Gusek, 2005; Behum *et al*, 2011). Field installations are typically designed for metal removal. A rule-of-thumb is to design the systems for 50% sulfate removal. Limited experience with bioreactor applications has suggested that most metals except Mn are retained within the bioreactor (Segid, 2010; Behum *et al*, 2011). Additional metal removal may occur within the bioreactor by either adsorption onto organics and hydroxides or cation exchange (Hong *et al*, 1995; Evangelou, 1998). Considerable dissolved Fe may discharge from bioreactors where loading is high (Table 1). However, due to the high alkalinity and favorable pH of a fully functional bioreactor discharge the remaining Fe will rapidly precipitate whenever adequate oxidation structures are constructed following the bioreactor cell.

Acidity and alkalinity trends

The high net acidity of the inlet AMD (median = 1,647 mg/L CCE; Table 1) is reduced by HCO_3^- alkalinity generated by the sulfate reduction reaction (Reaction 1), carbonate dissolution, and partial acidity storage in the form of sulfides (Reaction 2) with a total of a 96.1% reduction measured in the system discharge. During the operation of the treatment system there has been a parallel decrease in both the bioreactor inlet acidity from about 2,391 mg/L CCE (median 2008 and 2009) to 1,779 mg/L CCE (median 2010 and 2011) and the bioreactor outlet alkalinity from 403 mg/L CCE (median 2008 and 2009) to 221 mg/L CCE (median 2010 and 2011). The reduction in bioreactor discharge alkalinity is paralleled with an increase of dissolved Fe (2008 to 2009 median = 41.0 mg/L; 2010-2011 median = 156.1 mg/L). This increase may be due to: (1) a loss of available organic matter adsorption sites (Hong *et al*., 1995; Evangelou, 1998), (2) a decrease in retention time due to the reduction of compost pore space as a result of accumulation of metal precipitates and compaction, and 3) a decrease in the rate of bacterial sulfate reduction processes. Geochemical modeling indicates that the bioreactor discharge is saturated with respect to the minerals alunite, gibbsite, siderite, rhodochrosite, jarosite, and $Fe(OH)_3$ precipitates. Eventually, metal accumulation, dissolution of limestone, and degradation of compost material will require reconstruction of the reactor cell (Thomas and Romanek, 2002; Neculita *et al*., 2008a and 2008b). The large and steady increase of approximately 450 mg/L in calcium in the bioreactor discharge is an indicator that limestone dissolution is a major alkalinity-producing process (Fig. 9).

Sulfate removal

Between the 2008 and 2011 an average of 30.7% of the SO_4^{2-} is removed by the bioreactor cell. A 2009 study by the SIUC research team found that the average $\delta^{34}S$ value of the SO_4^{2-} in the untreated Tab-Simco AMD was 7.3 ‰; this value was similar to the $\delta^{34}S$ values of the pyrite in the coal seams, indicating that pyrite was the source of SO_4^{2-} (Segid, 2010). The $\delta^{34}S$ value of SO_4^{2-} increased in the bioreactor from an average value of 6.9‰ (inlet) to 9.2‰ (outlet), suggesting the presence of bacterial sulfate reduction processes (Segid, 2010). Geochemical analyses have showed a small seasonal variation in SO_4^{2-} removal rates with the seasons, with average values of 33.0% in the cooler months (October-March) and 38.6% in the warmer months (April – September; Figs. 10 and 11).

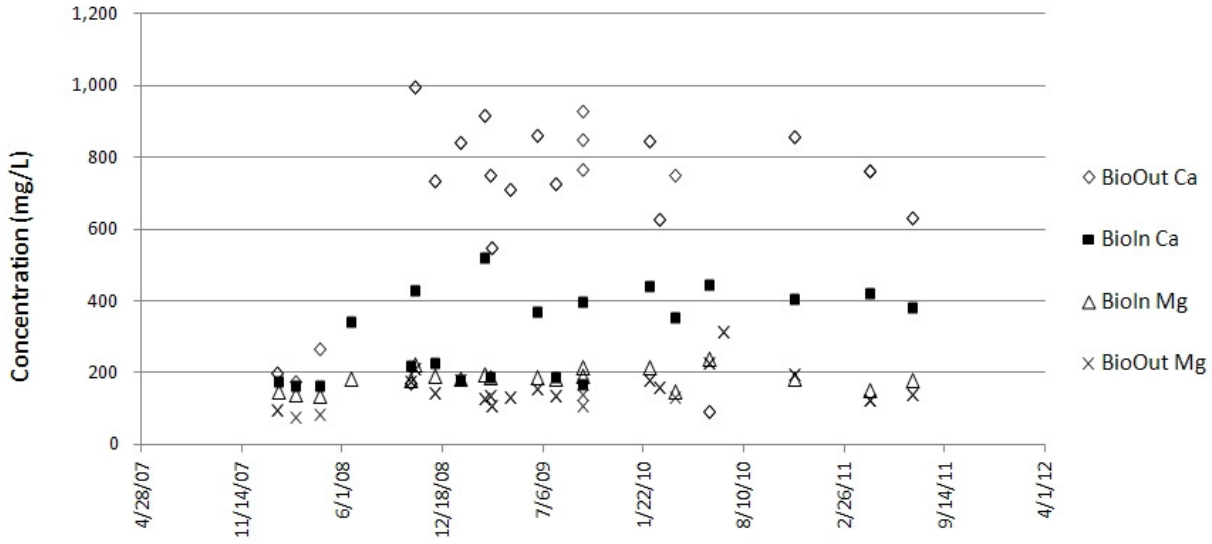


Figure 9. Trends in carbonate dissolution within the Tab-Simco bioreactor.

This cycle can be explained by a decline in bacterial sulfate reduction activity at low temperatures (Neculita et al., 2008a). Seasonal declines in sulfate reduction is offset in part by the continued production of alkalinity from carbonate rock within the structure (Fig. 9) as evidenced by large increase in average dissolved Ca concentration, from a median of 294.5 mg/L for the untreated AMD (bioreactor inlet) to 749 mg/L (bioreactor outlet) and dilution during the typically wet winter and spring months. The additional decrease in SO_4^{2-} measured in the system discharge (median = 1,750 mg/L CCE) may be due to: 1) additional sulfate reduction in the 1.2-meter deep oxidation pond, 2) precipitation of Fe sulfate minerals, and 3) dilution with fresh water runoff collected by a series of drain ways. Overall a respectable 43.4 % SO_4^{2-} decrease is produced by the Tab-Simco treatment system since operation began late in 2007 (Table 2).

Removal of metals

An estimated 14.6 metric tons of Fe and 5.2 metric tons of Al are retained in the bioreactor annually. The majority of Fe in the inlet AMD is removed by the bioreactor (Tables 1 and 2). Subsequent Fe precipitation occurs most likely as Fe oxyhydroxide and Fe sulfate minerals in follow up oxidation cells. Under the pH conditions of the bioreactor (pH > 4.5) Al is removed to a low level (0.83 mg/L). Due to the higher solubility of MnS at the cells pH and Eh conditions only 13.2 % of the Mn is removed by the bioreactor. (Fig. 11; Hedin *et al*., 1994). Variations in Mn removal approximate trends in SO_4^{2-} removal (Fig. 11). This trend may serve as an indicator of the rate of sulfate reduction processes. A small amount of additional Mn is removed in the follow up oxidation pond and of the surface flow wetland that results in a cumulative 36.1% Mn removal (Fig. 11). The limited removal in these structures is probably due to circumneutral pH (< 6.5), which does not favor the precipitation of Mn minerals (Hedin *et al*, 1994). The principle trace metals measures in the inlet AMD are Ni and Zn at 1.87 and 2.27 mg/L, respectively (median values, Table 1). Ni and Zn are removed by the system to low levels (0.16 and 0.23 mg/L, respectively).

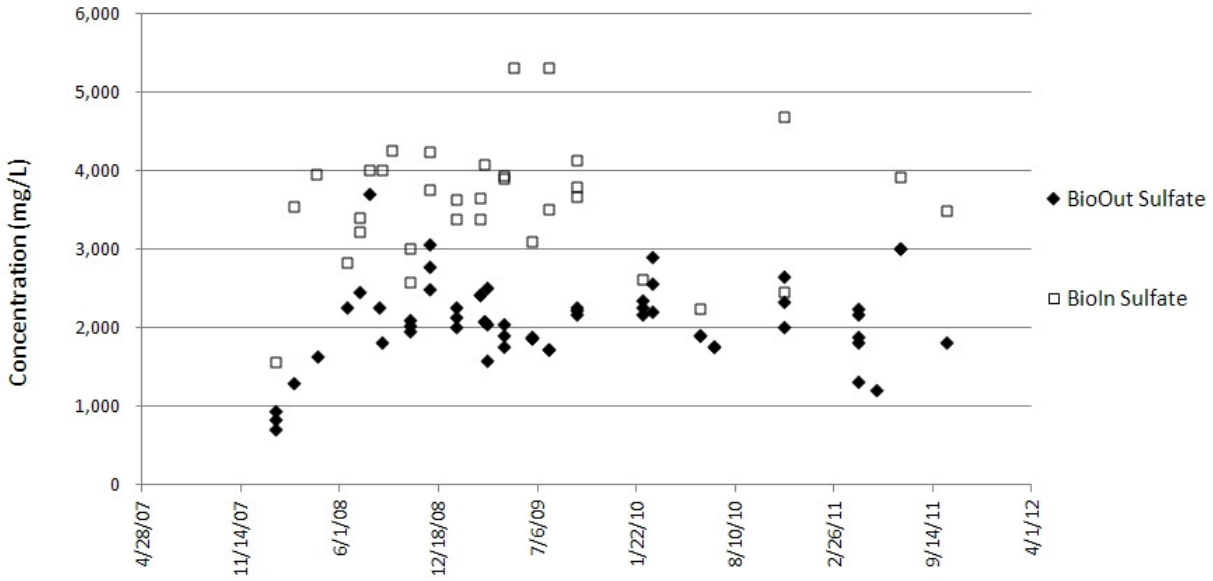


Figure 10. Changes in sulfate concentration in the Tab-Simco bioreactor discharge over time.

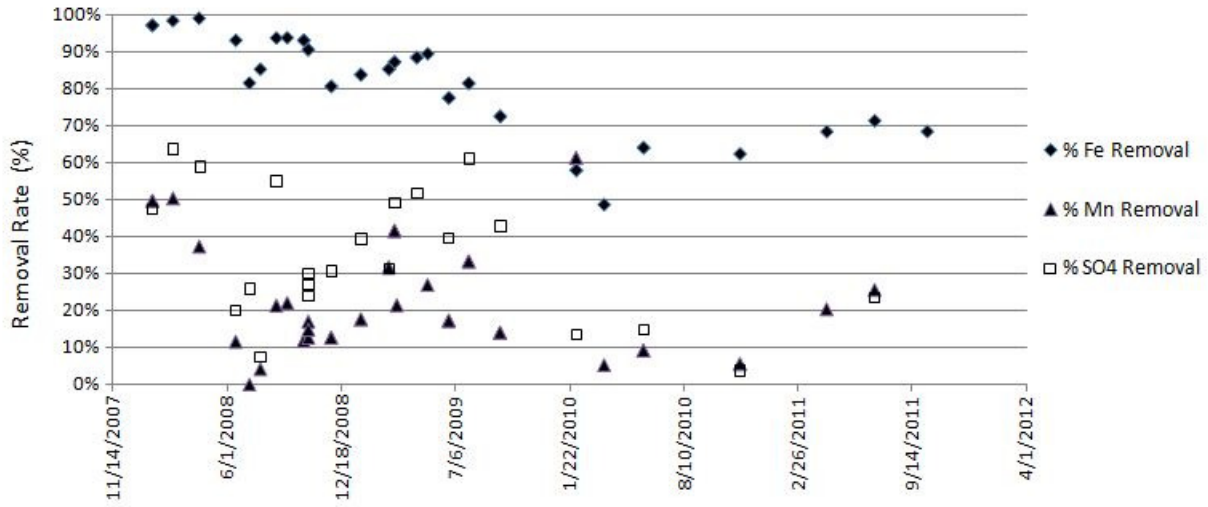


Figure 11. Sulfate and metal removal trends in the Tab-Simco Bioreactor discharge.

Conclusions

Between the end of 2007 and 2011 the Tab-Simco system has effectively treated AMD of a quality that heretofore has been untreatable by passive methods. Operation of the Tab-Simco treatment system typically reduces pollutant loads to a level which prevents significant degradation of Sycamore Creek. Operational issues include plugging of the bioreactor discharge with ferruginous precipitates and the seepage of untreated AMD into the "fresh" water bypass channel. System operational problems and to a greater extent the existence of an untreated AMD seep upstream have periodically impacted receiving stream water quality. A second bioreactor-based system has been proposed to treat the smaller (5 GPM, pH = 2.5) discharge and serve as a backup to the existing facility; construction is pending the results of an ongoing evaluation of biologic impact of AMD on Sycamore Creek.

Further study is ongoing that includes solid phase analyses and biological diversity to assess the conditions within the bioreactor, such as depletion of organic matter and armoring and clogging of substrate material by precipitated metal oxides and sulfides, conditions which will greatly affect performance and longevity. Identifying the mineralogy of these precipitates within the bioreactor using solid phase analyses would improve our understanding the geochemical conditions inside the bioreactor, which in turn can be helpful in designing the sulfate-reducing bioreactors in a manner that enhances longevity and performance. An improved understanding of biologic community especially sequences which are able to use complex carbon sources such as cellulose to produce simple organic compounds such as acetate, used by the sulfate-reducing bacteria as carbon sources will also aid in improving design efforts.

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