THE USE OF SULFATE REDUCING BACTERIA TO REMOVE SULFATE FROM IRON MINING TAILINGS WATER

Paul Eger, Tom Moe, and John Engesser

Abstract. A column experiment was conducted to evaluate the ability of various substrates to support sulfate reducing bacteria and remove sulfate from iron mining tailings basin water in northern Minnesota. The tailings water has a pH of around 7.5, 800 mg/L of sulfate and low levels of iron and trace metals. Although sulfate was removed in all columns, overall removal rates varied widely between substrates, ranging from 270 to about 3000 mmoles/m$^3$/day. The best removal occurred in the columns that were fed an organic carbon source, either ethanol or molasses. An organic substrate based column, biosolids + sawdust + hay, also had a high reaction rate but produced unacceptable levels of hydrogen sulfide. Effluent sulfate concentrations in some of these columns were below 50 mg/L and the reaction rate may have been sulfate limited. Methanol was also tried as an organic carbon source but the reaction rate was only about 50% of the rates achieved with ethanol and molasses. Based on the column results, a field pilot cell was designed and constructed in 2002. The cell was built solely with an inorganic iron rich substrate and ethanol was used as the carbon source. Although sulfate reduction occurred, flow problems developed and the system was redesigned in 2003. Through early December 2003, the system was treating about 400 L/minute and reducing sulfate from about 800 to 400 mg/L.


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Introduction

Iron is removed from taconite ore by crushing, grinding and magnetic separation. These operations increase the dissolved solid content of the process water. Minnesota taconite operations recycle their process water, reclaiming much of the water from their tailings basin. The water quality in the tailings basin is a function of the chemistry and mineralogy of the ore, reagents used in processing, the amount of fresh water added and the composition of other process streams that discharge to the tailings basin.

United States Steel Corporation (U. S. Steel), through its Minnesota Ore Operations, is the largest iron producer in Minnesota. The water in its tailings basin contains elevated levels of dissolved constituents, including sulfate. Sulfate concentrations have increased over time and the rate of accumulation has changed over time with adjustments to the process, including the installation of wet scrubbers to meet air quality standards. The waste gas scrubbers use water to remove particulates from the flue gas. Suspended solids from the scrubber slurry discharge are recovered in thickeners and a portion of the thickener overflow is discharged to the tailings basin. The scrubbers also remove a percentage of the SO\textsubscript{2} formed in the process, which is subsequently converted to sulfate and carried to the tailings basin in a dissolved form. Tailings basin water is recycled to the plant for use in the processing circuit. Sulfate concentrations in the basin water have increased about 40 mg/L each year since 1992 when the most recent set of scrubbers was installed. The increased concentration of dissolved constituents in the recirculating process water loop has caused problems in the processing circuit within the plant and a method is needed to reduce the total concentrations.

If water could be discharged from the tailings basin, lower concentration make-up water could be added to reduce the concentrations in the process water. Although the tailings basin water does not contain any constituents at toxic concentrations, sulfate concentrations are higher than the downstream Minnesota water quality standards. As a result, the Minnesota Pollution Control Agency (MPCA) has asked U. S. Steel to investigate various treatment alternatives to reduce sulfate concentrations. A variety of treatment alternatives were evaluated and the most cost effective approach of reducing sulfate concentrations was through the microbiological reduction of sulfate to sulfide (i.e., sulfate reduction), and subsequent precipitation as iron sulfide. A column test was designed to investigate the use of sulfate reducing bacteria to remove
sulfate from tailings basin water. Based on the results of the column test, a field demonstration test program began in 2002.

**Goal**

The ultimate goal is to build a system capable of treating 5000 gpm and achieving at least a 50% reduction in sulfate concentration.

**Objectives**

Investigate the ability of readily available materials to reduce sulfate.
Determine sulfate removal rates.
Based on laboratory results, design a pilot system that will be capable of removing sulfate throughout the year.

**Methods**

**Columns**

Clear acrylic columns (76 cm long, 14.6 cm diameter) with a perforated PVC support plate, were used for this study. Before putting the substrate into the columns, three 1.27 cm layers of crushed taconite ore were placed into each column (-0.64 cm, +6 mesh; -6, +8 mesh; and -8, +14 mesh).

**Substrates**

Locally available inorganic and organic materials were chosen. Organic substrates included sugar beet waste (called “tailings”), a peat mixture (fibric peat + screenings, a waste product from the preparation of horticultural peat), cow manure, exceptional quality biosolids, hay, sawdust, and cracked corn. Screened rod mill feed (-1.27 cm, +10 mesh taconite ore) from U. S. Steel was used as an inorganic component to provide permeability in the initial columns. Iron filings (10% by volume) were added to sugar beet waste, peat, and rod mill feed. New columns begun in April 2002 used a mixture of 90% of screened oxidized ore (-1.27 cm, +10 mesh) and 10% unscreened coarse tailings (100% -0.64 cm) as the inorganic component. For
columns containing organic substrates, the inorganic component comprised 25% by volume of the total substrate in the column (Table 1).

Ethanol was fed to columns containing sugar beet waste, peat, rod mill feed and oxidized ore + coarse tailings. Molasses was fed to columns with inorganic substrates, i.e., either oxidized ore + coarse tailings or rod mill feed. In August 2002, the molasses was switched to methanol. Columns that contained only an inorganic substrate received a bacterial seed addition of either cow or horse manure (~ 500 mL of manure as received or about 5% by volume).

After the columns were set up, the initial porosity was determined by slowing filling the void space with water. Estimates of the overall hydraulic conductivity of each column were made by using a falling head technique. The columns were then filled with tailings basin water and were maintained in a saturated condition without flow for about one week. Once the initial incubation period was complete, no additional incubation periods were included in the study.

**Sampling**

Feed water was pumped into the columns with a 12-channel peristaltic pump (Manostat Model CARTER 12/6, #74-126-00000). All columns were operated in down-flow mode. Columns, that received an organic feed, were fed from a carboy where the external carbon had been added to the tailings water. Flow rates were checked visually on a daily basis and volumetrically adjusted about every one to two weeks.

Initially, water quality samples were collected twice per week. Sample frequency decreased over time dropping to about once per month. Calcium, magnesium and iron were analyzed by an Inductively Coupled Plasma - Optical Emission Spectrometer (Perkin Elmer 4300 DV (Dual View )) while sulfate was analyzed with an ion chromatograph.

**Column Results**

**Flow Rates**

Initially, flow rates were selected to provide a residence time based on pore volume of approximately 48 hours and ranged from about 0.9 mL/min to around 2 mL/min. Flow rates were subsequently increased up to 2.5 mL/min and held there through the end of testing. Flow rates were generally maintained within ± 10% of these rates.
### Table 1. Column composition.

<table>
<thead>
<tr>
<th>Organic Substrate</th>
<th>% by volume</th>
<th>Zero Valen Iron</th>
<th>% by volume</th>
<th>Inorganic Substrate</th>
<th>% by volume</th>
<th>Bacterial Seed</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar beet waste</td>
<td>75</td>
<td></td>
<td></td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Sugar beet waste</td>
<td>75</td>
<td></td>
<td></td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>No</td>
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<td>Sugar beet waste</td>
<td>65</td>
<td>Iron filings</td>
<td>10</td>
<td>Rod mill feed</td>
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<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Peat</td>
<td>75</td>
<td></td>
<td></td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Peat</td>
<td>75</td>
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<td></td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Peat</td>
<td>65</td>
<td>Iron filings</td>
<td>10</td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Manure</td>
<td>10</td>
<td></td>
<td></td>
<td>Rod mill feed</td>
<td>25</td>
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<td>No</td>
</tr>
<tr>
<td>saw dust</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed corn(cracked)</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure</td>
<td>25</td>
<td>Rod mill feed</td>
<td>25</td>
<td>No</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sawdust</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hay</td>
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<td></td>
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<td></td>
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<tr>
<td>Sawdust</td>
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<td></td>
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<td></td>
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<tr>
<td>Hay</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Iron filings</td>
<td>10</td>
<td>Rod mill feed</td>
<td>90</td>
<td>Yes ³</td>
<td>No</td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Rod mill feed</td>
<td>100</td>
<td>Yes ³</td>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Oxidized ore</td>
<td>90</td>
<td>Yes ³</td>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Coarse tailing</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Oxidized ore</td>
<td>90</td>
<td>Yes ³</td>
<td>Molasses/methanol ⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Coarse tailing</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>Rod mill feed</td>
<td>100</td>
<td>Yes ³</td>
<td>Molasses/methanol ⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 - Columns discontinued on 4/18/02.
2 - Columns were discontinued on 5/20/02.
3 - Original columns 5 and 6 dismantled and replaced. New columns filled on 5/6/02 and flow began on 5/13/02.
4 - Seed source, “young” cow manure, 25 grams air-dried, ground powder. +500 mL “older” cow manure seed thoroughly mixed throughout column.
5 - Roughly 400 mL “as received” (not dried) horse manure; seed mixed into top portion of column only
6 - Feed was switched to methanol on 8/26/02.

**Water Quality**

**pH.** The pH of the tailings basin input water ranged from 7.9 to 8.6. Initially, the pH in all the column outflows was less than the input, with the lowest values measured immediately after startup. The pH values in the sugar beet column and the column with the cracked corn were
initially below 5, but increased above 5 after two and four weeks, respectively, and exceeded 7 after about two months. The column with rod mill feed and iron filings produced the highest effluent pH, routinely exceeding 8.5 after two months. The pH in the columns receiving ethanol were generally around 8, while those with molasses generally had lower pH values, between 6.5-7, but increased to around 8 when the feed was switched to methanol.

**Sulfate.** Sulfate in the tailings basin water input generally decreased over time from around 810 to 660 mg/L. After the first sample, all columns removed sulfate. During the first two months of the study, all the columns that received ethanol and the biosolids column had almost complete removal of sulfate. Since the organic substrate did not appear to increase sulfate removal when ethanol was added, the columns with organic substrates plus ethanol were discontinued after about 2 months. Removal was lowest in the columns with peat and these were also discontinued after about two months.

Outflow sulfate concentrations generally increased with time in the columns with manure but decreased over time in the columns that received molasses as an external carbon source. When the feed was switched from molasses to methanol the outflow concentrations increased by about 200 - 300 mg/L. Outflow concentrations were also much more variable with methanol than molasses.

**Iron.** Iron concentrations in the columns with sugar beets, peat and sawdust/manure/corn were initially above 100 mg/L. Concentrations decreased over time and were generally less than 1 mg/L after two months. Iron concentrations in the sawdust/biosolids/hay, sawdust/manure/hay and the rod mill feed with ethanol were about an order of magnitude lower and outflow concentrations decreased to <0.1 mg/L after about two months. Only the columns that received molasses continued to have iron in the column outflow. Iron in both columns ranged from around 5 to 20 mg/L. When the feed was switched to methanol, iron concentrations in both columns decreased to <0.1 mg/L within about one month.

The column with rod mill feed and iron filings never released any significant amount of iron. Iron concentrations never exceeded 10 mg/L and were below 0.1 mg/L for most of the four months the column was run.
**Sulfide.** A limited amount of quantitative data was collected for sulfide. Qualitative observations and semi-quantitative measurements using indicator paper (lead acetate) were used to monitor sulfide in the column effluent. If an H$_2$S odor was detected, the outflow would be checked with the indicator paper. This was done about once per month.

Measured sulfide ranged from $<0.5$ mg/L to about 60 mg/L. Indicator paper measurements ranged from $<5$ mg/L to $>25$ mg/L. Sulfide in the effluent from the biosolids column routinely exceeded 25 mg/L and produced enough H$_2$S that laboratory staff requested the column be terminated. With the exception of the columns fed molasses, sulfide in the other columns was variable, and ranged from an effluent with no odor to distinct odors. No odor was detected in the columns fed molasses and all indicator paper measurement suggested that sulfide was $<5$ mg/L. When the feed was switched from molasses to methanol, sulfide was periodically detected in the outflow from the columns.

**Sulfate Removal Rates.** Rates of sulfate reduction were calculated in terms of mmoles/m$^3$/day from the change in sulfate concentration, the average flow rate, and the initial volume of the column. Average rates for the first 2 months of the study ranged from about 270 mmoles/m$^3$/day for the mixture of peat and peat screenings to around 2400 mmoles/m$^3$/day for the rod mill feed with ethanol.

At the end of the first two months, changes in the experiment were made and sulfate reduction rates were calculated for periods with constant conditions or concentrations. Rates ranged from 515 mmoles/m$^3$/day for the rod mill feed and iron to 3130 mmoles/m$^3$/day for the rod mill feed with ethanol. The oxidized ore columns with molasses and ethanol feed also had rates around 3000 mmoles/m$^3$/day as did the biosolid column. When the feed was switched from molasses to methanol, removal rates decreased by 40 – 50%. The rates for both manure columns decreased substantially with time decreasing from around 2540 to 660 mmoles/m$^3$/day for the manure/sawdust/corn mixture and from 1530 to 610 mmoles/m$^3$/day for the manure/sawdust/hay mixture (Table 2).

**Sulfate Mass Removal.** For the organic substrate based columns, total sulfate removal ranged from around 10% for the peat column to about 87% for the biosolid column. In general, the best overall removal was in the columns fed ethanol where removal ranged from about 68% to 92%.
Table 2. Sulfate removal rates.

<table>
<thead>
<tr>
<th>Column</th>
<th>Substrate</th>
<th>Average SO₄ Removal (mmoles/m³/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2/8 – 4/17/02</td>
</tr>
<tr>
<td>1</td>
<td>Sugar beets + ethanol</td>
<td>932</td>
</tr>
<tr>
<td>2</td>
<td>Sugar beets</td>
<td>803</td>
</tr>
<tr>
<td>3</td>
<td>Sugar beets + iron</td>
<td>1047</td>
</tr>
<tr>
<td>4</td>
<td>Peat</td>
<td>268</td>
</tr>
<tr>
<td>5</td>
<td>Peat + ethanol</td>
<td>2179</td>
</tr>
<tr>
<td>6</td>
<td>Peat + iron</td>
<td>290</td>
</tr>
<tr>
<td>8</td>
<td>Manure, sawdust, corn</td>
<td>1304</td>
</tr>
<tr>
<td>9</td>
<td>Manure, sawdust, hay</td>
<td>2094</td>
</tr>
<tr>
<td>10</td>
<td>Biosolids, sawdust, hay</td>
<td>2282</td>
</tr>
<tr>
<td>11</td>
<td>Rod mill feed + iron</td>
<td>611</td>
</tr>
<tr>
<td>12</td>
<td>Rod mill feed + ethanol</td>
<td>2393</td>
</tr>
<tr>
<td>7</td>
<td>Rod mill feed + molasses/methanol</td>
<td>1990⁶</td>
</tr>
<tr>
<td>5A</td>
<td>Oxidized ore, coarse tailing, ethanol</td>
<td></td>
</tr>
<tr>
<td>6A</td>
<td>Oxidized ore, coarse tailing, molasses/methanol</td>
<td>3029⁷</td>
</tr>
</tbody>
</table>

Notes: Rates were calculated during periods of constant conditions and concentrations.
1Columns 2 was terminated 6/3/02.
2Columns 10 and 11 were terminated 5/20/02.
3Columns 8 and 9 were terminated by 11/25/02.
4Rate period from 8/26 – 10/28/02.
5Rate period from 7/9 – 11/25/02.
6Rate period from 6/3 – 8/26/02.
7Rate period from 6/10 – 8/26/02.
8Switched to methanol; rate period 9/5 – 11/25/02.

Sulfate removal rate (mmol/m³/day) = (SO₄ in – SO₄ out) mg/L x Flow L/day / 96.06 mg/mmol x substrate volume m³
Discussion

In general the highest rates of sulfate reduction were achieved in the columns that were fed ethanol and molasses. With the exception of the biosolids, the organic substrate based columns had lower reaction rates and the rates decreased with time as the amount of readily available organic carbon decreased. The pattern in removal rates for the organic substrates is fairly typical for these types of systems. Initial rates are very high but decrease over time and approach the recommended “design rate” of 300 mmol/m$^3$/day (Wildeman et al. 1993, Eger and Wagner 1995, 2001). By feeding the columns with an external organic carbon source such as ethanol or molasses, the reaction can be sustained at a rate almost an order of magnitude higher than the organic substrate mixtures. While both ethanol and molasses were readily used by the bacteria in the columns, reaction rates with methanol were lower. Methanol has not been a commonly used feed source for sulfate reducing bacteria, but it has been used in several systems designed to treat mine drainage (Tsukamoto and Miller 1999).

Although rates in the biosolids columns were comparable to the columns receiving ethanol and molasses, the column effluent contained so much sulfide that objectionable amounts of H$_2$S were generated. The general reactions that occur during the microbiological reduction of sulfate can be represented by:

$$SO_4^{2-} + 2CH_2O = H_2S + 2HCO_3^- \quad (1)$$

$$H_2S + M^{+2} = MS + 2H^+ \quad (2)$$

Most mine drainage contains elevated concentrations of iron and trace metals, which readily react with the sulfide generated from the reduction reaction and reduce the release of H$_2$S. Equilibrium calculations indicate that at pH 7, with effluent iron concentrations on the order of 0.2 mg/L, the concentration of sulfide would be less than 0.01mg/L. Even at this low sulfide concentration, H$_2$S would be about 1 ppm, which is below exposure limits but is well in excess of the odor threshold of 10 ppb. In order to prevent odor problems, sulfide must be controlled in the outflow, which would require iron concentrations exceeding 0.3 mg/L at pH 8, and 30.7 mg/L at pH 7 (Eger et al, 2003).
Since the tailings basin water at U. S. Steel contains essentially no trace metals or iron, the iron needed to react with the sulfide must come from the substrate. While all the columns had iron in the outflow initially, only the columns fed with molasses routinely had 5 – 10 mg/L of iron in the outflow. This appeared to control H$_2$S emissions but more quantitative data on sulfide concentration in the effluent is needed. When the feed was switched from molasses to methanol, iron concentrations decreased and H$_2$S could be detected in the outflow.

Iron release did not appear to be related to the substrate, since iron concentrations in the columns fed with ethanol were similar for both the rod mill feed and the oxidized ore substrates. Although the total iron content was similar for both substrates (~ 31%), the oxidized ore contained 92% ferric iron, compared to 60% for the rod mill feed. At neutral pH, iron reducing bacteria are needed to release iron from the substrate and typically reduce ferric to ferrous iron. Additional work is needed to examine iron release and the control of H$_2$S emissions.

**Field Demonstration 2002**

**Design and Operation.**

Although the initial laboratory tests were conducted with water from the tailings basin as influent, U. S. Steel would prefer to treat water from the waste gas scrubbers prior to discharge to the tailings basin. This stream contains elevated sulfate levels and leaves the plant at between 24 to 40.6 degrees C, with higher temperatures in the summer. The elevated temperature range should help to maintain treatment during the winter.

Based on the results from the column tests, U.S. Steel chose an inorganic substrate with an external carbon feed for the field demonstration. This decision was based on the high and constant reaction rates as well as the availability of inorganic substrate from waste rock at the mine. The initial design was a horizontal packed bed made of crushed oxidized waste rock (Fig. 1). (This material was similar to the “oxidized ore” used in the second set of columns). Process water discharged from the pelletizing plant was fed into a series of two settling ponds prior to entering the packed bed. A V-notch weir was used to measure process water feed flows and was positioned between the two influent settling ponds. Ethanol was used as the external carbon source throughout the demonstration testing in 2002 and was metered into the feed stream immediately after the weir. The process water/ethanol flowed by gravity into the downstream influent settling pond, through the packed bed, through a small effluent settling pond, and then
discharged to the tailings basin. A 60-mil HDPE liner was installed from the V-notch weir to the effluent discharge channel prior to rock placement to prevent seepage losses.

The reactive media for the packed bed was composed of about 90% crushed oxidized ore (100% -5 cm) and 10% coarse tailings (100% -0.6 cm). The packed bed was about 91 m long and trapezoidal in cross section (Fig. 1, and 2); 9.8 m wide at the base, 29.2 m wide at the top, with the depth varying from 1.8 – 2.4 m with the slope of the bottom. A 30 cm layer of coarse tailings was placed on the synthetic liner to protect it during placement of the reactive media. The top of the bed was covered with a 30 cm layer of ballast (-7.5 cm, + 2.5 cm coarse rock) as insulation. Aged horse manure, at about 1% by weight, was incorporated into the oxidized ore/coarse tailings mix as a biological seed.

Figure 1. 2002 demonstration bed

Figure 2. Cross section 2002 demonstration bed
Results

The system began operating in early July at a nominal process water feed rate of about 380 L/min and an ethanol feed rate of about 150 mL/min. Significant sulfate reduction occurred within about 4 weeks, and sulfate removal efficiencies averaged about 67% from late July through mid-September. However, sulfate reduction began to decrease in September and evaluations of system flow patterns suggested that up to 80% of the flow was through the top ballast layer, significantly reducing residence times. The system was shut down and additional laboratory studies were designed to address the hydraulic, residence time and media size issues raised from operation of the initial demonstration system.

2003 Field Demonstration

Design and Operation

Based on laboratory testing and hydraulic modeling, the demonstration system was redesigned to minimize pressure drop, provide much more flexibility in terms of hydraulic head across the system, and test treatment efficiencies using a coarser reactive media. A cross section of the new design is shown in Fig. 3. In the new system, the process water and external carbon is fed into drain tile at the base of ballast-filled trenches on either side of the system. The water flows up through the ballast and across the reactive media into a center ballast trench that contains drain tile to collect and convey the treated effluent out of the system. In-bed water levels are controlled at the outflow of the system using an in-line water level control structure containing removable stop logs. Since the new design is more compact than the original, 2 separate treatment cells were incorporated so that different types of reactive media could be tested at the same time (Fig. 4). The new design eliminated all open water pools, other than the initial settling pond, to minimize heat loss for winter operation.

Cell 1 was to be constructed using washed coarse tailings with a specified size distribution of 100% +6 mesh. Cell 2 was to receive crushed, and screened oxidized ore having a particle size specification of 100%, –1.27 cm, +6 mesh. Sieve analyses conducted after system reconstruction was completed indicated that the one-pass washing procedure used to remove fines from the
Figure 3. Cross section 2003 demonstration bed

Figure 4. Top view 2003 demonstration bed
coarse tailings was not effective and about 50% of the material was –6 mesh. The measured Cell 2 particle size distribution was fairly close to the design specifications. The reactive media in each cell was seeded with aged horse manure at about 1% by weight.

The new system was completed in late June and began operating on July 7 at nominal process water feed rates of 190 L/minute per cell. Denatured ethanol was used as the external carbon source until mid-September when the carbon feed was switched to a blend of ethanol and molasses (Molasses is less expensive than ethanol and columns fed molasses produced less H$_2$S). Carbon feed rates were set based on previous and on-going laboratory results and averaged about 0.35 mL ethanol/L process water during straight ethanol feed, and 0.25 mL ethanol/L and 0.3 mL molasses/L when feeding the carbon blend.

Significant efforts were made to winterize the demonstration system for year-round operation. The influent settling pond was insulated using hexagonal, closed-foam, polyethylene “lily pads,” a 30- 60 cm layer of straw was applied to the surface of the treatment cells, the influent weir boxes were fitted with insulated covers, and a ethanol/molasses blend was developed that would stay liquid to -40°C (-40°F).

Results

**Sulfate reduction.** Both treatment cells removed sulfate with the denatured ethanol feed. Sulfate removal efficiencies were close to 60% prior to the switch to an ethanol/molasses blend on September 19, 2003 (Fig. 5). Treatment efficiencies decreased for several weeks after the carbon switch, but steadily increased and were between 50 – 60% by the middle of December 2003.

**Sulfide.** Stabilization of sulfide produced by the reduction of sulfate in the process water is a critical issue from two perspectives: hydrogen sulfide is a hazardous air pollutant and subject to federal and state air emissions regulations, and at elevated concentrations is an industrial hygiene issue. When the system was fed just ethanol, sulfide was detected in the effluent but all concentrations were <2 mg/L. When the feed was switched to the mixture of ethanol/molasses, sulfide concentrations decreased and were routinely <0.4 mg/L.
Temperature. The efforts that were made to limit heat loss through proper design along with winterization procedures resulted in good heat retention throughout the system and should allow for uninterrupted operation throughout the northern Minnesota winter. The system consistently operated at or above 26°C (80°F) (Fig. 6). Influent temperatures are expected to decrease by 5 - 8°C (10 - 15°F) as air temperatures drop in January and February. While this change in temperature could slow the reaction rate, flow and sulfate reduction should continue.

Media Fouling. During construction, monitoring wells were installed across the width of each treatment cell so that water levels changes could be measured over time. Wells were placed in each of the feed ballast channels, the effluent ballast channel and three were equally spaced in the reactive media (North, Central, South). Figures 7 and 8 show the results of weekly water level measurements taken from the monitoring wells in treatment Cells 1 and 2, respectively. Water level increased substantially in the feed channel of Cell 1, but increases within the bed were much smaller, suggesting plugging of the bed material at the feed channel/reactive media interface. The water level increase in Cell 2 was much smaller and the largest increase occurred
at the effluent ballast channel, which suggests plugging may have been occurring at the effluent drain tile. In October 2003, the entire system was shut down and the treatment cells drained so that clean-out piping could be installed at each end of the feed drain tile lines. The feed lines were cleaned with high pressure water and a significant mass of biological growth was found in the lines (Fig. 9). After the initial cleaning, water levels began to increase in Cell 1, and operation of the cell was discontinued in early December 2003. Water levels also increased in Cell 2 but at a much slower rate. Routine cleaning was needed to maintain stable operation.

![Temperature vs. time, demonstration bed 2003](image)

Figure 6. Temperature vs. time, demonstration bed 2003
Figure 7. Water levels vs. time, Cell 1, demonstration bed, 2003
Discussion/Conclusions

Although the 2003 demonstration system has generally been successful in removing sulfate, several issues still need to be addressed. The operational problems associated with biological growth in the feed pipes appears to have been resolved with a routine maintenance program, but must be addressed in the design of the full-scale system to reduce operator intervention and downtime.

Aqueous sulfide control must be continually evaluated to insure that hydrogen sulfide emissions do not lead to industrial hygiene problems or violation of applicable air quality regulations. Jar testing with a number of different chemical reagents was conducted to evaluate effluent treatment options should hydrogen sulfide emissions become problematic. Hydrogen peroxide, chlorine bleach, and ferrous sulfate were all shown to be extremely effective at eliminating any H$_2$S emission problem (Moe, 2003).
Conditions conducive to anaerobic sulfate reduction are also favorable for the conversion of elemental mercury to methyl mercury. Limited sampling and analysis of the 2002 field demonstration system indicated that although total mercury decreased there appeared to be an increase in methyl mercury. Additional low-level mercury sampling must be conducted to more clearly define effluent mercury concentrations and develop tertiary treatment steps to prevent mercury release if needed.

Similarly, overall effluent quality must be determined under operating conditions that would likely be used in a commercial-scale system to define any additional treatment operations that may have to be included.

Figure 9. Biological growth in feed line to demonstration bed, October 2003

References


