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The Use of Sulfate Reducing Bacteria to Remove Sulfate from Tailings Basin Water at U.S. Steel

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Preliminary Column Studies Final Report, June 2004

Minnesota Department of Natural Resources Division of Lands and Minerals

The Use of Sulfate Reducing Bacteria to Remove Sulfate from Tailings Basin Water at U.S. Steel

Preliminary Column Studies Final Report

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> > June 2004

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1. EXECUTIVE SUMMARY

A column experiment was conducted to evaluate the ability of various substrates to support sulfate reducing bacteria and remove sulfate from U.S. Steel's tailings basin water. Although sulfate was removed in all columns, the amount of removal varied widely between substrates. Originally 11 columns were set up to examine different combinations of organic substrates and the use of an inorganic substrate, fed with ethanol as the organic carbon source. After two months poorly performing columns were eliminated and new columns were built to examine the use of a different feed, molasses, and an inorganic substrate with higher oxidized iron content.

Several columns were extremely effective in removing sulfate and had sulfate reduction rates on the order of 3000 mmoles/m³/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 ethanol and molasses.

Despite the use of iron rich inorganic substrates, iron concentrations were below the detection limit in all columns except those fed with molasses. If insufficient iron or metals are present, some of the sulfide generated by the reduction of sulfate will not be retained in the column. Since the tailings basin water contains very low concentrations of iron and trace metals, iron must be produced by the substrate. Data on sulfide in these columns is limited, but based on estimates, over 95% of the sulfur that is reduced is retained within the column (Appendix 4). Molasses columns have measurable iron in the effluent but additional data is needed to confirm that the release of sulfide is effectively controlled.

The control of sulfide is a major unresolved issue and additional data needs to be collected to accurately determine sulfide release. Additional columns have been built and will be used to examine methods to increase the amount of iron reduction.

Since sulfate reducing bacteria can also methlate mercury, the behavior of mercury in this system must be investigated. US Steel's original plan was to treat water directly from the agglomerator. However, this discharge contains water from the waste gas wet scrubbers and as a result contains low levels of mercury. The fate of this mercury in the sulfate reduction system needs to be determined. If methylation occurs, treating tailings basin water, which is extremely low in mercury, may limit the production of methyl mercury.

Once the inorganic substrate and carbon source have been selected, an optimization study should be conducted. The goals of the study would be to:

Determine optimal nutrient additions

Determine optimal residence time

Determine optimal carbon feed rate.

2. INTRODUCTION

Iron is removed from taconite ore by crushing, grinding and magnetic separation. These operations can increase the dissolved solid content of the process water. Minnesota taconite operations can recycle their process water, reclaiming much of the water from their tailings basin. The concentration 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, the composition of other waste streams that discharge to the tailings basin and the overall facility water management strategy.

Water in U.S. Steel's tailings basin contains elevated levels of dissolved solids, including sulfate. Sulfate concentrations have increased over time and are related to the installation of wet scrubbers to meet air quality standards. The wet scrubbers use water to remove particulate matter from the waste gas, which also results in the removal of a small percentage of flue gas SO₂. The dissolved SO₂ is oxidized to sulfate and discharged to the tailings basin. 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 solids in the tailings basin cause problems in the plant and a method to reduce the level of dissolved solids is needed.

If water could be discharged from the tailings basin, fresh water could be added to reduce the concentrations of all constituents in the process water. Although the tailings basin water does not contain any constituents at toxic concentrations, the high level of sulfate is a concern. 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 was to reduce sulfate through the microbical reduction of sulfate to sulfide (i.e., sulfate reduction). A column test was designed to investigate the use of sulfate reducing bacteria to remove sulfate from tailings basin water. This report summarizes the first year of data from these experiments. The rationale for column design and information on substrate selection, and column changes are presented in Appendix 1.

3. METHODS

3.1. Column Design

Clear acrylic columns (30 in. long, 5³/₄ in. diameter) were constructed by Jasper Engineering in Hibbing, MN. A 0.64 cm high acrylic sleeve was glued into the bottom of the column to support a 0.16 cm thick PVC plate, which was perforated with 0.32 cm holes spaced 0.48 cm on center. The bottom was sealed with an acrylic plate with a 0.85 cm outlet port (Figure 1). Prior to loading the columns, about a gallon of water was placed into each column to make sure that there were no leaks. A small leak was noted in only one of the columns and was repaired.

Before putting the substrate into the columns, three distinct size fractions of taconite ore (rod mill feed) were placed into the bottom of the column and were supported by the PVC plate. One-half inch layers of $-\frac{1}{4}$ inch, +6 mesh; -6, +8 mesh; and -8, +14 mesh material were placed into each column.

3.2. Substrates

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, biosolids, hay, sawdust, and cracked corn. Iron filings (10% by volume) were added to columns containing sugar beet waste (Column 3), peat (Column 6), and rod mill feed (Column 11). Screened rod mill feed (-1/2 inch, +10 mesh) from U.S. Steel was used as an inorganic component to provide permeability in the initial columns. New columns begun in April 2002 used a mixture of 90 % of screened oxidized ore (-1/2 inch, +10 mesh) and 10 % unscreened coarse tailings as the inorganic component. For columns containing organic substrates, the inorganic component comprised 25% by volume of the total substrate in the column.

Columns 1 (sugar beet waste), 5 (peat), 12 (rod mill feed) and 5A (oxidized ore + coarse tailing) were fed ethanol denatured with methanol as a supplemental food source for the bacteria, while Columns 6A (oxidized ore + coarse tailing) and 7 (rod mill feed) were initially fed molasses. In June, the ethanol feed was switched to ethanol denatured with methyl isobutyl ketone (MIBK) and in August,

the molasses was switched to methanol. Columns with only an inorganic substrate received a bacterial seed addition. Columns 11 and 12 received 25 grams of cow manure that was less than one day old, air-dried and ground to a powder as well as 500 mL of cow manure that had been stockpiled for several months. The seed was thoroughly mixed with the substrate prior to loading the column. Columns 5A, 6A, and 7 received roughly 400 mL of "as received" (not dried) horse manure that was less than one day old. The seed was mixed into the top portion of the column (~0-6") with a spatula after the column was constructed. 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 column mixtures are listed in Table 1 and detailed notes on the preparation of substrates, loading of the columns, and the measurements of porosity and hydraulic conductivity are provided in Appendices 1 and 2.

3.3. Experimental Setup

The initial eleven columns (1-6 and 8-12, Table 1) were filled with tailings basin water on February 1, 2002 and were maintained in a saturated condition without flow for about one week. The initial water quality samples were taken on February 11. Columns 1 (sugar beet waste + ethanol), 3 (sugar beet waste), 4 (peat), 5 (peat + ethanol), and 6 (peat + iron filings) were discontinued on April 18, 2002. Based on data from the initial columns three additional columns were added to the experiment. Columns 5A (oxidized ore + coarse tailing + ethanol), 6A (oxidized ore + coarse tailing + molasses), and 7 (rod mill feed + molasses) were filled with tailings basin water on May 6, 2002, and were maintained in a saturated condition without flow for about one week. Column 10 (biosolids) was discontinued on May 20, 2002, due to excess production of H₂S, while columns containing sawdust and other organic materials (columns 8, 9) were stopped on November 25, 2002. Appendices 1 and 5 contain a description of the columns, a timeline and a discussion of experimental changes.

3.4. Sampling

Feed water was pumped into the columns with a 12-channel peristaltic pump (Manostat Model CARTER 12/6, #74-126-00000). Columns, which received ethanol, were fed from a carboy where 1.3 mL of 63% ethanol (70% total alcohol) per liter had been added, and the molasses feed contained

0.7 mL of methanol/ L of solution. Flow rates were checked visually on a daily basis and volumetrically adjusted about every one to two weeks.

Initial water quality samples for the original eleven columns and the three new columns were collected twice per week and analyzed by U.S. Steel. Sample frequency for the six original columns still operating was reduced to once per week on April 22. At the end of May, the sample frequency for the sawdust columns was reduced to about once per month. Calcium, magnesium and iron were analyzed by ICP while sulfate was analyzed with an ion chromatograph. Nutrient samples were collected immediately after start up and after one month of operation. Several additional samples were collected for Biochemical Oxygen Demand (BOD), nutrients, Total Organic Carbon (TOC) and sulfide. These samples were analyzed by Northeast Technical Services in Virginia, MN.

4. RESULTS

4.1. Introduction

The initial results from the columns were described in a status report prepared in June of 2002 and revised in August 2002. This report will focus on the additional data collected from the original columns as well as the data from the new columns started in May 2002.

4.2. Substrate properties

The organic substrates contained 40-50% total organic carbon (TOC) and had a low ash content, ranging from 1.25% for the corn to 17.5% for the biosolids (Table 2). The 18% total carbon value for the cow manure appears to be anomalously low, 31.2% is an average value for fresh dairy manure (North Carolina University Extension web site). Metals were generally less than detection, except in the biosolids, which contained low but measurable amounts of all metals except cadmium and silver (Table 2).

Initial porosities ranged from 38% to 45 % for the sugar beet, rod mill feed, and oxidized ore columns and 49% to 62% for the remaining columns with the biosolids being the highest (Table 3). With the exception of the sugar beet columns, there was little settling of the substrate. The maximum settling occurred in Column 2 where the substrate settled about 50% (Appendix 2)

Initial permeability for all of the original substrates ranged from $1 \ge 10^{-1}$ cm/sec to $2 \ge 10^{-1}$ cm/sec. Permeability for the oxidized ore + coarse tailing columns were $2.7 \ge 10^{-1}$ cm/sec and $3.2 \ge 10^{-1}$ cm/sec (Table 4). (Subsequent tests showed that the permeability in the original columns was controlled by the diameter of the outlet and not the substrate. The initial permeabilites provide an estimate of the minimum permeability). Only a minimum head was necessary to provide the flow through the columns. The water level in all columns was less than an inch above the outlet and there was no evidence of a consistent or permanent increase in water level. Water levels have fluctuated periodically due to air bubble formation in the small outflow tubing, or possible plugging of the outlet tube by a black sludge like material (observed in Column 12).

4.3. Flow Rates

The flow rates for the initial eleven columns 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 (Table 5). Starting the week of April 15, the flow rates for Columns 8, 9, 10, 11, and 12 were increased to 2.5 mL/min while the flow rate for Column 2 was increased to 1.4 mL/min. The new columns (5A, 6A, and 7) were started at a flow rate of 2.5 mL/min (Table 5). Flow rates were generally maintained within \pm 10% of these rates for the year.

4.4. Water Chemistry

4.4.1 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 (Column 2) and the column with the cracked corn (Column 8) were initially below 5, but increased above 5 after two and four weeks, respectively. The pH exceeded 7 in both columns after about two months (Figures 3 and 5). Column 11, which contained rod mill feed

and iron filings, produced the highest effluent pH, routinely exceeding 8.5 after two months. The pH in Column 12 (rod mill feed and ethanol) generally stabilized around 8, except during periods when conditions in the columns were drastically altered. When the column siphoned at the end of July and the media was exposed to oxidizing conditions, pH dropped below 7, but returned to 8 after about six weeks (Figure 7). Column 5A (oxidized ore/tailings) also received ethanol and the pH generally stabilized around 8 (Figure 8).

Columns that received molasses (Columns 6A, 7) generally had lower pH values, between 6.5-7. The pH values for the rod mill feed (Column 7) were lower than the oxidized ore/tailings (Column 5A) (Figures 7, 8). When the feed was switched to methanol, pH increased to slightly above 8 for Column 7 to slightly below 8 for the oxidized ore/tailings Column (5A).

4.4.2 Sulfate

Sulfate in the column feed was relatively constant during the first two months of the study and averaged 814 mg/L. However, the concentration generally decreased over the course of the study and averaged 660 mg/L in November. After the first sample, all columns removed sulfate. Sulfate concentrations in the first sample ranged from 360 mg/L to 835 mg/L, with Column 12 (rod mill feed + ethanol) being the lowest and Columns 4 (peat), 8 (manure + sawdust + corn), and 11 (rod mill feed + iron) exceeding the feed water concentrations (Figure 5). During the first two months of the study, all the columns that received ethanol (Columns 1, 5, and 12) and the biosolids column had almost complete removal of sulfate. Since the organic substrates (sugar beets in Column 1 and peat in Column 5) did not contribute to a measurable increase in the overall performance of the columns receiving ethanol, they were discontinued. Column 3 (sugar beets + iron) showed good removal that increased slightly when the flow rate was increased but the column was discontinued due to the high cost of iron filings. Removal was lowest in Columns 4 (peat) and 6 (peat + iron) with generally less than 20% of the input sulfate being removed. These columns were also discontinued in April.

When flow rates were increased, the effluent sulfate concentrations remained low in the biosolid column, the manure + sawdust + corn column, and the rod mill feed + ethanol column (Columns 10, 8, and 12, respectively - Figures 5, 7). Effluent sulfate concentrations in Column 2 (sugar beets),

Column 9 (manure + sawdust + and hay), and Column 11 (rod mill feed + iron) increased when the flow increased (Figures 3, 5, 6). Outflow sulfate concentrations generally increased with time in Columns 8 and 9 and were at about 500 mg/L when they were terminated. Sulfate concentrations in Column 12 remained low throughout the study except when the column siphoned in July.

Sulfate concentrations decreased over time in the columns that received molasses. Sulfate dropped quickly in the column with the oxidized ore/tailings substrate (Column 6A), with concentrations almost at 0 after about one month. Concentrations in the column with the rod mill feed substrates dropped slowly, reaching a level of around 200 mg/L after two months. When the feed was switched from molasses to methanol the outflow concentrations shifted upward to between 300-500 mg/L in both columns (Figures 7, 8). Outflow concentrations were much more variable with methanol than molasses.

4.4.3 Iron concentrations

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 (Figure 6).

4.4.4 Nutrients, Sulfide and Total Organic Carbon

Data on nutrient release from the columns are limited. Initial nutrient release, with the exception of $NO_2 + NO_3$, was high from all substrates except the peat and iron filings. BOD in the initial sample was particularly high in the columns containing sugar beets and, as was the case with the remaining columns, showed a decreasing trend over time (Table 6). No nutrient data was collected from any of the columns after May 15 or on the feed water. Based on historical data for the tailings basin water, nitrate values would be expected to be from 3.5 to 4 mg/L and total phosphorus would be ≤ 0.03 mg/L.

A limited amount of quantitative data was collected for sulfide and total organic carbon (Table 6). Qualitative observations and semi-quantitative measurements using indicator paper (lead acetate) were used to monitor sulfide in the column effluent. If an H_2S 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 (Table 6). Indicator paper measurements ranged from <5 mg/L to >25 mg/L. The column with biosolids produced large amounts of H₂S and was shut down. 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. On July 16, sulfide was analyzed for the columns fed molasses (Columns 6A and 7) and ranged from 7-10 mg/L. When the feed was switched from molasses to methanol, sulfide was periodically detected in the outflow from the columns.

4.5 Sulfate Removal Rates

Rates of sulfate reduction were calculated in terms of mmoles/m³/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 /m³/day for the mixture of peat and peat screenings to around 2400 mmoles /m³/day for the rod mill feed with ethanol (Table 9).

At the end of the first two months, changes in the experiment were made based on the sulfate removal rate. Five columns were eliminated and three new columns were started (Appendix10). After the first two months, sulfate reduction rates were calculated for periods with constant conditions or similar treatment efficiency (Appendix 5).

Rates ranged from 515 mmoles/m³/day for the rod mill feed and iron (Column 11) to 3130 mmoles/m³/day for the rod mill feed with ethanol (Column 12) (Table 9). The oxidized ore columns with the molasses, and the ethanol feed (Columns 6A and 5A respectively) also had rates around 3000 mmoles/m³/day as did the biosolid column (Column 10). The rates for both manure columns decreased substantially with time decreasing from around 2540 to 660 for the manure/sawdust/corn (Column 8) mixture and from 1530 to 610 for the manure/sawdust/hay mixture. (Column 9). When the feed was switched from molasses to methanol, removal rates decreased by 40 - 50% dropping from 1990 to 1310 in Column 7 and from 3030 to 1650 in Column 6A.

4.6 Sulfate Mass Removal

The total mass of sulfate removed and removal efficiency was calculated for each column (Table 10). Removal ranged from around 10% for the peat column (Column 4) to 92% for the peat column with ethanol (Column 5). Removal also exceeded 80% in the biosolids column (Column 10), in the rod mill feed and oxidized ore columns that were fed ethanol (Columns 12 and 5A) and in the oxidized ore column that was fed molasses (Column 6A).

5. 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 mmoles/m³/day. By feeding the columns with an external 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.

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_2S were generated. (Based on semi-quantitative measurements made with lead acetate paper, sulfide was probably greater than 25 mg/L in the column effluent). Most mine drainage contains elevated concentrations of iron and trace metals. These metals readily react with the sulfide generated from the reduction reaction and reduce the concentration of sulfide in the effluent. Equilibrium calculations indicate that at a pH of 7 with iron concentrations in the effluent on the order of 0.2 mg/L, the concentration of sulfide in the effluent would be less than 0.01mg/L. At this sulfide concentration, the amount of H_2S emitted to the air would be about 1 ppm which is below exposure limits but is well in excess of 10 ppb which is the level at which most people can smell H_2S . In order to prevent odor problems, sulfide would have to be well below detection limits and the iron concentration would have to exceed 0.3 mg/L at pH 8, and 30.7 mg/L at pH 7 (Appendix 6).

The tailings basin water at U.S. Steel contains essentially no trace metals or iron, so in order to tie up the sulfide, the substrate must release iron. 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 H₂S 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 H₂S 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. The oxidized ore had both a higher total iron and a higher ferric iron content than the rod mill feed. Iron reducing bacteria are needed to release iron from the substrate, particularly at a neutral pH. These bacteria typically reduce ferric iron to ferrous iron. Additional work is planned to look at iron release (Appendix 10).

Although some of the sulfate that was reduced left the columns as sulfide, most of the sulfur was returned within the column. A sulfur balance was estimated for column 12 (ethanol), and over 95% of the sulfur that was reduced was retained within the column (Attachment A4.8, Appendix 4). The fate of the sulfide in the effluent is a function of pH and temperature. A portion of the sulfide may be released as H_2S but some may be oxidized back to sulfate (Appendix 6).

In order to minimize the size of the final treatment system, the rate of sulfate reduction should be maximized. The rate of sulfate reduction is a function of the concentration of sulfate, available carbon and temperature. In order to maximize the reaction rate, adequate concentrations of both sulfate and carbon must be maintained. The reaction rate has been reported to be sulfate limited when sulfate concentrations dropped below 50- 300 mg/L. Therefore, if the sulfate concentration exceeds 300 mg/L, the reaction rate should be independent of sulfate concentration.

The reaction rate will also be a function of the concentration of the electron donor, which in these columns is organic carbon. The amount of organic carbon required is a function of the specific carbon source and the reaction pathway. (Appendix 8). The general model for the sulfate reduction reaction can be represented by:

$$SO_4^{-2} + 2 CH_2O = H_2S + 2 HCO_3$$

To reduce the sulfur from S^{+6} to S^{-2} requires 8 electrons. In this model, 2 moles of carbon are needed to reduce 1 mole of sulfate. A 2:1 ratio was used to calculate the ethanol and methanol feed rates. (Appendix 8). Using this model, excess carbon in the effluent was predicted, and this was generally confirmed by a limited number of total organic carbon measurements (Table 7, Appendix 4).

Although a comprehensive literature search on the effect of organic carbon on the kinetics of the sulfate reduction reaction was not done, no rate limiting values were found. However, it is generally believed that the amount of readily available organic carbon limits the treatment rate in most mine drainage situations.

The rate of microbiological reactions is usually modeled as "Monod Kinetics", where:

$$-\underline{dS} = \underline{kSX} \\ \underline{dt} \quad K_{S} + S$$

• S is the substrate concentration [mg/L]

X is the biomass concentration [mg/L]

• k is the maximum substrate utilization rate [sec⁻¹]

• K_s is the half-saturation coefficient [mg/L]

When the substrate concentration is substantially greater than K_s , (S>>K_s), the equation can be written as:

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \mathrm{kX}$$

Therefore, if sufficient organic carbon is present, the reaction rate is zero order, and at a given temperature and biomass, the reaction rate is constant. Optimizing the reaction rate is important and should be pursued to determine the most cost effective size for this system. Additional information on microbiological reactions is presented in Appendix 9.

6. CONCLUSIONS and RECOMMENDATIONS

- 1. Biological sulfate reduction was effective in removing sulfate from U.S. Steels' tailings basin water and was capable of reducing sulfate concentrations to less than 25 mg/L, well below the secondary drinking water standard of 250 mg/L.
- 2. Reaction rates on the order of 3000 mmoles/m³/day were achieved in columns fed with ethanol and molasses. This is an order of magnitude higher than the typical design value reported in the literature for organic substrate-based systems.
- 3. The reaction rate may be sulfate limited. Flow rates should be increased incrementally until the sulfate concentration in the outflow approaches 250 mg/L. This test has been started.
- 4. Control of sulfide in the column effluent must be addressed. Columns fed with molasses had less odor and contained measurable iron in the discharge regardless of the type of inorganic substrate in the column. Actual measurements of the sulfide in the column effluent are needed to verify qualitative and semi-quantitative data.

- 5. Once the final substrate and feed solution have been chosen, an optimization study should be conducted to maximize reaction rates.
- 6. Performance in the field will be a function of the hydraulics of the system, the temperature and the input water chemistry. These need to be addressed prior to building a full-scale system.
- 7. The behavior of mercury in the system needs to be determined.

Column	Organic Substrate	% by volume	Zero Valent Iron	% by volume	Inorganic Substrate	% by volume	Bacterial Seed	Additive
1 1	Sugar beet waste	75			Rod mill feed	25	No	Ethanol
2	Sugar beet waste	75		•	Rod mill feed	25	No	No
3 1	Sugar beet waste	65	Iron filings	10	Rod mill feed	25	No	No
4 ¹	Peat	. 75			Rod mill feed	25	No	No
5 1	Peat	75			Rod mill feed	25	No	Ethanol
6 ¹	Peat	65	Iron filings	10	Rod mill feed	25	No	No
8	Manure	10			Rod mill	25	No	. No
	Saw dust	40	···· ·		iccu		- •	
	Feed corn(cracked)	25						
9	Manure	25			Rod mill feed	25	No	No
	Sawdust	40				-		
	Hay	10		•				
10.2	Biosolids	25			Rod mill	25	No .	No
10	Sawdust	40			Teed	5. S.	· · ·	•
-	Hay	10.						
11 2 .	None	0	Iron filings	10	Rod mill feed	90	Yes ⁴	No
12	None	0			Rod mill feed	100	Yes ⁴	Ethanol
5 4 3	None	0			Oxidized	90	×r 5	Ethanol
JA	· .	0		· .	Coarse tailing	10	res	•
6A ³	None	0			Oxidized	90	Yes ⁵	Molasses/methanol ⁶
· · ·		0			Coarse tailing	10		
7 ³	None	0			Rod mill feed	100	Yes ⁵	Molasses/methanol ⁶

Table 1. Column composition.

- Columns were discontinued on 4/18/02.

- Columns were discontinued on 5/20/02.

1

2

3 4 - Original columns 5 and 6 were dismantled and replaced. Columns were filled with water on 5/6/02 and flow began on 5/13/02.

- The seed source was "young" cow manure, which was air-dried, ground to a powder, and 25 grams were added to the columns. Five hundred milliliters (500 mL) of "older" cow manure were also added; seed was thoroughly mixed throughout the column. - Roughly 400 mL of "as received" (not dried) horse manure; seed mixed into top portion of column only.

5 6 - Feed was switched to methanol on 8/26/02.

					•			
Parameter	Substrate Analysis (dry wt.)							
	Corn	Sawdust	Peat	Biosolids	Sugar Beets	Manure		
As	LTD	LTD	LTD	0.6	LTD	LTD		
Ba	LTD	24	13.8	428	5.3	7.9		
Cd	LTD	LTD	LTD	LTD	LTD	LTD		
Cr	LTD	LTD	3.9	19.8	LTD	LTD		
Pb	LTD	LTD	LTD	35.4	LTD	LTD		
Hg	LTD	LTD	LTD	0.5	LTD	LTD		
Se	LTD	LTD	LTD	0.7	LTD	LTD		
Ag	LTD	LTD	LTD	LTD	LTD	LTD		
Ash %	1.25	1.94	6.51	17.5	1.81	1.95		
Carbon,	45.6	50.6	42.9	44.5	41.8	18.5		
Total %								
TOC (%)	43.0	50.4	44.0	43.3	40.8	17.6		
Kjeldahl N	177.8	58.9	226.0	638.3	307.7	160.0		
Nitrate	0.33	1.22	37.85	4.79	12.31	8.40		
Phos	173.33	5.58	12.23	93.62	123.08	24.00		
N Total	177.8	60.1	263.8	643.6	320.0	168.4		
% Solids	90	90	35.4	94	13	50		

Table 2. Substrate properties.

Notes: All values in mg/kg unless noted.
Bold, anomalous value
% moisture for manure is an estimate.
% moisture for biosolids is average based on historical data. Metals are total values.

LTD = Less than detection limit

Detection limits	mg/kg
As	0.2
Ba	5.0
Cd	2.5
Cr	2.5
Pb	2.0
Hg	0.2
Se	0.2
Ag	5.0

Table 3. Initial substrate porosity.

		Calculated	Water to	Water to	Estimated	Required
Column	Substrate	substrate	saturate	saturate	porosity	flow rate ²
		volume	column	substrate	%	mL/min
		(mL)	(mL)	(mL)	$\frac{1}{4} = \frac{1}{4} $	
1	Sugar beets	8300	3725	3415	41	1.2
2	Sugar beets	8300	3500	3190	38	1.1
3	Sugar beets + iron	8700	4000	3690	42	1.3
4	Peat	8600	4590	4280	50	1.5
5	Peat	8600	4565	4255	49	1.5
6	Peat + iron	8800	4840	4530	51	1.6
8	Manure, sawdust,	9000	5340	5030	56	1.7
	corn					-
9	Manure, sawdust,	9000	5500	5190	58	1.8
	hay					
10	Biosolids, sawdust,	9000	5920	5610	62	2.0
	hay		· · ·			·
11	Rod mill feed +	9000	4200	3890	43	1.4
	iron					·
12	Rod mill	9000	4400	4090	45	1.4
	Oxidized ore +					
5A	coarse tailing	9000	4075	3765	42	1.3
	Oxidized ore +					
6A	coarse tailing	9000	3950	3640	40	1.3
7	Rod mill feed	9000	3575	3265	40	1.1

1 - The amount of water needed to saturate the screened rod mill feed and the void space at the bottom of the column was calculated using Column 7 which did not contain any substrate. The distance from the bottom of the column to the top of the screened rod mill feed was 1.75 inches. When 500 mL was added, the water level rose to 2.19 inches.

2 - Flow rate required to provide a residence time of 48 hours, based on the pore volume in the column.

Column	Substrate	Permeability (cm/sec)
1	Sugar beets	0.17
2	Sugar beets	0.13
3	Sugar beets + iron	0.15
4	Peat	0.15
5	Peat	0.15
6	Peat + iron	0.13
8	Manure, sawdust, corn	0.10
9	Manure, sawdust, hay	0.18
10	Biosolids, sawdust, hay	0.14
11	Rod mill feed + iron	0.17
12	Rod mill feed	0.15
5A	Oxidized ore + coarse tailing	0.27
6A	Oxidized ore + coarse tailing	0.32
7	Rod mill feed	0.17

Table 4. Permeability of test columns.

Average value based on falling head tests (Appendix 2).

				Volume (mL)		Residence Times	
		Flow	rate range			(hrs.)	
		(m	L/min)		제일 것 같은		
Column	Substrate	2/8/02 to	4/17/02 to	Total	Estimated	Total Bed.	Pore
		4/16/02	11/30/02	Substrate	Pore		volume
11	Sugar beets + ethanol	0.9-0.95	Discontinued	8300	3415	150	62
2 ⁵	Sugar beets	1	1.4	8300	3190	99	38
31	Sugar beets + iron	1	Discontinued	8700	3690	145	62
4 1	Peat	1.8-2	Discontinued	8600	4280	75	38
5 ¹	Peat + ethanol	1.6-1.7	Discontinued	8600	4255	87	43
61	Peat + iron	1.8	Discontinued	8800	4530	81	42
8 ³	Manure, sawdust, corn	2	2.5	9000	5030	60	33.5
9 ³	Manure, sawdust, hay	2-2.05	2.5	9000	5190	60	34.5
10 ²	Biosolids, sawdust, hay	2-2.05	2.5	9000	5610	60	37.5
11 2	Rod mill feed + iron	2	2.5	9000	3,890	60	26
12 ⁶	Rod mill feed + ethanol	1.8-2	2.5	9000	4090	60	27
5A	Oxidized ore + coarse tailing + ethanol	2.5	2.5	9000	3765	60	. 25
6A ⁴	Oxidized ore + coarse tailing + molasses/methanol	2.5	2.5	9000	3690	60	24
7 ⁴	Rod mill feed + molasses/methanol	2.5	2.5	9000	3265	60	22

Table 5. Flow rates in columns (February – November 2002).

1 - Columns were discontinued on 4/18/02.

2 - Columns were discontinued on 5/20/02.

3 - Column 9 discontinued after 11/18/02 and Column 8 discontinued after 11/25/02.

4 - 8/26/02- changed to methanol feed. 12/9/02- converted Columns 6A and 7 back to molasses.

5 - Column discontinued 6/3/02

6 - 6/10/02 - Changed ethanol feed chemistry - 95.4% ethanol, 3.8% MIBK, 1% pet nap (0.6 mg/L).

Table 6. Column effluent nutrient data.

Column	Substrate		BO	D		Tł	٢N	TP	NO ₂ -	+NO ₃	NH3
		2/12/02	3/12/02	4/16/02	5/15/02	2/13/02	3/12/02	2/13/02	2/13/02	3/11/02	3/11/02
1	Sugar beets + ethanol	4920	1650	90.9 ¹		82	10.3	18.6	< 0.1	0.1	1.6
2	Sugar beets	2520	600	<2 ¹	48.1	54	14.4	28.8	< 0.1	< 0.1	2.8
3	Sugar beets + iron	4920	450	39.9		14.4	0.55	1.06	< 0.1	< 0.1	0.3
4	Peat	18.1	3.8			4	3.4	0.06	< 0.1	< 0.1	1.9
5	Peat + ethanol	750	460	60.9 ¹		4.1	2.8	0.18	0.1	< 0.1	1.2
6	Peat + iron	12.1	6.2			3.5	2.9	0.06	< 0.1	< 0.1	2.2
8	Manure, sawdust, corn	2520	1200		150	- 78	35	10.2	< 0.1	0.1	18.9
9	Manure, sawdust, hay	600	120	41.4	22.6^{1}	14.9	2.9	11.8	0.1	0.1	0.6
10	Biosolids, sawdust,	1410	780		240^{1}	300	64	175	0.1	0.1	63
	hay										
11	Rod mill feed + iron	21.7	10.6			2.4		0.26	0.1	NA	NA
12	Rod mill feed +	710	250	124	168	1.8	1.9	0.97	<0.1	0.1	< 0.1
	ethanol										-

1 – Dissolved oxygen depletion.
 2 – Blank; not analyzed.

BOD = biochemical oxygen demandTKN = Total Kjeldahl NitrogenTP = Total PhosphoousNA = not analyzed

All value reported in mg/L

Column	Substrate	Sul	fide (mg/L			ГОС (mg/L	
		25 March	15 May	16 July	25 March	15 May	16 July
1	Sugar beets + ethanol	2.54			392		
2	Sugar beets	< 0.5	21.1		196		
3	Sugar beets + iron	<0.5			75.8		
4	Peat	< 0.5			55.7	·	
5	Peat + ethanol	1.61			199		
6.	Peat + iron	<0.5			15.1		
. 8 .	Manure, sawdust, corn	<0.5	16.8	60.6	255		
9	Manure, sawdust, hay	6.11	8.49	30.6	32.3		
10	Biosolids, sawdust, hay	19.6	5.85		353		
11	Rod mill feed + iron	<0.5	1.35		8.1		
12	Rod mill feed + ethanol	<0.5	4.39		122	90.1	8.8
5A	Oxidized ore + coarse tailing + ethanol			6.15			98.8
6A	Oxidized ore + coarse tailing + molasses		N	7.3			95.2
7	Rod mill feed + molasses			10.8			311

Table 7. Effluent sulfide and TOC concentrations for 2002.

Bold = anomalous value

Blank = no data, sample not analyzed for these parameters

Percent passing Screen size Oxidized ore/tailings Oxidized ore² Rod mill feed¹ column³ Coarse tailings -1" 99.5 -3/4" 97.0 -1/2" 100.0 100 78.1 -3/8" 99.9 -1/4" 39.0 42.78 48.4 31.06 96.6 -4 mesh -37.6 25.0 19.89 -6 mesh -10 mesh 1.63 65.5 8.0 -20 mesh 13.0 3.98 -35 mesh 1.8 6.3 8.0 -65 mesh 0.6

Table 8. Particle size distribution of inorganic components.

¹Size distribution for rod mill feed in the plants; for the original columns the rod mill feed was screened and only the -1/2", +10 mesh size fraction was used.

²Oxidized ore was screened for the columns and only the -1/2", +10 mesh size was used.

³Calculated size distribution of column using 90% by volume of the oxidized ore

-1/2, +10 mesh, plus 10% of the unscreened coarse tailings.

		Average SO ₄ Removal (mmol/m ³ /day)					
Column	Treatment	2/8-4/17/02	4/18 - 8/26/02	8/27 - 11/25/02			
1	Sugar beets + ethanol	932					
2	Sugar beets	803	652 ¹				
3	Sugar beets + iron	1047					
4	Peat	268	•				
5	Peat + ethanol	2179					
6	Peat + iron	290					
8	Manure, sawdust, corn	1304	2541	660 ³			
9	Manure, sawdust, hay	2094 *	1529	614 ³			
10	Biosolids, sawdust, hay	2282	3108 ²				
11	Rod mill feed + iron	611	515 ²				
12	Rod mill feed + ethanol	2393	3130	2798 ⁴			
7	Rod mill feed + molasses/methanol		1990 ⁶	1315 ⁸			
5A	Oxidized ore, coarse tailing, ethanol			2805 ⁵			
6A	Oxidized ore, coarse tailing, molasses/methanol		3029 ⁷	1654 ⁸			

Table 9. Sulfate removal rates.

Notes: Rate periods were selected based on changes in columns (Appendix 5).

Columns 5A, 6A, and 7 first sample 5/13/02

¹Columns 2 was terminated 6/3/02.

²Columns 10 and 11 were terminated 5/20/02.

 3 Columns 8 and 9 were terminated by 11/25/02.

⁴ Rate period from 8/26 - 10/28/02.

⁵ Rate 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 $(mmol/m^3/day) = (SO_4 in - SO_4 out) mg/L x Flow L/day$ 96.06 mg/mmol x substrate volume m³

			Total	Total	Removal	
Column #	Substrate	Time period	volume (L)	SO ₄ input (g)	SO ₄ removal (g)	%
1	Sugar beets + ethanol	2/8 - 4/18	91.9	75.9	51.3	67.6
2	Sugar beets	2/8 - 6/3	190.7	154.0	64.3	41.8
3	Sugar beets + iron	2/8 - 4/18	99.4	82.1	60.4	73.6
4	Peat	2/18 - 4/18	188.8	155.9	15.3	9.8
5	Peat + ethanol	2/18 - 4/18	163.9	135.3	124.2	91.8
6	Peat + iron	2/18 - 4/18	178.8	147.7	16.9	11.4
8	Manure, sawdust, corn	2/8 - 11/25	987.8	745.9	413.6	55.4
9	Manure, sawdust, hay	2/8 - 11/18	965.1	730.5	338.9	46.4
. 10	Biosolids, sawdust, hay	2/8 - 5/20	313.5	253.8	220.2	86.8
11	Rod mill feed + iron	2/8 - 5/20	311.0	251.8	50.2	19.9
12	Rod mill feed + ethanol	2/8-11/25	978.0	738.5	616.7	83.5
5A	Oxidized ore, coarse tailing, ethanol	5/10 - 11/25	716.4	509.4	448.2	88.0
6A	Oxidized ore, coarse tailing, molasses	5/10 - 8/26	388.8	284.2	241.0	84.8
6A	Oxidized ore, coarse tailing, methanol	8/26 - 11/25	327.6	223.7	129.0	57.7
7	Rod mill feed + molasses	5/10 - 8/26	388.8	284.2	154.0	54.2
7	Rod mill feed + methanol	8/26 - 11/25	327.6	223.7	103.0	46.0

Table 10. Total mass of sulfate removal.

Total volume (L) = flow rate L/day x # days in period

Total sulfate input (g) = <u>Average SO₄ input mg/L x total volume L</u>

1000

Total sulfate removal was estimated by using the average rate of removal for the period when the output concentrations were relatively constant and using average output concentrations when conditions in the column changed.

Total sulfate removal (g) = sulfate reduction rate x # days x column volume + (Cin - Cout) x V

Total sulfate removal (g) = Average removal mmol/ m^3 /day x substrate volume m^3 x # days x 96.06 g/mole 1000

+ (average input concentration (mg/L) - (average output concentration) x total volume (L) 1000 mg/gm







Figure 2. pH and sulfate vs. time for the column feed water.

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Figure 3. pH, sulfate and iron vs. time for the sugar beet columns (1,2,3).

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Figure 4. pH, sulfate, and iron vs. time for the peat columns (4, 5, 6)

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Figure 6. pH, sulfate, iron vs. time for the rod mill feed and zero valent iron column (11).

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Figure 7. pH, sulfate, iron vs. time for the rod mill feed columns (7, 12).

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APPENDIX 1

Column Design and Substrate Information

Attachment A1.1.	Description of substrates
Attachment A1.2.	Size distribution of raw rod mill feed
Attachment A1.3.	Column design
Attachment A1.4.	Exceptional quality biosolids, produced at the Blue Lake Plant in Shakopee, MN
Table A1.1	Blue Lake heat-dried biosolids analysis, exceptional quality
Photo A1.1	Sugar beets, chopped
Photo A1.2	Rod mill feed, screened
Photo A1.3	Sawdust
Photo A1.4	Peat mixture (peat + peat screenings)
Photo A1.5	Manure
Photo A1.6	Cracked corn
Photo A1.7	Blended substrates by four corner method
Photo A1.8	Blending manure substrates by hand
Photo A1.9	Biosolids
Photo A1.10	Overall column setup with initial sample collection system

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Attachment A1.4. Exceptional Quality Biosolids, produced at the Blue Lake Plant in Shakopee, MN.

Rules governing treatment and use of biosolids can be found at

http://www.revisor.leg.state.mn.us/arule/7041/

From this rule, the requirements for the Blue Lake pellets are:

(2) Heat drying. Sewage sludge is dried by direct or indirect contact with hot gases to reduce the moisture content of the sewage sludge to 10 percent or lower. Either the temperature of the sewage sludge particles exceeds 80 degrees Celsius or the wet bulb temperature of the gas in contact with the sewage sludge.

Table A1.1. Blue Lake heat-dried biosolids analysis, exceptional quality sludge units (all values in kg/kg unless noted*)

Lab	Sample	Period	<u>%TS</u>	<u>%TVS</u>	<u>As</u>	<u>Cd</u>	<u>Ca*</u>	<u>Cu</u>	<u>Fe*</u>	Pb	Hg	Mo
MVTL	12/20/2000	02/04/2001	94.3	74.7	3.78	2.41	17560	760	8843	25.6	0.33	15.2
MVTL	02/05/2001	03/04/2001	94.5	73.2	3.17	3.03	15880	741	8587	37.5	0.43	13.9
MVTL	03/05/2001	04/01/2001	94.4	82.9	1.62	2.86	16490	793	8403	26.5	0.37	13.9
MVTL	04/02/2001	04/29/2001	94.5	75.3	1.51	2.63	20180	684	9800	24.8	5.29	20.4
MVTL	04/30/2001	06/01/2001	95.6	75.9	4.52	1.41	19280	727	10020	24.4	0.46	14.4
MVTL	06/04/2001	07/01/2001	95.3	78.0	2.81	0.74	17820	720	11370	18.5	0.50	13.6
MVTL	07/02/2001	07/29/2001	95.2	76.7	1.76	1.71	16820	731	10810	14.8	0,70	18.5
MVTL	07/30/2001	09/02/2001	94.8	75.7	4.72	0.65	23260	849	10650	24.7	0.45	26.6
MVTL	09/03/2001	09/30/2001	94.5	79.9	2.05	0.60	18690	810	4154	31.0	0.46	29.8
MVTL	10/01/2001	10/28/2001	94.6	75.8	1.81	0.35	15760	789	10200	14.6	0.54	21.5
MVTL	10/29/2001	12/02/2001	94.1	80.3	3.32	0.39	15620	578	8458	13.1	1.05	15.6
MVTL	12/03/2001	12/30/2001	93.2	80.2	2.95	0.12	19440	601	8151	0.9	0.44	14.5

<u>Ni</u>	<u>K as %K2O*</u>	<u>Se</u>	<u>%S*</u>	Zn	<u>%TKN</u>	<u>%Avail. P2O5*</u>	<u>%NH3-N</u>	FC (mpn/g)	pН
21	0.31	1.04	0.90	427	5.67	3.84	0.16	<140	6.0
19	0.39	1.47	0.77	420	5.68	4.18	0.17	5	5.9
32	0.35	0.90	0.69	523	5.46	3.96	0.19	< 140	5.8
24	0.30	0.19	0.76	511	5.23	3.33	0.21	16	5.9
24	0.26	1.76	0.76	545	4.92	3.52	0.20	16	6.0
15	0.29	3.03	0.78	535	5.06	3.68	0.21	2	5.8
15	0.26	0.53	0.77	561	5.11	3.77	0.19	16	. 5.8
17	0.29	0.75	0.82	633	5.26	4.42	0.20	16	5.7
19	0.38	2.05	0.89	532	5.44	4.72	0.26	2	6.0
25	0.32	0.56	0.96	561	5.21	4.13	0.20	2	5.9
15	0.39	1.82	0.83	448	5.59	4.85	0.20	2	5.7
25	0.41	2.21	0.69	445	5.74	4.90	0.18	16	5.8

Parameters: pH SC SO₄ S^{-2} Ca Fe nutrients BOD Total P NH₄N Fecal coliform Ethanol on columns with additive?

Ethanol analysis may only be possible on substrates without organic material, the organic substrates will release substantial quantities of organic material and will probably cause analytical interference.

Digital photos to record color:

Frequency: pH, SC, sulfate every sample
S⁻², Fe, Ca once per week
Nutrients, initial sample then monthly
Fecal coliform, initial sample then monthly, on columns with manure and Biosolids

Substrates: % moisture % ash Total C, organic C Total N Total P Metals (compost, EQ list) Attachment A1.3. Column design.

Mixtures: The goal is to have the maximum amount of organic material in the column yet still have permeability of at least 10^{-3} cm/sec.

Literature:

Some studies report mixtures by percent volume while others report by percent weight. Converting the percent weight studies (using estimated bulk densities) provide a range of about 25 - 50% by volume inorganic. Soudan columns have maintained a permeability of 10^{-3} cm/sec for about five years. The inorganic component for the Soudan columns was about 20% by weight (weight as received). Permeability in the field system should be at least an order of magnitude higher than in the lab.

Column mixtures are listed in Table 1.

Approach :

Mix with 25% by volume rod mill feed.

If the mixture looks "good", it will be loaded into the column. Measure column porosity.

Estimate permeability of the column.

Raise water level to maximum, record water level vs time, using falling head permeability calculation.

If permeability is at least 10^{-3} , column would be left saturated for one week to allow bacteria to grow.

If permeability too low, the amount of rod mill feed would be increased in the mixture and the procedure repeated.

Experimental Design:

Flow rate = 2 mL/minResidence time = 2 days

Rationale:

In order to minimize the size of the final system, need to have a sulfate reduction rate $> 300 \text{ mmoles/m}^3/\text{day}$. To determine the rate the sulfate in the column outflow must be measurable. A residence time of two days is within recommended range.

Sampling: Minimum of twice per week to generate sufficient data to do a preliminary Schedule: evaluation of the substrates.

Size	<u>% Cum Pass</u>
1"	99.55
3/4"	97.04
1/2"	78.11
1/4"	39.01
6M	25
8M	21.14
20M	13 (between 10 and 12 mesh)
65M	8.125
100M	7.29
270M	4.16
500M	3.02

Attachment A1.2. Size distribution of raw rod mill feed.

NOTE: -1/2, + 10 mesh ~ 60% of the sample

Used the -1/2", +10 mesh for inorganic substrate. The graded layer consisted of three $\frac{1}{2}$ " layers with the following size fractions (assuming mesh is U.S. series sand >.05):

-1/4, +6 mesh	(.2513 in)
-6 mesh, +8 mesh	(.13-0.9 in)
-8 mesh, +14 mesh	(.09056 in)

water treatment effluent were collected but these contained only a few percent solids and no hydrogen sulfide was produced.

For use in the original columns "fresh" cow manure (less than one day old) was collected from a barn, air dried, ground to a powder, and 25 grams was added as a bacteria source. Five hundred mL (500 mL) of the "mature" (several months old) manure were also added.

For the new columns, 400 mL of "fresh" horse manure was used (less than one day, old).

Zero valent iron

U.S. Steel has not yet been able to find a suitable inexpensive source. For the lab tests, material from Connely Iron will be used. This material is about 90% reduced iron and has been used extensively in permeable reactive barriers. The drawback is its high cost (over \$340/ ton + shipping). If this is selected for field trials scaling factors will have to be applied to account for the amount of reduced iron and surface area. Product 1022 was used in these experiments.

Rod mill feed

Crushed ore that will provide the inorganic component of the column. The primary function of this material is to increase the permeability of the substrate. Some iron will dissolve which should react with the sulfide generated as part of the reduction process. The size distribution will range from fine sand to gravel (100% passing ¹/₂ inch screen and 100% greater than 0.05 inches (10 to 14 mesh)) This product contains about the same amount of iron as ballast, so one would expect a similar iron release in the columns and the field. (Will need to provide a scaling or safety factor in final design)

Oxidized taconite

Taconite that has been oxidized to the point where no longer magnetic and can be processed in plant. Characterized by higher ferric iron content and red color. Material from U.S. Steel's pit.

Coarse tailings

Tailings collected from the coarse tailings stream in the plant.

Attachment A1.1. Description of substrates

Sugar Beets

These are chunks of sugar beets, including the bottom piece of the beet. This is a waste that they will give away for free. For column tests the chunks will have to be chopped into small pieces, suggest 100% -1/2 in. For field application will either have to devise a way to chop them (maybe something similar to a bale buster) or use them as received. Would have to use a scale factor to account for the difference in surface area.

Shreds

Tailings

A dry sugar beet product, looks like dry pulp after processing, would probably be less reactive than tailings although this material has much more surface area and would be easier to mix and handle (was not used in columns may cost for the material).

Peat

Purchased dry peat from Minnesota Sphagnum (MSI).

Peat screenings

Waste produced by screening peat. Contains sticks (several inches long) but also contains a lot of peat. Was screened to -1/2 inch for column tests.

Ideally, to replicate field run material would need to mix in the correct proportion. Should contact MSI. Since the screenings contained mostly peat, the exact proportion was not investigated.

Biosolids

Exceptional quality material from Shakopee, MN. Heat dried pellets. According to Met Council staff this material is not regulated and is sold as fertilizer. Currently Met Council is paying \$6/ton to take the material. Facility has excellent truck loading facilities and is near a railroad. A rail loading location and the cost of back haul must be determined.

Manure

The "mature" cow manure was collected by USS from a pile in a nearby area. The age of the manure was estimated as several months. The manure was still fairly fresh, had not decomposed, and had a strong odor. Pieces of corn were still visible.

Hay

The hay was collected by USS from a reclamation site at the mine.

Sawdust

USS provided the sawdust which is used as fuel for their kilns.

Bacterial source

Originally this was to be paper mill processing residue from Blandin. Blandin has now changed there processing procedure. Currently all waste water is combined (paper mill + Grand Rapids WWTP) and then filtered. Samples of the paper mill effluent before it was combined with the waste Photo A1.1 Sugar beets, chopped

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Photo A1.3 Sawdust

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Photo A1.4 Peat mixture (peat + peat screenings)





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Photo A1.6 Cracked corn





Photo A1.7 Blending substrates by 4 corner method

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Photo A1.8 Blending manure substrates by hand



Photo A1.9 Biosolids

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Photo A1.10 Overall column setup with initial sample collection system



APPENDIX 2

Notes on Column Setup and Substrate Data

Attachment A2.1.	Detailed notes on USS columns setup (January 23-25, 2002)
Table A2.1.	Final column mixtures
Table A2.2.	Excess substrate volumes
Table A2.3.	Initial volumes
Table A2.4.	Substrate porosity
Table A2.5.	Porosity and permeability testing on columns
Table A2.6.	Bulk density of individual components
Table A2.7.	Bulk density of column mixtures
Attachment A2.2.	Calculation of permeability for U.S. Steel columns
Table A2.8.	Hydraulic conductivity calculations

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Attachment A2.1. Detailed notes on USS columns setup (January 23-25, 2002).

The purpose of this experiment is to examine the ability of various substrates to remove sulfate from USS tailings water. The test method will be to use $5\frac{3}{4}$ -inch diameter acrylic columns, each 30 inches high, to evaluate a variety of substrates (Table A1.1). Jasper Engineering in Hibbing, who also built the stand for the columns, fabricated the columns. The bottom was glued into the columns and a screen support was placed on the substrate. Prior to loading the columns, about a gallon of water was placed into each column to make sure that it did not leak. A small leak was noted in only one of the columns, the other eleven were fine. Before putting the substrate into the columns a base consisting of three distinct size fractions of rod mill feed were placed into the bottom. One-half inch layers of three size fractions ($-\frac{1}{4}$ inch, +6 mesh; -6, +8 mesh; -8, +14mesh) were placed into each column. Typically, we would use sand but in order to get the columns started on time, the only material available was the rod mill feed, which was screened by USS and is the same material that was used for the inorganic component of the substrate mixture to provide permeability. The organic substrate was then prepared for each column. The substrates will be discussed separately.

Sugar Beet Tailings

The sugar beet tailings material consisted of the bottoms and tops or chunks of sugar beets; small whole beets were also included. The green part of the beet was also included in these tailings. The leafy portion of the beets appeared to be partly decomposed. The chunks of beets were quite large. The whole beets were on the order of several inches in diameter and 3-4 inches long. In order to have a good distribution of flow within the column, the beets had to be chopped. This was done manually and the beets were screened to pass a -1/2-inch screen. Once the beets were chopped, they were placed on a plastic sheet which was turned and mixed using the four-corners method. Each corner of the sheet was turned over, the complete cycle of the four corners was repeated ten times to thoroughly blend the different size fractions. The four-corners method of blending was used for most of the substrates. The only exception was the manure, which was wet and had to be worked in manually. Since the sugar beets were fairly coarse, it was decided that sufficient permeability would be obtained using 25% by volume rod mill feed which had been screened to be -1/2 inch, +10 mesh. The volume of material required for the column was 8.8 L. This volume would bring the substrate level up to the top of the upper support in the stand. This would allow 3¹/₂ inches of water head on each column and still allow sufficient volume to store water in case of column plugging. The required volume of sugar beets and rod mill feed was measured in a 2¹/₂-gallon bucket, which had been calibrated with water and marked with one liter markings. The combination sugar beet and rod mill feed was then placed on the plastic sheet and mixed using the four-corner method. Once the substrate was mixed, a 400 mL beaker was used to place the substrate into the column. By using a beaker, the substrate could be placed directly onto the bed and moved around carefully to avoid segregation of the material. This is particularly important when the material in the substrate has drastically different densities, such as the rod mill feed and the sugar beet material. A one-liter container of sugar beets was weighed to provide a bulk density of the material prior to putting in the column. The column was filled to the desired level and the residual volume; the volume that was not used was measured (Table A2.2). When the first sugar beet column was filled there was roughly .6 L left over. Since the calculated volume was 8.8 L and the initial volume was about 9 L, it was not

surprising that there was some volume remaining. Over time the sugar beet material settled and eventually the level settled below the top support of the column. Prior to starting the experiment the distance from the top of the column to the top of the substrate was measured (Table A2.3). Unfortunately, the residual volume for the first column was discarded but the residual volume for the second sugar beet column was retained and this material was distributed among Columns 1 and 2 that contained sugar beets.

Peat Column

USS had collected peat substrate from the material that was used for the pilot cell. One bucket of fibric peat and three buckets of screenings was blended for this experiment. The peat and screenings were obtained from Minnesota Sphagnum, which is the only company that screens their peat. The fibric material was light brown and dry; the screenings were darker and contained pieces of wood. The screenings were primarily peat and appeared more decomposed than the fibric peat. The screenings were passed through a ½-inch screen to remove the sticks. The material was placed on a piece of plastic and blended to provide a uniform mixture (four-corners method). This mixture was then coned and quartered, and one-quarter of each material was selected for the peat columns. The peat material was fibric in origin, it had sufficient permeability when it was mixed with 25% by volume rod mill feed. The method of loading the peat columns was the same as for the sugar beets. The volumes were estimated using the calibrated bucket, placed on a sheet of plastic and blended using the four-corners method. The residual volume after the columns were loaded was measured. The peat columns did not settle very much. Again, the distance from the top of the column to the substrate level was measured (Table 2.3).

Manure and Biosolids Columns

U.S. Steel collected the manure from a nearby area. Cow manure was collected from an outdoor pile and was still fairly fresh; it had a strong odor and had not decomposed. It was probably several months old. Pieces of corn were still visible in the manure. Since the manure was still wet, it could not be blended using the four-corners method. The calibrated bucket was used to estimate the volumes. U.S. Steel provided the sawdust. This material is collected and burned in their kilns. The hay was collected from U.S. Steel and had been used as a mulch on a revegetation project. It was cut with scissors to be approximately ½-inch long and was screened using a ¹/₂-inch screen. The hay, manure, sawdust and rod mill feed were placed on a sheet of plastic and mixed manually to provide a mixture. It was rolled several times using the quarter method, but most of the mixing was done by hand so the clumps of manure could be broken and distributed throughout the mixture. All columns were loaded using the 400 mL beaker and the residual volume was measured (Table 2.2). The manure columns had large excess volumes. By breaking up the clumps of manure the volume increased and the volume of sawdust also increased during mixing. The biosolids were exceptional quality and were obtained from the Shakopee plant in the Twin Cities. The material contained less than 10% moisture, resembled small fertilizer pellets and could be mixed with the four-corners method with the sawdust, hay and rod mill feed. The zero valent iron was produced by Connolly Iron in Chicago (Product 1022). The volume of iron was measured, placed with the substrate and mixed into the substrate using the four-corners method.

Two columns used rod mill feed as the primary substrate. One column received 10% by volume of zero valent iron. A bacteria source was needed for these columns. Fresh manure was airdried and ground to a powder with a mortar and pestle. Twenty-five grams were added to each column. Five hundred milliliters of the stockpiled manure was also added. The manure was blended manually.

For the new columns, 400mL of fresh horse manure (less than one day old) was mixed into the top several inches of the column.

Measurement of Porosity

Distance from the top of the column to the substrates was measured. Porosity was estimated by slowly adding water to the column with a 500 mL graduated cylinder (Table A2.4). The volume of water needed to completely saturate the substrate was measured . (Added water until water level was at the top of the substrate.) About 0.3 L was needed to saturate the screened rod mill feed at the bottom of the column.

Permeability Measurement

Once porosity was estimated the column was completely filled. Water was added to minimize disturbance of the substrate surface. Outlet water level was adjusted to the top of the stand and the change in water level over time was measured. Measurements were taken at each inch and a flow rate was measured when the water level had fallen to about $4\frac{1}{2}$ inches below the top of the column. (This level was chosen since it represents the approximate operating level for the column.) Three columns, 1, 6, and 9, were measured on 1/25/02. Measurements were taken on the other columns on 1/30/02 (Table A2.5).

Miscellaneous Notes

Rationale for Column Mixtures

Manure/sawdust/hay column was changed to be the same ratio as biosolids/sawdust/hay. This will allow a direct comparison of biosolids vs manure.

Manure is available, but if large quantities were needed, U.S. Steel would have to develop a collection system similar to its current system for sawdust. In the original plan, all manure columns were similar. It was decided to change Column 8 to use less manure and more cracked corn. Cracked corn is available, has structure, and should provide readily available organic carbon.

One column (Column 7) was left empty. If an inexpensive source of zero valent iron can be obtained or if there is an additional substrate, it can be tested.

Samples of each substrate were collected and were analyzed for metals and organic content (Table 2).

Table A2.1. Final column mixtures.

Column	Organic Substrate	% by volume	Zero Valent Iron	% by volume	Inorganic Substrate	% by volume	Bacterial Seed	Additive
1 ¹	Sugar beet waste	75	(1) W. C. Lindson, References, explored and a second se	Control States - 1 and	rod mill feed	25	No	Ethanol
2	Sugar beet waste	75			rod mill feed	25	No	No
3 1	Sugar beet waste	65	iron filings	10	rod mill feed	25	No	No
4 ¹	Peat	75			rod mill feed	25	No	No
5 ¹ .	Peat	75			rod mill feed	25	No	Ethanol
6 ¹	Peat	65	iron filings	10	rod mill feed	25	No	No
8	Manure	10			rod mill	25	No	No
	Saw dust	40						•
	Feed corn (cracked)	25		- - -				
9	Manure	25			rod mill	25	No	No
	Saw dust	40			ieed	an a		
	Нау	10			1 20			
10.2	Biosolids	25		1. S. S.	rod mill	25	No	No
10-	Saw dust	40			feed	÷ .		н. 1
	Нау	10						
11 2	None	0	iron filings	10	rod mill feed	90	Yes ⁴	No
12	None	0	2		rod mill feed	100	Yes ⁴	Ethanol
5 Å 3	None	0			oxidized ore	90	X7.5	Ethanol
· JA	None	0			coarse	10	res	
6A ³	None	0			oxidized ore	90	Yes ⁵	Molasses
	None	0			coarse tailing	10		
7.3	None	0			rod mill feed	100	Yes ⁵	Molasses

1 - Columns were discontinued on 18 April 2002.

2 - Columns were discontinued on 20 May 2002.

3 - Columns were filled on 06 May 2002 and flow began on 13 May 2002.

4 - The seed source was "young" cow manure, which was air dried, ground to a powder, and 25 grams were added to the columns. Five hundred milliliters (500 mL) of "older" cow manure were also added.

5 - Roughly 400 mL of "as received" (not dried) horse manure.

Column	Volume leftover (L)	Comments
1	.6 (initial)	
2	0	Substrate in all 3 columns settled. Residual
3	0	volume from column 1 was discarded;
		residual volume from columns 2 & 3 was distributed among the 3 columns.
4	not measured	
5	.3	
6	.3	
8	3.0	Substrate volume increased after mixed
9	1.3	manure sawdust, hay and biosolids.
10	1.8	
. 11	2.0	
12	1.3	

Table A2.2. Excess substrate volumes.

Column	Distance from top	Total depth	Initial substrate	Distance below
Column 1	o O		8300	1 3/8
2	9	19.5	8300	1 3/8
3	8	20.5	8700	1/4
4	8 1/4	20.25	8600	3/4
5	8 ¹ / ₄	20.25	8600	3/4
6	7 3/4	20.75	8800	1/2
8	7 1/4	21.25	9000	
9	7 1/4	21.25	9000	
10	7 1⁄4	21.25	9000	· ·= ·
11	7 1⁄4	21.25	9000	
12	7 1/4	21.25	9000	
5A	7 1⁄4	21.25	9000	
6A	7 1⁄4	21.25	9000	
7	7 1/4	21.25	9000	

Table A2.3. Initial volumes.

1 - Depth of substrate measurements taken prior to adding water (measurement does not include the screened rod mill feed).

2 - Initial volume rounded to nearest 100 mL.

3 - Some of the substrates settled, this is the distance from the top of the plywood to the top of the substrate.

		Calculated Substrate	Water to Saturate	Water to Saturate	Estimated	Required
Column	Substrate	(mL)	(mL)	(mL)		mL/min
1	Sugar beets + ethanol	8300	3725	3415	41	1.2
2	Sugar beets	8300	3500	3190	38	1.1
3	Sugar beets + iron	8700	4000	3690	42	1.3
4	peat	8600	4590	4280	50	1.5
5	Peat + ethanol	8600	4565	4255	49	1.5
. 6	Peat + iron	8800	4840	4530	51	1.6
8	Manure, sawdust, corn	9000	5340	5030	56	1.7
9	Manure, sawdust, hay	9000	5500	5190	58	1.8
10	Biosolids, sawdust, hay	9000	5920	5610	62	2.0
11	Rod mill feed + iron	9000	4200	3890	43	1.4
12	Rod mill feed + ethanol	9000	4400	4090	45	1.4
5A	Oxidized ore + coarse tailing + ethanol	9000	4075	3765	42	1.3
6A	Oxidized ore + coarse tailing + molasses	9000	3950	3640	40	1.3
7	Rod mill feed + molasses	9000	3575	3265	40	1.1

Table A2.4. Substrate porosity.

1 - The amount of water needed to saturate the screened rod mill feed and the void space at the bottom of the column was calculated using Column 7 which did not contain any substrate. The distance from the bottom of the column to the top of the screened rod mill feed was 1.75 inches. When 500 mL was added, the water level rose to 2.19 inches.

Volume in rod mill feed = 500 - ($(2.19-1.75) \times 425 \text{ mL/inch}$) = 313 mL, or approximately 310 mL

2 - Flow rate to provide 48 hr residence time.

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T = pore volume
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Q

Target flow rate:

Flow Rate (mL/min)
~1.2
~1.5
~1.8

Table A2.5. Page 1 of 2. Porosity and permeability testing on columns.

	Volume to saturate			Flow rate
Column material	column (mL)	Time	Water level ¹ (in.)	$(mL/min)^2$
<u> </u>	in the second	0:53	1	an a
		1.52	2	
1- sugar beets +	3725	3:00	3	200
ethanol		4:24	4	
		6:15	5	
		1:13	1	
		2:34	2	· · · · · ·
2 - sugar beets	3500	4:00	3	200
C		5:43	4	
		7:54	5	
		1:07	1	<u> </u>
3 - sugar beets &	4000	2:09	2	225
iron		3:32	3	
	•	5:02	4	
		1:13	. 1	
		2:16	2	1 m 11 m m
4 - peat	4590	3:30	3	220
-		5:03	4	*
	r	7:03	5	
		1:06	1	
		2:07	2	
5 - peat + ethanol	4565	3:26	3	235
		5:00	4	
		7:00	5	
		1:15	1	
		2:32	2	
6 - peat + iron	4840	4:09	3	125
filings		6:23	4	
		9:58	5	
		1:35	1	· · · · ·
0		3:25	2	
δ - manure,	5340	5:22	3	80
sawdust, teed corn		7:56	4	· ·
	· .	12:16	5	
	; ; ·	0:54		··· · · ·
		2:00		
9 - manure,	5500	3:06	3	200
sawdust, hay		4:36	4	
		6:45	5	

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Table A2.5. Page 2 of 2. Porosity and permeability testing on columns.

	Volume to saturate			Flow rate
Column material	column (mL)	Time	Water level ¹ (in.)	$(mL/min)^2$
		1:06	1 .	
		2:06	. 2	
11 - rod mill feed		3:15	3	230
+ iron filings	4200	4:35	4	
		6:35	5	
		1:08	1	
		2:30	2	
12 - rod mill feed	4400	3:51	3	210
+ ethanol		5:27	4	
		7:55	5	
5A- oxidized ore		0:41	1	
+ coarse tailing		1:30	2	
+ ethanol	4075	2:10	3	500
		2:57	.4	
		3:47	5	
6A- oxidized ore		0:31	1	
+ coarse tailing		1:09	2	
+ molasses	3950	1:49	3	500
		2:30	4	-
		3:20	5	
7 - rod mill feed		0:58	1	
+ molasses		2:13	2	
	3575	3:29	3	340
		4:16	4	• .
		6:11	5	

1 - Distance measured from top of column.

2 - Flow measured for one minute when water level was between 4" and 5". (Flow measured in beaker, so value represents an estimated value.)

Substrate	Grams	Net Weight (Bulk Density g/L)
Peat	376	325
Rod mill	1810	1759
Iron filings	2625	2574
Sugar beets	717	666
Sawdust	237	186
Corn	716	665
Hay	81	30
Manure	594	593
Biosolids	581	530
Oxidized ore	1729	1678
Coarse tailings	1883	1832

Table A2.6. Bulk density of individual components.

Note: Material was weighed in a one liter plastic bottle (tare = 51gram). Material was packed loosely into the bottle in an attempt to provide the same density as in the column.

Table A2.7. Bulk density of column mixtures.

	Column	Gross	Tore	Newyyveight	Bulk density
Manure	9	665	51	614	<u>(9</u> L) 614
sawdust hay					
rod mill feed		н 1	1		
Biosolids	10	787	51	736	736
sawdust hay					
rod mill feed			•		
Manure	8	666	51	615	615
sawdust corn					
rod mill feed					
Zero valent	11	1814	51	1763	1763
iron		•			
rod mill feed					· .

Note: Mixture was packed into a 1 liter bottle at a density similar to columns. Tare for 1 liter bottle = 51 grams. Attachment A2.2. Calculation of permeability for U.S. Steel Columns.

 $Q = K_h A \Delta H/L$

A = fixed for all substrates = $\pi r^2 = \pi \frac{[5.75 \text{ in } x \text{ } 2.54 \text{ cm/in}]^2}{[2007]^2} = 167 \text{ cm}^2$

L = fixed for each substrate, height of column

 $K_h =$ column property, to be measured

Data = time required for water level to drop 1"

Volume per inch of column = A x h = $167 \text{ cm}^2 \text{ x } 2.54 \text{ cm} = 425 \text{ cm}^3$

Compute $Q = \frac{\text{volume}}{\Delta \text{ time}}$

 $\Delta H = H_i - H_t$ (distance from top of column to top metal edge)

Since have measuring flow and head over one-minute intervals are actually measuring average values

$$K_{h} = \underbrace{Q_{ave}}_{\Delta H_{ave}} \underbrace{L}_{A}$$

so compute K_h for each $Q_{ave} \Delta H_{ave}$ all values should be reasonably close average values

		-							1	2	3	4	5	
	Hydraulic Co	onductivity Calc	ulations						2.54	5.08	7.62	10.2	12.7	
Column	Total Depth Substrate (in)	Total Depth Substrate (cm) L	Area (cm2)	T-1	T-2	T-3	T-4	T-5	Q1	Q2	Q3	Q4	Q5	Q ave
<u>· 1</u>	19.5	49.53	167.5	53	112	180	264	375	8.03	7.599	7.09	6.45	5.67	6.968
2	19.5	49.53	167.5	73	154	240	343	474	5.83	5.526	5.32	4.96	4.49	5.225
3	20.5	52.07	167.5	67	129	212	302	437	6.35	6.597	6.02	5.64	4.87	5.895
4	20.25	51.435	167.5	73	136	210	303	423	5.83	6.258	6.08	5.62	5.03	5.763
5	20.25	51.435	167.5	66	127	206	300	420	6.45	6.701	6.2	5.67	5.07	6.017
6	20.75	52.705	167.5	75	152	249	383	598	5.67	5.599	5.13	4.44	3.56	4.88
8	21.25	53.975	167.5	95	205	322	476	736	4.48	4.151	3.96	3.58	2.89	3.812
9	21.25	53.975	167.5	54	120	186	276	401	7.88	7.092	6.86	6.17	5.31	6.662
10	21.25	53.975	167.5	68	143	243	364	520	6.26	5.951	5.25	4.68	4.09	5.246
11	21.25	53.975	167.5	66	126	195	275	395	6.45	6.754	6.55	6.19	5.39	6.265
12	21.25	53.975	167.5	68	150	231	327	475	6.26	5.674	5.53	5.21	4.48	5.428
5A	21.25	53.975	167.5	41	90	130	177	227	10.38	9.46	9.82	9.62	9.37	9.73
6A	21.25	53.975	167.5	31	69	109	150	200	13.73	12.33	11.71	11.35	10.64	11.95
7	21.25	53.975	167.5	58	133	209	286	371	7.34	6.40	6.11	5.95	5.73	6.31

T-11- 100	n 1		TT 1 1'	1		1
I anie A / X	Page I	OF 7	Hydrauli	c conductiv	ITV COLO	ullafione
1 4010 1 12.0.	I ago I	UI 2.	IIYulauli		ity can	uiauons.
	0					

Note: T-1 = time in seconds for the water level to drop from the top of the column (0) to 1 inch below the top of the column. Q1 = Average flow in cm³/sec during the time it took the water level to drop the first inch from the top of the column.

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Table A2.8. Page 2 of 2. Hydraulic conductivity calculations.

Column	dH1	dH2	dH3	dH4	dH5	kH1	kH2	kH3	kH4	kH5	Average permeability cm/s
1	7	6	5	4	3	0.133504	0.147411	0.1651	0.187614	0.220133	0.170752
2	7	6	5	4	3	0.096928	0.107208	0.123825	0.144402	0.174156	0.129304
.3	7	6	5	4	3	0.111023	0.134548	0.147368	0.172417	0.198589	0.152789
4	· 7.	6	5	·4	3	0.100656	0.126066	0.146957	0.169752	0.20266	0.149218
5	7	6	5	4	3	0.111331	0.135	0.149811	0.17145	0.204107	0.15434
6	7	6.	5	4	3	0.10039	0.115581	0.127	0.137611	0.146892	0.125495
8	7	6	5	4	3	0.081165	0.087764	0.100575	0.113393	0.122226	0.101025
9	7	6	5	4	3	0.142791	0.149931	0.174113	0.195562	0.224335	0.177346
10	7 .	6	5	4	3	0.113393	0.125816	0.133272	0.148283	0.172997	0.138752
11	7	6	5	4	3	0.116829	0.142791	0.166077	0.196273	0.227743	0.169942
.12	7	6	5	4	. 3	0.113393	0.119944	0.140195	0.165061	0.189386	0.145596
5A	7	6	5	4	3	0.188	0.200	0.249	0.305	0.396	0.268
6A	7	6	5	4	3	0.249	0.261	0.297	0.360	0.450	0.323
. 7	7	6	5	4	3	0.133	0.135	0.155	0.189	0.242	0.171

Note: $dH1 = \Delta H$, head, in inches kH1 = permeability in cm/sec calculated first one inch drop in water level

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APPENDIX 3

Drainage Quality Results

- Table A3.1.Drainage quality data for column feed water
- Table A3.2.Drainage quality data for the sugar beets + ethanol column (1)
- Table A3.3.Drainage quality data for the sugar beets column (2)
- Table A3.4.Drainage quality data for the sugar beets + iron column (3)
- Table A3.5.Drainage quality data for the peat column 4
- Table A3.6.Drainage quality data for the peat + ethanol column (5)
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- Table A3.8.Drainage quality data for the sawdust, manure, corn column (8)
- Table A3.9.Drainage quality data for the sawdust, manure, hay column (9)
- Table A3.10. Drainage quality data for the sawdust, biosolids, hay column (10)
- Table A3.11. Drainage quality data for the rod mill feed + iron column (11)
- Table A3.12. Drainage quality data for the rod mill feed + molasses column (7)
- Table A3.13. Drainage quality data for the rod mill feed + ethanol column (12)
- Table A3.14. Drainage quality data for the oxidized ore, coarse tailings, ethanol column (5A)
- Table A3.15. Drainage quality data for the oxidized ore, coarse tailings, molasses column (6A)
- Table A3.16. Anomalous data

D	ate	pH (Conductivity	SO_4	Ca	Fe	Mg
	+		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Initi	al fill				129	< 0.1	193
02/0	08/02	•		881	127	< 0.1	191
02/1	.1/02	7.9	1540	807	134	< 0.1	198
02/1	5/02	8.2	1390	816	128	< 0.1	191
02/1	9/02	8.2	1750	807	133	< 0.1	197
02/2	22/02	8.1	1320	870	136	0.70	203
02/2	26/02	8.1	1680	809	129	< 0.1	194
03/0	04/02	8.0	1590	799	133	< 0.1	198
03/0	07/02	8.0	1520	827	132	< 0.1	197
03/1	2/02	8.0	1190	815	133	< 0.1	199
03/1	8/02	8.2	1720	845	136	< 0.1	202
03/2	22/02	8.0	1270	814	125	< 0.1	188
03/2	28/02	8.1	1590	868	136	< 0.1	204
04/0	01/02	8.2	1350	841	131	< 0.1	196
04/0	05/02	8.1	1530	819	134	< 0.1	201
04/1	.7/02	8.3	1910	808	129	< 0.1	195
04/2	22/02	8.4	1370	778	127	< 0.1	188
04/2	29/02	8.3	1520	729	122	< 0.1	179
05/0	03/02	8.4	1490	739	121	< 0.1	180
05/1	0/02			748	120	< 0.1	179
05/1	3/02	8.4	1420	727	122	< 0.1	181
05/1	7/02	8.4	1570	762	127	< 0.1	188
05/2	24/02	8.3	1560	756	121	< 0.1	182
06/0	07/02	8.4	1820	750	120	< 0.1	179
06/1	4/02	8.4	1820	772	124	< 0.1	185
06/2	21/02	8.4	1850	774	120	< 0.1	185
06/2	28/02	8.3	1820	782	125	< 0.1	189
07/0	08/02	8.4	1320	766	123	< 0.1	187
07/1	2/02	8.4	1830	774	128	< 0.1	192
07/1	9/02	8.4	1500	718	123	< 0.1	178
07/2	26/02	8.4	1540	691	120	< 0.1	173
07/2	29/02	8.2	1660	671	120	< 0.1	171
08/0	05/02	8.3	1830	683	121	< 0.1	172
08/1	2/02	8.4	1590	661	117	< 0.1	167
08/2	26/02			655	111	< 0.1	159
09/0)5/02	8.4	1570	680	117	< 0.1	170

Table A3.1. Drainage quality data for the column feed water.

Table A.	5.1. Drama	ige quality data for	the column 1	eeu water (t	commueu).	
Date	pН	Conductivity	SO_4	Ca	Fe	Mg
		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)
09/09/02	8.4	1590	692	117	< 0.1	167
09/16/02	8.4	1590	692	117	< 0.1	167
09/23/02	8.4	1580	705	117	< 0.1	170
09/30/02	8.6	1850	702	122	< 0.1	174
10/07/02	8.5	1620	719	121	< 0.1	170
10/14/02	8.2	1590	700	121	< 0.1	172
10/28/02	8.3	1410	657	114	< 0.1	163
11/04/02	8.4	1320	659	117	< 0.1	164
11/12/02	8.2	1500	656	. 119	< 0.1	165
11/18/02	8.4	1410	660	122	< 0.1	164
11/25/02	8.2	1480	670	124	< 0.1	170
12/09/02	8.2	1670	743	134	< 0.1	184
12/16/02	8.2	1530	749	139	< 0.1	187
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Table A3.1. Drainage quality data for the column feed water (continued).

Table A3.2. Drainage quality data for the sugar beets + ethanol column (1).

Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
+ . <u> </u>		(µS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	5.6	3250	522	889	810	422	0.93
02/14/02	5.3	2680	708	606	520	319	0.93
02/18/02	5.2	2460	769	347	280	232	0.93
02/21/02	5.2	2940	652	380	280	266	0.93
02/25/02	5.1	1820	676	413	290	278	0.93
02/28/02	5.2	2240	610	409	290	269	0.93
03/04/02	5.1	2020	308	368	200	223	0.93
03/07/02	5.3	1620	12	308	120	196	0.93
03/11/02	5.5	1870	1	286	83	200	0.93
03/14/02	5.5	1180	77	257	82	207	0.93
03/18/02	5.7	1690	2	223	69	203	0.93
03/21/02	6.0	1700	1	177	49	192	0.93
03/25/02	6.3	1200	17	117	3.3	147	0.93
03/28/02	6.6	1390	3	126	11	173	0.93
04/01/02	6.5	1700	2	199	2.7	203	0.93
04/04/02	6.7	1580	85	121	2.5	174	0.93
04/08/02	6.6	1440	124	128	2.9	184	0.93

Column was discontinued on 18 April 2002.

Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
 		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	4.7	2610	727	387	320	277	1.00
02/14/02	4.8	2190	791	432	350	267	1.00
02/18/02	4.9	2490	740	420	190	249	1.00
02/21/02	5.0	3230	786	590	270	286	1.00
02/25/02	5.1	1680	627	365	130	226	1.00
02/28/02	5.2	1930	642	437	200	249	1.00
03/04/02	5.3	1670	502	257	110	212	1.00
03/07/02	5.3	1630	272	250	150	206	1.00
03/11/02	5.8	1610	25	171	62	184	1.00
03/14/02	5.9	1140	85	148	36	188	1.00
03/18/02	6.4	1650	140	129	9.4	177	1.00
03/21/02	6.6	1870	148	131	4.9	183	1.00
03/25/02	6.9	1400	304	115	1.4	162	1.00
03/28/02	6.8	1670	55	124	1.8	175	1.00
04/04/02	7.3	1670	131	119	0.50	170	1.00
04/08/02	7.4	1400	157	128	0.30	180	1.00
4/22/02*	7.7	1370	437	126	< 0.1	181	1.40
04/29/02	8.0	1480	449	122	< 0.1	174	1.40
05/06/02	7.6	1480	434	120	< 0.1	173	1.40
05/13/02			509	118	< 0.1	171	1.40
05/20/02	7.9	1500	601	125	0.10	183	1.40
05/28/02	7.8	1520	615	121	< 0.1	178	1.40

Table A3.3. Drainage quality data for sugar beets column (2).

* Flow was increased to 1.4 mL/min on 17 April 2002.

Column was discontinued on 3 June 2002.

Date	pH	Conductivity	SO ₄	Ca	Fe	Mg	Flow
		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	6.1	3000	470				1.00
02/14/02	6.0	2180	612	159	1300	165	1.00
02/18/02	5.7	2600	661	141	1100	168	1.00
02/21/02	6.2	2340	686	144	650	197	1.00
02/25/02	6.4	1400	131	137	250	166	1.00
02/28/02	6.6	1630	17	106	160	169	1.00
03/04/02	6.3	1420	15	101	190	180	1.00
03/07/02	6.5	1410	17	91	210	170	1.00
03/11/02	6.5	1430	69	69	150	138	1.00
03/14/02	6.3	1050	5	73	140	155	1.00
03/18/02	6.8	1350	70	59	53	146	1.00
03/21/02	7.3	1410	86	55	19	147	1.00
03/25/02	7.7	100	133	48	1.8	132	1.00
03/28/02	8.0	1250	116	49	0.10	137	1.00
04/01/02	8.2	1380	169	40	0.10	140	1.00
04/04/02	8.4	1230	165	37	< 0.1	130	1.00
04/08/02	8.2	1090	303	45	0.10	131	1.00

Table A3.4. Drainage quality data for sugar beets + iron column (3).

Column was discontinued on 18 April 2002.

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	Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	02/11/02	5.6	1210	808	141	99	112	1.90
	02/14/02	5.8	1060	787	126	120	117	1.90
	02/18/02	5.7	1460	759	95	100	131	1.90
	02/21/02	6.0	1560	768	85	94	143	1.90
	02/25/02	6.1	1170	744	72	86	151	1.90
	02/28/02	6.2	1400	697	66	81	159	1.90
•	03/04/02	6.1	1350	766	63	65	174	1.90
	03/07/02	6.2	1280	742	65	56	177	1.90
	03/11/02	6.4	1490	776	76	48	186	1.90
	03/14/02	6.4	1090	755	83	42	190	1.90
	03/18/02	6.6	1500	732	93	37	188	1.90
· .	03/21/02	6.7	1570	733	94	26	189	1.90
	03/25/02	6.7	1170	692	93	6.0	177	1.90
	03/28/02	6.7	1430	735	106	12	193	1.90
	04/01/02	6.8	1620	726	110	10	189	1.90
	04/04/02	7.0	1390	744	116	7.8	192	1.90
•	04/08/02	6.8	1320	717	120	5.9	194	1.90

Table A3.5. Drainage quality data for peat column (4).

Column was discontinued on 18 April 2002.

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	Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
	санана. По во селото селото По селото село		(µS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	02/11/02	5.6	1140	406	122	180	96	1.65
	02/14/02	5.5	1170	323	128	210	119	1.65
	02/18/02	6.0	1390	166	90	120	128	1.65
	02/21/02	6.2	1240	8	57	83	109	1.65
	02/25/02	6.3	1010	18	48	64	115	1.65
	02/28/02	6.4	1210	16	47	51	126	1.65
	03/04/02	6.5	962	17	52	41	139	1.65
	03/07/02	6.5	1160	32	55	43	152	1.65
÷.	03/11/02	6.9	1380	17	58	25	163	1.65
	03/14/02	6.7	1070	25	61	14	165	1.65
	03/18/02	7.1	1410	11	70	12	154	1.65
	03/21/02	7.1	1480	32	68	14	159	1.65
	03/25/02	7.1	1160	10	61	5.6	137	1.65
	03/28/02	7.2	1320	20	70	5.7	164	1.65
	04/01/02	7.2	1460	22	70	5.3	162	1.65
	04/04/02	7.5	1400	39	76	3.5	169	1.65
•	04/08/02	7.5	1230	14	81	1.6	173	1.65

Table A3.6. Drainage quality data for the peat + ethanol column (5).

Column was discontinued on 18 April 2002.

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Date	pH	Conductivity	SO_4	Ca	Fe	Mg	Flow
· · · · · · · · · · · · · · · · · · ·		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	5.9	1080	683	69	210	83	1.80
02/14/02	6.0	1110	710	57	240	114	1.80
02/18/02	6.1	1420	721	49	160	140	1.80
02/21/02	6.4	1330	731	46	130	155	1.80
02/25/02	6.4	1250	740	48	100	163	1.80
02/28/02	6.6	1310	687	55	100	173	1.80
03/04/02	6.3	1430	750	72	74	175	1.80
03/07/02	6.7	1350	721	76	65	176	1.80
03/11/02	6.7	1430	730	83	57	177	1.80
03/14/02	6.7	1140	718	84	26	178	1.80
03/18/02	6.9	1500	772	98	34	184	1.80
03/21/02	7.0	1580	745	97	25	185	1.80
03/25/02	7.0	1220	780	95	1.4	176	1.80
03/28/02	7.1	1460	757	102	1.2	187	1.80
04/01/02	7.1	1610	726	102	1.1	183	1.80
04/04/02	7.3	1500	706	104	0.40	185	1.80
04/08/02	7.2	1340	773	110	3.2	193	1.80

Table A3.7. Drainage quality data for the peat + iron column (6).

Column was discontinued on 18 April 2002.
Date	pH	Conductivity	SO ₄	Ca	Fe	Mg	Flow
		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	4.3	1940	831	402	500	267	2.00
02/14/02	4.7	1740	785	279	260	251	2.00
02/18/02	4.7	2130	780	317	200	273	2.00
02/21/02	4.7	2020	718	301	180	269	2.00
02/25/02	4.6	1640	684	264	200	254	2.00
02/28/02	4.7	1850	535	221	200	238	2.00
03/04/02	4.7	1730	431	191	170	229	2.00
03/07/02	4.9	1480	248	151	120	211	2.00
03/11/02	5.3	1650	201	117	73	206	2.00
03/14/02	5.6	1090	289	104	79	208	2.00
03/18/02	5.9	1510	369	106	61	205	2.00
03/21/02	5.9	1510	484	106	52	197	2.00
03/25/02	6.1	1200	455	81	1	181	2.00
03/28/02	6.1	1440	324	71	1	194	2.00
04/01/02	6.2	1590	131	91	7	191	2.00
04/04/02	6.5	1490	95	105	5	187	2.00
04/08/02	6.7	1330	42	119	7	188	2.00
4/22/02*	7.3	1130	173	119	< 0.1	174	2.50
04/29/02	7.8	1280	103	121	< 0.1	172	2.50
05/06/02	7.7	1220	62	114	< 0.1	159	2.50
05/13/02			99	111	< 0.1	156	2.50
05/20/02	7.9	1260	142	118	< 0.1	168	2.50
05/28/02	8	1290	112	116	< 0.1	160	2.50
06/03/02	7.7	1380	104	111	< 0.1	159	2.50
06/24/02	7.9	1420	170	115	0.2	165	2.50
07/09/02	7.6	1350	192	107	0.1	161	2.50
08/12/02	7.6	1750	292	108	0.1	159	2.50
09/16/02	7.8	1490	451	110	< 0.1	160	2.50
09/23/02	7.8	1500	514	116	< 0.1	167	2.50
09/30/02	7.8	1610	542	118	< 0.1	166	2.50
11/04/02	7.8	1550	482	119	< 0.1	164	2.50
11/18/02	7.7	1380	557	124	< 0.1	169	2.50
11/25/02	7.6	1540	565	121	< 0.1	167	2.50

Table A3.8. Drainage quality data for the sawdust, manure, corn column (8).

* Flow was increased to 2.5 mL/min on 17 April 2002.

Column was discontinued on 25 November 2002.

	Date	pH	Conductivity	SO_4	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	02/11/02	5.9	1350	566	181	18	180	2.03
	02/14/02	6.1	1370	560	184	30	197	2.03
	02/18/02	6.4	1570	341	143	4.4	194	2.03
	02/21/02	6.6	1650	300	132	9.8	183	2.03
	02/25/02	7.0	1310	141	107	1.5	165	2.03
	02/28/02	7.0	1590	68	117	3.2	175	2.03
	03/04/02	7.0	1550	164	121	3.1	175	2.03
2	03/07/02	7.2	1460	189	118	0.7	174	2.03
	03/11/02	7.2	1630	227	124	0.5	182	2.03
	03/14/02	7.1	1200	142	119	1.7	178	2.03
	03/18/02	7.2	1570	49	113	0.4	165	2.03
	03/21/02	7.3	1660	95	135	4.2	171	2.03
	03/25/02	7.3	1310	112	100	0.40	151	2.03
	03/28/02	7.6	1470	118	119	0.60	180	2.03
	04/01/02	7.5	1620	81	115	0.30	172	2.03
	04/04/02	7.8	1530	170	119	0.10	176	2.03
·.	04/08/02	7.6	1310	181	125	0.20	185	2.03
	4/22/02*	7.6	1260	447	119	< 0.1	179	2.50
	04/29/02	7.9	1340	413	119	< 0.1	177	2.50
	05/06/02	7.6	1410	400	116	<0.1	169	2.50
	05/13/02			410	111	< 0.1	164	2.50
	05/20/02	7.6	1280	411	117	< 0.1	174	2.50
	05/28/02	7.8	1260	340	114	< 0.1	167	2.50
	07/15/02	7.8	1570	374	118	0.2	179	2.50
	09/30/02	8	1590	549	117	< 0.1	166	2.50
	11/04/02	7.9	1510	509	122	< 0.1	168	2.50
	11/18/02	7.8	1360	518	125	< 0.1	169	2.50
		•	and the second					

Table A3.9. Drainage quality data for the sawdust, manure, hay column (9).

* Flow was increased to 2.5 mL/min on 17 April 2002.

Column was discontinued on 18 November 2002.

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	Date	pH	Conductivity	SO ₄	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	02/11/02	5.5	2220	758	240	8.5	201	2.03
	02/14/02	5.8	2240	782	240	0.8	202	2.03
	02/18/02	6.2	2860	167	132	28	157	2.03
	02/21/02	6.2	2870	46	104	15	150	2.03
	02/25/02	6.4	2310	88	107	4.0	170	2.03
	02/28/02	6.5	2520	92	130	2.0	201	2.03
	03/04/02	6.5	2130	151	142	0.80	198	2.03
	03/07/02	6.4	1880	127	165	0.80	213	2.03
	03/11/02	6.4	1920	118	173	0.80	204	2.03
	03/14/02	6.2	1340	101	175	1.4	201	2.03
÷.	03/18/02	6.5	1740	23	157	1.9	183	2.03
· . · ·	03/21/02	6.5	1590	18	117	0.90	135	2.03
	03/25/02	6.6	1360	17	105	2.3	146	2.03
	03/28/02	6.8	1450	46	121 .	1.4	180	2.03
	04/01/02	6.8	1580	5	123	0.80	184	2.03
	04/04/02	7.0	1550	12	121	1.4	181	2.03
	04/08/02	7.0	1390	3	126	2.2	191	2.03
	4/22/02*	7.0	1270	52	108	< 0.1	164	2.50
	04/29/02	7.8	1250	22	122	< 0.1	180	2.50
	05/06/02	7.3	1400	3	121	< 0.1	169	2.50
	05/13/02			10	111	< 0.1	159	2.50

Table A3.10. Drainage quality data for the sawdust, biosolids, hay column (10).

* Flow was increased to 2.5 mL/min on 17 April 2002.

Column was discontinued on 20 May 2002.

Date	pH	Conductivity	SO ₄	Ca	Fe	Mg	Flow
		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
02/11/02	7.1	1300	835	126	4.6	174	2.00
02/14/02	7.4	1300	766	129	< 0.1	178	2.00
02/18/02	7.6	1540	662	112	2.4	174	2.00
02/21/02	7.7	1560	714	114	0.20	179	2.00
02/25/02	8.0	1330	704	108	0.10	179	2.00
02/28/02	8.1	1620	678	104	0.10	179	2.00
03/04/02	8.1	1380	641	89	0.60	170	2.00
03/07/02	8.3	1270	585	74	0.50	159	2.00
03/14/02	8.6	1070	603	82	< 0.1	152	2.00
03/18/02	7.9	1330	512	78	0.20	141	2.00
03/21/02	8.7	1280	521	67	0.20	135	2.00
03/25/02	8.8	1160	590	68	0.10	153	2.00
03/28/02	8.8	1180	616	70	< 0.1	165	2.00
04/01/02	8.7	1290	615	66	< 0.1	167	2.00
04/04/02	8.7	1280	612	68	0.10	172	2.00
04/08/02	8.7	1200	640	67	< 0.1	181	2.00
4/22/02*	8.9	1170	694	73	< 0.1	192	2.50
04/29/02	8.7	1240	653	70	< 0.1	187	2.50
05/06/02	8.7	1360	641	66	< 0.1	178	2.50
05/13/02	- * -		590	59	< 0.1	170	2.50

Table A3.11. Drainage quality data for the rod mill feed + iron column (11).

* Flow was increased to 2.5 mL/min.

Column was discontinued on 20 May 2002.

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	Date	pН	Conductivity	SO ₄	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	05/17/02	6.9	1700	716	205	2.0	192	2.50
	05/20/02	6.3	1590	713	156	4.8	188	2.50
	05/28/02	6.4	1440	539	126	16	178	2.50
•	06/03/02	6.6	1340	341	106	18	160	2.50
	06/10/02	6.7	1680	319	107	12	161	2.50
	06/17/02	6.9	1710	371	111	. 14	167	2.50
	06/24/02	6.7	1710	329	113	13	172	2.50
	07/01/02	6.7	1890	316	112	5.8	171	2.50
	07/09/02	6.5	1320	257	103	4.8	156	2.50
	07/15/02	6.7	1670	213	105	16	156	2.50
	07/22/02	7	1510	55	108	18	158	2,50
	07/29/02	6.7	1560	323	109	7.6	159	2.50
	08/05/02	7.1	1710	253	110	17	160	2.50
	08/12/02	6.6	1620	79	109	10	156	2.50
	8/26/02*	6.5	1560	299	109	21	156	2.50
	09/09/02	7.2	1370	244	95	2.7	144	2.50
	09/16/02	7.6	1470	476	102	0.2	151	2.50
	09/23/02	7.7	1480	247	104	0.1	155	2.50
	09/30/02	8	1640	513	111	< 0.1	159	2.50
	10/07/02	8.1	1650	94	85	< 0.1	125	2.50
	10/14/02	8.1	1440	495	111	< 0.1	158	2.50
	10/28/02	8.1	1330	176	102	< 0.1	145	2.50
	11/04/02	7.9	1580	446	115	0.2	157	2.50
	11/11/02	7.9	1600	532	119	< 0.1	162	2.50
	11/18/02	7.8	1310	367	112	< 0.1	155	2.50
	11/25/02	7.9	1540	459	116	< 0.1	161	2.50
	12/9/02**	6.9	1570	403	147	12	167	2.50
	12/16/02	6.9	1660	411	125	7.6	165	2.50
• .	12/23/02	7	1790	640	128	7.6	178	2.50

Table A3.12. Drainage quality data for the rod mill feed + molasses column (7).

* Feed changed to methanol on 8/26/02.

**Feed changed back to molasses on 12/9/02.

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	Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	02/11/02	6.3	1290	360	212	38	207	1.90
•	02/14/02	7.1	1270	444	212	32	211	1.90
	02/18/02	7.4	1440	12	113	3.6	169	1.90
	02/21/02	7.4	1470	2	110	1.6	169	1.90
	02/25/02	7.4	1280	14	109	2.8	169	1.90
	02/28/02	7.6	1520	15	113	1.2	175	1.90
	03/04/02	7.5	1430	10 .	111	1.4	174	1.90
	03/07/02	7.5	1380	7	111	2.6	173	1.90
	03/11/02	7.7	1510	2	108	1.4	171	1.90
	03/14/02	7.7	1190	15	116	0.20	175	1.90
	03/18/02	7.6	1570	136	120	0.80	179	1.90
	03/21/02	7.6	1360	4	118	1.3	172	1.90
	03/25/02	7.7	1130	10	99	0.40	147	1.90
	03/28/02	7.6	1130	1	109	0.80	169	1.90
	04/01/02	7.7	1250	44	111	0.40	173	1.90
	04/04/02	7.9	1350	. 114	129	0.50	190	1.90
	04/08/02	7.6	1120	11	113	0.90	172	1.90
	4/22/02*	7.9	1030	. 11	104	< 0.1	165	2.50
	04/29/02	8.1	1180	12	107	< 0.1	168	2.50
	05/06/02	8.0	1320	25	102	< 0.1	156	2.50
	05/13/02			18	95	< 0.1	150	2.50
	05/20/02	7.9	1200	14	99	0.20	154	2.50
	05/28/02	7.9	1220	204	108	< 0.1	161	2.50
	06/03/02	7.7	1280	5	97	0.3	150	2.50
	6/10/02**	7.9	1510	- 1	99	0.1	151	2.50
	06/17/02	8.2	1400	12	99	< 0.1	147	2.50
	06/24/02	8.3	1240	6	95	< 0.1	152	2.50
	07/01/02	8.2	1300	22	93	0.1	158	2.50
	07/15/02	8.2	1240	29	91	0.1	150	2.50
÷.,	7/29/02***	7.5	1720	690	191	3.9	184	2.50
•	08/05/02	7.1	1710	383	155	14	154	2.50
	08/12/02	6.6	1730	251	124	14	138	2.50
	08/26/02	7.9	1290	22.	87	< 0.1	139	2.50
	09/05/02	7.7	1290	8	84	0.3	131	2.50
	09/09/02	8.1	1300	6	89	< 0.1	144	2.50
	09/16/02	8.1	1320	11	89	< 0.1	143	2.50

Table A3.13. Drainage quality data for the rod mill feet + ethanol column (12)

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Date	pH	Conductivity	SO_4	Ca	Fe	Mg	Flow
		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
09/23/02	8.1	1290	12	85	< 0.1	143	2.50
09/30/02	8.1	1360	13	86	< 0.1	146	2.50
10/07/02	8.2	1370	7	86	< 0.1	150	2.50
10/14/02	8.5	1170	4	97	< 0.1	159	2.50
10/28/02	8.3	1200	75	92	< 0.1	157	2.50
11/11/02	7.7	1800	371	159	0.4	192	2.50
11/18/02	7.6	1230	13	102	< 0.1	134	2.50
11/25/02	7.8	1650	105	118	0.1	161	2.50
12/09/02	7.8	1570	377	153	0.1	204	2.50
12/16/02	7.5	1660	349	167	0.1	182	2.50
12/18/02			12				2.50
12/23/02	8	1450	36	111	0.1	146	2.50
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Table A3.13. Drainage quality data for the rod mill feed + ethanol column (12).

* Flow was increased to 2.5 mL/min on 17 April 2002.

** Feed chemistry changed on 6/10/02.

***Column siphoned, caused disruption of column; data in italics represents period of effected data.

Date	pН	Conductivity	SO_4	Ca	Fe	Mg	Flow
· · · ·		$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
05/17/02	7.3	1390	702	131	< 0.1	168	2.50
05/20/02	6.4	1410	598	127	2.9	182	2.50
05/28/02	7.5	1360	96	101	0.4	160	2.50
06/03/02	7.7	1570	16	96	1.1	155	2.50
6/10/02*	7.9	1620	16	99	0.5	162	2.50
06/17/02	7.9	1580	155	99	0.1	158	2.50
06/24/02	8.2	1580	146	91	< 0.1	159	2.50
07/01/02	8.1	1570	146	88	< 0.1	161	2.50
07/09/02	8.2	1060	60	75	< 0.1	142	2.50
07/15/02	8.1	1380	19	72	< 0.1	146	2.50
07/22/02	8.1	1180	9	65	< 0.1	146	2.50
07/29/02	8.1	1200	9	54	< 0.1	136	2.50
08/05/02	8.2	1320	. 7	50	< 0.1	149	2.50
08/12/02	8	1450	1	53	< 0.1	142	2.50
08/26/02	8.3	1290	52	49	< 0.1	141	2.50
09/05/02	8.1	1280	6	50	< 0.1	138	2.50
09/09/02	8.1	1260	10	52	< 0.1	146	2.50
09/23/02	8, .	1270	0.4	48	0.2	141	2.50
09/30/02	8	1500	7	48	0.1	153	2.50
10/07/02	8.1	1750	43	58	0.2	166	2.50
10/14/02	8.1	1450	12	56	0.1	159	2.50
10/28/02	8.1	1250	16	53	0.1	140	2.50
11/04/02	7.6	1750	171	107	2.1	177	2.50
11/11/02	7.5	1700	16	84	1.1	174	2.50
11/18/02	7.6	1160	28	60	< 0.1	143	2.50
11/25/02	8.1	1300	44	75	< 0.1	144	2.50
12/09/02	8.1	1350	15	52	< 0.1	147	2.50
12/16/02	8.1	1350	9	51	< 0.1	147	2.50
12/23/02	8.3	1480	37	47	< 0.1	158	2.50

Table A3.14. Drainage quality data for the oxidized ore, coarse tailings, ethanol column (5A).

*Feed chemistry changed on 6/10/02.

	Date	pH	Conductivity	SO_4	Ca	Fe	Mg	Flow
			$(\mu S/cm)$	(mg/L)	(mg/L)	(mg/L)	(mg/L)	mL/min
	05/17/02	6.7	1610	712	167	4.1	188	2.50
	05/20/02	6.3	1640	717	161	2.1	192	2.50
	05/28/02	6.8	1410	310	102	0.5	160	2.50
	06/03/02	6.9	1580	27	95	15	149	2.50
	06/10/02	7	1800	1	95	8.3	148	2.50
	06/17/02	7.1	1770	2	94	12	150	2.50
	06/24/02	7.1	1690	1	98	10	154	2.50
	07/01/02	7.2	1880	5	93	12	156	2.50
	07/09/02	7.2	1410	2	90	4.5	157	2.50
	07/15/02	7.1	1700	2	77	15	140	2.50
	07/22/02	7.2	1530	4	95	7	152	2.50
	07/29/02	6.9	1520	156	99	4.8	150	2.50
	08/05/02	7.7	1580	2	93	9.5	147	2.50
	08/12/02	6.9	1580	44	97	14	141	2.50
	8/26/02*	6.8	1540	13	102	18	151	2.50
	09/05/02	6.8	1470	428	94	10	139	2.50
· .	09/09/02	7.3	1380	219	92	7.6	144	2.50
	09/23/02	7.3	1500	407	106	2.7	160	2.50
	09/30/02	7.5	1620	3,13	101	1.3	149	2.50
	10/07/02	7.7	1690	281	105	0.5	153	2.50
	10/14/02	7.9	1500	447	109	0.2	158	2.50
	10/28/02	7.8	1370	167	100	0.1	148	2.50
1	11/04/02	7.9	1520	115	97	0.1	145	2.50
	11/11/02	7.7	1570	161	105	0.2	152	2.50
	11/18/02	7.6	1300	268	111	< 0.1	155	2.50
	11/25/02	7.6	1490	309	118	0.6	164	2.50
	12/9/02**	7.1	1690	414	150	9.6	166	2.50
	12/16/02	7.3	1680	198	126	1	157	2.50
	12/23/02	7.2	1810	598	128	7.5	177	2.50

Table A3.15. Drainage quality data for the oxidized ore, coarse tailings, molasses column (6A).

* Feed changed to methanol on 8/26/02.

** Feed changed back to molasses on 12/9/02.

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Column	Date	Anomalous Value	Typical Value	Comment
5A	11/4/02	$SO_4 = 171$	<20	Nothing unusual recorded
6A	7/29/02	SO ₄ = 156	<10	Nothing unusual recorded
12	5/28/02	$SO_4 = 204$	<20	Nothing unusual recorded
12	7/29/02	SO ₄ = 690	20-25	Column siphoned. Column operation and performance disrupted. Column did not return to presiphon
				performance until 8/26/02.
12	8/5/02	$SO_4 = 383$	20-25	Column performance
12	8/12/02	SO ₄ = 251	20-25	Column performance affected by siphon.
12	11/11/02	SO ₄ = 371	20-25	column. May have been partial siphon of column.
12	7/16/02	TOC = 8.8	~100	Calculated and other measured values suggest the correct value should be about 100 mg/L.

Table A 3.16 Anomalous Data

Anomalous data was not used in the calculation of the sulfate removal rates. Anomalous values are shown in bold in the data tables.

APPENDIX 4

Miscellaneous Notes and Calculations

Attachment A 4.1.	Flow issues
Attachment A 4.2.	Iron requirements to tie up sulfide
Attachment A 4.3.	Miscellaneous calculations
Attachment A 4.4.	Sulfate removal
Attachment A 4.5.	Feed Solutions – Calculations of carbon in feed
Attachment A 4. 6.	Effect of E _h on reduction process
Attachment A 4.7.	Molasses information
Table A 4.1.	Substrate costs
Table A 4.2.	Organic solutions used in column study, 2002
Table A 4.3.	Excess carbon – calculated vs. measured; July 16, 2002
Table A 4.4.	Iron content in organic substrate
Attachment A 4.8.	Sulfur retained in column 12: $2/18/02 - 11/25/02$

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Attachment A 4.1. Flow Issues

This attachment provides an analysis of the effect of the sulfate reduction on the treatment system size and residence time required to remove a fixed amount of sulfate.

The assumptions are that the input sulfate concentration is 1200 mg/L and that a reduction of 50% in sulfate (effluent = 600 mg/L) would be acceptable.

The specific outflow requirement will be determined by an ongoing EIS. If a lower effluent concentration is required, a larger system would be needed.

The purpose of this example is to relate the system size for a specific treatment design to the rate of sulfate reduction.

Assumptions: Input flow Input concentration Output concentration 5000 gal/min 1200 mg/L 600 mg/L

Desired sulfate reduction: 5000 gal/min x 1440 min/day x 3.785 L/gal x (1200-600 mg/L) 96 mg/mmole

 $1.7 \ge 10^8$ mmole/day

	<u></u>			
Sulfate	Volume	Depth of	Area	Residence Time
Reduction Rate	Required (m^3)	Substrate (m)	(ha) (acre)	(days)
(mmoles/m ³ /day)				
300	$5.7 \ge 10^5$	1	57 140	10 1/2
1000	$1.7 \ge 10^5$	1	17 42	3
2000	$0.85 \ge 10^5$	1	8.5 21	1 1/2

Table 1. Treatment system size.

 $1 \text{ ha} = 10,000 \text{ m}^2$

1 ha = 2.47 acres

Residence time is based on the pore volume of the bed and is calculated assuming 50% porosity.

To transmit 5000 gpm through a vertical bed with one meter of substrate and with one foot of water over the substrate would require a permeability on the order of 10^{-3} cm/sec. (This value would be comparable to sand).

In a field setting:

Assume a reaction rate of 2000 mmoles/m³/day and use data from Table 1

$$Q = 5000 \text{ gal/min}$$

 $A = 8.5 \times 10^4 \text{ m}^2$

Bed depth = 1 m Water depth above bed = 1/3 m

$$\Delta H/L = 1/3 = .33$$

To transmit this flow the requirements would be the following:

$$K_{h} = \underbrace{Q}_{A \Delta H/L} = \underbrace{5000 \text{ gal x } 3.785 \text{ L/gal x } 1000 \text{ cm}^{3}/\text{L}}_{8.5 \text{ x } 10^{4} \text{ m}^{2} \text{ x } (100 \text{ cm/m})^{2} \text{ x } .33 \text{ x } 60 \text{ sec/min}}$$

$$K_{h} = 1.1 \text{ x } 10^{-3} \text{m cm/sec}$$

If the bed depth was increased to 2 m, the area would have to be reduced by a factor of 2 and the depth of water to 2/3 m.

 K_h required = 2.2 x 10⁻³ cm/sec

By increasing the depth of water above the bed, the gradient Δ H/L remains constant. If the water depth was maintained at 1/3 m would need a $K_h = 4.4 \times 10^{-3}$ cm/sec.

This hydraulic conductivity value is similar to the conductivity at the Soudan columns.

Head calculations for the Soudan columns (6" diameter, 12" substrate, 2" water above substrate.)

These columns have an organic substrate, with $\sim 25\%$ by weight limestone. Much less permeable than U.S. Steel columns.

$$Q = 2 \text{ ml/min}$$

$$A = \pi (3 \text{ in } x \text{ 2.54 cm/in})^2 = 182 \text{ cm}^2$$

$$\underline{AH} = \underline{2''} = .167$$

$$L = \underline{12''}$$

$$K_h = \underline{2 \text{ ml/min}}_{182 \text{ cm}^2 \text{ x .167 x .60 sec/min}} = 1.1 \text{ x } 10^{-3} \text{ cm/sec}$$

These columns have run with this head for about 5 years. However, since K_h may decrease with time should include safety factor.

 K_h lab minimum 10^{-3} cm/sec K_h field 10^{-1} to 10^{-2} cm/sec

Vertical beds are more efficient at transmitting flow than horizontal ones due to the ability to increase the head and larger cross section areas.

For example:

Horizontal bed

A bed 100' wide x 20' deep with a slope of 3% (3' elevation drop in 100' bed) and a permeability of 10^{-1} cm/sec, could transmit only.

Q

K A H/L

 $\frac{10^{-1} \text{ cm/sec x } 2000 \text{ ft}^2 \text{ x } .03 \text{ x } 60 \text{ sec/min x } 7.48 \text{ gal/ ft}^3}{30.48 \text{ cm/ft}}$

88 gal/min

Vertical bed

In contrast a 100' wide and 100' long bed with 6' of media and a 1' head of water could transmit.

 $\frac{10^{-1} \text{ cm/sec x 10000 ft}^2 \text{ x .17 x 60 sec/min x 7.48 gal/ft}^3}{30.48 \text{ cm/ft}}$

2500 gal/min

In the horizontal bed the residence time would be.

Bed volume = 50% porosity (assumed) x 100 x 20 x 100' x 7.48 gal/ ft^3 = 750,000 gallons At an input flow of 88 gpm

Residence time = bed volume/flow = 8500 minutes ~ 6 days

If permeability was on the order of 10^0 cm/sec could transmit 10 times more flow, or about 880 gal/min, but this would reduce residence time to 0.6 days if increased length of bed to 200' would increase residence time to 1.2 days.

Permeability of lab columns appear to be controlled by something other than the substrate since the values were all very similar, could be tubing, or screened material in bottom of column, likely that the permeability of the rod mill feed is at least 10° cm/sec (USS ran some calculations with mathematical formulas (designed for sand type particles), and got about 10° cm/sec). Subsequent testing showed that permeability was being controlled by outlet and not media. Estimate of outflow concentration, assume year round average reaction rate of 300 mmoles/m³/day.

<u>Q gal/min x (C in - C out) mg/L x 3.785 L/min x 1440 min/day</u> = 300 mmoles/m³/day 96 mg/mmole x 1,500,000 gal x .003785 m³/ gal

If input rate is 880 gal/min then,

(C in - C out) = 34 mg/L

If the input concentration is around 1000 mg/L then to reduce concentration to 500 mg/L, would either need to reduce flow, or increase bed size, or increase reaction rates.

If the average rate could be maintained at 1500 mmoles/m³/day, then the change in sulfate would increase from 34 mg/L to 170 mg/L, not enough to approach the water quality value of 250 mg/L.

In general, for this design the bed size will be determined by reaction kinetics and not permeability or flow issues.

If the input rate was 88 gal/min (which would correspond to a permeability of 10^{-1} cm/sec) and the average reaction rate was 300 mmole/m³/day, then the change in concentration would be 340 mg/L.

Attachment A 4.2. Iron requirements to tie up sulfide.

The goal is to provide enough iron to tie up all sulfide generated as iron sulfide <u>within the</u> <u>treatment bed</u>.

It does not appear that there is sufficient iron release from the rod mill feed, since iron concentrations in many of the columns are less than 1 mg/L. This could be due to the form of the iron and/or the surface area. Would recommend changing the inorganic media to provide more ferric iron and iron hydroxides. The literature suggests that ferric forms particularily those present in the hydroxides may be more available to iron reducing bacteria.

Potential sources of ferric iron:

Pellet fines (~ 65% ferric iron).

Natural ore, comparable to that found in the Auburn pit (this contains iron hydroxides, limonite and goethite) (55% ferric iron).

Oxidized taconite typically distinguished by color (oxidized is red), may be about 30% total iron with about 97% of the iron in the ferric form.

Coarse tailings (around 15-20% total iron).

If we assume that during the summer we could achieve a reaction rate of:

 $\frac{1000 \text{ mmoles}}{\text{m}^3/\text{day}}$ of SO₄

which is one-half the maximum lab rate observed to date. Then if the maximum rate occurs at 20° C centigrade and we assume the average year around temperature is 10° , then the average rate would be about a factor of 3 times slower or:

 $\frac{300 \text{ mmoles}}{\text{m}^3/\text{day}} \text{ of } S0_4$

This generates $\frac{300 \text{ mmoles}}{\text{m}^3/\text{day}}$ of S⁻²

to tie up as FeS it would require $\frac{300 \text{ mmoles}}{\text{m}^3/\text{day}}$ Fe⁺²

So in one cubic meter of substrate, the following would be required.

300 mmoles x 56 mg Fe x 365 days/yr x $10^{-6} \text{ kg/mg} = 6.1 \text{ kg Fe required/year}$ mmole

Or for a 20-year lifetime, 120 kg iron/m³ would be required.

Based on laboratory measurements, rod mill feed had a density of 1.7 kg/L, or 1700 kg/m³. So inorganic media should contain at least 10% ferric iron. (This assumes that all inorganic media would have a density similar to the rod mill feed). Rod mill feed has 12.2% ferric iron so there would be 207 kg Fe⁺³/m³ of substrate.

Attachment A4.3. Miscellaneous calculations.

Carbon requirements

Using the simple model of the sulfate reduction reaction $2CH_2O + SO_4 = H_2S + 2 HCO_3$

Need two moles of carbon for each mole of S reduced.

So per liter of input water would be:

 $\Delta \text{ SO}_4 = \underline{600 \text{ mg/L}}_{96 \text{ mg/mmoles}} = 6.25 \text{ mmoles/L}$

Need 12.5 mmoles C and if all added C comes from added carbon.

ethanol - $C_2 H_5 OH$ MW = 46

 $% C = \frac{24}{46} = .52$

100% ethanol = .79 gm/cm³ x $\underline{.52}$ x 1000 mg/gm = $\underline{34 \text{ mmole}}$ (density at 20°C $\underline{12 \text{ mg}}$ cm³ Perry's Handbook) mmole

So, to provide 12.5 mmoles would need $\sim 0.4 \text{ cm}^3$ of 100% ethanol for liter of feed. (the actual value was 0.34, since this couldn't be easily measured rounded up to 0.4, so will have excess)

If have 1200 mg/L could need ~ 0.8 mL per liter (actually would need 0.68)

Purchased alcohol contained 63% ethanol.

<u>.8 mL ethanol</u> .63 <u>mL ethanol</u> mL solution

 $\sim 1.3 \text{ mL}$ alcohol

Currently, are adding 1.3 mL alcohol per liter of feed for columns that are receiving ethanol. Therefore, are adding:

1.3 mL solution x .63 mL ethanol* x .79 gm ethanol x .52 gm C = .336 gm C mL solution mL ethanol gm ethanol

*assume 63% by volume

This would correspond to an input TOC of ~ 336 mg/L for each liter input = 336 mg C = 28 mmoles, which would be enough C to reduce 14 mmoles of sulfate = 1344 mg/L.

If consume all of SO₄ in input ~ $\frac{818}{96}$ (avg of first 7 values) = 8.5 mmoles

would require 17 mmole C = 204 mg C.

So at the current sulfate input concentration would have about 132 mg C in excess.

Measured TOC from Column 12 (rod mill feed + ethanol) = 122 mg/L

Assuming tailings basin water has low levels of TOC, are consuming ethanol at about the stoichometric ratio -- very efficient.

Attachment A 4.4. Sulfate Removal

<u>Rate</u>

The overall removal rate is calculated from the rate of change in sulfate concentration in the column.

 $\frac{(C \text{ in } - C \text{ out}) (mg/L) \times \text{daily flow } (L \text{ day})}{\text{Total volume of column } (m)^3 \times 96 \text{ mg/mmole}} = \text{rate } \frac{(\text{mmoles})}{\text{m}^3 \text{day}}$

Assumptions:

- 1. The change in sulfate concentration is due only to sulfate reduction.
- 2. There is no sulfate contribution from any of the substrates.
- 3. The total volume of the column is equal to the original column volume. (The sugar beet columns settled up to about 50%)

For the original columns all the data was used to calculate the initial rates for the period 2/8 - 8/26/02 (Table 9 in the report).

For the new column (5A, 6A and 7) and for the long term columns (8, 9 and 12) rates were calculated for periods of constant feed or flow on outflow concentrations (Table A 5. 2).

This eliminated start up conditions when rates were not optimum and eliminated periods when column conditions changed drastically (e.g. the siphon in column 12).

By eliminating these periods, a better comparison of rates between feed source and as a function of time and flow could be made.

Mass of Sulfate removed in column:

The typical procedures for calculating input and output mass would be to compute the daily input and output masses from measured flow rates and concentration. Values for the days between sample points are estimated as the average of the measured values for the beginning and end of the period. This calculation requires measurement of flow and water quality.

Since actual flow measurements were periodic and input and output concentrations generally did not show large fluctuations, an estimate based on average values should be reasonably accurate.

The total mass was calculated by using the average removal rate for the periods of uniform operation and using average input and output concentrations during fluctuating conditions.

Total mass = average removal rate (mmoles). X column volumn (m³) x number of days. m^{3} day

Since removal occurred throughout the study even when there was fluctuation or changes in the column, a specific estimate was made for those time periods that were not included in the rate calculations.

The estimate used the average input concentration minus the average output concentration multiplied by total flow during the period.

Time periods and columns when average concentrations used were:

Column	Time Periods
12	7/16 - 8/25/02
7	10/29 - 11/25/02 5/10 - 6/2/02
5A	5/10 - 7/8/02
6A	5/10 - 6/7/02

Attachment A 4.5.

Feed Solutions - Calculations of carbon in feed.

<u>Methanol</u>

100% methanol at 20° has a density of 0.79 gm/ml

CH₃OH	<u>12 gm C</u>
	32 gm methanol

 $\frac{12 \text{ gm C}}{32 \text{ gm methanol}} x \frac{.79 \text{ gm methanol}}{ml} = \frac{.3 \text{ gm C}}{ml}$

Addition rate 0.7 ml methanol/liter of feed.

 $\begin{array}{ccc} 0.7 \text{ ml/L x} & \underline{0.3 \text{ gm C}} & \text{x} & 1,000 \text{ <u>mmole} = 17.5 \text{ mmole/L}} \\ \hline \text{ml 12 gm/mole} & & \text{mol} \end{array}$ </u>

Using a simple model* to reduce one mole of sulfate, requires 2 moles of carbon. Therefore if all carbon consumed could reduce:

8.75 mmole SO_4 x 96 mg/mmole = 840 mg SO_4/L

Ethanol 6/10 – present, 95.2% by volume.

Addition rate 0.6 ml/L feed water.

 $\begin{array}{c} 0.6 \ \underline{\text{ml}} \ x \ .952 \ \underline{\text{ml ethanol}} \ x \ .79 \ \underline{\text{gm ethanol}} \ x \ .52 \ \underline{\text{gm c}} = .235 \ \underline{\text{gm c}} \\ L \ \\ \end{array}$

 $\begin{array}{c} \underline{.235 \text{ gm c}} \ge 1000 \text{ mmole} = 19.6 \text{ mmole} \text{ C} \\ 12 \text{ gm/mole} & \text{mmole} & \text{L} \end{array}$

19.6 mmole C will reduce 9.8 mmole $SO_4 = 940 \text{ mg } SO_4$

* Simple model: $2CH_2 0+SO_4^{-2} \Rightarrow H_2 S+2HCO_3^{-1}$ Note actual use of carbon may be more complex, and the ratio may not be an exact 2:1 ratio. Attachment A 4.6 Effect of E_h on reduction process.

In "Wetlands" by Mitsch and Gosselink on p. 126 a description of what occurs as the E_h of the water decreases.

1) At 400 to 600 my oxygen is still present.

2) At 250 mv nitrate reduction begins. Nitrate is reduced to nitrite and eventually reduced to ammonia and/or nitrogen.

3) At 225 mv manganese reduction begins. Manganic (+4) to is reduced to manganous(+2).

4) At 120 mv iron reduction begins. Ferric is reduced to ferrous - the author gives the following reaction: $Fe(OH)_3 + e^- + 3H^+ - > Fe^+ + 3H_2O$.

5) At -75 mv to -150 mv sulfate reduction begins. Sulfate is reduced to sulfide.

6) At -250 mv carbon is reduced and methane gas is produced $CO_2 + 8e_1 + 8H_{+} -> CH_4 + 2H_2O_2$. This is the reaction that assists in the formation of methyl mercury.

 E_h of the large scale system that will be installed next spring should be tracked. Dropping E_h probes into the monitor wells or having E_h probes installed in each monitor well should give adequate E_h readings. E_h is a good indication of the type of reduction that is occurring in certain areas of the system. E_h readings should be taken on each column that is currently running so that you can get an idea of the E_h values that occur in each column test and relate that to iron and sulfate reduction and possibly methyl mercury production. Maybe E_h in certain areas of the large system can be controlled by purging the system with small amounts of air in certain areas so that we can enhance ferrous production in some areas, sulfide production in other areas and limit methane production in order to limit methyl mercury production.

Attachment A 4.7. Molasses information

General analysis of molasses.

Moisture	20%
Sugars	~60%
Sucrose	~40%
Glucose, fructose, etc.	~20%
Other carbohydrates	2-5%
Protein, amino acids	2.5 – 4-5% (all nitrogenous compounds)
Organic acids	2-7%
Waxes/sterols	0.1-1%
Vitamins	low levels

An analysis of the organic acids (good chelating agents) are as follows: (Percent of Dry Molasses Solids)

Aconitic	1.54
Citric	0.18
Malic	0.12
Oxalic	0.11
Glycolic	0.05
Mesaconic	0.04
Succinic	0.02
Fumaric	trace
Syringic	trace
Tartaric	tropical cane only

It appears that by adding molasses as a food source, nitrogen (amino acids) and chelating agents (organic acids) are both being added which assist in iron dissolution and reduction.

Table A 4.1. Substrate Costs

Substrate	Delivered Cost	Source of Information
Peat	\$12.00/yd	Based on cost to build original peat based pilot system.
Sawdust/hay	\$8.50/yd	Based on costs from other projects at U.S. Steel.
Iron Filings	\$340.00/ton + shipping	Cost of product from Connelly Iron in Chicago, Illinois.
Manure	~ \$10.00/yd	Estimate based on other organic materials purchased by U.S. Steel.

Organic	Dates	Composition	Chemical	Feed	Feed Rate	Maximum
Feed			Additives	Rate		concentration
						of sulfate
			•	mL/L	mmole	reduced
					C/L	(mg/L)
Ethanol	2/08/02 to	63%	3.5%	1.3	28	1340
	6/10/02	ethanol ³	methanol			
			3.5%			
			isopropyl			
Ethanol	6/10/02 to	95.2%	3.8% MIBK	0.6	19.5	940
	11/29/02	ethanol	1% pet. nap. ¹			,
Molasses	5/13/02 to 8/30/02	36.4% TOC	None	0.9	27.3	1310
Molasses ²	11/29/02 to 2/6/03	31.0% TOC	None	0.5	12.9	620
Methanol	8/30/02 to	99.9%	none	0.7	17.5	840
	11/29/02					

Table A 4.2. Organic feed solutions used in column study, 2002.

1. MIBK = methyl isobutyl ketone., pet. nap = petroleum naphthalene

2. This was molasses from a different plant and a different batch than the first molasses. This material had become rancid and was replaced with a new batch in February, 2003.

3. Ethanol percent by volume.

4. Calculated by assuming all the carbon is consumed and used to reduce the sulfate at a 2 moles of carbon per mole of sulfate ratio.

Carbon calculation: for ethanol used chemical formula and assumed only the carbon in the ethanol as available (did not include any carbon from additives)

For molasses used TOC measurements and assumed all carbon was available and could be used by bacteria.

					mmoles	mmoles	•	TOC	
•		Input	Input	Output	SO_4	С	mg	mg in O	utflow
Column	Feed	SO_4	TOC	SO_4	Reduced	Required ²	Consumed	Calculated ⁴	Measured
12	Ethanol	774	234	29	7.8	15.5	186	48	8.8
5A	Ethanol	774	234	19	7.9	15.7	188	46	98.8
6A	Molasses	774	328	2	8.0	16.0	192	136	95.0
7	Molasses	774	328	213	5.8	11.7	140	188	311.0
7	Methanol	683 ³	210	368 ³	3.3	6.6	79	131	NA

Table A4.3. Excess Carbon – Calculated vs. Measured; July 16, 2002

Need data on rate of sulfate reduction as a function of ethanol or TOC concentration.

- 1. TOC calculated from carbon content of feed, for ethanol used only carbon in ethanol and did not include carbon in additives.
- 2. Assume 2 moles of carbon are required for each mole of sulfate reduced.
- 3. Average values for time period methanol was used. No TOC measurements were made.

4. Input TOC as calculated—TOC consumed = Calculated TOC in outflow.

NA = not analyzed

T ' ' '	•		1 / /
Iron content	110	01001010	anhatrota
		ULVALUC	SUDSUALE
THOIL COMPOSIT		OI Sound	Duobuut

Iron in %					
Subsrate	Total Fe	Fe ⁺²	Fe ⁺³		
Rod Mill Feed	30.96	12.23	18.73		
Oxidized Ore	31.39	2.5	28.89		
Coarse Tails	18.25	8.3	9.95		

Attachment A4.8. Sulfur retained in Column 12; 2/8/02 - 11/25/02.

Total sulfate removal for column 12 = 617 grams.

The total amount of sulfur retained in the column = total sulfur removal – mass of sulfide in effluent.

Only 2 samples were analyzed for sulfide (<0.5 mg/L, 4.4 mg/L).

Periodic analyses with lead acetate indicator paper indicated that sulfide varied in the outflow from less than detection limit (no color change, <5 mg/L) to slight color change (5 – 10 mg/L).

If assumed that the average sulfide in the outflow was 5 mg/L, then Mass of sulfur released = total flow through column (L) x average concentration (mg/L) = 978 L x 5 mg/L =4890 mg

at 10 mg/L = 978 L x 10 mg/L = 9780 mg

Total sulfur removed = 617 grams sulfate $\underline{x \ 32 \ gmS}$ 96 gmSO₄

= 206 grams S = 206,000 mg S

% retained (a) 5 mg/L S⁻² in out flow = $\sim 97.5\%$

(a) 10 mg/L S⁻² in out flow = $\sim 95\%$

APPENDIX 5

Experimental Changes, Timeline and Rationale

Attachr	nent.	A	5.1	. Т	imeline

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- Attachment A 5.2. Time periods for sulfate reduction rates
- Attachment A 5.3. Rationale for experimental changes

Attachment A 5.1.	Timeline:
1/23 - 25/02	Columns set-up.
2/01/02	Columns saturated.
2/08/02	Flow into columns begins.
2/11/02	First sample.
3/11/02	Column 11 leaky discharge hose, no sample collected.
4/17/02	Feed rate increased (Column 2: 1 to 1.4 ml/min, Columns 8-12 to 2.5
	mL/min).
4/18/02	Columns 1, 3, 4, 5 and 6 were stopped.
5/6/02	New columns 5A, 6A, and 7 were filled.
5/28/02	High water in Column 12.
6/10/02	Ethanol feed chemistry changed; new feed, 95.4% ethanol, 3.8% MIBK,
	1% pet nap - (new feed rate 0.6 ml/L).
7/29/02	Column 12 had siphoned over the weekend, severe drain.
8/26/02	Switched feed to methanol (Columns 6A and 7) flow rate
	decreased to 0.7 mL/min
9/05/02	No sample on Column 7 due to plumbing problems.
10/14/02	Column 6A high water.
11/04/02	Column 12; no sample could be collected*.
11/25/02	Column 9 stopped.
12/09/02	Convert feed back to molasses (Columns 6A and 7).
12/18/02	Resampled Column 12, wanted to check the elevated SO ₄ value from
	12/16/02.

*Water level was high on Friday, could not get column to flow even by lowering outlet tube. On Monday the column was checked and the water level was below top of substrate and there was no flow from the column.

Attachment . <u>Columns:</u>	A 5.2. Time Periods for Sulfat <u>Time Period:</u>	e Reduction Rates: <u>Anomalous:</u> <u>Data</u>	Justification:
12	4/18-7/15	5/28	On 4/16 increased flow to 2.5 ml/mn, this period is a
		7/29 to 8/12	Siphon caused disruption of anaerobic conditions, column
			7/26 (Friday) and was not corrected until Monday, July
· .			29 sulfate concentrations increased in outflow for 3 weeks.
	8/26-10/28	12/9-12/16	Sulfate on 12/9 = 371, 12/16 = 349 on 12/18 = 12
5A	7/9-11/25	11/4	Stable period after column equilibrated to new ethanol feed
6A	6/8-8/26	7/29	Eliminated initial set-up period, this time period represents stable period with molasses food
	9/5-11/25		Methanol feed: outflow concentrations more variable.
7	6/3-8/26		Eliminated initial start-up period, this time period represents stable period with molasses feed.
	9/9-11/26		Methanol feed: outflow concentrations more variable.
8	4/18-8/26 8/26-11/25		* Period of consistency, higher outflow concentrations
9	4/18-8/26 8/26-11/25		* Period of consistency,
Notor	· .		ingher outriow concentrations.

Notes:

*The flow for column 8 and 9 remained constant throughout the entire time period, but concentrations appeared to increase toward the end of the year. The time periods were chosen to represent the difference in removal.

On 6/10/02: Switched ethanol, went to ethanol denatured with MIBK instead of methanol.

Column 12 did not seem to change.

Column 5A, sulfate removal decreased for about 3 weeks.

For explanation of anomalous data, see Table A3.16.

Attachment A 5.3. Rationale for Experimental Changes.

Experimental changes (4/18/02)

1. Stop all peat columns, and the sugar beets with iron and ethanol.

Rationale:

Ethanol columns: the organic substrate did not appear to make a difference in the performance of the column. The column with the rod mill feed + ethanol (Column 12), performed as well, or better, than the columns with the organic substrate. Adding the organic substrate would not be a cost effective approach and may cause permeability problems in the long term.

Iron filings: Although the iron filings improved the performance of the peat column and the initial performance of the sugar beet column, it is too expensive. U.S. Steel has not found an inexpensive source of iron. Column 11 (iron filings and rod mill feed) will be continued to provide some longer term data on the behavior of the iron filings.

Peat: this mixture had the lowest removal rate.

Columns that were discontinued are shown in the timeline, (attachment A 5.1) and summarized in Table 1 in the report.

2. Change flow rates. (4/17/02)

Flow rates will be increased in all columns to insure that the reaction rate will not be sulfate limited. Initial changes are shown in Table 5. If the outflow sulfate concentrations are routinely below 250 mg/L (drinking water standard), the flow rate will be increased. The objective will be to determine the maximum sulfate reduction rate that can be achieved in the columns

3. Change sampling frequency. (4/18/02)

For columns that are currently running, switch sampling frequency to once per week. For the new columns, twice per week. Flow rates for the new columns will begin at approximately 2.5 mL/min. The flow rates for the original columns still in operation will be increased to 2.5 mL/min with the exception of Column 2 (sugar beets), which will remain unchanged.

At the end of May sampling frequency for columns 8 and 9 was decreased. Column 8 was sampled every 2-3 weeks, while column 9 was sampled periodically.

4. Add new columns. (5/02)

A replicate of Column 12 (rod mill feed + additive) will be constructed. This column will be fed with a sugar beet molasses additive instead of ethanol. The initial estimated cost for the molasses would be about 20% of the ethanol (\$0.35 vs. \$1.50 per gallon).

Two columns will be constructed with an inorganic material that will attempt to maximize the surface area of ferric iron to insure that there is sufficient iron available to tie up all the sulfide produced due to the reduction of sulfate. Options include, oxidized taconite, coarse tailings, pellet fines and ore from the Auburn Mine near Virginia. One column would be fed with

ethanol, the other with molasses. (The plan was to start with ethanol, then switch to molasses. While this could be done, it would delay the results, since the column should run about one month before the feed is switched).

5. Change ethanol. (6/10/02)

The original columns were fed with an ethanol denatured with methanol. To use this in the field requires a special permit from the US Bureau of Alcohol, Tobacco and Firearms. This permit is not required if the denaturing agent is MIBK (methyl isobutyl ketone), so the ethanol in the columns was switched to use ethanol denatured with MIBK.

6. Switch from molasses to methanol. (8/26/02)

U.S. Steel wanted to have the flexibility of switching the source of organic carbon based on cost. The objective was to see how the columns would respond to a change in food source.

APPENDIX 6

Sulfide Equilibrium

Attachment A 6.1	Sulfide Equilibrium
Attachment A 6.2	Hydrogen Sulfide in Air (Sample Calculations)
Attachment A 6.3	Sample Calculation for FeS solubility
Table A 6.2	Calculation of Sulfide and Iron Equilibrium
Table A 6.3	Relationship between iron and sulfide in solution, with H_2S in air
Table A 6.4	Hydrogen Sulfide in Air
Figure A 6.1	Hydrogen Sulfide Liberated from Sulfide Solution – Concentration in Air
	at Equilibrium – pH 7, 8, and 9
Figure A 6.2	Hydrogen Sulfide Liberated from Sulfide Solution – Concentration in Air
	at Equilibrium – pH 7, 8, and 9

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Attachment A 6.1. Sulfide Equilibrium

In the system being studied at US Steel, sulfide is generated through the reduction of sulfate. Sulfide will react with trace metals or iron present in the water to form insoluble metal sulfide precipitates. If there is a lack of metals to bind with the sulfides, sulfide will be present in the outflow from the columns. Sulfide could then be released as H_2S , potentially causing health affects and other environmental problems.

In order to examine the potential for H_2S release, the equilibrium concentrations in air and water were calculated. Sulfide solubility is a function of pH and temperature. As pH increases, the tendency for sulfide to convert to H_2S decreases.

Since iron sulfides are extremely insoluble, the amount of iron needed to control the concentration of sulfide in the effluent was calculated. Between pH 7 and 8 (the typical range for the column outflow), a ferrous iron concentration greater than 0.02 mg/L in the effluent should result in a sulfide concentration below 0.1 mg/L in the effluent. Even though the sulfide concentration is low, the amount lost to the atmosphere would create odor problems. At pH 8, 0.1 mg/L concentration in the effluent, would have an equilibrium concentration in air of 2.7 ppm, which is well in excess of the "smell" detection limit of 10 ppb. At pH 7, the H₂S concentration would be 14.2 which is above the exposure limit of 10 ppm. (TLV = 10 ppm, threshold limit value; a time weighted averaged value, TWA; reference ACGIH 1998-99 Threshold Limit Values for Chemical Substances and Physical Agents)

This appendix contains calculations and tables relating sulfide and iron in water to hydrogen sulfide in air. Two sets of tables and figures are presented to cover a broad range of concentrations. This was done since there is a three order magnitude difference between the typical odor threshold of 10 ppb and the TLV of 10 ppm.

Attachment A 6.2. Hydrogen Sulfide in Air (Sample Calculation)

Equilibrium Reactions of Hydrogen Sulfide in Water $H_2S \leftrightarrow HS^- + H^+$ $K_1 = 9.1 \times 10^{-8}$ $HS^- \leftrightarrow S^= + H^+ \quad K_2 = 1.1 \ge 10^{-12}$ Assume pH = 7 $\overline{[\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}]} = 10^{-7}(\text{x})/(1-\text{x}) = 9.1 \text{ x } 10^{-8}$ Solve for x x = 0.47644 $[H_2S] = 1-x = 1-0.47644 = .52356 =$ fraction of H_2S in solution Henry's Constant for Hydrogen Sulfide at 68F is 483 Henry's Law \rightarrow Partial Pressure = Mole Fraction x Henry's Constant

Assume the concentration of sulfide is 5 mg/liter (MW $S^2 = 32$, MW $H_2O = 18$)

 $5 \text{ mg/L}=(5/(1000 \text{ x} 32))/(1000/18)=2.8125 \text{ x} 10^{-6} \text{ as mole fraction of total sulfide in water}$

 H_2S mole fraction = 0.52356 x 2.8125 x 10⁻⁶ = 1.473 x 10⁻⁶ Partial Pressure = 1.473 x 10⁻⁶ x 483 = 7.112 x 10⁻⁴ atmospheres

 $7.112 \times 10^{-4} \times 10^{6} = 711.2 \text{ ppm}$ assuming the atmospheric pressure = 1 atm.

1 able A 6.1. H_2S Concentration in Air at Equilibrium	Гable A б	.1. H_2S	Concentration	in Air	at Equilibrium
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at pH 7			• .	H₂S	H₂S	H₂S
Sulfide	Sulfide	H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/l	mole/l	mole frac	H = 367	H = 483	H = 609
0	0	0	0	0.0	0.0	0.0
0.1	3.125E-06	1.636E-06	2.945E-08	10.8	14.2	17.9
0.5	1.563E-05	8.181E-06	1.473E-07	54.0	71.1	89.7
1	3.125E-05	1.636E-05	2.945E-07	108.1	142.2	179.4
5	1.563E-04	8.181E-05	1.473E-06	540.4	711.2	896.8
10	3.125E-04	1.636E-04	2.945E-06	1080.8	1422.4	1793.5
20	6.250E-04	3.272E-04	5.890E-06	2161.6	2844.9	3587.0
at pH 8			· .	H₂S	H ₂ S	H₂S
Sulfide	Sulfide	·H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/I	mole/l	mole frac	H = 367	H = 483	H = 609
0	0 -	0	0	0.0	0.0	0.0
0.1	3.125E-06	3.094E-07	5.569E-09	2.0	2.7	3.4
0.5	1.563E-05	1.547E-06	2.784E-08	10.2	13.4	17.0
1	3.125E-05	3.094E-06	5.569E-08	20.4	26.9	33.9
5	1.563E-04	1.547E-05	2.784E-07	102.2	134.5	169.6
10	3.125E-04	3.094E-05	5.569E-07	204.4	269.0	339.1
20	6.250E-04	6.188E-05	1.114E-06	408.7	537.9	678.3
·						
at pH 9				H₂S	H₂S	H ₂ S
Sulfide	Sulfide	H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/I	mole/l	mole frac	H = 367	H = 483	H = 609
0	0	0	0.	0.0	0.0	0.0
0.1	3.125E-06	3.394E-08	6.109E-10	0.2	0.3	0.4
0.5	1.563E-05	1.697E-07	3.054E-09	1.1	1.5	1.9
1	3.125E-05	3.394E-07	6.109E-09	2.2	3.0	3.7
5	1.563E-04	1.697E-06	3.054E-08	11.2	14.8	18.6
10	3.125E-04	3.394E-06	6.109E-08	22.4	29.5	37.2
20	6.250E-04	6.788E-06	1.222E-07	44.8	59.0	74.4

Note 1: K₁ and K₂ for H₂S – 66th Edition of Handbook of Chemistry and Physics, CRC Press Note 2: Henry's Constants for H₂S – Table 14-21 Fourth Edition of Perry's Chemical Eng. Handbook
Attachment A 6.3.

Sample Calculation for FeS solubility

 $[H_2S] + [HS^-] + [S^-] =$ Total concentration of sulfide (sulfide analysis)

 $K_1 = 9.1 \times 10^{-8} = [H^+][HS^-] / [H_2S]$

 $K_2 = 1.1 \times 10^{-12} = [H^+][S^-] / [HS^-]$

Assume pH = 8, then $[H^+] = 10^{-8}$

Using K₁ at pH 8 then $[H_2S] = 10^{-8} [HS^-] / (9.1x10^{-8}) = 1.0989 x 10^{-1} [HS^-]$ Using K₂ at pH 8 then $[S^-] = (1.1x10^{-12})[HS^-]/10^{-8} = 1.1 x 10^{-4}[HS^-]$

Substitute in the top equation for $[H_2S]$ and $[S^=]$ and assume 1 ppm total sulfide 1 ppm total sulfide = 1 mg/liter = $1/(32*1000) = 3.125 \times 10^{-5}$ moles/liter

 $1.0989 \ge 10^{-1} [HS^-] + [HS^-] + 1.1 \ge 10^{-4} [HS^-] = 3.125 \ge 10^{-5}$ solve for [HS⁻]

 $[HS^{-}] = 2.8153 \times 10^{-5}$

then $[S^-] = 2.8153 \times 10^{-5} \times 1.1 \times 10^{-4} = 3.097 \times 10^{-9}$

For Fe S the $K_{sp} = 6.3 \times 10^{-18} = [Fe^{+2}][S^{=}] = [Fe^{+2}] (3.097 \times 10^{-9})$ solve for $[Fe^{+2}]$

 $[Fe^{+2}] = 2.034 \times 10^{-9}$ moles/liter as ppm or mg/l $Fe^{+2} = 1.136 \times 10^{-4}$ ppm

Therefore at pH 8, as long as the concentration of iron is greater than 0.0001136 ppm then the concentration of total sulfide will be less than 1 ppm.

Table A 6.2. Calculation of Sulfide and Iron Equilibrium

 $K1 = 9.1 \times 10-8$ $K2 = 1.1 \times 10-12$ FeS Ksp = 6.3 x 10-18

	At pH 8					•	
	•	Sulfide	H2S	HS-	S=	Fe++	Fe++
	Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
	1	0.0000313	3.094E-06	2.815E-05	3.097E-09	2.034E-09	1.14E-04
	5	0.0001563	1.547E-05	1.408E-04	1.548E-08	4.069E-10	2.27E-05
	20	0.0006250	6.188E-05	5.631E-04	6.194E-08	1.017E-10	5.68E-06
	50	0.0015625	1.547E-04	1.408E-03	1.548E-07	4.069E-11	2.27E-06
	•	· * .					
	At pH 7						
	1	Sulfide	H2S	HS-	. S=	Fe++	Fe++
	Sulfide.ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
	1	0.0000313	1.636E-05	1.489E-05	1.638E-10	3.847E-08	2.15E-03
	5	0.0001563	8.181E-05	7.444E-05	8.188E-10	7.694E-09	4.30E-04
	20	0.0006250	3.272E-04	2.978E-04	3.275E-09	1.923E-09	1.07E-04
	50	0.0015625	8.181E-04	7.444E-04	8.188E-09	7.694E-10	4.30E-05
			· · · · ·		· · ·		
÷	At pH 6	• • • • •	· .	· .			· . · · ·
		Sulfide	H2S	HS-	S=	Fe++	Fe++
	Sulfide.ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
	1	0.0000313	2.864E-05	2.607E-06	2.867E-12	2.197E-06	0.1227
	5	0.0001563	1.432E-04	1.303E-05	1.434E-11	4.395E-07	0.0245
	20	0.0006250	5.729E-04	5.213E-05	5.734E-11	1.099E-07	0.0061
	50	0.0015625	1.432E-03	1.303E-04	1.434E-10	4.395E-08	0.0025
						•	
	At pH 4			· •			
	•	Sulfide	H2S	HS-	S=	Fe++	Fe++
	Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
	1	0.0000313	3.122E-05	2.841E-08	3.125E-16	2.016E-02	1125.8
	5	0.0001563	1.561E-04	1.421E-07	1.563E-15	4.032E-03	225.2
	20	0.0006250	6.244E-04	5.682E-07 · :	6.251E-15	1.008E-03	56.3
	50	0.0015625	1.561E-03	1.421E-06	1.563E-14	4.032E-04	22.5
						•	
	At pH 3	· ·			· ·		
		Sulfide	H2S	HS-	S=	Fe++	Fe++
	Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
	. 1	0.0000313	3.125E-05	2.843E-09	3.128E-18	2.014	112491
	5	0.0001563	1.562E-04	1.422E-08	1.564E-17	0.403	22498
	20	0.0006250	6.249E-04	5.687E-08	6.256E-17	0.101	5625
	50	0.0015625	1.562E-03	1.422E-07	1.564E-16	0.040	2250

K1, K2 from 66th Edition of the Handbook of Physics and Chemistry published by CRC Press. Ksp from 13th Edition of Lange's Handbook of Chemistry published by McGraw Hill. Table A 6.3. Relationship between iron and sulfide in solution, with H₂S in air

K1 = 9.1 x 10⁻⁸ K2 = 1.1 x 10⁻¹² FeS Ksp = 6.3 x 10⁻¹⁸ * - Iron concentration that would limit the hydrogen sulfide equilibrium concentration to 10 ppb in air

At pH 9 H2S HS-S= Fe++ Fe++ Sulfide Sulfide,ppm mole/L mole/L mole/L mole/L mole/L ppm 0.0035 1.1888E-10 5.2997E-08 0.0030 1.0938E-07 1.1876E-09 1.0807E-07 0.01 3.3964E-10 1.8549E-08 0.0010 3.1250E-07 3.3930E-09 3.0877E-07 0.1 3.3930E-08 3.0877E-06 3.3964E-09 1.8549E-09 1.04E-04 3.1250E-06 1.04E-05 1 3.1250E-05 3.3930E-07 3.0877E-05 3.3964E-08 1.8549E-10 5 1.5438E-04 1.6982E-07 3.7098E-11 2.07E-06 1.5625E-04 1.6965E-06 20 6.2500E-04 6.7861E-06 6.1753E-04 6.7929E-07 9.2744E-12 5.18E-07 At pH 8.5 Sulfide H2S HS-S= Fe++ Fe++ Sulfide,ppm mole/L mole/L mole/L mole/L mole/L ppm 0.0013 0.0258 4.0625E-08 1.3639E-09 3.9247E-08 1.3652E-11 4.6146E-07 0.01 3.0190E-07 1.0502E-10 5.9990E-08 0.0034 3.1250E-07 1.0491E-08 0.1 3.1250E-06 1.0491E-07 3.0190E-06 1.0502E-09 5.9990E-09 0.0003 1 3.1250E-05 1.0491E-06 3.0190E-05 1.0502E-08 5.9990E-10 0.0000 5 1.5625E-04 5.2456E-06 1.5095E-04 5.2509E-08 1.1998E-10 0.0000 20 6.2500E-04 2.0982E-05 6.0381E-04 2.1003E-07 2.9995E-11 0.0000 At pH 8 Sulfide H2S HS-S= Fe++ Fe++ Sulfide,ppm mole/L mole/L mole/L mole/L mole/L ppm 0.00036 1.1250E-08 1.1138E-09 1.0135E-08 1.1149E-12 5.6509E-06 0.316 0.001 3.1250E-08 3.0938E-09 2.8153E-08 3.0968E-12 2.0343E-06 0.114 0.01 3.1250E-07 3.0938E-08 2.8153E-07 3.0968E-11 2.0343E-07 0.011 0.1 3.1250E-06 3.0938E-07 2.8153E-06 3.0968E-10 2.0343E-08 1.14E-03 1 3.1250E-05 3.0938E-06 2.8153E-05 3.0968E-09 2.0343E-09 1.14E-04 5 1.5625E-04 1.5469E-05 1.4077E-04 1.5484E-08 4.0687E-10 2.27E-05 20 6.2500E-04 6.1875E-05 5.6306E-04 6.1937E-08 1.0172E-10 5.68E-06 Table A 6.3. Relationship between iron and sulfide in solution, with H_2S in air (cont.)

At pH 7.5	,				· · · · ·	
	Sulfide	H2S	HS-	S=	Fe++	Fe++
Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
0.00016	5.0000E-09	1.2894E-09	3.7105E-09	1.2907E-13	4.8811E-05	2.726
0.001	3.1250E-08	8.0587E-09	2.3190E-08	8.0668E-13	7.8098E-06	0.436
0.01	3.1250E-07	8.0587E-08	2.3190E-07	8.0668E-12	7.8098E-07	0.044
0.1	3.1250E-06	8.0587E-07	2.3190E-06	8.0668E-11	7.8098E-08	0.004
1	3.1250E-05	8.0587E-06	2.3190E-05	8.0668E-10	7.8098E-09	0.000
5	1.5625E-04	4.0294E-05	1.1595E-04	4.0334E-09	1.5620E-09	0.000
20	6.2500E-04	1.6117E-04	4.6381E-04	1.6134E-08	3.9049E-10	0.000
At pH 7				• .		
	Sulfide	H2S	HS-	S=	Fe++	Fe++
Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
0.00007	2.1875E-09	1.1453E-09	1.0422E-09	1.1464E-14	5.4956E-04	30.6929
0.01	3.1250E-07	1.6362E-07	1.4888E-07	1.6377E-12	3.8469E-06	0.2149
0.1	3.1250E-06	1.6362E-06	1.4888E-06	1.6377E-11	3.8469E-07	0.0215
. 1	3.1250E-05	1.6362E-05	1.4888E-05	1.6377E-10	3.8469E-08	0.0021
5	1.5625E-04	8.1809E-05	7.4440E-05	8.1884E-10	7.6938E-09	0.0004
20	6.2500E-04	3.2724E-04	2.9776E-04	3.2754E-09	1.9235E-09	0.0001
· ·	1997 - A.					
At pH 6						
	Sulfide	H2S	HS-	S=	Fe++	Fe++
Sulfide,ppm	mole/L	mole/L	mole/L	mole/L	mole/L	ppm
0.001	3.1250E-08	2.8643E-08	2.6065E-09	2.8672E-15	2.1973E-03	122.718
0.01	3.1250E-07	2.8643E-07	2.6065E-08	2.8672E-14	2.1973E-04	12.272
0.1	3.1250E-06	2.8643E-06	2.6065E-07	2.8672E-13	2.1973E-05	1.227
1	3.1250E-05	2.8643E-05	2.6065E-06	2.8672E-12	2.1973E-06	0.123
5	1.5625E-04	1.4322E-04	1.3033E-05	1.4336E-11	4.3946E-07	0.025
20	6.2500E-04	5.7287E-04	5.2131E-05	5.7344E-11	1.0986E-07	0.006

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Table A 6.4. Hydrogen Sulfide in Air

at pH 7				H₂S in air	H₂S in air	H ₂ S in air
Sulfide	Sulfide	H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/I	mole/l	mole frac	H = 367	H = 483	H = 609
0	0	0	0	0.000	0.000	0.000
0.00007	2.188E-09	1.145E-09	2.062E-11	0.008	0.010	0.013
0.001	3.125E-08	1.636E-08	2.945E-10	0.108	0.142	0.179
0.01	3.125E-07	1.636E-07	2.945E-09	1.081	1.422	1.794
0.1	3.125E-06	1.636E-06	2.945E-08	10.8	14.2	17.9
0.5	1.563E-05	8.181E-06	1.473E-07	54.0	71.1	89.7
1	3.125E-05	1.636E-05	2.945E-07	108.1	142.2	179.4
5	1.563E-04	8.181E-05	1.473E-06	540.4	711.2	896.8
10	3.125E-04	1.636E-04	2.945E-06	1080.8	1422.4	1793.5
at pH 8			·	H₂S in air	H₂S in air	H₂S in air
Sulfide	Sulfide	H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/l	mole/I	mole frac	H = 367	H = 483	H = 609
0	0	0	0	0.000	0.000	0.000
0.00036	1.125E-08	1.114E-09	2.005E-11	0.007	0.010	0.012
0.001	3.125E-08	3.094E-09	5.569E-11	0.020	0.027	0.034
0.01	3.125E-07	3.094E-08	5.569E-10	0.204	0.269	0.339
0.1	3.125E-06	3.094E-07	5.569E-09	2.0	2.7	3.4
0.5	1.563E-05	1.547E-06	2.784E-08	10.2	13.4	17.0
1	3.125E-05	3.094E-06	5.569E-08	20.4	26.9	33.9
5	1.563E-04	1.547E-05	2.784E-07	102.2	134.5	169.6
10	3.125E-04	3.094E-05	5.569E-07	204.4	269.0	339.1
				· · ·		·
at pH 9				H₂S in air	H₂S in air	H₂S in air
Sulfide	Sulfide	H2S	H2S	ppm at 50F	ppm at 68 F	ppm at 86F
mg/l	mole/l	mole/i	mole frac	H = 367	H = 483	H = 609
0	0	0	0	0.000	0.000	0.000
0.0035	1.094E-07	1.188E-09	2.138E-11	0.008	0.010	0.013
0.01	3.125E-07	3.394E-09	6.109E-11	0.022	0.030	0.037
0.1	3.125E-06	3.394E-08	6.109E-10	0.224	0.295	0.372
0.5	1.563E-05	1.697E-07	3.054E-09	1.12	1.48	1.86
1	3.125E-05	3.394E-07	6.109E-09	2.24	2.95	3.72
5	1.563E-04	1.697E-06	3.054E-08	11.21	14.75	18.60
10	3.125E-04	3.394E-06	6.109E-08	22.42	29.51	37.20

Note: .010 odor threshold for hydrogen sulfide



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APPENDIX 7

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Zero Valent Iron

The role of zero valent iron in sulfate reduction reactions.

Metallic iron (Fe^o) initially consumes the oxygen in solution.

Under aerobic conditions, dissolved oxygen is the preferred electron acceptor and will reduce to O_2 (Reaction consumes oxygen)

aerobic reactions

 $2 \operatorname{Fe}^{\circ} + \operatorname{O}_{2} + 2\operatorname{H}_{2}\operatorname{O} \rightarrow 2 \operatorname{Fe}^{+2} + 4 \operatorname{OH}^{-}$ $4 \operatorname{Fe}^{+2} + 4 \operatorname{H}^{+} + \operatorname{O}_{2} \rightarrow 4 \operatorname{Fe}^{+3} + 2 \operatorname{H}_{2}\operatorname{O}$ $\operatorname{Fe}^{+3} + 30\operatorname{H}^{-} \rightarrow \operatorname{Fe}(\operatorname{OH})_{3}$

Once the oxygen is consumed, the anaerobic reactions occur.

anaerobic reactions

Fe^o (S) \rightarrow Fe⁺² + 2e⁻ 2 H₂O + 2e⁻ \rightarrow H₂ + 20H⁻

 $Fe^{\circ}(S) + 2 H_2O \rightarrow Fe^{+2} + H_2 + 20H^{-1}$

Sulfate reducing bacteria can utilize the hydrogen as an electron donor

 $4 H_2 + SO_4^{-2} \rightarrow S^{-2} + 4 H_2O$

To reduce one mole of sulfate to sulfide requires 8 electrons, and each mole of H_2 provides 2 electrons.

Therefore, for each mole of sulfate reduced requires 4 moles H_2 and 4 moles of $Fe^{\circ}(s)$

Sources of Zero Valent Iron

Zero valent iron is being used in permeable reactive barrier walls to primarily treat chlorinated hydrocarbons in groundwater. Several companies are manufacturing iron filings for use in these walls. For the US Steel study we evaluated several products from Connelly Iron Products in Chicago, Illinois. The products that were examined included:

cc-1004- flow characteristics similar to sand

cc-1022- some of larger size fractions have been removed so this product has larger surface area

Information on each of these products is included.



CONNELLY - GPM, INC.

ESTABLISHED 1875 3154 SOUTH CALIFORNIA AVENUE · CHICAGO, ILLINOIS 60608-5176 PHONE: (773) 247-7231 ConnellyGPM@aol.com FAX: (773) 247-7239

DEC

December 13, 2001

Lounder to

VIA: UPS GROUND

Mr. Paul Eger Minnesota Department of Natural Resources Division of Lands and Minerals Box 45, 500 Lafayette Road St. Paul, MN. 55155-4045

Dear Mr. Eger:

As per our phone conversation this morning, we are pleased to offer you the following quotations on several grades of IRON AGGREGATE. As the time frame and quantity are unknown at this time, please understand that these numbers are for your budgetary purposes only.

Pricing for IRON AGGREGATE CC-1004 is as follows:

Total:	\$363.35/NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 EA.)	<u>\$ 4.35/NT</u>
Bulk Bags (\$21.00 ea.) @ 3000 lbs.	\$ 14.00/NT
IRON AGGREGATE CC-1004	\$345.00/NT

CC-1004 is the most sought after IRON AGGREGATE for Groundwater Remediation. We also offer the following:

Pricing for IRON AGGREGATE CC-1107 is as follows:

	F.O.B.	Ch	icago	, IL
	Total:	\$46	58.35/	NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 EA.)		<u>\$</u>	4.35/	NT
Bulk Bags (\$21.00 ea.) @ 3000 lbs.		\$ 1	4.00/	NT
IRON AGGREGATE CC-1107		\$45	50.00/	NT

Page 2, Mr. Paul Eger

December 13, 2001

Minnesota Department of Natural Resources

Pricing for IRON AGGREGATE CC-1022 is as follows:

	F.O.B.	Chicago, IL
• • • • • • • • • • • • • • • • • • • •	Total:	\$393.35/NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 ea.)		<u>\$ 4.35/NT</u>
Bulk Bags (\$21.00 ea.) @ 3000 LBS.		\$ 14.00/NT
IRON AGGREGATE CC-1022		\$375.00/NT

Pricing for IRON AGGREGATE CC-1021 is as follows:

	F.O.B.	Chicago, IL
	Total:	\$454.35/NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 EA.)		<u>\$ 4.35/NT</u>
Bulk Bags (\$21.00 ea.) @ 3000 lbs.		\$ 14.00/NT
IRON AGGREGATE CC-1021		\$436.00/NT

Pricing for IRON AGGREGATE CC-1163 is as follows:

	F.O.B.	Chicago, IL
	Total:	\$490.35/NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 EA.))	<u>\$ 4.35/NT</u>
Bulk Bags (\$21.00 ea.) @ 3000 lbs.	•	\$ 14.00/NT
IRON AGGREGATE CC-1163	•	\$472.00/NT

Pricing for IRON AGGREGATE CC-1118 is as follows:

	F.O.B.	Chicago, IL
	Total:	\$525.35/NT
42" x 42" Pallets - <u>RECONDITIONED</u> (\$6.50 EA.)	. • · · ·	<u>\$ 4.35/NT</u>
Bulk Bags (\$21.00 ea.) @ 3000 lbs.		\$ 14.00/NT
IRON AGGREGATE CC-1118		\$507.00/NT

The Bulk Bags have a plastic liner for weather protection.

We have enclosed ½# samples of each IRON AGGREGATE so that you can choose which one you would like for your tests. You stated in your fax that you would require approximately 50# for your column tests. The samples are identified by CC numbers and when you make your selection, use the CC number to designate your choice. After you have made your choice, let us know and we will send you the material. Page 3, Mr. Paul Eger

December 13, 2001

Minnesota Department of Natural Resources

We have gotten a freight rate for you, via flatbed over the road truck, of \$835.00/TL. These trucks carry 15-3000# Bulk Bags for a payload of 22.5NT of material. The freight cost would be \$37.11/NT, based on full truckloads of material. Due to the current fuel cost situation, all freight charges are subject to a fuel surcharge that varies from week to week. They have gone from 3.5% to as high as 10.5%, so when planning your costs you need to add a buffer in the freight allowance.

Freight rate information given to you by CONNELLY-GPM, INC. is our understanding of the freight charges in effect at that time. CONNELLY-GPM, INC. takes no responsibility for the completeness or accuracy of such information and you are encouraged to obtain confirmation of freight rates on your own.

CONNELLY-GPM, INC. has been in business since 1875 and we take pride in being the world's largest manufacturer of IRON AGGREGATE. We have supplied the three largest sites to date: over 1000 Net Tons to one, over 2000 Net Tons to another, and over 3500 Net Tons to another. Our record of delivering these large orders on time and within specifications has made us the supplier of choice for this rapidly growing technology.

Please advise when you have made your selection and we will send the 50# that you need. If you have any questions, please do not hesitate to contact us.

Very truly yours,

CONNELLY-GPM, ING

Judi A. Donegan Vice-President

/jd Encl.

D:\WORD\WT\M THRU P\MNDNRSMPLS121301



CONNELLY - GPM, INC.

TO:

COTABLISHED 1878 3154 SOUTH CALIFORNIA AVENUE * CHICAGO, ILLINOIS 60808-5176 PHONE: (773) 247-7231 ConnellyGPM(2)aol.com FAX: (773) 247-7239

December 20, 2001

VIA: FAX 651-296-5939 (total of 4 pages)

Mr. Paul Eger Minnesota Department of Natural Resources Division of Lands and Minerals Box 45, 500 Lafayette Road St. Paul, MN. 55155-4045

Dear Mr. Eger:

As per your phone conversation this morning with Mr. Klein and myself, attached please find the MSDS on IRON AGGREGATE and the requested Analysis of Iron.

As discussed, CC-1004 is the most commonly used TRON AGGREGATE for Groundwater Remediation. The water flows through as it would through sand or gravel. If you are looking for better surface area, CC-1022 would be the better choice. Either one might serve your purpose and these two are the least expensive.

If you would like to test these two, let us know and we will be happy to send you the amount you need for your testing. Just provide us with your selections and required pounds and we will send them to you in a pail or pails using your Fed-Ex or UPS account number.

We would also like to wish you Happy Holidays. Our office will be closed from Monday, December 24, 2001 through Wednesday, December 26, 2001.

Very truly yours,

CONNELLY-GPM INC.

Judi A. Donegan Vice-President

/jd Attach. D:WORD/WT/M THRU F/MND/RSMFL\$121301

Material Safety Data Sheet May be used to comply with OSHA's Hazard Communication Standard, 29 CFR 1910.1200. Standard must be consulted for specific requirements. IDENTITY (As Used on Label and List)

U.S. Department of Labor Occupational Safety and Health Administration (Non-Mandatory From) Form Approved OMB No. 1218-0072 NOTE: Blank spaces are not permitted. If an item is not applicable

·	IRON AGGF	REGATE	or inform	ation unavailable, ti	he appoor muct be	eo markod.
Section I						
Manufacturer's Name	<u>میں اگر نے پیدی پر میں میں میں میں میں اسا</u> لی اور ا		Emergency Tele	phone Number		
CONNELLY-GPM, INC			(773) 247-72	31		
Address (Number, Street, Cit	y, State, and ZIP Code	3)	Telephone Numb	per for Information		
3154 South California	Avenue	-	(773) 247-72	31		
			Date Prepared			
Chicago, IL 80608-517	6			04/25/2000		
			Signature of Pres	parer (optional)		
		•		•		
Section II - Hazardou	s ingredients/Id	entity Inform	nation			
Hazardous Components	میں کا بہتر <u>میں میں میں میں میں میں میں میں میں میں </u>			ACGIH	Other Limits	(1)
(Specific Ci	iemical Identity; Comm	non Name)	OSHA PEL	TLV	Recommended	% (optional)
IRON	CAS #130	9-37-1	10 mg/m ³	5 mg/m ³	10 mg/m ³	
		· · · · · · · · · · · · · · · · · · ·	(as i	mn oxide fur	ne)	
CARBON	CAS #123	3 86 4	3.6 ma/m	3.6 ma/m	7	
	0/0 #100	3-00-4	5.5 fig/ii-	3.5 mg/m	<u>/ Ing/in-</u>	
			(as c	arbon black)	
SILICON	<u>CAS #744</u>	<u>0-21-3 </u>	(2)	(3)	20 mg/m ³	
*8 hour time weig	hted average					
1) ACGIH Stel (1	984-1985)					
2) <1% () (artz 1)	5 malmi of tota	dust or f		irable dust		
2) -170 QUAIL2 10	mg/m of tota	i dust, or		irable dust		
	J mg/m or tota		o ingini resp	il able dust		
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Firefighters should	wear self-contain	ed breathing	apparatus and	protective clo	thina.	
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TO:

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December 20, 2001

TO:

TYPICAL ANALYSIS OF IRON

	
Metallic Iron	89.82
Total Carbon	2.85
Manganese	0.60
Sulphur	0.107
Phosphorous	0.132
Silicon	1.85
Nickel	0.05 - 0.21
Chromium	0.03 - 0.17
Vanadium	Nil
Molybdenum	0.15
Titanium	0.004
Copper	0.15 - 0.20
Aluminum	Trace
Cobalt	0.003

GALEN DIXON QUALITY CONTROL MANAGER

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APPENDIX 8

General Information on Sulfate Reduction Reactions

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Sulfate reduction reactions.

This appendix discusses issues related to sulfate reduction reactions, the amount of electron donors needed to reduce sulfate, and variations in electron donor source and reaction pathways.

Dissimulatory sulfate reduction, in which sulfate serves as electron acceptor is carried out by variety of bacteria, collectively called sulfate reducing bacteria. These bacteria can use a variety of compounds as electron donors.

Sulfate reduction, to go from S^{+6} in SO_4^{-2} to S^{-2} requires 8 electrons;

 $SO_4^{-2} + 8e^- + 8H^+ \leftrightarrow H_2S + 2H_2O + 2OH^-$

The form of S^{-2} in equilibrium is a function of pH.

Most sulfate reducers can use lactate as electron donor.

2 lactate + $SO_4^{-2} \rightarrow 2$ Acetate + 2 CO_2 + HS⁻ + H₂O + OH⁻

In this reaction the ratio of carbon oxidized to sulfate reduced is 2 moles of lactate: 1 mole of sulfate

Most desulfovibrio strains have hydrogenase and can also utilize H_2 as an energy substrate (electron donor)

 $4H_2 + SO_4^{-2} + 2 H^+ \rightarrow 4 H_2O + H_2S$

In this reaction, the ratio of hydrogen oxidized to sulfate reduced is 4 moles hydrogen: 1 mole of sulfate.

Two genera Desulfovibrio Desulfotomaculun

Variety of species exists, can use different electron acceptors—so when switch feeds may be looking at different strains of bacteria.

Tsukamoto and Miller found that with lactate the bacteria took 14 days to equilibrate while if took 49 days with methanol.

Bacteria don't use sugars directly--must be broken down by fermenters that can yield lactate, acetate, ethanol and hydrogen. These breakdown products can then be used by sulfate reducing bacteria.

In dissimulatory metabolism, only a small amount of sulfur is incorporated with the cells; the majority is used in energy metabolism as electron acceptor or donor similar to oxygen in aerobic organisms.

Some of the carbon is incorporated with biomass. Hammack (DOE, personal communication, 2003) estimated about 10% of the supplied carbon would go into cell mass.

Carbon not oxidized completely to CO₂ by Desulfovibrio but excreted partly as acetate.

Lactate Acetate
CH₃ CH OH COO⁻⁺ SO₄⁻²
$$\rightarrow$$
 2 CH₃ COO⁻ + 2HCO₃⁻ + H₂S

In order to determine exactly how much carbon is needed to reduce all the sulfate in the input, the carbon source, the breakdown pathway, and the number of electrons donated must all be known.

For example, each mole of ethanol that goes completely to CO₂, generates 12 electrons,

which is more electrons than the simple model in which

$$2 \text{ CH}_2\text{O} + \text{SO}^2 \rightarrow \text{H}_2\text{S} + 2 \text{ HCO}_3$$

2 moles CH_2O – generates 8 electrons

1 mole SO₄ – requires 8 electrons

The lactate to acetate model and the simple model both require 2 moles of Carbon for each mole of SO_4 reduced.

The ethanol to carbon dioxide model generates 12 electrons which will reduce 1.5 moles of

SO₄ Therefore, when the ethanol columns were designed on a 2: 1 C:S ratio, there would be

about $\sim 50\%$ excess C.

For methanol,

1 mole methanol = 1 mole C = 6 electrons which will reduce .75 mole SO₄. Therefore, if added 2 moles C would reduce 1.5 moles SO₄ so would also have excess carbon.

Since molasses is a mixture it is not immediately known what the specific reaction pathways will be or what the C:S ratio will be. Original columns had enough to fully consume SO₄.

The number of electrons is also a function of the pathway, for example:

lactate \rightarrow acetate + CO₂: 4 electrons

lactate \rightarrow acetate + CO₂ \rightarrow 3 CO₂: 12 electrons

Summary:

The feed rate into the columns with ethanol and methanol assumed that 2 moles of carbon were needed to generate 8 electrons. If the reaction goes completely to CO_2 , the carbon will actually generate 12 electrons which should be sufficient to reduce all the sulfate. In order to determine the exact amount of carbon required, an optimization study should be conducted.

APPENDIX 9

Reaction Kinetics

Attachment A9.1	Introduction
Figure A9.1	Microbial Growth
Figure A9.2	Biodegradation Kinetics
Figure A9.3	Monod Kinetics

Attachment A9.1 Introduction

The reaction rate is one of the key variables in the design of the final treatment system. The faster the reaction rate, the smaller and less costly the system.

Factors that influence the reaction rate include:

Concentration of reactants; sulfate and organic carbon Bacteria population Temperature

In most microbial systems, there is acclimitation period, or lag phase when microbes are adjusting to the food source and environment (Figure A9.1).

Once the bacteria have become established, and assuming an adequate supply of both sulfate and carbon, the reaction rate should be constant (zero order kinetics) (Figure A9.1). Reaction rate will vary with temperature. For sulfate reduction, the literature suggests that for every 10° C change, the reaction rate changes by a factor of 3. If Q_{20} is the reaction rate at 20° C, and Q_{10} is the reaction rate at 10°, then:

Q10

If the concentrations of either sulfate and/or carbon decrease, the reaction rate will most likely follow "Monod Kinetics" (Figure A9.2).

Monod Expression (Assume the carbon source is lactate)

 $\mu = (\mu \max \circ C) / (K_{Lac} + C)$

 μ = specific growth rate (M⁻¹) μ max = maximum growth rate (M⁻¹)

C = lactate concentration (mg/L)

 K_{Lac} = half saturation coefficient for lactate

For example:

$$\mu = \frac{.360 \,(\text{hr}^{-1}) \,\text{C mg/L}}{44 \,\text{mg/L} + \text{C mg/L}}$$

but if C >> K

then $\mu = \mu \max$, or the rate of reaction is constant and independent of the carbon concentration.

 μ max and K are functions of temperature.

Other variables may also affect the reaction rate, since they can affect the total microbial population.

Nutrients

Although the bacteria require N and P, there currently does not appear to be a nutrient limitation in the U.S. Steel columns, since both Column 12 and Column 5A consistently reduced all the sulfate without any supplemental additions of N or P.

But literature and the need for N and P in biological processes would suggest that at some point N and/or P may become limiting. In one experiment using lactate as the carbon source, the ratio at which P became limiting was 1 mg P to 1000 - 2000 mg lactate. Converting this to TOC gives ratio of TOC: P 400-800:1

Other studies have suggested that the limiting C: N ratio 45-120:1 Optimization studies are needed to determine the amount of N and P needed in these columns.

Sulfide

In general it appears that the bacteria can withstand substantial concentrations of sulfide in the column. One study found a 50% inhibition of lactate use at $S^{-2} \sim 500 \text{ mg/L}$, while another study found that Desulfovibrio had very high tolerance, with pure cultures reportedly growing even at 50mM H₂S. However, one study showed that when sulfide reached 20mM in the sediment it was completely toxic.

In general, column effluents appear to be less than 25 mg/L (based on indicator paper measurements), so sulfide toxicity should not be an issue at this time.

Chemical Structures

<u>Ethanol</u>

 C_2H_5OH

H H | | H- C- C- OH | | H H

Lactate	Lactic Acid
ННО	ННО
H- C- C- C- O	H- C- C- C- OH
	I I
Н Н	ΗH

Reference:

Contaminant Fate and Transport Processes Philip B. Bedient Environmental Science and Engineering Rice University, Houston, TX



Figure A9.1 Microbial Growth

Biodegradation Kinetics

- The rate of biodegradation or biotransformation is generally the focus of environmental studies
- Microbial growth and substrate consumption rates have often been described using 'Monod kinetics'



S is the substrate concentration [mg/L] X is the biomass concentration [mg/ L] k is the maximum substrate utilization rate [sec⁻¹] K_S is the half-saturation coefficient [mg/L]

Figure A9.2 Biodegration Kinetics



Figure A9.3 Monod Kinetics

APPENDIX 10

New Columns/Experimental Changes

Attachment A10.1	Rationale for experimental changes	
Table A10.1	Minntac sulfate-reducing test columns	
Table A10.2	Minntac process water sulfate treatment 2002-2003 bench-pilot-scale	
	test matrix, original plan 1-03	
Table A10.3	Minntac process water sulfate treatment 2002-2003 bench-pilot-scale	
	test matrix, revised 5-03	
Attachment A10.2	Procedure to follow before changing existing columns	
Attachment A10.3	Correspondence related to nutrients and iron reducing bacteria	
Attachment A10.4	New column porosity tests	

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Attachment A10.1 Rationale for experimental changes

Changes in the column experiment were initiated to attempt to answer the following questions. What is the maximum sulfate reduction rate achievable in the column?

The plan was to increase the input flow rate (by 0.5 ml/mm) in a step-wise fashion until SO_4 concentrations in the effluent increased to around 250 mg/L. This concentration is the secondary drinking water standard and within the reported range of sulfate concentrations at which the reaction rate should be independent of sulfate concentration.

What is the effect of particle size on iron release?

In this system, iron must be released from the substrate in order to tie up the sulfide that is produced during the reduction of sulfate.

How can iron reduction be stimulated?

Effluent from columns fed molasses did not release detectable (by smell) H_2S . Initial thoughts were that nutrients or chelators in the molasses stimulated iron- reducing bacteria. The plan is to add these components in a step-wise manner to a column fed with ethanol.

In addition, effluent from one of the columns was fed through a new column to see if iron reduction would occur after most of the sulfate was removed.

What is the effect of temperature on reaction rate?

A laboratory chiller was wrapped around one of the columns and is being used to lower the temperature at 5° F intervals to examine the change in reaction rate.

Table A10.1 and Table A10.2 provide information on the original experimental plan designed to address these issues. The plan was modified and the current experimental setup is shown on Table A10.3. Attachment A10.2 describes how the columns should be monitored so that changes in treatment can be quantified.

Table A10.1 Minntac Sulfate-Reducing Test Columns

Existing columns (set up in February or May 2002)

Substrate/Carbon Source	Current Feed Rate	Proposed Feed Rate
Ox. Ore + Ethanol	2.5 mL/min.	2.5 mL/min.
Ox. Ore + Molasses	2.5 mL/min.	2.5 mL/min.
RMF + Molasses	2.5 mL/min.	3.0 mL/min.
RMF + Ethanol	2.5 mL/min.	3.0 mL/min.
	<u>Substrate/Carbon Source</u> Ox. Ore + Ethanol Ox. Ore + Molasses RMF + Molasses RMF + Ethanol	Substrate/Carbon SourceCurrent Feed RateOx. Ore + Ethanol2.5 mL/min.Ox. Ore + Molasses2.5 mL/min.RMF + Molasses2.5 mL/min.RMF + Ethanol2.5 mL/min.

New Columns (12-18-02)

<u>Column</u>	Substrate/Carbon Source	Substrate Particle Size	Proposed Feed Rate
13	Ox. Ore + Molasses	-1/4"	2.5 mL/min.
14	Ox. Ore + Molasses	-1/2" +8 mesh	2.5 mL/min.
15	Ox. Ore + Effluent Feed	-1/2"	2.5mL/min.
*.	From #12	•	
16	Ox. Ore + Alternate Carbon Source	-1/2"	2.5 mL/min.
17	Ox. Ore + Molasses/Ethanol Blend	-1/2"	2.5 mi./min.

Table A10.2

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Minntac Process Water Sulfate Treatment 2002-2003 Bench-/Pilot-scale Test Matrix, original plan 1-03

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Column			HRT,		
Number	Substrate	Carbon Source	days	Test rationale	Comments
Existing	Columns				
5A	Oxidized taconite	Ethanol	2.5	Nutrients/	1 month of acclimation, 2 months of nitrogen addition,
				Chelating agent	2 months of chelator addition (sodium citrate)
6A	Oxidized taconite	Molasses	2.5	Baseline	
7	Rod mill feed	Molasses	2	Minimum HRT	Reduce HRT by 0.5 day increments until effective minimum is
					reached
12	Rod mill feed	Ethanol	2	Minimum HRT	Same as Column 7 with ethanol
New Colu	umns				
13	Oxidized taconite	Molasses	2.5	Surface area	$PSD^{1} = -\frac{1}{4}$ ", Evaluate constituent reduction with increased
					substrate surface area/decreased hydraulic potential
14	Oxidized taconite	Molasses	2.5	Surface area	$PSD = -\frac{1}{2}$, +8 mesh, Evaluate constituent reduction with
*					decreased substrate surface area/increased hydraulic potential
15	Oxidized taconite ²	Ethanol	2.5	Temperature effects	Laboratory chiller used to control temperature of reactor
16	Oxidized taconite ²	Molasses	2.5	Temperature effects	Laboratory chiller used to control temperature of reactor
17	Oxidized taconite ²	Molasses-ethanol	2.5	Effect of carbon feed	50/50 blend by volume (initially)
		blend		source	
New Pilo	t Reactor				
NA	Oxidized taconite ²	Ethanol	2.5	Hydraulics,	Horizontal operating configuration, 8" I.D. x 6' long. Operated to
				Fate of sulfur,	model the 2002 demo unit initially. Will likely be converted to
				Iron reduction	molasses in the future

¹PSD = Particle size distribution ²Particle size distribution = $-\frac{1}{2}$ "

Table A10.3

Minntac Process Water Sulfate Treatment 2002-2003 Bench-/Pilot-scale Test Matrix, revised 5-03

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Column			HRT,		
Number	Substrate	Carbon Source	days	Test rationale	Comments
Existing	Columns				
5A	Oxidized taconite	Ethanol	2.5	Nutrients/	1 month of acclimation, 2 months of nitrogen addition,
				Chelating agent	2 months of chelator addition (sodium citrate)
6A	Oxidized taconite	Molasses	2.5	Baseline	· · · · · · · · · · · · · · · · · · ·
7	Rod mill feed	Molasses	2	Minimum HRT	Reduce HRT by 0.5 day increments until effective minimum is reached
12	Rod mill feed	Ethanol	2	Minimum HRT	Same as Column 7 with ethanol
New Colu	umns				
13	Oxidized taconite	Molasses	2.5	Surface area	$PSD^1 = -\frac{1}{4}$, Evaluate constituent reduction with increased
					substrate surface area/decreased hydraulic potential
14	Oxidized taconite	Molasses	2.5	Surface area	$PSD = -\frac{1}{2}$ ", +8 mesh, Evaluate constituent reduction with
					decreased substrate surface area/increased hydraulic potential
15	Oxidized taconite ²	Ethanol	2.5	Temperature effects	Laboratory chiller used to control temperature of reactor
16	Oxidized taconite ²	Molasses	2.5	Temperature effects	Laboratory chiller used to control temperature of reactor
17	Oxidized taconite ²	Molasses-ethanol	2.5	Effect of carbon feed	50/50 blend by volume (initially)
		blend		source	
New Pilo	t Reactor				
NA	Oxidized taconite ²	Ethanol	2.5	Hydraulics,	Horizontal operating configuration, 8" I.D. x 6' long. Operated to
				Fate of sulfur,	model the 2002 demo unit initially. Will likely be converted to
				Iron reduction	molasses in the future
Newer Co	olumn(s)				
18	Coarse Tailings	Ethanol	2.5	Media/Hydraulics	Test treatment efficiency using coarse tailings as media vs. fouling
					potential

 1 PSD = Particle size distribution

²Particle size distribution = $-\frac{1}{2}$ "

Column 18 was put into service on or about April 15, 2003. Column 13 was taken out of service at the end of April 2003 because of chronic plugging. Column 16 was taken out of service after the first week of May 2003 because of chronic plugging.

Attachment A10.2

Procedure to follow before changing existing columns

The objective is to have a stable baseline prior to making a change in column operation so that the effect of the change can be determined.

Establish baseline Stabilize flow at existing rate run for 2 weeks sample 2 times/week SO_4 , S^{-2} , Fe

Make the change to the column Allow 1/week to stabilize Sample 1/week for first 3 weeks (new equilibration period) If stable then repeat intensive sampling, i.e., twice per week for 2 weeks

If the intensive sampling shows stable conditions then could either

continue columns as is, reduce sampling 1 week

or make a new change and repeat equilibration period sampling and then intensive sampling

Substrate (existing)

Rod mill feed

calculate surface area estimate area of Fe^{+2} and Fe^{+3}

Repeat for

oxidized ore and tailings

Estimate K_h based on size distributions

If molasses reactors are producing sufficient Fe now, could argue that existing surface area is adequate, so probably look at a smaller surface area, more permeable material. (Should look at what size fractions are already available and are cost effective)

Attachment A10.3 Correspondence related to nutrients and iron reducing bacteria.

If I remember correctly, we expected about 90% of the nutrient (ethanol) to result in sulfate reduction...about 10% went to cell growth and inefficiency. Other nutrients included KH2PO4 and NH4Cl. Micronutrients came from the mine water. That's all that was added and the system ran for years. I believe that the main problem in a passive system is the buildup of sulfide, which inhibits the activity of acetogenic bacteria. Paques uses 500 ppm sulfide as an upper limit for sulfate reducing bioreactors using ethanol. On the other hand, sulfate reducing bioreactors using hydrogen (the activity of acetogens not needed) can tolerate sulfide concentrations of about 2000 ppm with no deleterious effect.

Rick

Richard W. Hammack Research Geochemist US Dept. of Energy National Energy Technology Laboratory Pittsburgh, PA (412) 386-6585 FAX (412) 386-4459 hammack@netl.doe.gov

I'm afraid I don't have any straight-forward answers for you. Rick Hammack used to take whatever sulfide-rich effluent came from SRB bioreactors and would run it through a bioreactor with sulfide oxidizers to generate elemental sulfur. You may have more success changing your carbon source.....HRC from Regenesis is one commercially available polylactate material.....you might try regular lactate first to see if it is worth it. I don't know....there are a lot of complicating factors in this type of system. If your redox potential is low (if you smell sulfide, it must be), that is typically going to solubilize any "reducible" iron that is available, and the high organic content will tend to keep it in solution in a complexed form. If you have substantial iron in your solid medium, it is surprising you don't have an excess in solution. Is this all solid iron, and you want to solubilize it with iron-reducing bacteria? In a recent study where I added polylactic acid to smelter tailings, sulfate reduction was eventually stimulated and a lot of iron was reduced and precipitated as FeS. In the absence of added sulfate (as gypsum), the iron was reduced/solubilized but not precipitated as FeS. But these were static cultures....residence times and relative level of bacterial activity in the columns can be tricky things to balance. The "proper" flow rate for your current system may just be unacceptably slow to you.

Again, you may need more nutrients than just ethanol to support bacterial activity long-term. If you haven't done bench-scale experiments, it might be worthwhile to do them in batch at first and modify your various amendments to screen for optimal sulfate reduction/FeS precipitation conditions.

I am not a real expert on iron-reducer physiology, but my guess is that in a sulfate-rich environment, they would tend to play a role in the transition of conditions from aerobic to anaerobic, and that you might not be able to achieve the side-by-side activity with SRBs it sounds like you want. Can you run iron rich water in from a second reactor that has little sulfate in it?

Hope this is of some help. I'll cc this to Rick in case he has any ideas to add.

Hank Edenborn US Dept. of Energy National Energy Technology Laboratory Pittsburgh, PA
Attachment A10.4 New Column Porosity Tests

Substrate target volume is 8670 cm³. The top 1/3 of each new column was seeded with material from the old column 8 (manure, sawdust, cracked corn with rod mill feed) at 5% (434 cm³) of the total column volume. The columns were filled with water to determine initial (dry) void space volume and allowed to drain over night. The columns were again filled to determine the functional (wet) void space volume. The second volume was determined using an ethanol mixture at 50% concentration of the current ethanol feed which provides a carbon source for the sulfate-reducing microorganisms as they acclimate to their new environment. Columns will be allowed to acclimate for at least one week before active feeding begins.

Column	Initial void space	Functional void space	Percent of column volume
13	2630 ml.		30.34%
13		780 ml.	9.00 %
14	4312 ml.	·	49.74%
14		3434 ml.	39.61%
15	2753 ml.		31.75%
15	· -	1382 ml.	15.94%
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The "functional void space" is an estimate of the field capacity of the material in the column.

APPENDIX 11

Monitoring Recommendations for Field Test

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MN DNR's Recommendations for Monitoring USX's Sulfate Reduction Field Test

Solid Phase Analysis

Oxidized ore Tailings Manure Ethanol

Oxidized ore and Tailings

Size distribution Chemistry trace elements --either RCRA metals --or ICP/MS scan Iron Speciation Total Fe, Fe⁺³/ Fe⁺² Total S

Manure

% moisture trace elements

<u>Ethanol</u>

composition

Water Sampling

Input and Output

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Flow – continuous monitor
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--daily measurements and inspection (reduce after system stabilizes)

Water Quality

Routine Parameters

pH specific conductance temperature total suspended solids Fe

 $\begin{array}{l} Sulfur \ Species \\ Input \\ SO_4 \ / \ SO_3, \ sample \ S^{2^-} \ on \ initial \ sample \\ Output \\ SO_4 \ / \ SO_3 \ / \ S^{2^-} \end{array}$

Sample Frequency

2/week for first month 1/week after first month

Periodic Parameters

Nutrients BOD TKN NH4 NO3 / NO2 Total P Fecal Coliform TOC Ca Mg

Frequency - 1/wk for first month

every 2 wks or until results are below water quality standards

Metal Issues

Metals, RCRA or ICP/MS scan Hg issues

Total (low level)

If detectable Hg, will need to do methyl Hg

Recommend doing a complete scan on an initial sample (maybe after one week so the system is stable)

Based on the results of the metal scan, select parameters with elevated levels and determine sample frequency.

e.g., if above water quality standard, sample at same frequency as nutrients

At a minimum repeat scan / Hg in September

Ethanol, denatured products:

Same frequency as nutrients

Wells

Water level readings weekly for first month Reduce frequency based on data

Sample wells after first week for routine parameters Determine frequency based on data and system performance

Concerns/Issues

1. Fine particulates in scrubber water --settling tests (run prior to start up)

--determine rate of settling

size of pond flocculent?

Consider adding flocculent to scrubber water and sending to thickener, then take overflow to settling pond, this should minimize the amount of fines that reach the bed

2. Ethanol

Add enough to fully remove sulfate reduce based on outflow sulfate

3. Wells

Survey

Fully screened, 6'

2" PVC, schedule 80

select screen size based on particle size we have used .012 in slot material with Inland's discharge tailings

4. Fill bed at design flow rate (100 gpm) Include ethanol Let set saturated 1 week

5. Evaluate Hydraulics

What are the expected flow paths through the bed With the current outflow, how much of the bed near the outflow will be used Consider alternate outflow structures to allow an increase in head

If flow moves uniformly through the entire cross section of the bed, a permeability of around 3-4 cm/sec will be required to transmit all the flow. With the current design if the permeability is less than this value, there is no easy way to increase the head through the system. Water level will rise in the settling pond and the flow rate through the system will have to be decreased.

APPENDIX 12

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Preliminary feasability report

THE USE OF SULFATE REDUCTION TO REMOVE SULFATE FROM AGGLOMERATOR WATER AT USX

D R A F T - 12/20/01 Revisions 2/14/02

Paul Eger Minnesota Department of Natural Resources Division of Lands & Minerals St. Paul, MN

Introduction

This report provides background information on rates of sulfate reduction in both natural systems and in systems constructed to treat mine drainage, the use of additives to stimulate sulfate reduction and a suggested experimental approach. Additional information and data have been requested and will be added to this report when received.

The primary objective of this report was to review the literature and current practice to determine a list of potential substrates and additives to be used in laboratory column studies.

Substrates

The primary functions of the substrate are to:

- Provide sulfate reducing bacteria
- Consume the oxygen from the feed water to create an anaerobic condition
- Provide small chain organics to the sulfate reducing bacteria directly or indirectly through fermentative bacteria

Sulfate reducing bacteria are ubiquitous and it is generally accepted that they will become established if the substrate is held in a saturated condition for one to two weeks (Wildeman et al., 1993). In some studies, bacteria sources were added either through direct cultures (Engesser et al., 1998) by adding sewage sludge, or by adding substrate from an operating system (Wildeman et al, 1997). However, as long as the input acid load was less than the sulfate reduction rate, treatment was not dependent on the addition of cultured bacteria or on a saturation period. Equivalent treatment was obtained when the drainage was added directly to the substrate (Reynolds et al., 1997).

The dissolved oxygen content of water is low, (around 8 mg/L at 25 degrees C), and if the flow is also low, the substrates ability to provide an anaerobic environment has not been a determining factor in the selection of a substrate. The key factor is the substrate's ability to provide the small chain organic molecules required by the sulfate reducing bacteria. To provide a background for substrate selection, sulfate reduction rates in both constructed and natural systems are summarized in the following sections.

Sulfate Reduction Rates in Constructed Systems

In the initial studies with mine drainage, many of the substrates consisted entirely of organic substrate, primarily spent mushroom compost. Although the exact composition of the compost varies based on the specific type of mushroom and location, the major ingredients are generally horse manure and straw. After the mushroom crop is harvested, the substrate is replaced and becomes a waste. Since it was readily available in the eastern U.S., it became the substrate of choice in many of the initial studies with coal mine drainage.

Since mushroom compost was not available in all areas, the use of locally available organic materials was investigated. Municipal solid waste compost, yard waste compost, manure, and wood chips were used in a study in northeastern Minnesota (Eger, 1992), chicken litter and rice hulls in an Arkansas study (Gross et al., 1993), wood products, manure and peat systems were tried in Colorado (Howard, et al., 1989) and leaf compost was studied in Canada (Waybrant et al., 1995).

Despite the difference in substrate, the overall rate of sulfate reduction generally ranged from 200-600 mmoles/m³/day and a general "rule of thumb" design value of 300 mmoles/m³/day has been proposed by Wildeman, Brodie and Gusek, (1993). In newly constructed systems, the initial rates have exceeded 1000 mmoles/m³/day and a value of 2000 mmoles/m³/day was measured in a pilot system (Wildeman et al., 1997). (Table 1)

Later systems added inorganic material to the organic substrate to increase permeability and sometimes to provide for additional neutralizing capacity for acid mine drainage. Most often limestone was added since it added neutralization capacity and increased the overall permeability of the substrate. In some studies gravel (Gammon, et al., 2000; Anderson, personal communication; Miller, personal communication) and coarse taconite tailings (Engesser et al., 1998) have been used.

Sulfate reducing bacteria require small chain organic molecules, which must be available directly or are supplied by bacteria which break down the more complex organic material. Since composting tends to decease the amount of readily available reactive organics, more recent systems have been built with aged materials. Several new systems were built with limestone (increase overall permeability and provide additional neutralizing capacity), "aged" saw dust (material that had been stockpiled for several years, so breakdown had begun and was thought to provide a long term organic source), "fresh" material, usually alfalfa (immediately available organic material) and a "seed" organic, usually manure (source of sulfate reducing bacteria) (Gusek et al., 1998).

However, since the rate of sulfate reduction did not vary widely with substrate, the common approach has been to use the most cost effective material, which usually means the material is locally available. A batch test procedure to screen mixtures of locally available materials has been developed. (Wildeman and Updegraff, 1998)

Recently zero valent iron has been used to decrease the redox potential and facilitate conditions for sulfate reduction. As the iron reacts it initially consumes oxygen. Once the oxygen is removed, sulfate can become the electron receptor and the sulfate can be reduced. Although the incorporation of zero valent iron reduces the redox potential and may stimulate sulfate reduction, the reactions increase the concentration of ferrous iron in solution. This can increase the overall acidity of the solution.

Zero valent iron has been tested alone and incorporated into substrates in Canada (Blowes, personal communication). Based on unpublished laboratory studies, a mixture of organic matter and iron was more effective than just zero valent iron. Although eventually the iron should produce enough H₂ to supply the bacteria, it takes some time to establish the appropriate conditions. A successful substrate has been made from 30% iron, 40-50% gravel (~ $\frac{1}{2}$ ") and 20-30% leaf compost (percent by volume). Using this mixture, sulfate reduction rates on the order of 1-5 mg/L S0₄/day/gm dry weight have been observed.

Sulfate Reduction Rates in Natural Systems

Reported rates of sulfate reduction in natural systems have generally been on the same order as those reported for constructed systems (Table 2). Rates in surface marine sediments which contain the most reactive material are 1000-2000 mmoles/m³/day but rates in deeper sediments can be as much as an order of magnitude lower. The decrease is attributed to the reactivity of the organic matter (Westerich and Berner, 1988).

In natural peatlands the reported rates are generally lower than in surface sediments of fresh water and marine environments. Measured rates are on the order of 100 -200 mmoles/m³/day. Sulfate reduction rates were measured in a variety of wetland soils, both organic and mineral (Angelo and Reddy, 1998). Rates per unit mass in organic soils were generally higher than those in mineral soils and were correlated to the amount of total carbon in the soil. Rates expressed on a volumetric basis were similar and ranged from 76-288 mmole/m³/day for mineral soils to 59-216 mmole/m³/day for organic soils. The maximum rate was 880 mmoles/m³/day and was measured in soil collected from a wetland that received treated waste water.

Effect of Temperature

The rate of sulfate reduction decreases as temperature decreases, with a reported Q_{10} of around 3.0 (Westrich and Berner, 1988). (The Q_{10} is defined as the change in reaction rates for a 10° C change in temperature). For less reactive organic matter, (for example, deeper sediments) the Q_{10} is greater than 3.0 (Westrich and Berner, 1988). In field studies, winter rates were up to an order of magnitude lower than summer rates, and in some studies approached zero (Gammons et al., 2000, Hedin et al., 1991, McIntire et al., 1990; Weider, 1992).

Additives

By adding material that contains small chain organics, the rate of sulfate reduction should increase. The most common successful additives have been lactate, acetate, ethanol and hydrogen. Methanol was hardly used by sulfate reducing bacteria in some studies, but was quite effective in stimulating sulfate reduction in a depleted substrate (Widdel, 1988, Tsukamoto and Miller, 1999). In several studies the addition of lactate increased the rate of sulfate reduction and metal removal. The rate of sulfide production increased by a factor 2.4 when sodium lactate was added and by 4.3 when a hay extract was added (Reynolds et al., 1991). Hay addition also

provided a short-term increase in sulfate reduction rates in a field study in northeastern Minnesota. Nickel and sulfate concentrations were lower immediately after the hay was added, but returned to original values in less than a year. (Eger et al., 1997,2000).

At the Mike Horse Mine in Montana, methanol has been used as the carbon source for a gravel subsurface treatment bed. A proprietary organic material produced by Greenworld Science has also been used. The system was initially designed to run off the organic material produced from the vegetation that was planted on the surface of the gravel bed. Despite good vegetation growth of several native Carex species, insufficient organic matterial increased zinc removal (either reduction and remove zinc. The addition of organic material increased zinc removal (either methanol or the proprietary material) from about 75% to over 98% in the summer and from 0 to 75% in the winter (Anderson, personal communication). Although waste products were considered, methanol was chosen because of its relatively low cost, its purity and consistency, and its low freezing point.(Anderson, personal communication)

Several companies produce lactate products for adding to groundwater (JRW, Regenesis), but these products are fairly expensive (about \$.60/lb for the JRW product which is a pharmaceutical grade and about 10 times that amount for the Regenesis compound which is a slow release proprietary chemical). Molasses has been used to create reducing zones in groundwater at sites in Pennsylvania and California. By creating reducing conditions, it was possible to reduce Cr⁺⁶ to Cr⁺³. Since sulfate has not been a parameter of concern at these sites, no information was immediately available. (Dennis, personal communication)

Methanol was used as an additive in a wetland in Nevada. The original system was a vertical flow system, constructed from horse manure mixed with sand. Although successful initially, efficiency decreased and after several months there was little iron or sulfate removal. Adding methanol to the system increased removal efficiency. Ethanol and ethylene glycol (the main component of antifreeze) were also tried and were very effective. A gravel replacement system was built from 3/4" to 3" rock. This system is fed with ethanol and has been very successful in treating the drainage.(Miller, personal communication) (Ethanol cost was comparable to methanol, about \$2/gallon, and was the most environmentally acceptable additive)

Not all organic additions have produced significant increases in sulfate reduction rates. When dairy whey was added to a recently constructed wetland, little to no effect was observed (Stark et al., 1994). Neither lactate or acetate stimulated sulfate reduction in Lake Mendota sediments, but ethanol and hydrogen did increase the reaction rate.

Substrate Selection

The ideal substrate would supply small chain organics at a constant rate over an extended period of time. If this condition was met, the sulfate reduction rate would be constant.

Kuyucak and St. Germain (1992) suggest that the optimum substrate should have a C:N:P ratio of 110:7:1. They analyzed a series of organic materials including those with high cellulose contents (Table 3). In order to achieve the correct C:N:P ratio, a mixture of wood pulp, manure, and brewers dried grain was used. This substrate produced a sulfate reduction rate comparable to the rate achieved by an inorganic solution of lactic acid, ammonium sulfate, and potassium biphosphate.

Although a variety of substrates have been used, the most common and most successful have been the manure based systems (this includes spent mushroom compost). In general, these systems had the highest rates and formed stable metal sulfides (Weider, 1992). One possible explanation for the success of the manure based systems is that the C:N:P is close to the ideal ratio of 110:7:1.

Unfortunately, the rate of organic decomposition is exponential (Tarutis and Unz, 1994). Substrates initially have a high concentration of small chain organics and breakdown fairly rapidly. As the organic material ages the residual material reacts more slowly ("refractive") and the supply of small chain organics decreases and the rate of sulfate reduction also decreases (Eger and Wagner, 2001, 1995). To maintain high reaction rates requires either an input of organic matter or substrate replacement.

The typical method of substrate selection is to survey the available materials, to conduct short term laboratory tests, and select a suitable substrate, based primarily on availability and cost. To treat the entire flow of agglomerator water will require large amounts of substrate. If we assume an input flow of 5000 gal/min with 1200 mg/L sulfate, and the goal is to reduce the concentration by at least 50% the volume of substrate would range from 110,000 to 750,000 yd³, depending on the rate of sulfate reduction (Table 4). Given the large volume requirement the final selection will be largely based on availability and cost.

The recommended substrates for the column tests are:

Organic

The substrates that perform the best overall were manure based. Manures contain sulfate reducing bacteria and available carbon. A single organic substrate should be developed based on availability of material. Aged manure should be a part of the final substrate.

Inorganic: Coarse material

Coarse material is needed to provide structure and permeability to the substrate. For the column studies ½ inch material would be suitable, although field systems have generally been constructed with 3/4 to 3" material. Either coarse tailings or ½ inch ballast material could be used since these are produced on site and will supply iron to the system to help tie up the sulfide

generated from the sulfate reduction reactions. (Taconite pellets might also work). Systems currently being constructed typically contain about 40- 50% by volume inorganic material.

Zero valent iron.

Zero valent iron promotes reducing conditions, provides hydrogen which will stimulate the sulfate reducing bacteria, and will release ferrous iron to help tie up the sulfide generated from the sulfate reduction reactions. The most commonly used form is iron filings.

Organic Additives

Although there are several potential additives, field trials have been done with methanol, ethanol and ethylene glycol. Ethanol has been shown to be an effective additive in both laboratory and field studies. Cost, availability and handling issues will most likely drive the selection of the specific additive.

Recommendations for Column Experiments

Details on the suggested column design are provided in Appendix 1. To keep the number of columns manageable, it is suggested that one organic substrate, one coarse material, one source of zero valent iron and one additive be used. The recommended combinations for the column tests are:

Controls

Column 1 water only

Preliminary lab tests by USX showed that sulfate concentrations in the agglomerator water decreased to levels seen in the pilot cell when the water was allowed to sit in the laboratory.

Column 2 coarse material

This column is included since sulfate concentration in the pilot system appears to be solubility controlled. One possible explanation for the constant sulfate concentration in the pilot cell is that the concentration of sulfate is controlled by gypsum solubility, and that the calcium is supplied by the materials used to construct the system. Column 2 will also provide a control for the organic additive column, column 7.

Substrate columns

Column 3: organic substrate + coarse material

Column 4: organic substrate + coarse material + iron filings

Column 5: coarse material + zero valent iron

The most commonly used form of zero valent iron has been iron filings, although waste foundry sources also contains iron. One source of iron filings is Connelly in Chicago; 773-247-7231. The substrate should contain about 10 - 30% zero valent iron by volume.

Column 6: Peat/screenings mixture

This is the material from the pilot cell. A similar mixture was tested in a field trial at the old Amax site. Sulfate reduction rates were lower than for the more reactive municipal solid waste composts and ranged from 228 mmoles/m³/day in the first year to 92 mmoles/m³/day in the second year (Appendix 2). Should there be 2 columns, one for peat screenings mixture (used in 6 cells) and one for the screenings alone (used in 3 cells)

Organic Additives

Column 7: coarse material + organic additive

In columns with organic substrate, there is usually enough reactive carbon available initially, so it would not be necessary to add additional organic material. There may not be a sufficient bacterial population to use the additional carbon. However, as the readily available material in the substrate is consumed the additive becomes more important.

To determine the effect of the organic additive:

Column 8: organic substrate + coarse material + organic additive

Column 9: organic substrate + coarse material + iron filings + organic additive

Column 10: coarse material + iron filings + organic additive

Column 11: Peat/screenings mixture + organic additive

Residence Time

The current practice and recommendation for residence times are on the order of 2 - 4 days. When large flows need to be treated, the residence time is critical in sizing the system. In order to minimize the number of columns, one flow rate (which will determine the residence time) should be selected. If the rate of sulfate reduction in a column is so high that all the sulfate is removed, the flow rate will need to be increased.

References

Anderson, Bob. 2001. Hydrometrics, personal communication.

Angelo, Elise M. and K.R. Reddy. 1999. Regulators of heterotrophic microbial potentials in wetland soils. In: *Soil Biology and Biochemistry*, Vol. 31, p. 815-830.

Blowes, Dave. 2001. University of Waterloo, personal communication.

Boudreau, B.P. and J.T. Westrich. 1984. The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments. Geochim. Cosmochim. Acta 48. p. 2503-2516.

Dennis, Eugene. 2001. EPA remedial project manager, personal communication.

Dvorak, D.H., Hedin, R.S., Edenborn, H.M. and P.E. McIntire. 1991. Treatment of metal contaminated water using bacterial sulfate reduction; results from pilot-scale reactors. In: *Proceedings of the 1991 National Conference of the American Society of Surface Mining and Reclamation*, May 14-17, 1991, Durango, CO.

Eger, P., Wagner, J. 2001. Sulfate reduction - decreases in substrate reactivity and the implication for long term treatment. In Land Reclamation - A Different Approach. 18th Annual Meeting ASSMR, Albuquerque, New Mexico, June 3-7, 2001. p. 542-557.

Eger, P., Wagner, J. 2001. Sulfate reduction - designing systems for long term treatment. In 2001: A Mining Odyssey. CD-Rom. Society of Mining Engineers Annual Meeting, Denver, CO, February, 26-28, 2001. Paper 01-115.

Eger, P., Wagner, J., Melchert, G., Antonson, D., Johnson, A. 2000. Long term treatment of mine drainage at LTV Steel Mining Company's Dunka Mine. MN Dept. Nat. Resour., Div. of Lands and Minerals, St. Paul, MN. 54 p. plus appendices.

Eger, P., Wagner, J. 1995. Sulfate reduction for the treatment of acid mine drainage: Long term solution or short term fix? <u>In</u> Proceedings of Sudbury '95 - Mining and the Environment. May 28-June 1, 1995, Sudbury, Ontario, Canada. p. 515-524

Eger, Paul. 1992. The use of sulfate reduction to remove metals from acid mine drainage. <u>In</u>: *Proc. of American Society for Mining and Reclamation Meeting*. Duluth, MN, June 14-18, 1992. p. 563-575.

Engesser, John. 1998. The removal of sulfate and fluoride from process water - the effect of water chemistry on filtering and flotation. Natural Resources Research Institute - Coleraine Minerals Research Laboratory, Coleraine, MN. 20 p. plus appendices.

Gross, M.A., Formica, S.J., Gandy, L.C. and J. Hestir. 1993. A comparison of local waste materials for sulfate-reducing wetlands substrate. In: Constructed Wetlands for Water Quality

Improvement. p. 179-185.

Gusek, James, Mann, Carl, Wildeman, Thomas and Denis Murphy. Operational results of a 1,200 gpm passive bioreactor for metal mine drainage, West Fork, MO. <u>In</u>: *ICARD 2000, proceedings from the 5th Int'l. conference on acid rock drainage*, Vol. 2, p. 1133-1137.

Howard, Edward A., Emerick, John C. and Thomas R. Wildeman. 1989. Design and construction of a research site for passive mine drainage treatment in Idaho Springs, CO. <u>In:</u> Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural. Donald A. Hammer, ed. p 761-773.

Howarth, Robert W., and Susan Merkel. 1984. Pyrite formation and the measurement of sulfate reduction in salt marsh sediments. In: Limnol. Oceanogr., 29(3), p. 598-608

Ingvorsen, K., Zeikus, J.G., and T.D. Brock. 1981. Dynamics of bacterial sulfate reduction in a eutrophic lake. In: *Applied and Environmental Microbiology*, p. 1029-1036.

Kuyucak, Nural and Pascale St-Germain. In situ treatment o acid mine drainage by sulphate reducing bacteria in open pits: scale-up experiments. Noranda Technology Centre, Point-Clare, PQ, Canada.

McIntire, P.E., Edenborn, H.M. and R.W. Hammack. 1990. Incorporation of bacterial sulfate reduction into constructed wetlands for the treatment of acid and metal mine drainage. <u>In</u>: *Proceedings of National Symposium on Mining*, Knoxville, TN. May 14-18, 1990.

Miller, Glenn. 2001. University of Nevada-Reno, personal communication.

Reynolds, J.S., Machemer, Steven D., Updegraff, David M. and Thomas R. Wildeman. 1997. Potentiometric titration method for determining rates of sulfate reduction in a constructed wetland. In: *Geomicrobiology Journal*, Vol. 14, p. 65-79.

Reynolds, Julia S., Bolis, Judith L., Machemer, Steven D. and Thomas R. Wildeman. 1991. Sulfate reduction in a constructed wetland. Colorado School of Mines, Golden, CO.

Stark, Lloyd R., Wenerick, William R., Williams, M. and Paul J. Wuest. 1995. The effects of pH, flow rate, and carbon supplementation on manganese retention in mesocosm wetlands. In: *J. Environ. Qual.*, Vol. 24, p. 816-826.

Spratt, Jr., Henry G., Morgan, Mark D., and Ralph E. Good. 1984. Sulfate reduction in peat from a New Jersey pinelands cedar swamp. <u>In</u>: *Applied and Environmental Microbiology*, July 1987, p. 1406-1411.

Tarutis, W.J. and R.F. Unz. 1994. Using decomposition kinetics to model the removal of mine water pollutants in constructed wetlands. <u>In Water Science and Technology</u>, Vol. 29. p. 219-226.

Tsukamoto, T.K., and G.C. Miler. 1999 Methanol as a carbon source for microbiological treatment of acid mine drainage. In *Water Science and Technology*, Vol. 33. p. 1365-1370.

Waybrant, K.R., Blowes, D.W. and C.J. Ptacek. 1995. Selection of reactive mixtures for the prevention of acid mine drainage using porous reactive walls. Presented at the 1995 Sudbury Conference on Mining and the Environment, Sudbury, ON, Canada.

Westrich, Joseph T. and Robert A. Berner. 1988. The effect of temperature on rates of sulfate reduction in marine sediments. In: *Geomicrobiology*, Vol. 6, p. 99-117.

Widdel, F. 1988 In: Biology of Anaerobic Microorganisms, Alexander J.B. Zehnder, ed., John Wiley & Sons, p.469-586

Wildeman, Thomas, Gusek, James J., Miller, Aaron, and James Fricke. 1997. Metals, sulfur, and carbon balance in a pilot reactor treating lead in water. *Insitu and On-Site Bioremediation*, Vol. 3, Battelle Press, Columbus, OH. p. 401-406.

Wildeman, T.R., Brodie, G.A., and Gusek, J.J. 1993. Wetland design for mining operations. Bitech Pub., Vancouver, BC. 300 p.

					Results			
Substrate	Drainage Type	Test	Description	Residence Time	Sulfate Reduction Rate mmoles/m ³ /day	Duration of Experiment	Treatment	Reference
Alfalfa Composted manure Limestone	Neutral mine drainage	Full scale anaerobic bed	2 cells, each ~1/2 acre; substrate depth 6 ft.; flow ~1200 gpm downflow	~12 hours	~2000	2 years	Pb removed	Gusek et al., 2000
Alfalfa Composted manure Limestone	Neutral mine drainage	Pilot cell		~12 hours	200-2000 (winter- summer); rate calculated from sulfide production	60 days	Pb removed	Wildeman et al., 1997
Municipal solid waste compost	Acid mine drainage	Field	Small scale field test; different substrates		400	:		Eger, 1992
85% pea gravel 15% leaf compost (by volume)	Metal contaminated groundwater		Permeable reactive wall, wall 6.7 m deep, 10 m long, 2.5 m thick; Kn 1.5 x 10 ⁻¹ cm/sec	3.8 days	Not calculated	1 ½ years	Metal removal	
Wood pulp manure, brewers' dried grains	Mine water AMD	Laboratory study	Tests conducted in 280 L drums and column 5 m high, 160L volume		300	1.4 months	Ph increased metals removed	Kuyucak, St. German, 1992
Mushroom compost	Acid mine drainage (coal)	Field			150-200			McIntire et al., 1990

Table 1. Sulfate reduction rates in constructed systems.

					Results			
Substrate	Drainage Type	Test	Description	Residence Time	Sulfate Reduction Rate mmoles/m ³ /day	Duration of Experiment	Treatment	Reference
Mushroom compost	Acid mine drainage (coal)	Field			377			Dvorak et al., 1991
Mushroom compost	Circumneutral drainage	Field			250			Dvorak, et al., 1991
Fresh mushroom compost 50% animal manure; 50% barley mash waste	Acid mine drainage	Lab	Compared rates calculated from S^{-2} production, SO_4 removal and radio- active tracer; all rates are equal		1600 initial rate (t <35 days) 800 (35 < t <110 days)			Reynolds et al., 1997
Peat, sand, grass, grass seed, bacteria & tailings	USX Tailings Basin water	Laboratory study	Short term column test	2.6	average: 1380; maximum: 2490			Engesser, 1998

Table 2. Sulfate reduction in neutral systems.

Substrate	Description	Results	Rate - mmoles/m ³ /day	Reference
Salt water marsh sediments	Radioactive tracer	Rates decreased with depth	Surface sediments 1000- 2000; rate decreased with depth	Howarth and Merkel, 1984
Eutrophic Lake sediments	Radioactive tracer	Rate varied with date of sampling and temperature	50-600; rate decreased with depth	Ingvorsen et al., 1981
Wetland soils	Change in sulfate concentration	Rates generally correlated with total carbon in soil	59-288 (880 for wetland receiving waste water)	Angelo and Reddy, 1999
Peat	Radioactive tracer	Rates varied with season (lowest in winter)	1-173 (rates decreased in winter and with depth in peat)	Spratt et al., 1987
Acid mine lake			Deep sediments 18-41 Shallow 0-128	Boudreau et al, 1998
Maine sediments		Rates varied with location, season and depth; rate at least 10 x slower at depth	Surface sediments 15-130 (winter-summer); 600-1800 (winter-summer); (for anoxic basin with very high sedimentation rate)	Westrich and Benner, 1988

Table 3. C, N, P ratios in waste materials.

		······································	
Substrate	Organic Carbon	Organic Nitrogen	Organic Phosphorus
Raw wastewater sludge	26.2	2.8	1
Brewers' yeast	31.5	1.06	1
Digested wastewater sludge	32.3	2.4	1
Distillers' grains	58.4	3.84	1
Whey	60.3	2.38	1
Brewers' grains	85.6	4.65	1
Cow manure	100	3.16	1
Sugar maple leaves	191	7.18	1
Oat straw	209.5	3.85	1
Bark (3 years)	519.2	14.6	1
Fuel peat	743.8	61.3	1
Straw	915	5.97	1
Cane molasses	1481.8	13.6	1
Wood pulp	1595	56.7	1
Bark (30 years old)	1610	64	1
Corn starch	2322	18.3	1
Oak leaves	1660	11.4	1
Newspaper	2760	0.42	1
Sawdust	11300	65	1
Pine sawdust	30200	26.9	1

Data from Kuyucak et al., 1991, and Kuyucak and St. Germain, 1992.

Table 4. Treatment system size.

Sulfate Reduction	Volume	Depth of	Aı	ea	Residence
Rate mmoles/m ³ /day	Required (m ³)	Substrate (m)	(ha)	(acre)	Time (Days)
300	5.7 x 10 ⁵	1	57	140	10 ½
1000	1.7 x 10 ⁵	. 1	17	42	3
2000	$0.85 \ge 10^5$	1	8.5	21	1 1/2

Assumptions: Input flow Input concentration Output concentration 5000 gal/min 1200 mg/L 600 mg/L

D 1 10 1 5000	1// 1 1 1 1 0 1 / 1	A FOFT / 1	
Degred gultate reduction: 5000	$\sigma_0 / m_1 n \mathbf{v} / / / (1 m_1 n / d_0 \mathbf{v} \mathbf{v})$	2 /85 1 /ool v /	1'200 600 ma/1
Desired surface reduction. JUN	$2a_1//10111 \times 1440/10111/0a_V \times$	$J_{1}0J_{1}2a_{1}x_{1}$	

96 mg/mmole 1.7 mmole/day

 $1 ha = 10,000 m^2$ 1 ha = 2.47 acres

Residence time calculated assuming 50% porosity.

Appendix 1

Laboratory Column Design for USX (vertical downflow system)

Columns (30" high) are to be constructed from clear $5\frac{3}{4}$ " I.D. acrylic plastic. A $\frac{1}{4}$ " high acrylic support fabricated from the tubing is glued into the bottom of the cell to support a 1/16" thick PVC plate, which is perforated with $\frac{1}{8}$ " holes spaced 7/32" on center. The bottom is sealed with an acrylic plate with a $\frac{1}{4}$ " outlet port in the center and a removable cover, with a $\frac{1}{4}$ " vent hole for the input tubing, is placed on top of the column. (Both the top and bottom plates will need to be fabricated). One-half inch layers of graded silica sand are placed on the perforated plate in the bottom of the column prior to loading the substrate. The bottom sand layer is $-\frac{1}{4}$ / +6 mesh, then a layer of -6 / +8, and the final layer is -8 / +14.

All substrates and additives, if applicable, are blended individually on a plastic sheet using the four corner method. In this method, each corner is grabbed and pulled over the pile. This procedure is repeated ten times. The pile is then split into four equal sections. The amount needed for a column is taken from as many sections as needed. The material is then loaded into the column. This process is repeated for each of the materials required for the column experiment. Depth of material for each column will be 12 inches.

Water is fed into the top of the column using a peristaltic pump and the input water flows by gravity through the column. The flow rate for the input water will be on the order of 0.25 to 2 mL/minute. Flow from the columns can be collected in 5 gallon pails, or larger containers, except when taking a sample. Sample events should be collected in clean plastic bottles sized to ensure adequate sample for all parameters.

Contact Dave Antonson with any questions on column design.

Materials

Vender for plastic materials

United States Plastic Corp. 1390 Neubrecht Rd. Lima, OH 45801 1-800-537-9724 Fax: 1-800-854-5498 www.usplastic.com

Material	Order #	Estimated Cost
5 ³ / ₄ " I.D. Acrylic tubing for columns ¹	44077	\$13.33 / ft.
Acrylic sheet for bottom and cover (48" x 48")	44368	\$41.60
PVC perforated sheet for bottom plate (48" x 48")	45172	\$47.64
¹ / ₄ " Adaptor of outlet port (one per column)	62006	\$.20 each
¹ / ₄ " I.D. tubing for outlet port	59006	\$8.16 / 50ft.
Solvent cement for acrylic (5 oz. tube)	44629	\$4.82 / tube

1 - Available in 5' lengths only. Discount: less 5% in 10 ft.; less 10% in 20 ft.; less 15% in 60 ft.

Vender for peristaltic pumps and tubing

Barnant Company 28W092 Commercial Avenue Barrington, IL 60010-2392 1-888-626-6782 Fax: 1-847-381-7053 www.barnant.com

Pump Head: Manostat (Carter 12/6), model #: 74-126-12131. Comes standard with 8 small cassettes and 2 large cassettes. Cost: \$2125

Small cassettes have a flow range of .0012 - 14 mLs/min. model #: 72-560-000 Large cassettes have a flow range of .016 - 74 mLs/min. model #: 72-560-100 Cost for additional cassettes: \$50/each

Tubing for the pump is included but the tubing from the feed bucket and a connector to the supplied tubing will have to be ordered separately.



Figure A1-1. Schematic of column design for USX experiments.

Appendix 2

Engesser 1998

Rate of sulfate reduction calculated from

Assumptions	
input concentration constant	531 mg/L
flow rate constant	1 ml/min
total volume in column	3.7 L
porosity in column	50%

Calculation Procedure

For the days between samples, an average outflow concentration for the time period was used. The only exception was the beginning of the experiment. The outflow concentration on day 3 was used for days 1 and 2.

total sulfate removed = 13725 mg SO_4				
(column ran for 2	28 days)			
average rate	=	<u> </u>		
(sulfate reduction)		96 mg/mmole 28 days 3.7 L m ³		
	-	1380 <u>mmoles</u> m ³ day		

Maximum daily rate

During the last week the average outflow concentration was 85 mg/L; 642 mg sulfate were removed each day, so

 $\frac{642 \text{ mg}}{96 \text{ mg/mmole 1 day 3.7 L}} \quad 1000 \text{ L/m}^3$

 $= 2490 \ \underline{\text{mmoles}}{\text{m}^3 \text{ day}}$

Column Calculations and Notes (corrected 2-14-02)

substrate

5.75" ID
12" depth
$$V = \pi r^2h$$

 $V = \pi \frac{(2.88)^2(12) \times 28.316L/ft^3}{1728 in^3/ft^3} = 5.1L$ substrate

assume reduction rate 300 mmoles/m³/day

input 1200mg/L, reduce 50%, outlet 600mg/L

$$\underbrace{1}_{1000 \text{ L/m}^3} \text{ x } \underbrace{300 \text{ mmole } \text{x } 5.1 \text{ L}}_{\text{m}^3 \text{ day}} = Q \underbrace{\text{L}}_{\text{day}} \text{ x } \underbrace{600 \text{ mg/L}}_{\text{day}}$$

$$Q \underline{L} = \underline{300 \text{ mmoles}} \times 5.1 \text{ L} \times \underline{96 \text{ mg}}$$

$$\underline{\text{mmole}}{1000 \text{ L/m}^3} \times \underline{600 \text{ mg/L}}$$

$$= .25 \text{ L/day}$$

$$= .25 \underline{L} \times \underline{1000 \text{ ml}}$$

$$\underline{\text{day}} \underline{L} = 0.17 \text{ ml/min}$$

residence time

assume porosity ~ 50% pore volume 2550 ml

 $\tau = \frac{\text{Pore volume}}{\text{Q}} = \frac{2550 \text{ ml}}{.17 \text{ ml/min x } 60 \text{ min/hr x } 24 \text{ hr/day}} = 10.4 \text{ days}$

if input flow is 1 ml/min

get $\tau = 1.78$ days ~ 2

and an expected reduction of

 $\Delta C = \frac{300 \text{ mmole/ x } 5.1 \text{ x } 96}{1.44 \text{ L/day x } 1000 \text{ L/m}^3}$

= 102 mg/L

sample schedule ~ 2 /week: if start on Monday could sample on Thursday and Monday since substrate will be new, should have an initial rate greater than 300.

if the rate of reaction ~ 1000 mmoles/m³/day, then Δ C ~ 500 mg/L

To minimize the development of preferential flow channels and short circuiting through the column, the rule of thumb for column design are:

column diameter ≥ 10 x maximum particle column length ≥ 10 x column diameter

if a $\frac{1}{2}$ " coarse particle is used then diameter should be at least 5" depth of substrate 50"

in the Soudan columns, the column diameter was 6"; column length was 12"; these contained substrates that were fairly uniform and could be mixed to give a consistent material

in order to determine the lifetime of the substrate the diameter of the column was kept to a minimum

In the USX columns a variety of mixtures will be used, so a larger column would be beneficial.

increase column length to 24"; this doubles the volume of substrate in column so new values would be:

column summary

substrate volume10.2 Linput flow1 ml/minestimated residence time~ 4 daysestimated change in sulfate concentration

- at 300 mmoles ~ 204 mg/L m³/day
- at 1000 mmoles ~ 680 mg/L m³/day

Procedure

shorten columns to accommodate

24" substrate

screened sand

flange

6" head

(if need more than this substrate too impermeable)

Need to fill to insure no segregation

slowly add input water to fill up all pore space record volume of water needed to completely saturate solid measure of porosity

bring water up to outflow level let columns sit for 1 week

begin to add input at 1 ml/min using tailings basin water as feed will have around 1000 mg/L sulfate in input water

rate	estimated output
300	796
1000	320

may need to increase flow if flow 2 ml/min

rate	estimated output
300	898
1000	660

residence time ~ 2 days

to $\tau = 4$ days sample schedule ~ 2/week if start on Monday could sample on Thursday and Monday

Notes

Need to ventilate room or install collection bottles in hood

Rate of Sulfide Generation

 $\begin{array}{c} \text{if reduce } \underline{300 \text{ mmoles}} \text{ of SO}_4 \\ \text{m}^3\text{/day} \end{array}$

generates $\frac{300 \text{ mmoles}}{\text{m}^3/\text{day}}$ of S⁻²

to tie up as FeS would require $\frac{300 \text{ mmoles}}{\text{m}^3/\text{day}}$ Fe⁺²

or 300 mmoles x 56 mg Fe x 365 days/yr x 10^{-6} Kg/mg = 6.1 Kg Fe required/year mole

or 6.1 Kg x 2.2 lb/Kg x (.3048 m/ft)³ - 0.41 lb/ft³/year

bulk density iron filings 160 lbs/ft³

 $K_h 5 \ge 10^{-2}$ cm/sec grain size (typical) 2 mm to 0.25 (-8 to +50 mesh)

so, if had 30% zero valent iron by volume

 $160 \text{ x} .3 = 48 \text{ lb Fe/ft}^3$

to tie up sulfide could reduce Fe even at 10%, would have 16 lb/ft³ or 432 lbs/yd

therefore, 1 ton of iron filings would be needed for 5 yds of substrate at cost of \$345/ton + shipping would mean that the iron for the substrate would be over \$60/yd of substrate

if system operated for 10 years would require ~ 4 lbs if reaction rate faster, for example 1000 then would need ~ 12 lb over 10 years.

So system should contain at least 10% by volume, will also get some iron from rod mill feed, but probably best to design assuming all Fe from zero valent

Carbon requirements

need 2 moles of carbon for each mole of S reduced

so per liter of input water

 $\Delta \text{ SO}_4 = \underline{600 \text{ mg/L}}_{96 \text{ mg/mmoles}} = 6.25 \text{ mmoles/L}$

need 12.5 mmoles C

if all added C comes from added carbon

ethanol - C₂ H₅ OH MW = 46
% C =
$$\frac{24}{46}$$
 = .52

100% ethanol = .79 gm/cm³ x $\underline{.52}$ x 1000 mg/gm = $\underline{34 \text{ mmole}}$ (density at 20°C $\underline{12 \text{ mg}}$ Perry's Handbook)mmole

so, to provide 12.5 mmoles would need $\sim 0.4 \text{ cm}^3$ 100% ethanol for liter of feed

to treat 5000 gal/min x 3.785 L/gal x .0004/L = 7.6 L/min or about 2 gal/min = 2800 gal/day

at \$2/gal:

annual cost \$2/gal x 2880 gal/day x 365 day/yr ~ \$2.1 million

Insert methanol calc.

Flow through column

Q = K_h A
$$\Delta H$$

L Q = 1 ml/min
A = $\pi \frac{(5.75 \text{ in})^2}{(2.54 \text{ cm/in})^2} = 167 \text{ cm}^2$

$$K_{h} = \underline{Q} \qquad \Delta H = \underline{2 \text{ in head}} = .083$$

$$A \underline{\Delta H} \qquad 24 \text{ in total column}$$

$$L$$

$$K_{h} = \frac{1 \text{ ml/min}}{167 \text{ cm}^{2} \text{ x .083 x 60 sec/min}} = 1.2 \text{ x } 10^{-3} \text{ cm/sec}$$

In field setting

Assume reaction rate 2000 mmoles/m³/day and using data from table 4

Q = 5000 gal/min A = 8.5 x 10^4 m² bed depth = 1 m water depth above bed = 1/3 m

$$\Delta H/L = \frac{1/3}{1} = .33$$

to transmit this flow would require

$$K_{h} = \underline{Q} = \underline{5000 \text{ gal x } 3.785 \text{ L/gal x } 1000 \text{ cm}^{3}/\text{L}}$$

A Δ H/L 8.5 x 10⁴ m² x (100 cm/m)² x .33 x 60 sec/min

 $K_{h} = 1.1 \text{ x } 10^{-3} \text{ cm/sec}$

if were to increase bed depth to 2 m

reduce area by 2 and increase the depth of water to 2/3 m

 K_h required = 2,2 x 10⁻³ cm/sec

if by increasing the depth of water above the bed, the gradient A Δ H/L remains constant

if the water depth was maintained at 1/3 m would need a $K_h = 4.4 \text{ x } 10^{-3} \text{ cm/sec}$

Soudan columns (6" diameter, 12" substrate, 2" water above substrate)

Q = 2 ml/min A = π (3 in x 2.54 cm/in)² = 182 cm²

$$\underline{\Delta H} = \underline{2"} = .167$$

 $K_{h} = \frac{2 \text{ ml/min}}{182 \text{ cm}^{2} \text{ x} .167 \text{ x} .60 \text{ sec/min}} = 1.1 \text{ x} 10^{-3} \text{ cm/sec}$

These columns have run with this head for about 5 years However, since K_h may decrease with time should include safety factor

 $\begin{array}{ll} K_h \ \mbox{lab minimum} & 10^{-3} \\ K_h \ \mbox{field} & 10^{-1} \ \mbox{to} \ 10^{-2} \end{array}$

USX update column design

flow rate = 2 ml/min residence time = 2 days

Rationale: In order to minimize the size of the final system, need to have a sulfate reduction rate > 300 mmoles/m³/day. To determine the rate the sulfate in the column outflow must be measurable. A residence time of 2 days is within recommended range.

Sampling Minimum of twice per week to generate sufficient data to do a preliminary evaluation Schedule: of the substrates.

Parameters:

SC SO_4 S^{-2} CaFe nutrients B

pН

BOD Total P

 $\rm NH_4N$

Ethanol on columns with additive?

This may only be possible on substrates without organic material, the organic substrates will release substantial quantities of organic material and will probably cause analytical interference

Digital photos to record color

Frequency: pH, SC, Sulfate every sample S^{-2} , Fe, Ca once per week nutrients, initial sample then monthly

Substrates: % moisture % ash Total C, organic C Total N Total P Metals (compost, EQ list) Columns:

Mixtures should designed to provide maximum organic substrate with enough inorganic material to maintain permeability.

Blowes recommendations are for inorganic to be about 50% by volume, Wildeman uses about 50% by weight (as received)

Soudan columns were less than that

limestone $\sim 25\%$ by weight

Determine mixtures by volume then weigh substrate to determine weight percentage (as received)

Estimate porosity after pack column

Additive:

To supply 100% of required carbon to reduce 600 mg/L would require 0.4 cm³ per Liter of feed

Supply carbon in excess, so if have 1000 mg/L input add 0.8 cm³ per Liter or 8 ml of 100% ethanol for every 10 L
Column	Organic Substrate	% by volume	Zero Valent Iron	% by volume	Inorganic Substrate	% by volume	Bacterial Seed	Additive
1	sugar beet waste				rod mill feed		No	No
2	sugar beet waste			·	rod mill feed	·	No	Yes
3	sugar beet waste		mill waste		rod mill feed		No	No
4	peat		·		rod mill feed		No	No
5	peat				rod mill feed		No	Yes
6	peat		mill waste		rod mill feed		No	No
7	manure				rod mill feed		No	No
	saw dust							
8	manure	-			rod mill feed		No	No
ļ	saw dust							
	feed corn							
9	manure						· · · · · · · · · · · · · · · · · · ·	
[hay				. •			
10	biosolids				rod mill feed		No	No
	saw dust	· · ·			• •			
· · · · · · · · ·	hay							
11	None		mill waste		rod mill feed		Yes	No
12	None				rod mill feed		Yes	Yes

3 most prevalent organics:

- sugar beet waste
 - alone
 - iron
 - additive
- peat
 - alone
 - iron
 - additive
- saw dust
 - manure
 - iron
 - additive
- How much iron?
- How much saw dust?
- Difference in sugar beet pulp & tailings are their 2 products or one?

 $K_{\rm h}$ column ~ 10⁻³ cm/sec = 4 days

@ 1 ml/min minimum

safety factor at least 10 x faster $\sim 10^{-2}$ cm/sec

Miscellaneous

compost 40-50% water 50-60% organic material

Sodium lactate - Na $C_3 H_5 O_3$

To have anaerobic conditions, need to consume oxygen $\frac{8 \text{ mg } O_2 \times 0.5 \text{ ml}}{L} \propto \frac{1440 \text{ min}}{\text{ day}} \times 5 \text{ day} = 28,800 \text{ mg } O_2$

31

could measure the BOD per gram of substrate

Rate of sulfate reduction/screenings mixture

Year	Days of operation	Total sulfate removed (grams)			
1992	98	1098			
1993	123	533			

Rate of reduction (1992) = $1098 \text{ gm SO}_4 \times 1000 \text{ mg/gm}$

96 mg/mmole

98 day x <u>135 gal x 3.785 L/gal</u> 10000 L/m³

= $228 \text{ mmoles/m}^3/\text{day}$

Rate for 1993 = $92 \text{ mmoles/m}^3/\text{day}$

Note: Volume of substrate in 3 barrels \approx 135 gallons