INNOVATIVE TREATMENT OF ALKALINE MINE DRAINAGE USING RECIRCULATED IRON OXIDES IN A COMPLETE MIX REACTOR[1]

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Abstract. A demonstration study was undertaken to develop an abiotic iron oxidation process to increase the Fe(II) removal rates (IRR) at low pH (6 to 7) compared to conventional oxidation ponds and aerobic wetlands (typical IRR is 10 to 20 $g/m^2/d$) while producing a high-quality sludge. An alkaline mine drainage from an underground mine pool containing 60 to 80 mg/L Fe(II) was used in the study. Batch tests were conducted in a 330 gal tank at various initial concentrations ranging from 5 to 1300 mg/l added Fe(III) solids. Results indicated test durations to obtain less than 1 mg/L of Fe(II) decreased from greater than 48 hours for low initial Fe(III) to less than 2 hours in tests with initial Fe(III) greater than 1000 mg/L. Following batch tests a flow-through reactor system was employed consisting of two-330 gal tanks, a complete-mix oxidation reactor followed by a clarifier tank. Fe(III) solids were recirculated from the clarifier to the reactor to obtain reactor concentrations ranging from 10 to 2000 mg/L. The reactor lowered Fe(II) to approximately 3 mg/L when Fe(III) was 2000 mg/L and contact time was 2.3 hours. IRR of 0.52 mg/min or 740 $g/m^2/d$ were achieved during this flow-through test. IRR exceeding 1 mg/min or 1300 $g/m^2/d$ were obtained when Fe(III) was 1800 mg/l and contact time was 1.3 hours, but with a slightly higher effluent of 14 mg/l Fe(II). The recirculated Fe(III) sludge had a specific resistance to filtration (SRF) of 4×10^{11} m/kg, a coefficient of compressibility of 0.37 and solids concentrations greater than 20%. The SRF is similar to that observed for flocculent solids formed at high pH (>8), but the compressibility is similar to high-density sludges. This research demonstrated the effectiveness of a recirculated sludge process to increase IRR over passive treatment and to obtain similar IRR as conventional chemical (lime) treatment.

Additional Key Words: AMD treatment, iron removal, heterogeneous iron oxidation

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Introduction

Mine drainage in the eastern portion of the United States is a byproduct of coal extraction and can be produced from either surface or deep mining practices. The chemistry of mine drainage will vary considerably depending on coal and overburden characteristics, and mining and reclamation techniques. Two broad categories of mine drainage are Acidic Mine Drainage (AMD) and Neutral/Alkaline Mine Drainage (NAMD). AMD is defined as having "hot peroxide" acidity exceeding alkalinity, if present, and NAMD is defined as having alkalinity equal to or exceeding mineral acidity. Both AMD and NAMD contain iron, primarily as ferrous-Fe(II), at concentrations as high as several hundred milligrams per liter (mg/L).

Iron can be removed from mine drainage by employing active or passive treatment technologies. Active treatment requires continuous metering of chemicals (e.g., lime) to raise the pH to increase the rate of iron oxidation and precipitation as oxides. Passive treatment systems rely on natural abiotic and biotic processes. Performance of passive systems has been described by a number of investigators including Hedin *et al*. (1992, 1993, 1994) and Dempsey *et al*. (2001). Typically, AMD pretreated with an alkalinity producing system (e.g., anoxic limestone drain - ALD) or NAMD passes through open water ponds or aerobic wetlands where abiotic processes usually dominate at pH above 5 and aerobic conditions (Kirby *et al.* 1999). In aerobic systems, iron is removed by means of oxidation and precipitation of iron oxides. Passive treatment systems usually remove between 10 and 20 grams of Fe(II) per square meter of pond surface area per day (GMD) as reported by Hedin & Nairn (1992). The IRR in passive treatment systems can vary with season, influent flow and concentration. In addition, treatment areas that are required to remove iron can become excessive for high flow and/or concentration of Fe(II) in AMD or NAMD discharges. The focus of this study was on improving IRR by increasing the rate of Fe(II) oxidation, which is usually the limiting step in the removal or iron.

Fe(II) is oxidized to Fe(III) in the presence of oxygen described in the following stoichiometric equation:

$$\mathbf{Fe^{2+} + \tfrac{1}{4}\,O_2 + \tfrac{1}{2}\,H_2O = Fe^{3+} + OH^-} \qquad (1)$$

Followed rapidly by hydrolysis/precipitation in the following equation:

$$\mathbf{Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+} \qquad (2)$$

The oxidation process (equation 1) can involve soluble Fe^{2+}, $FeOH^+$, $Fe(OH)_2°$ species, or sorbed Fe(II). Oxidation of the three dissolved species of Fe(II) is called *homogeneous* oxidation, while oxidation of sorbed Fe(II) is *heterogeneous* oxidation (Sung and Morgan 1980 and Tamura *et al* 1976). The overall abiotic oxidation rate at pH greater than 5 is the sum of the homogeneous and the heterogeneous reactions, as described in the equation:

$$\textbf{Overall abiotic rate}_{\text{(for pH>5)}} = (-d[Fe(II)]/dt) = (k_1 + k_2\,[Fe^{3+}][H^+])[Fe^{2+}][O_2][H^+]^{-2} \qquad (3)$$

Rate constants have been reported by a number of investigators in studies using synthetic ferrous iron solutions in batch reactors. Reported homogeneous rate constants (k_1) range from$1.0x10^{-14}$ to $1.0x10^{-12}$ mol $L^{-1}s^{-1}$ (Millero *et al.* 1987; Liang *et al.* 1993; and Ames 1998). Reported heterogeneous rate constants (k_2) range from $2.6x10^{-8}$ to $3.6x10^{-8}$ $(mg/L)^{-1}s^{-1}$ in studies by Tamura & Nagayama (1976), Sung & Morgan (1980) and Ames (1998), where the concentration of Fe(III) was expressed in mg/L. Millero *et al.* (1980) and Ames (1998) determined the effect of temperature on the homogenous reaction rate by determining activation energy (E_{act}) for the homogeneous reaction (k_1) of 237 and 324 kJ/mol (units of $L^3mol^{-3}\,min^{-1}$), respectively. Ames also estimated an E_{act} of 179 kJ/mol for the heterogeneous reaction (k_2).

Solid characteristics are also an important consideration in mine drainage treatment. Active treatment with chemical addition typically produces a flocculent, low-density (1-4%) iron oxide sludge that is frequently contaminated with carbonates and sulfates and oxides of manganese, calcium and other metals. A chemical treatment process, known as the high-density sludge (HDS) process, uses lime to increase pH (>9) and recirculates solids to improve coagulation and settling characteristics has been reported to achieve solids content of 20 percent (Murdock e*t al.* 1994). Sludge from passive treatment systems has this much higher sludge density (15-30%) than chemical treatment and similar to the HDS process, but with less contamination (Dempsey & Jeon, 2001; Jeon, 1998).

Study Objectives

Enhancing the oxidation and removal of Fe(II) in mine drainage while producing a high density and high quality sludge could have substantial economic and environmental consequences. Some abiotic oxidation ponds have utilized design features that have been found to increase the IRR to greater than 50 GMD, more than 2 times reported conventional passive treatment removal rates (Dempsey *et al.* 2001; Budeit 2001). Dempsey *et al*. indicated the observed increased iron removal was, at least in part, due to the heterogeneous iron oxidation process in the passive treatment system. Enhancing iron removal by utilizing heterogeneous oxidation could have the benefits of reducing treatment area while retaining the benefits of a denser and cleaner sludge that may have greater potential for reuse.

The following were the objectives for this study:

- Modify the mixing and chemistry of the mine drainage to obtain enhanced oxidation at an actual mine drainage discharge;
- Evaluate the importance of heterogeneous oxidation and enhance the process by mixing and recirculation to suspend and increase the concentration of catalytic iron hydroxide particles;
- Evaluate whether abiotic iron oxidation rate constants (k_1 and k_2) in a “real” mine drainage are consistent with reported values obtained from studies with synthetic ferrous iron solutions;
- Demonstrate the potential of heterogeneous oxidation processes to decrease treatment area requirements and reduce/eliminate chemical usage;
- Evaluate the characteristics of the sludge produced in the enhanced oxidation process to determine similarities and differences to passive treatment system sludges.

Study Site & Demonstration Setup

The demonstration location was at the Bird Mine near Tire Hill, Pennsylvania (in the vicinity of Johnstown, PA). The Bird Mine is a closed deep mine operation that currently pumps mine drainage as high as 12,000 liters per minute (3,000 gpm) from a deep mine complex with two groundwater pumps, to prevent release of mine water into local waterways. Mine drainage is currently treated by active chemical treatment that employs lime addition, mechanical aeration, polymer addition and settling. The mine drainage characteristics, summarized in table 1, vary depending on the number of pumps in operation, but is generally neutral to slightly acidic with between 50 and 100 mg/L of Fe(II).

Table 1. Average mine drainage characteristics of the influent to and effluent from the Anoxic Limestone Drain (ALD)[1]

Parameter	Temp.	pH	Alkalinity	Conduct.	SO_4^{-2}	Total Fe	Total Mn
Units	°C	s.u.	mg/L as $CaCO_3$	µS/cm	mg/L	mg/L	mg/L
Influent to ALD	12.9	6.30	140	2320	1240	92	3.1
Effluent from ALD	12.7	6.50	250	2450	1250	88	3.1

[1] Data provided by Robert Hedin, Ph.D.

The treatment system was located upslope of the existing treatment. A small amount of the pumped flow, approximately 190-380 L/min (50-100 gpm), was redirected through an anoxic limestone drain (ALD). The ALD treated mine water characteristics are summarized in table 1 and are similar to the discharge, but with added alkalinity.

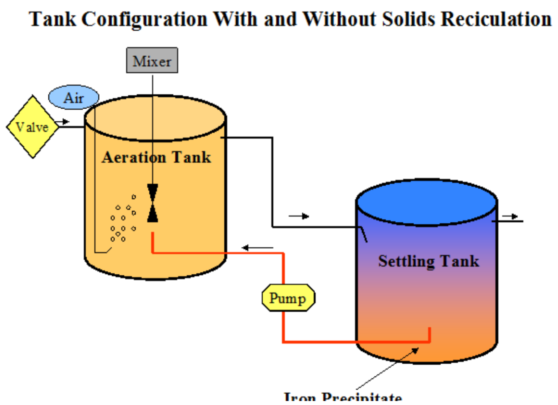

Figure 1. Reactor and settling tank setup during of the study.

The demonstration setup is depicted in figure 1 and consisted of two 400-gal HDPE tanks, a reactor and settling tank. Water capacity dimensions of 3.90 feet diameter and 3.75 feet height provided a tank volume of 1250 liters (330 gallons). The tanks, PVC piping and valves were installed near the ALD by the Bird Mine maintenance staff. A sludge return system consisting of 2-inch PVC piping and a variable-speed pump with various diameter Tygon® tubing was installed in the settling tank in order to recirculate sludge from the settling tank to the reactor tank. A submersible pump provided mixing in the reactor and was capable of recirculating 130 L/min (35 gpm) within the reactor tank. Aeration was provided by a portable air compressor at a total rate of between 15 and 30 L/min (0.5 and 1 ft^3/min).

Study Plan

The study was conducted in two phases: batch tests conducted in a reactor tank; and flow-through tests in the reactor and settling tank.

A number of batch tests were conducted in the reactor tank in which mixing and aeration were provided at various initial concentrations of Fe(III) solids (determined to be ferrihydrite by Mössbauer Spectroscopy) ranging from 0 to 1,400 mg/L, analytically measured as Total Fe. Results of all field batch tests are reported in this paper. Fe(III) solids used in the batch tests were obtained from the holding pond prior to chemical treatment system at the Bird Mine treatment facility. Batch test durations were a minimum of either 24 hours or until reactor Fe(II) concentrations were less than 2 mg/L. Samples were collected and analyzed prior to initiating the batch tests and periodically during each batch. The frequency of sampling was dependent on the rate of Fe(II) removal. For example, batch test 1 (no initial Fe(III) solids) was sampled every 2 to 5 hours while batch test 6 (Fe(III) ~ 1000 mg/L) was sampled every 15 to 20 minutes. The results of the batch tests were used to evaluate the importance of iron oxide solids as a catalyst in the oxidation of Fe(II) and to establish flows and reactor tank Fe(III) concentrations to be examined during flow-through tests.

Flow-through tests were conducted in the two-tank system for two operating conditions: mixing and aeration; and mixing and aeration with solids recirculation. Recirculation was necessary to increase iron oxides as Fe(III) in the reactor. All flow-through tests are reported in this paper. Influent flow was varied from 3.8 L/min (1 gpm) to 17 L/min (4.5 gpm). Sludge recirculation rates were varied from 50 to 2000 mL/min depending on influent flow and the target concentration for total Fe(III) in the reactor. Reactor total Fe(III) concentrations ranged from 400 to 2000 mg/L in the flow through tests. Slug tests with addition of tracers demonstrated that the reactor tank was a complete-mixed reactor. Flow-through tests were run until steady-state conditions were achieved in the reactor. Influent, reactor effluent, and recirculated sludge were periodically sampled and analyzed during the start-up period to determine progress towards steady-state conditions. After all system parameters were constant, effluent samples were collected and analyzed every 15 to 20 minutes until a total of 6 samples were collected. Mine drainage influent and recirculated sludge were sampled and analyzed at the beginning and end of the reactor steady-state sampling.

Field & Laboratory Analytical Methods

Table 2 lists the parameters monitored and the analytical methods used in the batch and flow-through tests. In addition to the methods in table 2, a number of samples were analyzed for total iron, after digestion, by ICP spectroscopy, as a quality-control check on the field measurement techniques. The results of the colorimetric and ICP methods were found to be comparable with all differences less than 10 per cent, which indicates the field total iron colorimetric field measurement technique was accurate.

Table 2. Parameters monitored on water samples during each phase of the abiotic iron oxidation demonstration.

Parameter	Units	Method Description	Equipment
pH	s.u.	Electrode	Orion Model 290A
Alkalinity	mg/L as $CaCO_3$	Potentiometric Endpoint Titration	Hach Digital Titrator
Dissolved Oxygen	mg/L	Electrode	YSI Model 54A
Total Iron	mg/L	Unfiltered, Sodium Citrate, Sodium Hydrosulfite, & 1,10 Phenanthroline	Hach Pocket Colorimeter
Ferrous Iron	mg/L	0.2 μm Filtered & 1,10 Phenanthroline	Hach Pocket Colorimeter
Total Ferrous Iron	mg/L	1-hr 0.5 N HCL, 0.2 μm Filtered & 1,10 Phenanthroline	Hach Pocket Colorimeter
Temperature	°C	Electrode	YSI Model 54A

Recirculated sludge was evaluated periodically for total iron and pH during flow-through tests. Sludge was also collected and characterized at the conclusion of the study for resistance to filtration, settling rate, total solids, particle size distribution and surface area. Resistance to filtration was conducted in a positive pressure filtration chamber, with Whatman No. 3 filter paper, that was attached to a top-loading Mettler PE 160 portable balance to measure filtrate with time. Settling rate was determined at a total solid concentration of 3.5 g/L, the maximum concentration in several recirculation tests, using a 100-mL graduated cylinder and measuring clarified water depth with time. Total solids were measured by filtration and drying at 105°C

(APHA 1989). Particle size distribution was measured with a Malvern Mastersizer operating at a wavelength of 633 nm. Surface area was estimated with a Gemini 2370 BET, which measures multipoint surface area under flowing nitrogen gas.

Batch Test Results

Seven batch tests were conducted in the reactor tank to evaluate the effects of iron oxides on the rate of Fe(II) oxidation. Aeration and mixing were provided in all experiments. Initial and final reactor characteristics, along with batch test durations, are summarized in table 3. All batch tests had similar pH ranging from 6.2 to 6.6 and temperature ranging from 13 to 18 °C. With the exception of batch test 1 and 5, all batch tests were similar in dissolved oxygen, with initial dissolved oxygen ranging between 3 and 5 mg/L and increasing to between 8 and 10 mg/L by the end of the test. Also, as would be expected, alkalinity decreased throughout the batch test as a result of precipitation of Fe(III), although measured alkalinity was slightly higher than would be expected based on the removal of Fe(II) and equations (1) and (2). The stoichiometric anomaly may be due to the presence of sorbed Fe(II). Results summarized in tables 3 indicate increasing the iron oxide solids from 5 to 1,200 mg/L in the reactor decreased the time for oxidation of the ferrous iron to less than 3 mg/L from greater than 24 hours to less than 2 hours.

The data from the batch tests were further evaluated by estimating the slopes, from the linear portions of the curves, of the Fe(II) concentration decrease, or Fe(II) removal rate ($-d\mathrm{Fe(II)}/dt$) in moles per liter-second using data. Table 4 summarizes the removal rates in various forms including milligrams per liter-minute, grams per day and grams per square meter-day (GMD). Batch test 5 results are not included in table 4 because of the slightly higher initial dissolved oxygen in this test versus other batch tests, which would result in significantly higher Fe(II) oxidation rates (see equation 3). The effect of Fe(III) on Fe(II) removal rates is obvious from this analysis with Fe(II) removal rates increasing by more than an order of magnitude. Batch test 1 Fe(II) removal rates were approximately 40 GMD, which are in the range of maximum IRR observed in passive treatment systems (i.e., oxidation ponds and aerobic wetlands). Batch test 2 produced an 160% increase in Fe(II) removal rates due to the addition of only 6 mg/L of suspended Fe(III). Fe(II) removal rates in batch tests with Fe(III) greater than 1,000 mg/L demonstrated Fe(II) removal rates of more than 1000 GMD, an increase of 3000% over Batch test 1 conditions. These results clearly demonstrate the importance of Fe(III) on the Fe(II) removal rates, and demonstrate that very high Fe(II) removal can be achieved, in spite of pH values that are slightly acidic (6.3-6.6).

Table 3. Summary of initial and final reactor conditions for batch tests conducted at the Bird Mine site.

Parameter	Units		Batch Test						
			1	2	3	4	5	6	7
Duration	Hrs		23	24.3	14.5	3.1	3.5	2	1.7
Fe(II)	mg/L	Initial	86	85	85.5	80.5	84.5	62.5	63
		Final	52	15.8	1.2	0.8	1.7	2.9	2.8
Fe(III)	mg/L	Initial	1	6	410	719	436	1252	1087
		Final	23	51	360	819	456	1247	1353
D.O.	mg/L	Initial	1.6	4.3	3.5	4.8	6.5	4.5	3.7
		Final	4.4	7.6	8.2	8.2	9.6	8	8.4
pH	s.u.	Initial	6.48	6.3	6.6	6.54	6.5	6.25	6.37
		Final	6.46	6.81	6.68	6.57	6.65	6.46	6.43
Alkalinity	mg/L	Initial	203	218	220	245	248	220	232
		Final	154	115	105	125	107	135	168
Temperature	°C	Initial	13	17	15	16	16	12	13
		Final	16	15	13	18	14	16	14

Table 4. Summary of Fe(II) removal rates at various batch reactor Fe(III) concentrations.

Parameter	Units	Batch Test					
		1	2	3	4	6	7
Avg. Reactor Fe(III)	mg/L	5	30	410	790	1240	1260
dFe(II)/dt	mol/L-s	-7.0×10^{-9}	-1.8×10^{-8}	-4.8×10^{-8}	-1.3×10^{-7}	-2.1×10^{-7}	-2.1×10^{-7}
Avg. Fe(II) Removal Rate	mg/L-min	0.02	0.05	0.10	0.43	0.50	0.59
Fe Removal	g/day	42	108	288	795	1284	1257
Areal Fe Removal Rate	g/m^2-day	38	96	257	710	1146	1122

<u>Flow-Through Test Results</u>

Seven flow-through runs were completed during the study, including two tests without recirculation of ferric oxide sludge and five tests with sludge recirculation. Aeration and mixing were provided in all experiments. The results of steady-state conditions during each sample run are summarized in table 5. Influent chemistry was very consistent during these tests and only average values are provided for influent conditions. Effluent from the reactor varied slightly and the means and standard deviations of the six samples collected during steady-state are shown in table 5. For the most part, the standard deviations were low (coefficients of variability less than

10% during steady-state operation) indicating the system functioned consistently and without upsets. Steady-state Fe(II) concentrations during the Recycle #2 and #4 tests with variability as high as 30 percent were the only exceptions. However, the measured concentrations were below 3 mg/L and increased variability was due to the field measurement technique. The results in table 5 indicate Fe(II) was significantly ($\rho<0.001$) lowered (removed to below 5 mg/L) in a flow-through reactor with recirculation of iron oxide solids (compared to flow-through reactors without recirculation of solids). In addition, higher reactor Fe(III) produced significantly ($\rho<0.001$) lower effluent Fe(II) concentrations at comparable flows.

Table 5. Summary of influent and average effluent results from flow-through runs with and without recirculation of sludge[1].

	Influent Characteristics					Reactor & Effluent Characteristics					
Flow-through Run	Flow gpm	pH s.u.	Alkal. mg/L as $CaCO_3$	FeII mg/L	Tot. Fe mg/L	pH s.u.	Alkal. mg/L as $CaCO_3$	D.O. mg/L	Fe(II) mg/L	Fe(III) mg/L	Temp. °C
No Recycle #1	3.19	6.39	214.0	62.9	70.5	6.56 (0.031)	199.3 (2.5)	7.08 (0.30)	55.4 (4.1)	12 (3.4)	16.0 (0)
No Recycle #2	0.92	6.47	208.2	55.5	60.8	6.73 (0.014)	170.3 (6.1)	7.77 (0.23)	38.0 (0.27)	14 (0.80)	16.8 (0.41)
Recycle #1	1.25	6.39	259.5	67.5	67.5	6.36 (0.033)	177.5 (4.5)	6.05 (0.05)	9.3 (0.31)	472 (24.4)	14.5 (0.27)
Recycle #2	1.25	6.44	270.0	78.2	78.5	6.52 (0.010)	172.7 (5.3)	7.93 (0.10)	2.2 (0.19)	1007 (21.2)	15.9 (0.78)
Recycle #3	3.33	6.40	262.0	77.8	79	6.37 (0.014)	177.2 (3.1)	6.92 (0.08)	13.5 (0.82)	875 (32.3)	14.7 (0.33)
Recycle #4	2.40	6.37	258.5	66.4	67.5	6.42 (0.018)	213.3 (10.8)	7.38 (0.29)	3.1 (0.66)	1960 (120)	16.6 (0.24)
Recycle #5	4.38	6.46	263.0	78.5	79	6.34 (0.020)	212.0 (3.5)	6.52 (0.16)	14.3 (0.57)	1772 (89)	13.3 (0)

[1] Value in parentheses is the standard deviation of the sampling results (***s***)

The steady-state reactor pH values remained between 6.3 and 6.5 in all flow through tests. Reactor pH is a function of alkalinity (HCO_3^-) and carbonic acid (H_2CO_3) in the reactor with two driving forces involved in the steady-state pH: 1) conversion of HCO_3^- to H_2CO_3 due to acidity generated by the oxidation of Fe(II) and precipitation of iron oxide; and 2) CO_2 lost from the reactor due to volatilization. The continuous generation of carbonic acid in the reactor, from the Fe(II) oxidation, offset the volatilization of CO_2 from the reactor thereby maintaining the slightly acidic pH.

Effluent alkalinity was lower than influent alkalinity as a result of the precipitation of iron oxides in the reactor. Based on stoichiometric considerations and equations (1) and (2), 1.8 mg/L (as $CaCO_3$) of alkalinity should be required in the oxidation and precipitation of 1 mg/L of Fe(II). Ratios ranging from 2.1 during no recycle tests to 1.0 in high Fe(III) recirculation tests were found. Discrepancies between stoichiometric and actual may be due in part to “sorbed” Fe(II) or incorporation of sulfate in the precipitates.

The dissolved oxygen in the reactor was provided by transport of oxygen to the water at the surface of the reactor and the aeration provided by the compressor. Low aeration was needed to maintain the reactor dissolved oxygen because of the low oxygen demand of the Fe(II) oxidation; 1 mg/L of dissolved oxygen will oxidize 7 mg/L of Fe(II). As a result, reactor dissolved oxygen concentrations were all between 6 and 8 mg/L at the airflow of 0.5 cfm. Lower dissolved oxygen levels in Recycle #3 and #5 may have been due to the slightly higher oxidation rates during these runs.

Table 6 summarizes the Fe(II) removal in various units, which indicate greater removal was achieved in the flow-through reactor with iron oxide recirculation; Fe(II) removal in flow-through with recirculation had between 400 and 2000% greater iron removal than flow-through without recirculation. Results also indicate that greater removal was achieved by increasing reactor Fe(III) concentrations; highest removal was observed in Recycle #5. Recirculation produced unit area removal rates 4000% greater than conventional passive treatment and similar to oxidation rates in chemical treatment (pH~8). Higher removal rates were achieved where reactor effluent Fe(II) was higher (see Recycle #2 versus Recycle #3 and Recycle #4 versus Recycle #5). This is expected since equation 4 indicates removal should be first-order with respect to the steady-state Fe(II) concentration.

“Sorbed” Fe(II), the difference between reactor total ferrous iron and solution ferrous iron, increased with increasing concentration of Fe(III). Averages of “sorbed” Fe(II) from the flow through runs with recirculation were 2.9 mg/L for Recycle #1, 4.5 mg/L for Recycle #2, 6.4 mg/L for Recycle #3, 8.6 mg/L for Recycle #4, and 10.2 mg/L for Recycle #5. Comparison between Recycle #2 and #3, and Recycle #4 and #5 also indicates effluent ferrous iron may affect “sorbed” Fe(II). Using the averages from the flow-through tests and the reactor Fe(III) concentrations yielded an average “sorbed” Fe(II) of 5.6 mg Fe(II) per gram of Fe(III). Based on the level of "sorbed" Fe(II) observed it appears all strong sorption sites are occupied; i.e., about 0.2 to 0.35 sites per nm^2 of surface area.

Table 6. Ferrous iron (Fe(II)) removal rates measured at steady-state during flow-through runs.

Flow-Through Run	Flow gpm	Influent Fe(II) mg/L	Effluent Fe(II) mg/L	Fe(II) Removal Rates Instantaneous mg/min	Daily g/d	Unit Area $g/d/m^2$
No Recycle #1	3.19	62.9	55.4	0.08	131	117
No Recycle #2	0.92	55.5	38.0	0.05	88	79
Recycle #1	1.25	67.5	9.3	0.24	396	354
Recycle #2	1.25	78.3	2.3	0.31	518	462
Recycle #3	3.33	77.8	13.5	0.70	1165	1060
Recycle #4	2.40	66.5	3.1	0.52	829	740
Recycle #5	4.38	78.5	14.3	1.01	1532	1368

Solids Evaluation

Recirculated solids from the settling tank were analyzed for total iron and pH during each of the flow-through with recirculation tests. The sludge pH increased slightly from 6.17 to 6.26 and total iron concentration in the return sludge decreased slightly from 44 to 31 g/L over the flow-through tests, possibly a result of rat-tailing or short-circuiting in the settling tank; the settling tank was modified to assist in recirculating sludge, but was not specifically designed for this purpose. Sludge samples collected at the end of the flow through tests were analyzed for a number of parameters including total iron, total solids, specific resistance, particle size and surface area. The results are summarized in Table 7.

The total solids and total iron concentrations in recirculated solids equate to a 6% solids sludge. Settleability testing performed on the recirculated sludge is representative of zone settling that would occur in a settling tank with a reactor concentration of 2,000 mg Fe(III)/L. Additional settling of the 6% sludge, in long-term settling tests, increased solids to 19%. The settling tests indicated the sludge zone-settled at a rate 3.6 cm/hr for the first 2 hours, and 0.2 cm/hr during the compaction stage of settling. The maximum sludge density was reached at approximately 48 hours. Particle sizes measured on the recirculated sludge were normally distributed about the mean particle diameter of 3.61 μm with a 10th and 90th percentile of 1.24 and 9.27 μm, respectively.

Table 7. Summary of analyses conducted on recirculated sludge from the flow-through runs and comparisons to other iron oxide solids.

Parameter	Units	This Study	Passive Systems[1]	Chemical Systems[1]
Recirculated Sludge	%	5.8	--	--
Recirculated Iron	g/L	33	--	--
Settling Rate	cm/sec	1.5	1.8	--
Sp. Resistance to Filtration	m/kg	4.3×10^{11}	2 to 4×10^{10}	26 - 125×10^{10}
Coeff. of Compressibility	--	0.37	0.38	0.46
Settled Sludge Density	%	19.1	20	1
Ave. Particle Dia.	μm	3.6	2.5	--
Surface Area	m^2/gr	230	--	--
Specific Gravity	g/cm^3	2.2	--	--

[1] Dempsey and Joen (2001)

Discussion

Kinetic Evaluation

The results of the demonstration study indicate the Fe(II) removal rate can be enhanced to levels several orders of magnitude greater than has been observed in passive treatment systems. The data from the batch tests provide an evaluation of the overall kinetics of the reaction. However, data from flow-through tests were more useful for this purpose since the reactor was completely mixed and the reaction is *pseudo* first-order. The *pseudo* first-order kinetic assumption is valid since all parameters except Fe(II) remained approximately constant during the test.

With this information the overall rate coefficient k_{total} can be determined using the following equation:

$$k_{total} = (Fe(II)_{influent} - Fe(II)_{effluent}) * Q_{total}/V_{reactor} \,/\, Fe(II)_{effluent} \qquad (4)$$

where $V_{reactor}$ is the reactor volume and Q_{total} is the sum of influent flow and sludge recirculation flow. $Fe(II)_{influent}$ is the mixed influent Fe(II) concentration, which must also include dilution by the recirculated sludge flow in which Fe(II) is 0 mg/L. Table 8 summarizes the inputs and results using equation 4.

Table 8. Summary of kinetic calculations input values and reaction kinetic coefficients for the flow-through reactor.

Flow-Through Run	Influent Flow gpm	Sludge Flow gpm	Influent Fe(II)[1] mg/L	Effluent Fe(II) mg/L	Reactor Fe(III) mg/L	k_{total} /sec
Flow Through #1	3.19	0	62.9	55.4	12	2.33×10^{-5}
Flow Through #2	0.92	0	55.5	38.0	14	2.27×10^{-5}
Sludge Recycle #1	1.25	0.011	66.9	9.3	472	4.16×10^{-4}
Sludge Recycle #2	1.25	0.036	76.1	2.3	1007	2.26×10^{-3}
Sludge Recycle #3	3.32	0.068	76.2	13.5	875	8.45×10^{-4}
Sludge Recycle #4	2.4	0.15	62.5	3.1	1960	2.62×10^{-3}
Sludge Recycle #5	4.38	0.55	69.7	14.3	1772	1.02×10^{-3}

[1] Corrected for dilution by recirculated sludge.

The flow-through runs contained slight variability in influent Fe(II), pH, and dissolved oxygen all of which are important components in the Fe(II) abiotic oxidation reaction (see equation 3). Rearranging the overall abiotic oxidation rate presented in equation 5 yields:

$$\mathbf{(-d[Fe(II)]/dt)[H^+]^2/([Fe^{2+}][O_2]) = k_2\,[Fe^{3+}][H^+] + k_1} \qquad (5)$$

By inspection ***(-d[Fe(II)]/dt)/[Fe^{2+}]*** is the $\boldsymbol{k_{total}}$., which results in the equation:

$$\mathbf{k_{total}\,[H^+]^2/[O_2] = k_2\,[Fe^{3+}][H^+] + k_1} \qquad (6)$$

The above equation is in the form of a straight line. A regression analysis of ***[Fe^{3+}][H$^+$]*** versus ***K_{total} [H$^+$]^2/[O$_2$]*** yielded a significant ($\rho < 0.01$) straight line with an R^2 of 0.84. The slope and y-intercept of the line are the heterogeneous ($\boldsymbol{k_2}$) and homogenous rate ($\boldsymbol{k_1}$) constants, which were 1.67×10^{-9} (mg/L)$^{-1}$s^{-1} and 8.35×10^{-14} mol L^{-1}s^{-1}, respectively. The two rate constants are for a temperature of 15°C, which is the average temperature of all the flow-through tests. The $\boldsymbol{k_2}$ from this study is lower than previous studies, but the study temperature is 10°C lower than the literature studies. Adjusting for the temperature difference using the Arrhenius equation and the activation energy (E_{act}) of 179 kJ/mol reported in Ames (1998) results in a $\boldsymbol{k_2}$ of 2.1×10^{-8} (mg/L)$^{-1}$s^{-1} at 25°C. This $\boldsymbol{k_2}$ is similar to but slightly lower than reported values, which may be due to the larger particle sizes in the recirculated iron oxide sludge used in this study versus freshly formed iron oxides used in the experiments that have been reported in the literature.

The only previous work in which ferrous oxidation was studied using the high concentrations of ferric oxides as in this demonstration, was a study by Tufekci and Sarikaya (1998). They used Fe(III) up to 600 mg/L in batch reactors, and their results seem to be in conflict with results from this demonstration, i.e. Tufekci and Sarikaya found heterogeneous oxidation that was proportional to Fe(III) concentrations of about 400 mg/L with minimal effect above this concentration of ferric oxide. However, their study used only 3 mg/L of initial ferrous iron. Based on reported adsorption by Tamura *et al* (1976) and adsorption measured in this study, nearly all of the ferrous iron would have been adsorbed at Fe(III) concentrations exceeding 200 mg/L and probably explains their lack of observed catalytic effect at Fe(III) concentrations greater than 400 mg/L. Our study provides evidence that heterogeneous iron oxidation continues at Fe(III) concentrations up to and exceeding 2000 mg/L. Rate coefficients from this study are comparable to the literature values representing much lower concentrations (below 100 mg/L) of Fe(III).

Sludge Characteristics

Sludge density, specific resistance (SR) and the coefficient of compressibility (S_o) obtained from this study (summarized in table 7) demonstrated that the recirculation process produced a high-density sludge. The high-density sludge was easily pumped at this concentration with minimal increased viscosity. Higher concentrations of solids approaching 20 percent were obtained by wet packing the recirculated iron oxide sludge. The high-density sludge had properties consistent with a viscous liquid and could be poured from a container.

Characteristics of iron oxide sludges from conventional passive treatment systems and rapidly precipitated ferric hydroxide (similar to chemically treated mine drainage sludge) are also summarized in table 7. The high-density sludge from this study is within the range of sludge characteristics typically observed for passive treatment sludge. Ferric hydroxide sludge settled to only 1 percent solids compared to 20 percent for the sludges that were produced in this study. Mechanisms for the formation of high-density and low-density sludges have been reported in the literature (Herman & Korb 1989; Dempsey 1993). Chemically treated sludge may also be heavily contaminated with other metals (e.g., manganese and calcium) and carbonates, hydroxides and sulfates. Due to the lower pH, sludge produced using this demonstrated approach would be less contaminated with other metals than chemical treatment sludge.

There are a number of benefits resulting from production of a denser and cleaner sludge. Increased sludge density will decrease the costs of sludge handling and disposal. In simple terms the increased solids content will decrease sludge handling efforts (and costs) by a factor of at least 20 over conventional chemical treatment. Since the resulting sludge is purer than sludge produced by other treatment processes, there could be a greater potential for reuse in a variety of applications, such as pigments or as a coagulant-aid and contaminant adsorbent in water and wastewater treatment.

Reactor Sizing & Design

Based on the overall abiotic iron oxidation rate equation (equation 3), the size of a continuously stirred reactor (CSTR) would be dependent on a number of AMD discharge characteristics and reactor conditions including flow, influent Fe(II) and alkalinity and CSTR pH, Fe(III) concentration, dissolved oxygen and temperature. The effects of influent Fe(II) and reactor pH and Fe(III) on CSTR detention time (DT) were evaluated using equation 3, equation 4, reactor conditions and influent chemistry. A CSTR temperature of 15°C and dissolved oxygen of 7 mg/L (70% saturation) were assumed for calculating the $\boldsymbol{k_{total}}$.

Figure 2 shows the effects of varying influent Fe(II) and CSTR pH on the DT (or size) of a CSTR. As expected, based on equation 3, DT decreases by a factor of 10 with each pH unit change. It is likely that most CSTRs employing this process, which have sufficient alkalinity, will have a CSTR pH between 6.0 and 6.6, similar to the operating conditions

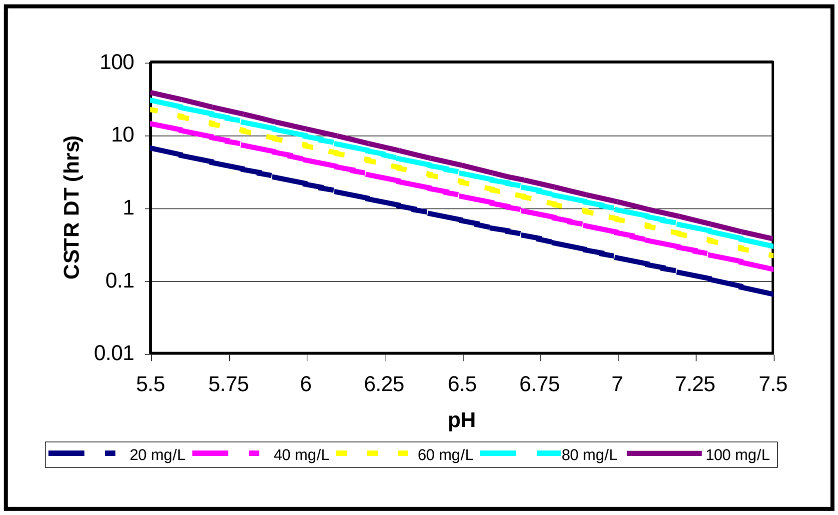

Figure 2. Continuously stirred reactor (CSTR) detention time (DT) to achieve 3 mg/L Fe(II) at various influent Fe(II) concentrations; CSTR Fe(III)=2000 mg/L, DO=7 mg/L and Temp=15°C.

observed in this study. Higher CSTR pH above this range is possible by increasing the mass transport of CO_2 from the CSTR, but is likely to be at the expense of increased aeration. Figure 2 also provides CSTR DT for various influent Fe(II). At pH of 6.3, DT ranges from approximately 1 hour for a 20 mg/L discharge to 6 hours for a 100 mg/L discharge, which equate to 85 and 97 percent removal, respectively.

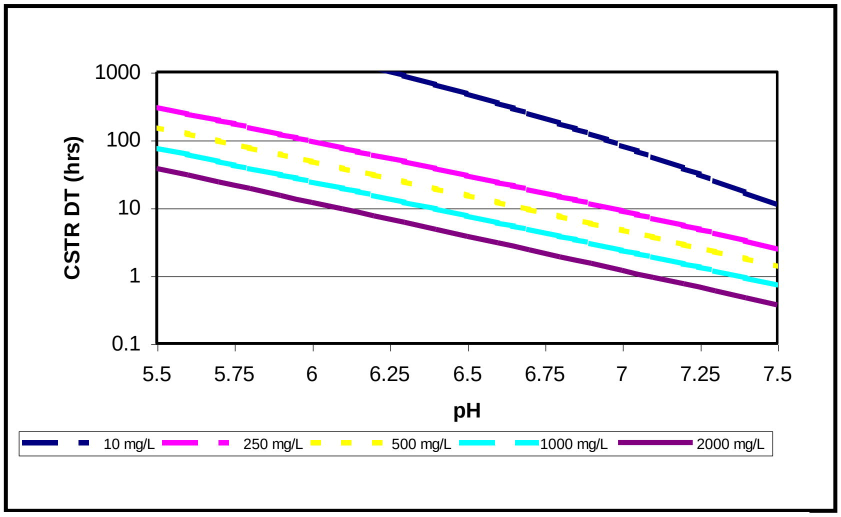

Figure 3. Continuously stirred reactor (CSTR) detention time (DT) to achieve 3 mg/L Fe(II) at various CSTR Fe(III) concentrations; influent Fe(II)=100 mg/L, DO=7 mg/L and Temp=15°C.

Figure 3 shows the effects of varying CSTR pH and Fe(III) concentrations on the CSTR DT on achieving an effluent Fe(II) of 3 mg/L at an influent Fe(II) of 100 mg/L (97% removal). The CSTR DT in figure 3, as expected and as was observed on figure 2, decreases as CSTR pH increases. The 10 mg/L CSTR Fe(III) line is provided in figure 3 as an estimate of a CSTR with no sludge recirculation and is similar to this studies observed reactor Fe(III) concentrations with no recirculation (see table 5). All other CSTR Fe(III) concentrations provided in figure 3 would be a result of sludge recirculation. At pH 6.5 the DT for a CSTR Fe(III) equal to 10 mg/L (i.e., no sludge recirculation) would approach 1000 hours versus less than 4 hours at a CSTR Fe(III) equal to 2000 mg/L. This later DT is similar to the DT calculated from the results of this study when an effluent Fe(II) of less than 3 mg/L was observed (see recycle #2 and #4 in table 5). This clearly demonstrates the importance of Fe(III) solids recirculation in the size of a CSTR.

This evaluation demonstrates the ability to determine the size of a CSTR system using the abiotic iron oxidation equation (equation 3) with minimal assumptions regarding CSTR dissolved oxygen and pH. As was discussed previously CSTR pH is a function of the alkalinity and carbonic acid. The later is a function of the dissolution of CO_2 from the CSTR. Estimation of CSTR pH and dissolved oxygen can be made for the design of a CSTR system using mass transport calculations for various mechanical and bubble diffuser aeration approaches.

Summary

This demonstration study provided compelling evidence regarding the benefits of recirculating and suspending iron oxide solids in an oxidation reactor. The study demonstrated the following:

- Abiotic Fe(II) oxidation can be enhanced in the presence of iron oxides at pH that is typical of neutral/alkaline mine drainage.
- Heterogeneous Fe(II) oxidation rate constants at Fe(III) concentrations between 400 and 2000 mg/L are similar to rate constants reported in studies for Fe(III) of less than 100 mg/L. Therefore, abiotic oxidation kinetics can be applied to this treatment approach.
- The "modified" treatment process using recirculated iron oxides can achieve Fe(II) removal rates similar to conventional chemical treatment and 50-fold greater than passive treatment systems (oxidation ponds and aerobic wetlands).
- Iron oxide sludge produced by the "modified" treatment process contained much higher solids than for conventional chemical treatment (20% versus 1%) and equal to or greater solids than reported for passive treatment. Sludge produced by this process is likely to be cleaner than chemical or passive treatment and have a greater potential for reuse.

The mining industry, government agencies, and a variety of public groups can utilize the enhanced removal process to treat NAMD from both active and abandoned mined lands. Application of this treatment approach is currently limited to alkaline mine waters or mine waters that can be pre-treated to add alkalinity. Additional studies are needed to determine applicability of this treatment approach to net acidic mine waters.

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