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Field determination of Fe^{2+} oxidation rates in acid mine drainage using a continuously-stirred tank reactor

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Abstract—A gravity-fed, battery-powered, portable continuously-stirred tank reactor has been developed to directly measure aqueous reaction rates in the field. Dye and tracer experiments indicate the reactor is well-mixed. Rates of Fe^{2+} oxidation at untreated and passively treated coal mine drainage sites in Pennsylvania were measured under ambient conditions and with the addition of either O_2 gas or NaOH solutions. Rates at 5 sites ranged from below the detection limit for this technique (approximately 10^{-9} mol L^{-1} s^{-1}) to $3.27 \pm 0.01 \times 10^{-6}$ mol L^{-1} s^{-1}. Uncertainties in rates ranged from 70% near the lower limit of measurement to as little as 1% at higher rates of reaction. Multiple linear regressions showed no universal correlations of rates to Fe^{2+}, dissolved O_2, and pH (*Thiobacillus* populations were not measured), although data for two more acidic sites were found to fit well for the model log rate = log K + a log $[Fe^{2+}]$ + b log $[OH^-]$ + c log $[O_2]$. Field rates of Fe oxidation from this and other studies vary by 4 orders of magnitude. A model using the ambient field rate of Fe oxidation from this study successfully reproduced independently-measured Fe^{2+} concentrations observed in a passive wetland treatment facility. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The rate of aqueous Fe^{2+} oxidation has been very extensively studied, more so in the laboratory than in the field. However, it is the field rate that has significant ramifications for the design of mine drainage treatment facilities, particularly with regard to sizing requirements of constructed wetlands. The results of Stumm and his colleagues (Stumm and Lee, 1961; Singer and Stumm, 1968; Singer and Stumm, 1970) are cited in most papers about Fe^{2+} oxidation kinetics and are commonly accepted as correct for abiotic conditions. Singer and Stumm (1968) acknowledged that the Fe^{2+} oxidation rate is catalyzed by microorganisms in the field. In field studies of acid mine drainage (AMD) where *Thiobacillus ferrooxidans* bacteria are present (Noike *et al.*, 1983; Nordstrom, 1985; Williamson *et al.*, 1992), the rates measured are 5 to 8 orders of magnitude faster than abiotic laboratory studies. In addition, several laboratory kinetic studies have introduced *Thiobacillus* into the experimental design (e.g., Lazaroff, 1963; Noike *et al.*, 1983; Pesic *et al.*, 1989; Okereke and Stevens, 1991).

The oft-cited reactions for production of AMD include

$$FeS_{2,s} + H_2O + 7/2O_2 = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_{3,s} + 3H^+ \quad (3)$$

where Reaction 1 is the oxidation of pyrite, Reaction 2 is the oxidation of Fe^{2+}, and Reaction 3 is the precipitation of ferric hydroxide (ochre). The solid formed in Reaction 3 is often referred to as "amorphous ferric hydroxide", but Bigham *et al.* (1992); Bigham *et al.*, 1996) suggest that the solid takes other forms, sometimes including SO_4 in a crystalline structure. Other acid SO_4 solid phases also contribute to acid generation (Cravotta, 1994). Reaction 2 is the main reaction of interest in this study.

Previous studies

Abiotic rates. Some studies provide rate laws for Reaction 2, while others report only rates. There are several ways in which the rates have been fitted to rate laws. Stumm and Lee (1961) proposed

$$\frac{d[Fe^{2+}]}{dt} = -k[Fe^{2+}][OH^-]^2P_{O_2} \quad (4)$$

where k is a rate constant, brackets indicate mol L^{-1} (except for OH^- and H^+), and P is partial

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pressure, Millero (1985) gives the rate law

$$\frac{-\mathrm{d}\ln[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = \frac{k_1\beta_1\alpha_{\mathrm{Fe}}}{[\mathrm{H}^+]} + \frac{k_2\beta_2\alpha_{\mathrm{Fe}}}{[\mathrm{H}^+]^2} \tag{5}$$

where β's are hydrolysis constants for Fe^{2+} species, and α is the fraction of free Fe^{2+}. The rate law of Millero *et al.* (1987) has the same form as Stumm and Lee's (Stumm and Lee, 1961) with the rate constant dependent on ionic strength and temperature. Hustwit *et al.* (1992) gave a rate law for near-neutral pH solutions (primarily for AMD treatment systems) that is independent of pH and Fe^{2+} concentrations:

$$-\frac{\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = 7k_{\mathrm{O}_2}[\mathrm{O}_2]_{\mathrm{sat}}. \tag{6}$$

Rates in the presence of Thiobacillus. Okereke and Stevens (1991) counted *Thiobacillus* bacteria, measured Fe^{2+} and temperature, performed stepwise regressions and gave 3-dimensional plots of rate *versus* these parameters for pH 2.4; rates are reported as optical density units min^{-1} and thus cannot be compared directly to other rates. Pesic *et al.* (1989) included terms for initial bacteria, pH, redox potential, and temperature to derive the rate law

$$-\frac{\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = 1.62 \times 10^{11} C_{\mathrm{bacteria}}[\mathrm{H}^+][\mathrm{Fe}^{2+}]P_{\mathrm{O}_2} \times \exp\left(-\frac{58.77}{RT}\right) \tag{7}$$

for $\mathrm{pH} > 2.2$. Schnaitman *et al.* (1969) and Noike *et al.* (1983) used Michaelis-Menten microbial rate laws to describe their laboratory data. For their field data, Noike *et al.* (1983) wrote an integrated rate law that is first-order in Fe^{2+}, and independent of pH

$$\ln\frac{\mathrm{Fe}^{2+}}{\mathrm{Fe}^{2+}_{\mathrm{init}}} = -kt. \tag{8}$$

Williamson *et al.* (1992) give a similar rate law by combining their own field data with field data from Noike *et al.* (1983) and Nordstrom (1985).

Field mine drainage solutions vary dramatically in chemical compositions from extremely acidic, metal-laden waters to net alkaline waters (alkalinity > acidity) with low metal concentrations. Bacterial populations also vary considerably in both numbers of organisms and their importance to the chemical processes associated with mine drainage. There is not yet a consensus on how best to model the rate of Fe^{2+} oxidation.

Our objectives in this paper are two-fold: to introduce a design for a field continuously-stirred tank reactor (CSTR, also referred to as a mixed-flow reactor) which should have uses beyond this study, and to present field rates of Fe^{2+} oxidation in untreated and treated acid mine drainage determined using this CSTR. One advantage of using a CSTR is the ability to measure the rate of reaction directly without resorting to a differential method requiring much more data collection. In addition, the CSTR may more closely approximate flow conditions in a stream than a batch reactor.

In the first trial of this reactor system, we have not attempted to explicitly account for all parameters which might influence Fe^{2+} oxidation rates; most notably we have not counted *Thiobacillus* bacteria. Other factors to be considered include those listed in Table 1.

METHODOLOGY

Reactor design. The reactor vessel (Fig. 1) is a modified Fisher® plexiglass water bath. The original battery powered drill that turned a plastic propeller for mixing was later replaced with a small AC stirrer motor because the drill battery pack discharged too quickly. The original plastic spigot mounted for outflow 3 cm above the reactor floor was replaced by a PVC pipe outlet to achieve steady flow rates. A similar spigot was mounted on the top edge of the reactor vessel for the inflow. A hose submerged in the stream fed the reactor by gravity flow; the maximum flow rate was approximately 2.5 L min^{-1}, depending on the available hydraulic head. Later experiments used smaller diameter PVC tubing to achieve low flow rates. Flow rates were measured at the inlet and outlet using a graduated cylinder and stopwatch. Steady state flow was assumed once the inflow and outflow rates were equal within 2%. For this study, "ambient" conditions were defined by setting up the reactor and allowing it to reach steady state pH and dissolved O_2 levels, i.e., no NaOH nor dissolved O_2 were introduced into the reactor. Operation of the stirrer *does* introduce dissolved O_2 into the reactor at levels slightly elevated above the stream levels (e.g., at Site 3 for runs 1–4, the dissolved O_2 concentration increased from 4.0 to 4.5 mg/L over 30 min. For non-ambient condition runs, either O_2 gas or NaOH solutions were introduced. Compressed O_2 gas was supplied by a small O_2 tank. Gas was introduced through a 35 cm-long diffuser stone on the reactor floor to maintain dissolved O_2 levels. Sodium hydroxide solutions between 0.2 and 4.0 mol L^{-1} were introduced by a cassette pump to maintain pH values to within 0.04 units during a run. The pump and stirrer motor were driven by a 12V car battery through a DC/AC inverter. Samples for Fe^{2+} were collected at the inflow and outflow 2–4 times for each run condition. Dissolved O_2 and pH were measured within the reactor by suspending probes in the reactor. After collecting data and samples for a run, conditions were changed (NaOH solution or O_2 was added continuously), and 0.75–1.5 h allowed the reactor to reach steady state before the next set of measurements were made.

Visual dye studies were used to evaluate mixing properties. In addition, NaCl solution was used as a conservative tracer to evaluate average residence times for non-reactive species. Sodium chloride concentrations at the outlet flow were tracked with a conductivity probe.

Field sites. The field sites included discharges from the Southern Anthracite Region and the western bituminous coal fields in Pennsylvania. Sites 1 and 2 (Fig. 2) were from the Anthracite Region and had experienced no treatment. Sites 3–5 were located in passive treatment facilities

Table 1. Variables suggested to influence the rate of Fe^{2+} oxidation

Variable	Investigators
Fe^{2+} concentration	Stumm and Lee, 1961; Wilmoth *et al.*, 1974; Davison and Seed, 1983; Noike *et al.*, 1983; Millero, 1985; Pesic *et al.*, 1989; Okereke and Stevens, 1991; Williamson *et al.*, 1992
H^+ (or OH^-) concentration	Stumm and Lee, 1961; Wilmoth *et al.*, 1974; Davison and Seed, 1983; Millero, 1985; Pesic *et al.*, 1989
Na^+ concentration (authors note that "Na^+" influence may actually be due to SO_4^{2-})	Okereke and Stevens, 1991
O_2 concentration	Stumm and Lee, 1961; Kim, 1968; Sung and Morgan, 1980; Davison and Seed, 1983; Millero *et al.*, 1987; Pesic *et al.*, 1989
Presence of ferric hydroxide solids	Tamura *et al.*, 1976a; Sung and Morgan, 1980
Organic acids	Theis and Singer, 1974; Miles and Brezonik, 1981; Deng and Stumm, 1993
Ionic strength, Cl^-, SO_4^{2-}	Sung and Morgan, 1980
ClO_4^-, NO_3^-, Cl^-, Br^-, I^-, SO_4^{2-}	Tamura *et al.*, 1976b
Cu^{2+}, Mn^{2+}, Co^{2+}	Stumm and Lee, 1961
Light intensity	Singer and Stumm, 1968; McKnight *et al.*, 1988
Colloidal silica and aluminum oxide, bentonite clay	Singer and Stumm, 1968
Temperature	Sung and Morgan, 1980; Okereke and Stevens, 1991
Thiobacillus concentration	Nordstrom, 1985; Pesic *et al.*, 1989; Okereke and Stevens, 1991
Nutrients (glucose—indirect effect)	Noike *et al.*, 1983

combining anoxic limestone drains and constructed wetlands in the bituminous region [see Hedin *et al.* (1994) for a discussion of passive coal mine drainage treatment].

- Site 1 – Ephemeral drainage through fractured rock and coal spoils, tributary to the North Branch of Shamokin Creek, Northumberland County, PA.
- Site 2 – Flooded shaft draining a deep mine pool, tributary to Carbon Run, Northumberland County, PA.
- Site 3 – Rate measured at outlet of second oxidation pond (downstream of two anoxic limestone drains) at Howe Bridge Passive Treatment Site (see Fig. 3), tributary to Mill Creek, Jefferson County, PA.
- Site 4 – Rate measured at overflow of large wetland pond at Howe Bridge Passive Treatment Site (see Fig. 3), tributary to Mill Creek, Jefferson County, PA.
- Site 5 – Rate measured approximately 100 m downstream of the westernmost anoxic limestone drain at Filson Passive Treatment Site, tributary to Little Mill Creek, Jefferson County, PA.

Analytical methods. Dissolved O_2 was measured with a YSI model 57 meter and probe. The pH was measured with a HANNA HI 9025C pH meter. Samples for Fe^{2+} were filtered (0.2 μm), acidified with HCl immediately, and analyzed in the field within 0.2–6 h of sampling. Fe^{2+} was determined using a HACH DR2000 spectrophotometer and 1,10 phenanthroline according to standard methods (Greenberg *et al.*, 1992). The Fe^{2+} standards were prepared daily using a stock solution prepared from $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$, concentrated HCl, and distilled deionized water. The stock solution was found to be stable within analytical error for several hours. Each time standards were checked, they were mixed from stock solution in the field. The sensitivity was 0.972 A L mg^{-1}, where A is absorbance units, and the detection limit was 0.02 mg L^{-1} ($\bar{x}_0 + 3\sigma$).

Reaction rates were determined at steady state Fe^{2+} concentrations (variation in outlet $[Fe^{2+}] < 1\%$) using the following equation

$$r_{Fe^{2+}} = \frac{dn_{Fe^{2+}}}{dt} = -\left[\left(\frac{n_{Fe^{2+}}}{V}\right)_{in} - \left(\frac{n_{Fe^{2+}}}{V}\right)_{out}\right]\left[\frac{dV}{dt}\right]$$
$$= ([Fe^{2+}]_{in} - [Fe^{2+}]_{out})(\text{flow rate}) \quad (9)$$

where n is moles, V is volume in L, $[Fe^{2+}]$ is in mol L^{-1}. The rate in mol s^{-1} was converted to mol L^{-1} s^{-1} by dividing by 15 L (the reactor volume). Modeling results using Stella®, a differential equation solver, and analytical uncertainty estimates (i.e., $\{[Fe^{2+}_{in}]-[Fe^{2+}_{out}]\} > 0.1$ mg L^{-1}) suggest that the minimum measurable rate at flow rates used in this study is approximately 10^{-9} mol L^{-1} s^{-1}.

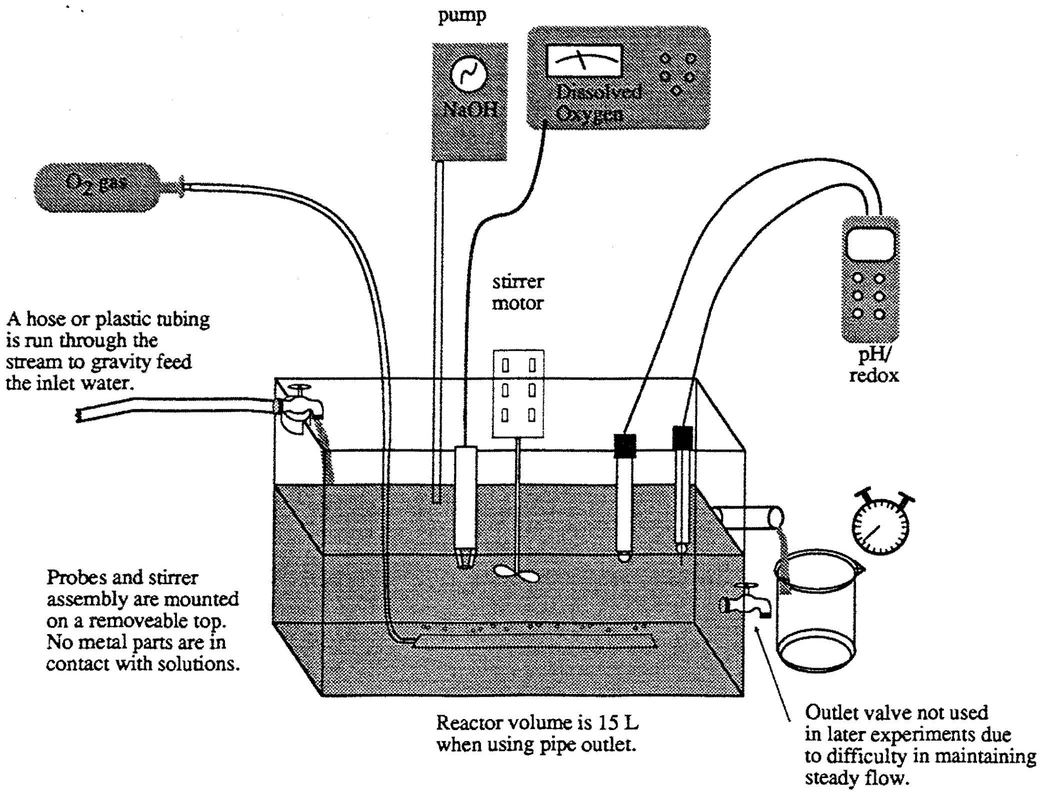
RESULTS AND DISCUSSION

Reactor performance

Visual dye studies suggested that mixing was rapid when the propeller was driven at maximum speed. To check mixing properties further, the average residence time, τ_{res}, was determined by using the equation

$$\tau = \frac{\Sigma\, t_i C_i}{\Sigma\, C_i} \quad (10)$$

where C_i is the concentration of NaCl at time t_i (Levenspiel, 1972). The NaCl concentration was



A hose or plastic tubing is run through the stream to gravity feed the inlet water.

Probes and stirrer assembly are mounted on a removeable top. No metal parts are in contact with solutions.

Reactor volume is 15 L when using pipe outlet.

Outlet valve not used in later experiments due to difficulty in maintaining steady flow.

Fig. 1. Field CSTR design.

estimated from the relationship C_{NaCl} (mg L^{-1}) = 0.5 (conductivity, mS/cm). The τ_{res} for a 2.2 L min^{-1} flow rate was 5.3 min; field flow rates ranged from 0.13 to 1.8 L min^{-1}, thus τ_{res} for field runs were higher than the laboratory-determined residence time. Figure 4 shows a plot of NaCl concentration *versus* time for a pulse input (3 mL of 3 mol L^{-1} NaCl solution). Complete mixing occurs within 1 min as evidenced by the rapid increase in conductivity, followed by exponential decay. τ_{res} was also determined by fitting the normalized concentration of NaCl (E) to the equation $E = 0.23 - 0.87 \log(\text{time})$ according to the method of Levenspiel (1972). This fit gave $\tau_{res} = 4.2$ min.

Experimental

Field data and calculated reaction rates are reported in Table 2. Data in Table 2 for which rate determinations were conducted under "ambient"

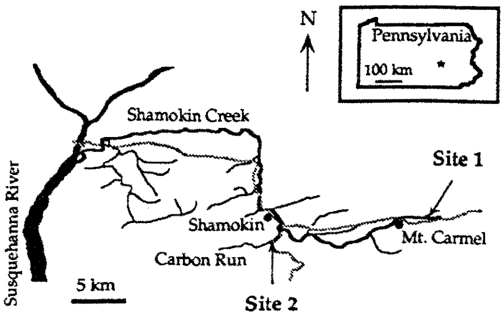


Fig. 2. Map of the Shamokin Creek watershed showing field Sites 1 and 2.

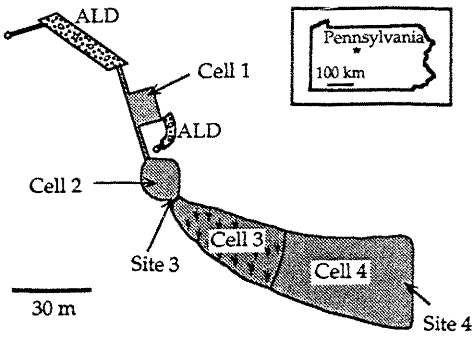


Fig. 3. Schematic drawing of the Howe Bridge passive mine drainage facility, Jefferson County, PA. The outflow is to Mill Creek. ALD stands for underground anoxic limestone drain.

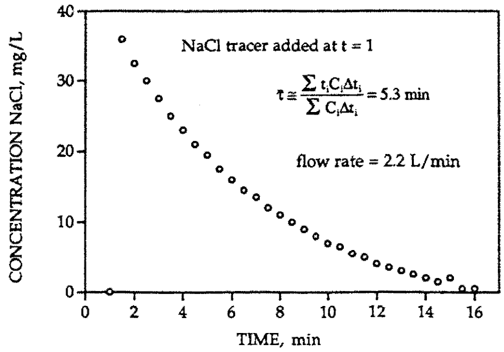


Fig. 4. Concentration of NaCl versus time for tracer experiment.

conditions (described in Section 2, Methodology) are identified with an asterisk.

We initially planned to take replicate inlet samples approximately 3 times during a several-hour field experiment, with outlet samples taken much more frequently for each run. This proved a poor design because the inlet Fe^{2+} concentrations varied significantly (approximately 0.2 to 1.0 mg L^{-1}) over a period of minutes in almost every experiment. The reproducibility of individual samples was approximately 0.1 mg L^{-1}, which suggested that the variation in inlet Fe^{2+} concentration with time was not an artifact. Therefore, samples of inlet and outlet solutions were taken successively for each run. The individual rates reflect run conditions (Fe^{2+} concentration, pH, DO, temperature) over 2–5 min intervals. Figure 5 shows the variation observed during the experiments at Sites 2 and 4. The variation at Site 4 generally trends towards lower Fe^{2+} concentrations with time and is probably due to groundwater infiltration; for 3 days prior to the experiment, the area received heavy rains. Site 2 exhibited more and shorter-term variation than any other site.

We were not able to measure a rate of Fe^{2+} oxidation at Site 2 even though the dissolved O_2 concentration was varied between 2.7 and 12 mg L^{-1}, and the ambient pH and Fe^{2+} concentrations were higher than Site 1 (where a rate of $2 \pm 1 \times 10^{-9}$ mol L^{-1} s^{-1} was measured). Copious ferric hydroxides coating the stream substrate indicate that Fe is being oxidized at Site 2. Based on the abiotic rate law given in equation 4 (Stumm and Lee, 1961), the rate of Fe^{2+} oxidation under ambient conditions (Runs 1–3, Site 2) would be 9.5×10^{-10} mol L^{-1} s^{-1}. Therefore, the rate of Fe oxidation at Site 2 is below the minimum measurable rate for this reactor. It should be possible to measure the rate by decreasing the flow rate, thereby increasing the residence time of Fe^{2+} in the reactor. However, at low flow rates, the time required to reach steady state goes up significantly. We were unsuccessful in an attempt to measure a change between inlet and outlet Fe^{2+} concentration at a flow rate of 7.8 mL s^{-1} at this site (data not displayed).

Limitations of interpretation

The Fe^{2+} oxidation rates determined under "ambient" conditions in this study are likely to be more realistic than the rates determined with altered pH values or dissolved O_2 (DO) concentrations, especially if Fe-oxidizing bacteria are affecting the measured rates. Bacterial populations may not have sufficient time to adapt to new pH and DO levels in the reactor (average residence times are between 20–40 min). For this reason, future use of this reactor for determination of Fe^{2+} oxidation rates will not involve altering pH or addition of O_2.

Under some run conditions, $Fe(OH)_3$ solids were observed visually in the CSTR at all field sites except Site 2, although ferric hydroxides were not always visually observed on the filters (where they are concentrated during sampling) under ambient conditions. The inlet water at Site 3 contained visible ferric hydroxides. Tamura *et al.* (1976a) suggest that Fe^{2+} oxidation is both a homogenous and heterogeneous reaction and that the oxidation rate is catalyzed by ferric hydroxides due to adsorption of Fe^{2+} onto $Fe(OH)_3$ surfaces at circumneutral pH values. Evidence for such a catlytic effect was not examined in this study.

Rate laws

Method of isolation. A rate law from data in this study cannot be developed by using the method of isolation (Lasaga, 1981) wherein the concentrations of some species are held constant while allowing one other species to vary. For example, upon changing the dissolved O_2 concentration, the pH and outlet Fe^{2+} concentrations also changed.

Least squares regressions. We attempted to determine a rate law based on a linear least squares model with form similar to Stumm and Lee (1961)

$$\log \text{rate} = \log k + a \log[Fe^{2+}] + b \log[OH^-] + c \log[O_2] \qquad (11)$$

Multiple regressions were performed on the entire data set and on subsets of the data. Table 3 presents the results using equation 11, considering Sites 1, 3, 4 and 5 together, separately, and in two subsets. The r^2 for the entire data set was only 0.42. Sites 1 and 4 were grouped because the pH values are relatively low at these sites, and it has been reported that *Thiobacillus ferroxidans* catalyze Fe^{2+} oxidation significantly at pH values of less than 3.5 (Lacey and Lawson, 1970). This grouping results in an r^2 of only 0.65, and relatively high $P > F$ values.

Table 2. Field data from this study

Site	Run #	Flowrate ($mL\ s^{-1}$)	Fe^{2+} mg^{-1} inlet	outlet	DO, $mg\ L^{-1}$	pH pH	T, °C	Rate $mol\ s^{-1}$	Rate $mol\ L^{-1}\ s^{-1}$	Log rate $mol\ L^{-1}\ s^{-1}$	Mean rate $\pm 1\sigma$ (mean log rate) $mol\ L^{-1}\ s^{-1}$
1	1*	14	3.56	3.39	3	3.36	12	4.21×10^{-8}	2.81×10^{-9}	−8.55	$2 \pm 1 \times 10^{-9}$
	2*	14	3.49	3.43	3	3.36	12	1.54×10^{-8}	1.03×10^{-9}	−8.99	(−8.7)
	3	14	3.74	2.80	4	4.38	12	2.93×10^{-7}	1.59×10^{-8}	−7.80	$1.3 \pm 0.4 \times 10^{-8}$
	4	14	3.39	2.83	4	4.38	12	1.45×10^{-7}	9.64×10^{-9}	−8.02	(−7.89)
	5	14	3.37	2.22	5	4.82	12	2.92×10^{-7}	1.95×10^{-8}	−7.71	$1.91 \pm 0.04 \times 10^{-8}$
	6	14	3.31	2.20	5	4.82	12	2.82×10^{-7}	1.88×10^{-8}	−7.73	(−7.72)
	7	14	3.42	1.71	6	5.10	12	4.35×10^{-7}	2.90×10^{-8}	−7.54	$2.94 \pm 0.05 \times 10^{-8}$
	8	14	3.38	1.62	6	5.10	12	4.46×10^{-7}	2.97×10^{-8}	−7.53	(−7.53)
2	1*	31	23.2	24.7	2.7	5.85	14	nd	nd	nd	nd
	2*	31	25.9	26.2	2.7	5.85	14	nd	nd	nd	(nd)
	3*	31	26.1	22.0	2.7	5.85	14	nd	nd	nd	
	4	32	22.9	21.6	5.6	5.95	14	nd	nd	nd	nd
	5	32	22.8	23.7	5.6	5.95	14	nd	nd	nd	(nd)
	6	32	21.4	21.1	5.6	5.95	14	nd	nd	nd	
	7	31	20.1	22.1	8.9	5.98	14	nd	nd	nd	nd
	8	31	23.2	23.1	8.9	5.98	14	nd	nd	nd	(nd)
	9	31	24.5	21.6	8.9	5.98	14	nd	nd	nd	
	10	31	22.4	22.5	8.9	5.98	14	nd	nd	nd	
	11	31	22.9	21.9	12	6.00	14	nd	nd	nd	nd
	12	31	22.5	22.4	12	6.00	14	nd	nd	nd	(nd)
3	1*	7.4	163	161	4.0	6.31	11	2.81×10^{-7}	1.87×10^{-8}	−7.73	$2.0 \pm 1.0 \times 10^{-8}$
	2*	7.4	159	156	4.1	6.31	11	3.93×10^{-7}	2.62×10^{-8}	−7.58	(−7.76)
	3*	7.4	159	156	4.3	6.31	11	4.50×10^{-7}	3.00×10^{-8}	−7.52	
	4*	7.4	154	153	4.5	6.31	11	9.37×10^{-8}	6.24×10^{-9}	−8.20	
	5	8.0	153	144	6.7	6.07	11	1.39×10^{-6}	9.28×10^{-8}	−7.03	$9.9 \pm 4.4 \times 10^{-8}$
	6	8.0	163	157	7.3	6.07	11	8.88×10^{-7}	5.92×10^{-8}	−7.23	(−7.03)
	7	8.0	173	158	7.3	6.07	11	2.20×10^{-6}	1.47×10^{-7}	−6.83	
	8	7.4	165	160	11.2	6.08	11	5.64×10^{-7}	3.76×10^{-8}	−7.42	$4.7 \pm 1.3 \times 10^{-8}$
	9	7.4	164	158	11.2	6.08	11	8.46×10^{-7}	5.64×10^{-8}	−7.25	(−7.34)
4	1*	14.2	32.8	33.2	7.3	3.14	15	nd	nd	nd	nd
	2*	14.2	32.3	32.3	7.3	3.15	15	nd	nd	nd	(nd)
	3*	14.2	31.8	32.2	7.3	3.12	15	nd	nd	nd	

	4	14.2	31.2	31.0	7.4	3.20	15	5.39×10^{-8}	3.59×10^{-9}	−8.44	$9 \pm 6 \times 10^{-9}$
	5	14.2	31.7	31.3	7.6	3.20	15	1.08×10^{-7}	7.19×10^{-9}	−8.14	(−8.05)
	6	14.2	31.7	30.7	7.8	3.20	15	2.43×10^{-7}	1.62×10^{-8}	−7.79	
	7	14.2	30.2	27.9	7.5	3.32	15	5.93×10^{-7}	3.95×10^{-8}	−7.40	$4 \pm 1 \times 10^{-8}$
	8	14.2	29.8	27.1	7.5	3.32	15	6.74×10^{-7}	4.49×10^{-8}	−7.35	(−7.33)
	9	14.2	30.5	27.2	7.5	3.32	15	8.49×10^{-7}	5.66×10^{-8}	−7.25	
	10	14.2	29.8	20.0	7.0	3.62	15.5	2.49×10^{-6}	1.66×10^{-7}	−6.78	$1.7 \pm 0.1 \times 10^{-7}$
	11	14.2	30.5	20.0	7.0	3.62	15.5	2.66×10^{-6}	1.78×10^{-7}	−6.75	(−6.78)
	12	14.2	29.1	20.1	7.0	3.65	15.5	2.30×10^{-6}	1.53×10^{-7}	−6.82	
	13	14.2	28.9	13.1	6.6	4.16	15.5	4.01×10^{-6}	2.67×10^{-7}	−6.57	$2.6 \pm 0.1 \times 10^{-7}$
	14	14.2	28.1	12.9	6.6	4.19	15.5	3.58×10^{-6}	2.56×10^{-7}	−6.59	(−6.58)
5	1*	9.3	29.2	21.9	7.9	7.17	11	1.20×10^{-6}	8.00×10^{-8}	−7.10	$8.9 \pm 0.9 \times 10^{-8}$
	2*	9.3	28.2	20.2	7.7	7.16	11	1.33×10^{-6}	8.89×10^{-8}	7.05	(−7.05)
	3*	9.3	29.3	20.5	7.8	7.15	11	1.47×10^{-6}	9.83×10^{-8}	−7.01	
	4	9.3	27.2	18.4	9.0	7.09	11	1.47×10^{-6}	9.77×10^{-8}	−7.01	$9.3 \pm 0.6 \times 10^{-8}$
	5	9.3	27.0	18.6	9.0	7.09	11	1.40×10^{-6}	9.36×10^{-8}	−7.03	(−7.03)
	6	9.3	26.7	18.9	9.0	7.09	11	1.30×10^{-6}	8.65×10^{-8}	−7.06	
	7	9.4	26.7	16.6	11.8	6.87	10	1.70×10^{-6}	1.13×10^{-7}	−6.95	$1.10 \pm 0.03 \times 10^{-7}$
	8	9.4	26.6	17.0	11.8	6.87	10	1.61×10^{-6}	1.08×10^{-7}	−6.97	(−6.96)
	9	94	26.5	17.0	11.8	6.87	10	1.60×10^{-6}	1.23×10^{-7}	−6.91	

* denotes "ambient" conditions prior to changing pH or dissolved oxygen levels.

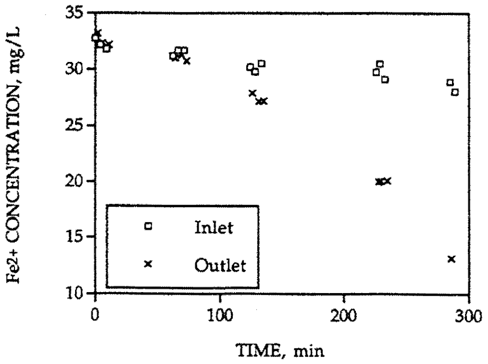


Fig. 5. Fe^{2+} concentration variations at Sites 2 and 4.

Sites 3 and 5 are also grouped because they are located in treatment facilities with $pH > 6.0$. The r^2 for this grouping is 0.57, with high $P > F$ values. Scatterplots of log rate versus log Fe^{2+} concentration indicate that our data do not fit models that are either zeroth or first order with respect to Fe^{2+} concentration. Stepwise regression based on equation 11 did not produce good fits to our data. No regression technique employed, including normalization of rates to initial Fe^{2+} concentrations, produced satisfactory fits to the entire data set from this study (see Section 3.3, Limitations, above).

Figure 6 (after Waddell, 1978) illustrates the hypothesized effects of the activity of bacteria on Fe^{2+} oxidation rates. If a scenario similar to that depicted in Fig. 6 does control Fe^{2+} oxidation, the rate law required to model mine drainage processes in the field would be a composite of both the abiotic and biotic rate laws.

Comparison to other published rates. Figure 7 graphically compares Fe^{2+} oxidation rates from this study with rates from other workers. The "abiotic" lines are from the laboratory rate law of Stumm and Lee (1961), and the two lines with positive slopes bracket the ranges of Fe^{2+} and dissolved O_2 concentrations in this study. The field rates in this figure are plotted directly rather than relying on rate laws. Three field studies (Noike *et al.*, 1983; Nordstrom, 1985; Williamson *et al.*, 1992) represented in Fig. 7 all define the rate as

$$\text{rate} = \frac{\Delta C_i}{\Delta x_i} \cdot \frac{\Delta x_i}{\Delta t_i} \tag{12}$$

where ΔC_i is the difference in Fe^{2+} concentration over the distance Δx_i, and Δt_i is the time required for a dissolved species to travel the distance Δx_i. However, in order to compare these rates consistently, ΔC, Δx and Δt were defined as in Nordstrom (1985), i.e., the measured values were used between each sampling station rather than from the farthest upstream station to each downstream station. This approach results in a significantly greater range of rates for the data from Noike *et al.* (1983), and a

Table 3. Results of multiple linear regressions on field data (rate as mol L^{-1} s^{-1}). Model: log rate = log k + a log [Fe] + b log [OH] + c log [O_2]

Site(s)	N	r^2	k	a	P>F	b	P>F	c	P>F
1, 3, 4, 5	37	0.42	0.92	0.017	0.89	0.056	0.31	2.1	0.0002
1	8	0.94	−53	−4.4	0.56	2.0	0.24	−12	0.48
4	11	0.92	−125	−30	0.0019	−8.7	0.0065	21	0.054
1, 4	19	0.65	19	4.4	0.0083	2.2	0.0043	−3.9	0.16
3	9	0.76	−44	4.6	0.54	−5.2	0.039	−2.0	0.19
5	9	0.90	−24	−1.5	0.044	−0.94	0.055	−1.7	0.51
3, 5	18	0.57	−10	−0.81	0.30	−0.54	0.44	0.67	0.38

somewhat smaller increase in range from the data from Williamson *et al.* (1992).

Figure 7 shows a very wide variation (4 orders of magnitude) in field Fe^{2+} oxidation rates in untreated and treated mine drainage. This simple graphical analysis does not account for differences in any variables other than pH. The Fe^{2+} concentrations vary by a factor of 100; dissolved O_2 varies from 3 mg L^{-1} up to saturation. Temperature varies from 6–20°C, bacteria levels vary, and other dissolved constituents also vary. However, unless a rate law is assumed, the data cannot be compared directly. A statistical approach incorporating variables in Table 1 might help elucidate a rate law, but insufficient data are available. Okereke and Stevens (1991) suggest that a statistical model to predict field Fe^{2+} oxidation rates will require extensive field experimentation, accounting for wide differences in factors such as those in Table 1.

Table 4 compares the common logarithm of rates for ambient conditions in this study to rates calculated using the Stumm and Lee (1961) and Pesic *et al.* (1989) rate laws, equations 4) and (7, respectively. We assumed 1 or 6 mg mL^{-1} *Thiobacillus* concentrations for the Pesic rate law calculations. The highest pH value in the Pesic *et al.* (1989) study was 3.1, thus we did not calculate rates from this rate law for the higher pH sites. For Sites 2 and 4, no field rate could be determined at ambient conditions, thus the rate must be less than 10^{-9} mol L^{-1} s^{-1} (see Section 2, Methodology).

The Stumm and Lee (1961) abiotic rate law is within one-half an order of magnitude of the field rate for Site 3 (Table 4). Hedin *et al.* (1994) provide evidence that Fe^{2+} oxidation in net alkaline mine drainage (alkalinity > acidity) may be mainly by abiotic processes. Within uncertainty, they find no difference in rate between filtered (0.22 μm) and unfiltered samples for a sample at pH 6.1 (*T. ferrooxidans* will not pass a 0.2 μm filter). Both Hedin *et al.* (1994) and Nordstrom (1985) find filtering samples with pH 2.4 to 3.5 dramatically slows the oxidation rate compared to unfiltered samples. Data from Sites 3 and 5 in this study were from net alkaline samples, and the rates are near those for abiotic oxidation (see Fig. 7 and Table 4). These comparisons suggest that Fe^{2+} oxidation is both abiotic and biologically influenced, depending on pH, in acid and alkaline mine drainage in the field.

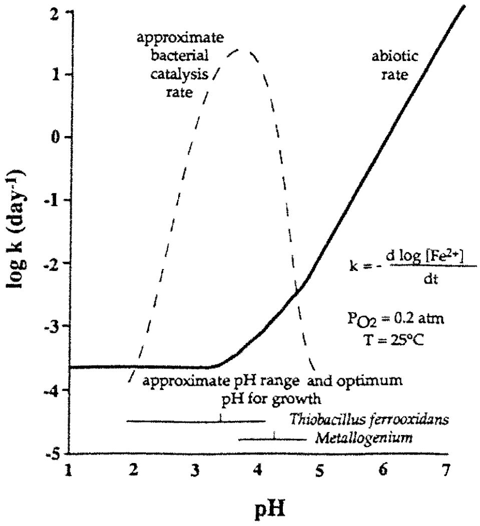


Fig. 6. Hypothesized abiotic and biotic influences on Fe^{2+} oxidation rates (diagram after Waddell, 1978 and Singer and Stumm, 1970).

Modeling

Figure 7 shows that, with the exception of the two Hedin *et al.* (1994) data points, our ambient field rates are slower than other field rates reported. Figures 8 and 9 represent one method of comparing our rates with other field data to determine if our rate measurements give reasonable results. Figure 8 shows the modeling approach used to simulate the steady state Fe^{2+} concentrations in the 4 settling ponds (Cells 1–4, numbered moving downstream) at the Howe Bridge treatment facility (Fig. 3). The software employed was the differential equation solver Stella®. Data used in the input were the measured raw water Fe^{2+} concentration, pond-full volume of the cells, volumetric flow rates, and the Fe^{2+} oxidation rates measured in this study. Simulations assumed the wetland cells were originally empty; as time proceeds, the cells fill up and the Fe^{2+} reaches steady state concentrations. The Fe^{2+} oxidation rates employed in the simulations

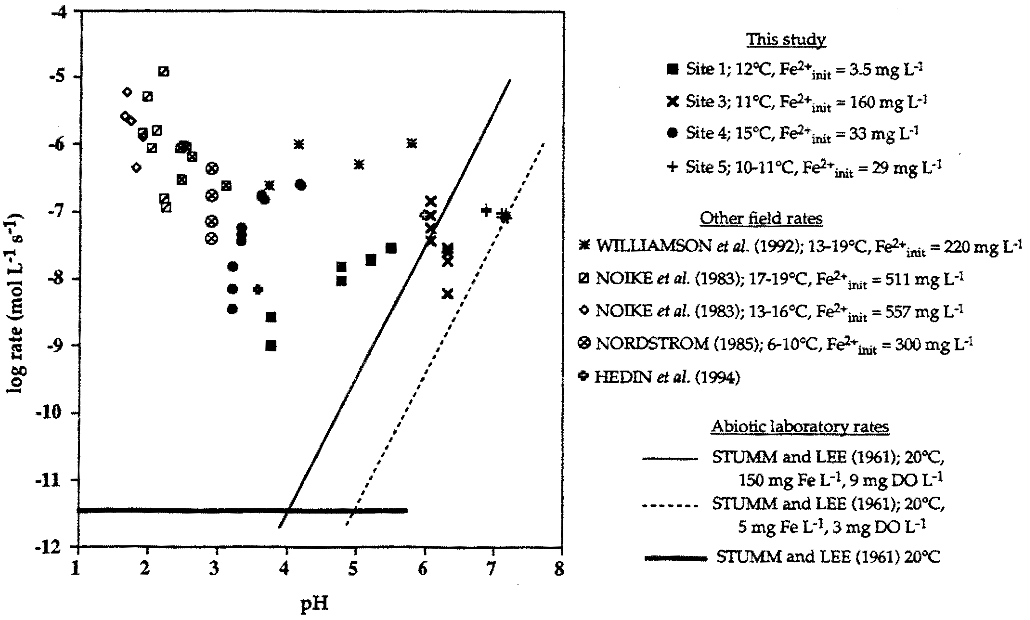


Fig. 7. Comparison of field and laboratory rates of Fe^{2+} oxidation. See text for explanation of rates from Noike *et al.* (1983).

Table 4. Comparison of field CSTR ambient rates to rates derived using equation 4 and equation 7 with data from this study

		Log rate (mol L^{-1} s^{-1})			
		Average,	Pesic *et al.* (1989)		Stumm and Lee (1961)
Site	pH	this study	$C_{bact} = 1$ mg mL^{-1}	$C_{bact} = 6$ mg mL^{-1}	20°C
1	3.36	−8.7	−10.1	−9.27	−11.5
2	5.85	nd; <−9.0	na	na	−9.02
3	6.31	−7.41	na	na	−7.09
4	3.14	nd; <−9.0	−8.42	−7.64	−11.5
5	7.17	−7.05	na	na	−5.98

(na = not applicable; outside the range of experimental conditions).

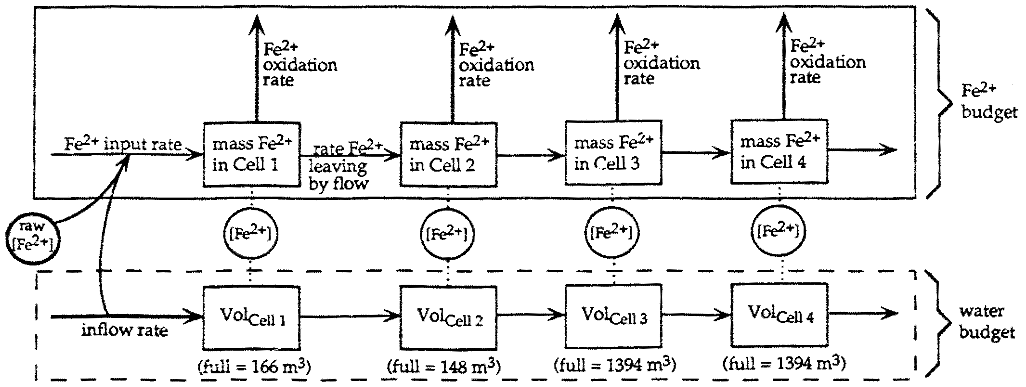


Fig. 8. Schematic of the modeling approach for the Howe Bridge facility (see Fig. 3 and Fig. 9). Dark lines indicate field data used in model. The volume of water in each cell (pond) is initially zero, and is limited by the pond-full volume of the cell. Ferrous iron concentrations ($[Fe^{2+}]$) are predicted and then compared to independently measured $[Fe^{2+}]$.

are shown in Fig. 9. The choice of rates in Fig. 9 was made based on the following:

Figure 9a: We used the rate measured at Site 3 (see Fig. 3) for Cells 1 and 2. Because no rate was measurable at Site 4, we assumed that the rate for Cells 3 and 4 was slightly lower than the 10^{-9} mol L^{-1} s^{-1} minimum measurable rate.

Figure 9b: We again used the rate measured at Site 3 for Cells 1 and 2. We assumed that the rate for Cell 3 was slightly lower than the rates in Cells 1 and 2, and that the rate for Cell 4 was slightly lower than the rate for Cell 3 and was below the 10^{-9} mol L^{-1} s^{-1} minimum measurable rate.

Figure 9c: This graph presents a sensitivity analysis of this model. Rates for all cells were divided or multiplied by 2 (the uncertainty reported for the ambient rate at Site 3) in order to test the effect of uncertainty on the Fe^{2+} concentration for a single cell.

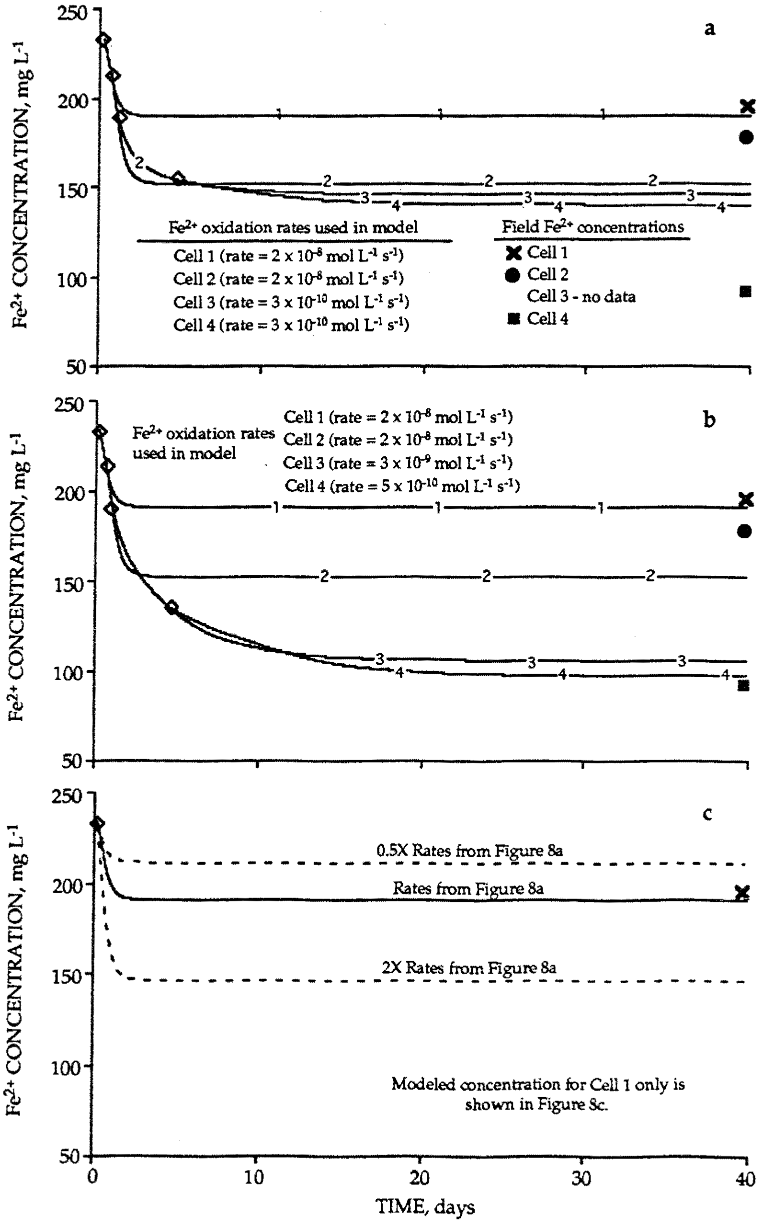


Fig. 9. Modelled Fe^{2+} concentrations for Howe Bridge Treatment Facility compared to measured concentrations (unpublished data from Watzlaf, US Department of Energy). Cells (ponds) are modelled as initially empty; ◇ indiates the initial of filling of each cell. C is a sensitivity analysis showing concentrations for Cell 1 only.

Figure 9a predicts well the observed Fe^{2+} concentration of Cell 1, but overestimates the concentrations for Cells 2 and 4. Figure 9b predicts the observed concentrations for Cells 1 and 4, but overestimates the value for Cell 2. This simulation does not account for dilution; Hedin *et al.* (1994) estimate a dilution factor of 0.89 at the Howe Bridge site (due to influence "clean" water), suggesting that predicted Fe^{2+} concentration should be approximately 10% lower than those modeled in Fig. 9.

Figure 9c shows that the model is fairly sensitive to changes in oxidation rates. Except for one rate (Hedin *et al.*, 1994), the field rates (Noike *et al.*, 1983; Nordstrom, 1985; Williamson *et al.*, 1992) presented in Fig. 7 would predict Fe^{2+} concentrations that are much lower than those observed in the Howe Bridge facility. For example, if the Williamson *et al.* (1992) rate law is used in this model, all Fe^{2+} is oxidized in Cell 1 and the concentration goes to zero. We do not suggest that these previously published field rate laws are incorrect, rather, we suggest that the field conditions in our study were different than in other studies; in particular, most of the previously published rate laws were derived in low-pH systems which likely contained *T. ferrooxidans* populations. Taken together, these model results confirm that the CSTR measurements produce accurate estimates of field Fe^{2+} oxidation rates.

The simulations and field observations in Fig. 9 also suggest that the most rapid oxidation of Fe^{2+} occurs in Cells 1 and 2. Although the model predicts that more Fe^{2+} is oxidized in Cell 3 than in either Cell 1 or 2, Cell 3 is much larger (see Fig. 8), allowing for longer retention times. In addition, the ambient pH of Cell 4 was 3.3, which was much lower than upstream cells because the treatment system has insufficient alkalinity to neutralize the mineral acidity (Fe^{2+}) present. The low pH may cause a slower rate of oxidation as suggested by abiotic laboratory models (see equation 4). If Fe^{2+} oxidation (as opposed to hydrolysis, precipitation, and physical settling of Fe^{2+} solids) is the rate-limiting step in the passive treatment of mine drainage, a more thorough understanding of the factors that influence Fe^{2+} oxidation rates should lead to more efficient treatment systems.

CONCLUSIONS

A field continuously-stirred tank reactor has been successfully used to determine Fe^{2+} oxidation rates in acid and alkaline mine drainage. Dissolved O_2, Fe^{2+} and pH were determined, while other factors which may influence rates were not controlled in this study. Given the complexity of the field setting, it is not surprising that no single rate law could be developed to predict field rates based on Fe^{2+}, O_2 and pH alone. Rates ranged from less than 10^{-9} to $3.27 \pm 0.1 \times 10^{-6}$ mol L^{-1} s^{-1}. Uncertainties are in the order of 70% near the lower limit of rate measurement using this reactor, whereas uncertainties of approximately 1% are achievable at higher rates of reaction. The comparison of modeling results to field Fe^{2+} concentrations in a treatment wetland confirm the accuracy of the measured rates.

In the future, we plan to examine the influence of more variables, especially SO_4 and *Thiobacillus* concentrations in order to determine a field-based rate law, although it is unlikely that this field method will help elucidate mechanisms involved in mine drainage reactions. It remains to be seen whether a single rate law can describe Fe^{2+} oxidation in mine drainage systems. It may be possible that some combination of rate laws or a composite rate law is necessary to cover the range of conditions encountered in mine drainage. The field CSTR holds promise for obtaining further data in an attempt to obtain a "universal" field rate law, if such a relationship exists. Remediation efforts should benefit from this study or from other field studies using this methodology. The field CSTR should also have numerous other applications; it should prove useful in determining aqueous reaction rates of natural and anthropogenic chemical processes. Some possible applications include metal hydroxide precipitation, travertine and siliceous sinter precipitation, mineral dissolution, and sorption phenomena.

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