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Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage

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Abstract

The oxidation of Fe(II) is apparently the rate-limiting step in passive treatment of coal mine drainage. Little work has been done to determine the kinetics of oxidation in such field systems, and no models of passive treatment systems explicitly consider iron oxidation kinetics. A Stella II® model using $Fe(II)_{init}$ concentration, pH, temperature, *Thiobacillus ferrooxidans* and O_2 concentration, flow rate, and pond volume is used to predict Fe(II) oxidation rates and concentrations in seventeen ponds under a wide range of conditions (pH 2.8 to 6.8 with Fe(II) concentrations of less than 240 mg L^{-1}) from 6 passive treatment facilities. The oxidation rate is modeled based on the combination of published abiotic and biological laboratory rate laws. Although many other variables have been observed to influence Fe(II) oxidation rates, the 7 variables above allow field systems to be modeled reasonably accurately for conditions in this study.

Measured *T. ferrooxidans* concentrations were approximately 10^7 times lower than concentrations required in the model to accurately predict field Fe(II) concentrations. This result suggests that either 1) the most probable number enumeration method underestimated the bacterial concentrations, or 2) the biological rate law employed underestimated the influence of bacteria, or both. Due to this discrepancy, bacterial concentrations used in the model for pH values of less than 5 are treated as fit parameters rather than empirically measured values.

Predicted Fe(II) concentrations in ponds agree well with measured Fe(II) concentrations, and predicted oxidation rates also agree well with field-measured rates. From pH 2.8 to approximately pH 5, Fe(II) oxidation rates are negatively correlated with pH and catalyzed by *T. ferrooxidans*. From pH 5 to 6.4, Fe(II) oxidation appears to be primarily abiotic and is positively correlated with pH. Above pH 6.4, oxidation appears to be independent of pH. Above pH 5, treatment efficiency is affected most by changing design parameters in the following order: pH > temperature ≈ influent Fe(II) > pond volume ≈ O_2. Little to no increase in Fe(II) oxidation rate occurs due to pH increases above pH 6.4. Failure to consider Fe(II) oxidation rates in treatment system design may result in insufficient Fe removal. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Mine drainage from coal and ore mines is a significant problem worldwide. Herlihy et al. (1990) estimate that 10 000 km of streams are strongly impacted by mine drainage in the eastern United States alone. Active chemical treatment of mine drainage is well understood and effective, but few active treatment facilities are being constructed for treatment of abandoned mine drainage due to cost constraints. Passive treatment, often employing settling ponds or wetlands with or without the addition of limestone (see Hedin et al., 1994a,b), is being widely used to treat mine discharges, particularly for coal mine drainage, in which metal loadings are often lower than for ore-generated mine drainage. The main objectives are to raise pH (where necessary) and precipitate Fe, Al, and Mn. The

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effectiveness of pond/wetland treatment has varied considerably. Successful treatment requires nearly complete oxidation of Fe (II) to Fe (III)

$$Fe^{2+}(aq) + 1/4\,O_2(aq) + H^+_{(aq)} = Fe^{3+}_{(aq)} + 1/2\,H_2O \qquad (1)$$

which must be followed by the precipitation of an Fe hydroxide

$$Fe^{3+}_{(aq)} + 3H_2O = Fe(OH)_{3(s)} + 3H^+_{(aq)}. \qquad (2)$$

Although several other processes such as flocculation, settling, and filtration or uptake by plants may be involved in Fe removal, if Eq. (1) and Eq. (2) do not proceed far enough to the right, treatment will not be effective. Singer and Stumm (1970) suggest that Fe(III) hydrolysis and precipitation proceed more rapidly than Fe(II) oxidation, thus oxidation is apparently the rate-limiting step. In agreement with this assessment, Kirby (unpublished data) found that the field rate of precipitation of Fe hydroxide is faster than the field rate of Fe oxidation (Kirby and Elder Brady, 1998). Knowledge of the field rate of Fe(II) oxidation is crucial for understanding mine drainage and treatment systems. While Fe sulfide mineral oxidation must be considered if one is examining mines or spoils, it need not be considered for a system where the sulfide has already has been oxidized, which is the case for the surface environment where mine drainage treatment takes place.

Stumm and Lee (1961) proposed a rate law for Fe(II) oxidation under abiotic laboratory conditions, and Stumm and Morgan (1981) present this rate law, recast with H^+ instead of OH^- and O_2 concentration instead of partial pressure as

$$\frac{d[Fe^{2+}]}{dt} = \frac{-k[Fe^{2+}]\,[O_2]}{[H^+]^2} \qquad (3)$$

where [] indicates aqueous concentration in mol L^{-1}, k is the rate constant in mol L^{-1} min^{-1}, and t is time in minutes. The rate of Fe(II) oxidation has also been proposed to be affected by numerous other inorganic and biological parameters (see Kirby and Elder Brady, 1998, for a list).

There is a broad range of Fe-oxidizing bacteria which may contribute to the biogeochemical oxidation of Fe in natural systems. They include *Thiobacillus* spp. which are acidophiles preferring an optimum growth pH < 3 (Trafford et al., 1973; Amaro et al., 1991) typically associated with sulfidic mine tailings and neutrophilic filamentous organisms such as *Gallionella* spp. (Ivarson and Sojak, 1978), *Leptothrix* spp. (Crerar et al., 1979), *Metallogenium* (Walsh and Mitchell, 1972) and *Sphaerotilus* spp. (Stokes, 1954), which typically occur at groundwater seeps containing Fe(II) (Emerson and Revsbech, 1994). Emerson and Moyer (1997) recently isolated two unamed strains of neutrophilic Fe-oxidizing bacteria. Ehrlich (1996) suggests that there is as yet no unequivocal evidence that *Gallionella* significantly promotes Fe oxidation at circumneutral pH. Schrenk et al. (1998) demonstrated high concentrations of Leptospirillum ferrooxidans under extremely low pH conditions, but their exact role in acid mine drainage generation is unclear.

It is well documented that *Thiobacillus ferrooxidans* catalyzes Fe(II) oxidation (e.g., Lacey and Lawson, 1970; Nordstrom, 1985) such that at low pH, field rates can be 10^5 to 10^6 times faster than abiotic laboratory rates. Optimal conditions for *T. ferrooxidans* growth occur at pH values near 3 (Schnaitman et al., 1969). Several laboratory rates or rate laws which include *T. ferrooxidans* terms have been produced (Schnaitman et al., 1969; Lacey and Lawson, 1970; Okereke and Stevens, 1991; Chavaire et al., 1993; Nyavor et al., 1996). Nemati and Webb (1997) use modified Michaelis–Menten kinetics to obtain a rather comprehensive Fe(II) oxidation rate law that includes temperature, Fe(II) and *T. ferrooxidans* concentrations. This rate law was developed under O_2-saturated conditions, and pH was not controlled, although the initial pH was 2.0. Pesic et al. (1989) also present a comprehensive rate law which includes Fe(II), dissolved O_2, and *T. ferrooxidans* concentrations, temperature, and pH.

Few field rates or rate laws have been published for Fe(II) oxidation. For low pH conditions not typical of those found in many treatment facilities, Nordstrom (1985) and Williamson et al. (1992) give a rate of approximately 5×10^{-7} mol L^{-1} s^{-1}, and Noike et al. (1983) give rates between 10^{-7} and 10^{-5} mol L^{-1} s^{-1}. Both Williamson et al. (1992) and Noike et al. (1983) present first order rate laws which suggest dependence on Fe(II) concentration alone. Kirby and Elder Brady (1998) measured field Fe(II) oxidation rates in untreated coal mine drainage and in wetland treatment systems using a continuously-stirred tank reactor; they found rates from less than 10^{-9} mol L^{-1} s^{-1} to $3.27 \pm 0.01 \times 10^{-6}$ mol L^{-1} s^{-1}. This study found no statistical correlation between pH, Fe(II), and dissolved O_2 with oxidation rates, and no rate law was proposed.

There is not a consensus on a rate law which applies in the field, nor is there consensus on which variables are most important in determining the field rate of Fe(II) oxidation in mine drainage. Complexation, presence of solids, photoreduction, biological activity, and many other factors (see Kirby and Elder Brady, 1998, for a more complete list) have been reported to influence Fe(II) oxidation rates. Davison and Seed (1983) provide a review of Fe(II) oxidation kinetics in water of circumneutral pH, and many of their conclusions support the idea that development of a "universal" rate law that applies to natural water is achievable.

Their work strongly supports the form of the rate law given in Eq. (3). Based on their own work and a literature review, Davison and Seed (1983) suggest that while different species can increase or decrease the rate, "the O_2 oxidation of Fe(II) is described by the same rate expression in natural systems and in analogous synthetic systems. The catalytic or inhibiting effect of other substances appears to be no greater in natural waters and in some cases the effect may be less pronounced". Although the Davison and Seed (1983) conclusions are not directly applicable to *acidic* mine drainage, their work lends credence to the idea that a relatively simple rate law with only a few variables may apply to a wide range of mine drainage solution compositions.

1.1. Previous models of mine drainage wetlands (ponds)

Published mathematical models of passive mine drainage treatment do not include Fe(II) oxidation. Flanagan et al. (1994) predict Fe and Al retention, but they suggest that their model is probably not applicable where Fe(II) concentrations are high. Other approaches (Dietz et al., 1994; Hedin et al., 1994a) model Fe removal on the basis of Fe loading to predict Fe removed per area of wetland (mass Fe removed m^{-2} d^{-1}). Although these models, which imply that Fe removal is dependent upon pond area rather than pond volume, have been reasonably effective, there are numerous cases in which ponds that were built based on loading/area removal-based criteria are inadequate for treatment (Hedin, personal communication). Wieder (1989) has also noted a significant percentage of passive treatment systems that have low treatment efficiencies. The authors are not aware of previous studies that directly link oxidation by acidophilic Fe-oxidizing bacteria to passive treatment of mine drainage. The Hedin et al. (1994a) criteria have proven quite useful and are often widely employed to design treatment facilities; however, insufficient Fe(II) oxidation may explain why some facilities so designed fail to remove as much Fe as expected.

1.2. Model employed in this study

Passive mine drainage treatment facilities offer natural laboratories because they can be modeled as continuously-stirred tank reactors, albeit non-ideal reactors. The authors hypothesize that by combining the abiotic laboratory rate law of Stumm and Lee (1961) (recast as in Stumm and Morgan, 1981) with the biological rate law of Pesic et al. (1989), field Fe(II) concentrations and oxidation rates in passive mine drainage treatment systems can be predicted for the relatively wide range of conditions in this study. The model delineates the relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. Although the authors recognize that many processes other than those considered by this model may influence Fe oxidation, this model represents an application of the principle of parsimony (Gauch, 1993)—choosing a simpler explanation over a more complex explanation. Field data from treatment systems in Pennsylvania and the two rate laws are used in a differential equation solver to predict Fe(II) concentrations in treatment systems with pH between 2.8 and 6.4. The variables in the model include influent Fe(II) concentration, volumetric flow rate, *T. ferrooxidans* and dissolved O_2 concentrations, temperature, pH, and pond volume. Other abiotic or biotic parameters have not been employed in the model, nor is the actual retention (precipitation, settling, filtration) of metals within wetlands addressed. This model provides an alternative approach to passive treatment design which is based on oxidation kinetics, volume, and flow rather than the loading and area-removal approach. The results suggest that wetlands may be undersized unless Fe(II) oxidation is considered during facility design.

The authors have chosen to refer to the water compartments of the treatment systems in this study as ponds rather than wetlands. The rationale for this choice is that the term pond aptly describe all of the systems, whereas the term wetland is not as generally applicable. Many of the ponds have high suspended solids, little vegetation, and are relatively deep (>1 m) over much of their area. Although some wetlands constructed for mine drainage treatment have aquatic plants that play a significant role in Fe removal, the role of plants in Fe oxidation in the ponds in this study is likely minimal.

2. Methodology

2.1. Field sites and data collection

Systems in this study treat mine drainage from the bituminous coal fields of western Pennsylvania. Descriptions and locations of the facilities are given in Table 1. Figure 1 shows site maps and sample locations for 4 facilities. The Howe Bridge site is further described in Hedin et al. (1994b). The pH in all facilities except Mead Run is raised by anoxic limestone drains (ALD) or successive alkalinity producing systems (SAPS). The Filson 1 site includes an "aluminator" (Kepler and McCleary, 1997), which is a SAPS designed to prevent clogging of the drain by $Al(OH)_3$ precipitation. Hedin et al. (1994a) describe treatment wetlands combined with anoxic limestone drains. Kepler and McCleary (1994) describe SAPS treatment, which incorporates an ALD underneath a layer of organic matter in treatment ponds. Data for the Mead

Table 1
Characteristics of wetland treatment systems in this study

Facility	Location in PA	Characteristics	Pond volume (m^3)			
			Pond 1	Pond 2	Pond 3	Pond 4
Howe Bridge	Jefferson Co.	2 discharges, 2 ALD's, 3 ponds, 1 SAPS	20	330	1620	–
Morrison	Clarion Co.	1 discharge, 1 ALD, 3 ponds, 1 SAPS	150	275	200	–
Filson 1	Jefferson Co.	1 discharge, 1 aluminator, 2 other ponds	nm	280	150	–
Filson 5 and 6	Jefferson Co.	2 discharges, 2 ALD's, 6 ponds, 1 SAPS	100	70	8.5	650
Mead Run	Elk Co.	1 discharge, 1 pond, no alkaline addition	360	–	–	–
Argentine	Cambria Co.	1 discharge, 1 ALD's, 4 ponds	430	580	80	63

ALD stands for anoxic limestone drain; SAPS stands for successive alkalinity producing system; nm indicates not modeled because influent solution could not be sampled.

Run treatment system were provided by the Headwaters Charitable Trust. Data for the Argentine treatment system were provided by Hedin Environmental.

All samples were collected during daylight hours in June and September of 1997; atmospheric conditions ranged from sunny to completely overcast. The pH was measured using field-calibrated portable meters. Dissolved O_2 (DO) was measured with a meter calibrated in the field against water-saturated air, and with the exception of the DO profiling sampling at Howe Bridge, measurements were made at a depth of approximately 10 cm. Samples for Fe(II) were filtered (0.45 μm), acidified with concentrated HCl, diluted, and analyzed within 15 min of collection using a Hach DR2000 spectrophotometer and 1,10 phenanthroline according to standard methods (Greenberg et al., 1992). Acidified Fe standards were prepared daily from

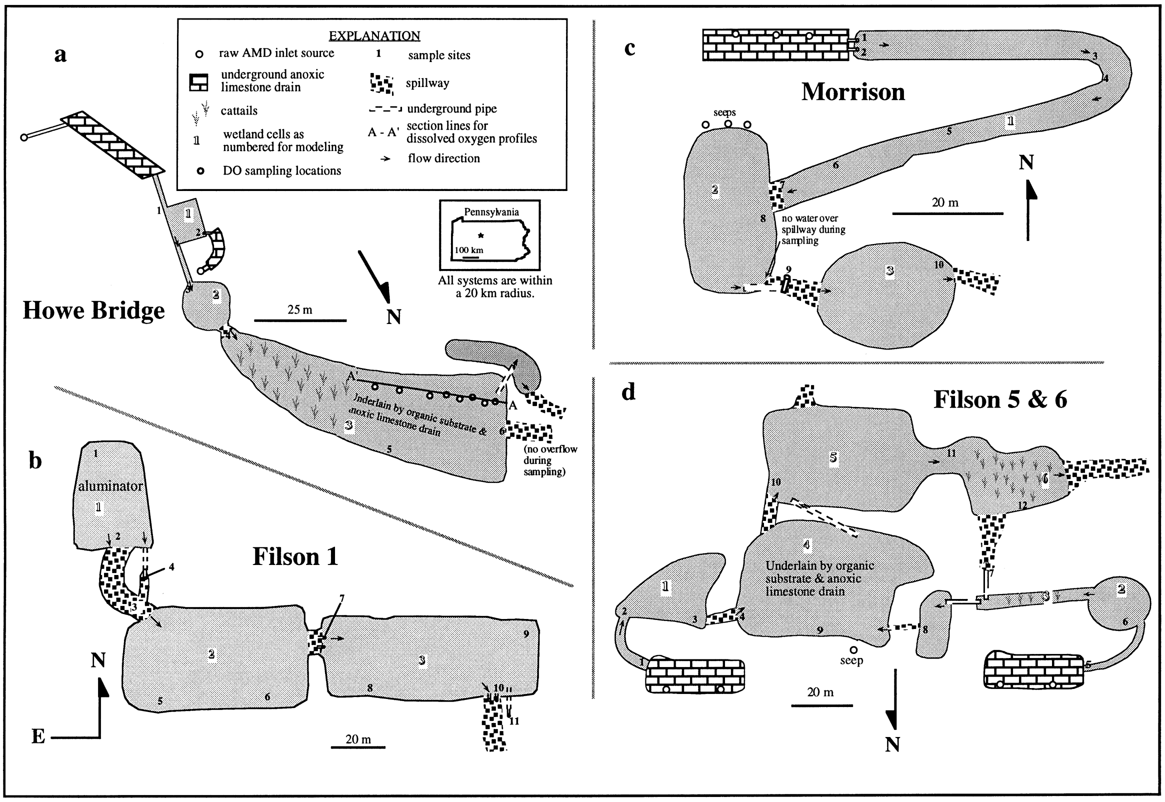

Fig. 1. Schematic maps of four treatment systems including locations of sampling sites.

Table 3
Field data, total dissolved Fe, and *T. ferrooxidans* concentrations for treatment systems

System and Date	Sample No.	flow rate (L hr^{-1})	pH	T (°C)	Concentration (mg L^{-1})			
					Fe(II)	Fe_{tot}	DO	C_{bact} (dry wt.)
Howe Bridge	1	5060	6.0	9.8	236	265	0.5	nd
6/97	2	420	nd	nd	214	nd	nd	nd
	3	nd	6.1	15	208	235	4.4	nd
	4	nd	5.9	23	179	191	2.7	nd
	5	nd	2.9	30	14	61	6.6	nd
	6	5660	2.8	30	8	56	7.1	nd
Howe Bridge	1	4910	6.43	10.7	230	nd	2.88	BDL
9/97	2	2875	6.43	10.2	209	nd	0.18	nd
	3	7785	6.41	11.8	207	nd	4.07	BDL
	4	nd	6.15	14.8	152	nd	4.96	6×10^{-7}
	5	nd	3.08	20.8	nd	nd	6.76	BDL
	6	nd	3.08	20.8	30	nd	6.66	BDL
Filson 1	1	nd	3.7	18.7	29.9	nd	6.14	nd
9/97	2	nd	3.65	17.3	nd	nd	5.86	4×10^{-5}
	3	2200	3.63	18.3	nd	nd	6.98	nd
	4	3400	5.21	15.6	63.3	nd	0.3	9×10^{-6}
	5	nd	3.56	20.7	29.8	nd	7.33	nd
	6	nd	3.54	20.1	24.4	nd	7.71	6×10^{-7}
	7	6390	3.6	20.2	21.5	nd	8.58	BDL
	8	nd	3.48	21.4	16.2	nd	6.55	nd
	9	nd	3.53	21	18.9	nd	6.98	nd
	10	1430	3.53	21.5	19.4	nd	7.76	BDL
	11	4000	4.8	20.7	10.2	nd	0.18	BDL
Morrison	1	3000	5.8	11.2	145	161	0.5	nd
7/97	2	1250	5.8	11.7	159	164	0.4	nd
	3	nd	nd	17.0	nd	nd	5.6	nd
	4	nd	6.1	17.0	182	205	6.7	nd
	5	nd	nd	19.5	nd	nd	7.0	nd
	6	nd	7.0	22.2	nd	nd	7.0	nd
	7	nd	5.2	21.9	97.2	109	3.5	nd
	8	nd	5.2	22.9	105	106	7.2	nd
	9	8300	6.1	18.4	86.0	97	2.7	nd
	10	nd	5.8	20.8	63.8	72	6.0	nd
Filson5&6	1	nd	6.2	11.8	53.4	58.7	0.30	nd
6/97	2	nd	6.4	22.9	nd	nd	4.4	nd
	3	2160	6.4	23.3	7.4	20.5	5.1	nd
	4	nd	6.7	25.0	nd	nd	7.4	nd
	5	nd	6.5	11.6	58.6	70.6	0.22	nd
	6	nd	6.3	24.0	58.8	69.2	2.1	nd
6/97	7	4180	6.4	24.2	22.2	20.0	5.1	nd
	8	2970	6.6	26.7	17.6	16.5	6.8	nd
	9	nd	6.8	27.0	0.46	0.6	13	nd
	10	5150	6.8	27.8	2.98	3.1	7.9	nd
Mead Run	influent	nd	6.4	20	7.5	8.0	6.0	nd
	effluent	85200	6.67	20	4.0	4.3	6.0	nd
	influent	nd	6.45	10.4	37.6	nd	0.1	nd
Argentine	Pond 1	nd	6.78	12.2	23.4	nd	7.4	nd
	Pond 2	nd	6.57	14.8	6.9	nd	8.2	nd
	Pond 3	nd	6.62	15.5	4.3	nd	8.9	nd
	Pond 4	35400	6.80	15.6	2.1	nd	9.5	nd

"nd" represents not determined. The detection limit for bacteria was 5×10^{-7} mg L^{-1}.

an acidified 100 mg Fe(II) L^{-1} stock solution. The Fe concentrations of the field standards ranged from 0.10 to 2.1 mg Fe(II) L^{-1}.

Volumetric flow rate was measured at several points in each facility using the bucket and stopwatch method, using vessels of 7L, 15L and 20 L. The containers were filled several times at each discharge site, and a total filling time was recorded. Weirs and pipes were already in place at some locations; at other sites, weirs were constructed to channel water through a PVC pipe. Where water was lost around the weirs ($<10\%$), the amount lost was estimated and added to the flow rate.

In Pond 3 of the Howe Bridge facility (see Fig. 1a and Fig. 5), the depth to the sediment-water interface was determined by lowering a lightly weighted 12×15 cm plexiglass plate into the water until it contacted the sediment-water interface.

Water samples were also collected at some facilities for laboratory analysis. The filtered (0.45 μm) samples were acidified with HNO3, placed on ice, and analyzed for K, Na, Mg, Mn and Ca using an atomic absorption spectrophotometer. Iron and Al were analyzed in a commercial laboratory by atomic absorption. Unfiltered samples for alkalinity, acidity, and anions were placed on ice and then refrigerated. Alkalinity and hot H_2O_2 acidity were determined within 1 to 3 days of collection according to standard methods (Greenberg et al., 1992). Sulfate was determined using an ion chromatograph. From these laboratory analyses, only total dissolved Fe concentrations are reported here for brevity.

Table 2
Symbols, descriptions, units, sources of information, and mathematical relationships used in models

Input data	Description	Units	Source
$[Fe]_0$	Fe(II) concentration entering system	mol L^{-1}	field data
Q	volumetric flow rate between ponds	L hr^{-1}	field data
$[O_2]$	dissolved oxygen concentration	mol L^{-1}	field data*
pH	pH of influent water and water in ponds	–	field data
T	water temperature	°C	field data
C_{bact}	*T. ferrooxidans* concentration	mg L^{-1} (dry)	see text*
k_{abio}	abiotic Fe(II) oxidation rate constant as f(T)	mol L^{-1} min^{-1}	Stumm and Morgan, 1981
k_{biol}	biological Fe(II) oxidation rate constant as f(T)	mol L^{-1} min^{-1}	**Pesic et al., 1989
V_{full}	total volume of each pond	L	field data*
Calculated values	**Description**		
H^+	activity of hydrogen ion	–	calculation
V_t	Volume of cells at time, *t*	L	calculation
Fe	mass of Fe(II) in cells	mol	calculation
$[Fe]_t$	Fe(II) concentration in cells at time, *t*	mol L^{-1}	calculation
$R_{Fe,ox}$	absolute rate of Fe(II) oxidation	mol hr^{-1}	calculation
r_{abio}	volumetric rate of abiotic Fe(II) oxidation	mol L^{-1} hr^{-1}	Stumm and Morgan, 1981
r_{abio}	volumetric rate of biological Fe(II) oxidation	mol L^{-1} hr^{-1}	Pesic et al., 1989
Fe_{infl}	rate of Fe(II) mass transfer from influent water	mol hr^{-1}	calculation
Fe_{outfl}	rate of Fe(II) mass transfer between cells	mol hr^{-1}	calculation

Description	Mathematical relationships
water volume change in cells	$dV_t/dt = Q_{in} - Q_{out}$
mass transfer and oxidation of Fe^{2+}	$dFe/dt = Fe_{infl} - Fe_{outfl} - R_{Fe,ox}$
mass transfer of Fe^{2+} into system	$Fe_{infl} = [Fe]_0 Q_{in}$
Fe^{2+} concentration in ponds	$[Fe]_t = Fe/V_t$
mass transfer of Fe^{2+} between ponds or as effluent	$Fe_{outfl} = [Fe]_t Q_{out}$
abiotic rate constant	$K_{abio} = A_{abio} \exp(-E_{a,abio}/RT)$
**biological rate constant	$K_{biol} = A_{biol} \exp(-E_{a,biol}/RT)$
abiotic Fe(II) oxidation rate	$r_{abio} = -k_{abio}[Fe]_t[O^2]/(H^+)^2$
**biological Fe(II) oxidation rate	$r_{bio} = -C_{bact}k_{biol}[Fe]_t[O^2](H^+)$
absolute Fe(II) oxidation rate	$R_{fe,ox} = -(r_{abio} + r_{biol})V_t$

*See text for discussion of pond volumes and dissolved O_2 and bacteria concentrations.**The value for the frequency factor, *A*, was modified after discovering a mathematical error in Pesic et al. (1989); see text for details.

Unfiltered, near-surface water samples for microbiological analysis were taken at the Howe Bridge and Filson 1 systems during the September sampling. Thirty-mL water samples were collected using sterilized pipettes, transferred to sterilized polyethylene bottles, and kept on ice or refrigerated until analysis within 3 days of collection. Acidophilic Fe-oxidizing bacteria were enumerated using the Most Probable Number (MPN) technique (Cochran, 1950) and 9K buffer (Silverman and Lundgren, 1959) containing 33 g of $FeSO_4{\cdot}7H_2O$ per liter. This medium has been utilized to culture *Thiobacillus ferrooxidans* from natural systems (Southam and Beveridge, 1992, 1993). MPN counts were converted to mg *T. ferrooxidans* L^{-1} (dry weight) by assuming that *T. ferrooxidans* have approximately the same density (2.8×10^{-13} g $cell^{-1}$ [dry]) as *Escherichia coli* which is the same size (Neidhardt and Umbarger, 1996). The MPN method consists of 5 replicate inoculations from a 10-fold serial dilution to reduce variability and produce a single (most probable) value. The MPN table does not list standard deviations, therefore, no uncertainty estimates are included in the analysis. Values for *T. ferrooxidans* concentration used in the model are explained in the discussion section.

2.2. Modeling

The rate law of Stumm and coworkers as given in Stumm and Morgan (1981) was employed to model abiotic Fe(II) oxidation

$$r_{\text{abiotic}} = \frac{\mathrm{d}[Fe^{2+}]}{\mathrm{d}t} = \frac{-k_{\text{abiotic}}[Fe^{2+}][O_2]}{[H^+]^2} = \frac{-\left\{A_{\text{abiotic}} \exp\left(\frac{-E_{\text{a,abiotic}}}{RT}\right)\right\}[Fe^{2+}][O_2]}{[H^+]^2} \qquad (4)$$

where k_{abiotic} is the rate constant in mol L^{-1} s^{-1}, and [] indicates concentration in mol L^{-1}. A_{abiotic} (value $= 4.00 \times 10^5$) and $E_{\text{a,abiotic}}$ (value = 96 kJ mol^{-1}) are the pre-exponential factor and activation energy, respectively; R is the gas constant in kJ mol^{-1} K^{-1}; and T is temperature in K. The temperature dependence of k_{abiotic} was developed from the activation energy and (Arrhenius) temperature dependence given in Stumm and Morgan (1981).

To model the contribution of *T. ferrooxidans* to Fe(II) oxidation, the rate law of Pesic et al. (1989) was employed:

$$r_{\text{bio}} = \frac{\mathrm{d}[Fe^{2+}]}{\mathrm{d}t} = -k_{\text{bio}}\, C_{\text{bact}}[Fe^{2+}][O_2][H^+] = -\left\{A_{\text{bio}} \exp\left(\frac{-E_{\text{a,bio}}}{RT}\right)\right\} C_{\text{bact}}[Fe^{2+}][O_2][H^+] \qquad (5)$$

where k_{bio} is the rate constant in L^3 mg^{-1} mol^{-2} s^{-1}, C_{bact} is the concentration of *T. ferrooxidans* in mg L^{-1} (dry weight), [] indicates aqueous concentration in mol L^{-1}. $E_{\text{a,bio}}$ (value = 58.77 kJ mol^{-1}) is the activation energy, R is the gas constant in kJ mol^{-1} K^{-1}; and T is temperature in K. The original form of this equation expressed O_2 as pO_2; it has here been recast to $[O_2]$ using the Henry's Law constant. Pesic et al. (1989) give the value of the frequency factor, A_{bio}, as 1.62×10^{11}. The authors discovered a mathematical mistake in their paper, and have corrected the frequency factor, resulting in a value for A_{bio} of 1.02×10^9. Eq. (4) and Eq. (5) are summed to give

$$\left(\frac{\mathrm{d}[Fe^{2+}]}{\mathrm{d}t}\right)_{\text{overall}} = -r_{\text{abiotic}} - r_{\text{biol}}. \qquad (6)$$

The program Stella II™ 3.02 (High Performance Systems, Inc.) for Macintosh™ computers was employed for all models. Stella II™ has a graphical interface which facilitates visualization of the mathematical relationships between variables. Flanagan et al. (1994) describe the operation of the Stella II™ program. The models were run using Euler's method for integration and 0.5 hr time steps.

Table 2 describes parameters and mathematical relationships employed in the model. A model for a single-pond system is graphically represented similarly

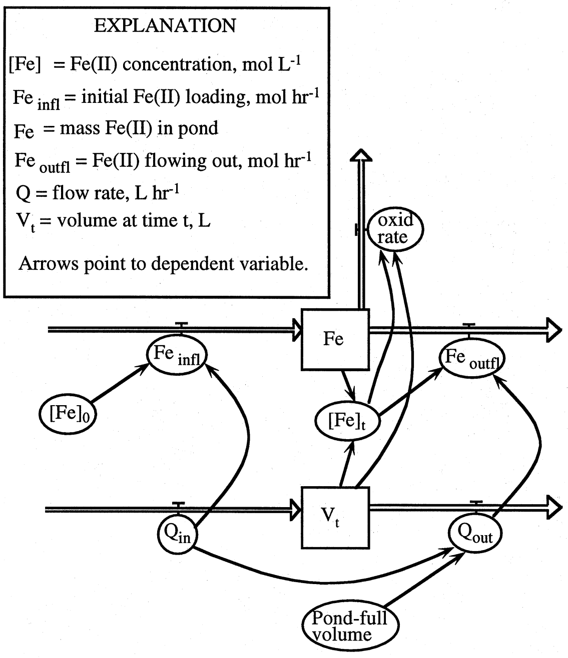

Fig. 2. Schematic diagram representing the mathematical relationships in the model for a single-pond treatment system. See Table 2 for definitions of symbols, mathematical relationships, and units.

Table 4
Input values for model verification

No bacteria included in model Facility	influent Fe(II) (mg L^{-1})	flow rate (L hr^{-1})	Pond 1			Pond 2			Pond 3			Pond 4		
			DO (mg L^{-1})	pH	T (°C)	DO (mg L^{-1})	pH	T (°C)	DO (mg L^{-1})	pH	T (°C)	DO	pH	T (°C)
Morrison	145 (159)	3010 (1250)	6.0	6.00	20.1	5.5	5.17	22.9	5.0	5.75	29.8	–	–	–
Filson 5 and 6	53 (59)	1980 (2980)	4.7	6.42	23.3	2.0	6.34	24.3	5.1	6.38	24.3	7.0	6.76	27.8
Mead Run	7.5	83300	6.0	6.40	20	–	–	–	–	–	–	–	–	–
Argentine	38	35430	3.0	6.78	12.2	8.2	6.57	14.8	8.9	6.62	15.5	9.5	6.80	15.6
Argentine (assume pH = 6.45)	38	35430	3.0	6.45	12.2	8.2	6.45	14.8	8.9	6.45	15.5	9.5	6.45	15.6

Bacteria included in model Facility	influent Fe(II)	flow rate	Pond 1				Pond 2				Pond 3			
			DO (mg L^{-1})	pH	T (°C)	C_{bact}	DO (mg L^{-1})	pH	T (°C)	C_{bact}	DO (mg L^{-1})	pHT (°C)	T (°C)	C_{bact}
Howe Bridge, 6/97	236 (210)	6280 (2440)	3.0	6.00	14.0	0	2.0	5.76	25.1	0	3.0	2.89	29.7	158
Howe Bridge, 9/97	230 (209)	4910 (2875)	2.5	6.4	10.5	0	3.0	6.25	13.3	0	3.0	3.08	19.0	158
Filson 1, 6/97	8.6 (48)	3150 (4180)	nm	nm	nm	nm	8.3	3.26	24.3	237	8.1	3.15	25.4	237
Filson 1, 9/97	29.9 (63.3)	2200 (3400)	nm	nm	nm	nm	5.5	3.54	20.2	395	5.0	3.50	21.2	395

Two influent Fe(II) concentrations and flow rates are given for systems which have two inflows. C_{bact} is in mg L^{-1} (dry weight), and nm indicates not modeled because influent solution could not be sampled.

Table 5
Measured and predicted effluent Fe(II) concentrations (mg L^{-1}) and predicted range of Fe(II) oxidation rates within facilities with lower pH values (pond 3 for Howe Bridge; ponds 2 and 3 for Filson 1)

Facility	Pond 1			Pond 2			Pond 3		
	meas	pred	Range of predicted rates (mol L^{-1} s^{-1})	meas	pred	Range of predicted rates (mol L^{-1} s^{-1})	meas	pred	Range of predicted rates (mol L^{-1} s^{-1})
No bacteria in model									
Howe Bridge, 6/97	208	230	8.8 to 9.0×10^{-9}	172	175	6.6 to 8.3×10^{-9}	8	175	3.3 to 3.6×10^{-14}
Howe Bridge, 9/97	209	207	2.5 to 2.8×10^{-8}	152	139	1.5 to 2.2×10^{-8}	30	139	1.5 to 1.8×10^{-14}
Filson 1, 6/97	25	nm	nm	11	25	3.4×10^{-14}	9.5	25	2.5×10^{-14}
Filson 1, 9/97	50	nm	nm	22	31	9.3×10^{-14}	19	31	8.5×10^{-14}
Bacteria in model									
Howe Bridge, 6/97	208	230	8.8 to 9.0×10^{-9}	172	175	6.6 to 8.3×10^{-9}	8	13	0.44 to 6.4×10^{-8}
Howe Bridge, 9/97	209	207	2.5 to 2.8×10^{-8}	152	139	1.5 to 2.2×10^{-8}	30	20	0.26 to 1.5×10^{-8}
Filson 1, 6/97	25	nm	nm	11	13	1.6 to 6.5×10^{-9}	9.5	9	1.0 to 2.7×10^{-9}
Filson 1, 9/97	50	nm	nm	22	21	0.25 to 1.0×10^{-8}	19	20	1.3 to 3.4×10^{-9}

The slower rates are steady-state values; nm indicates not modeled.

to the Stella II® interface in Fig. 2. The boxes are reservoirs, the valves represent forcing functions, i.e., the rates of fluid flow or Fe(II) transfer. The solution volume is handled in the lower portion of the diagram and is linked mathematically to the mass of Fe (upper portion). The circles are mathematical functions that do not accumulate or act as a forcing function. An arrow indicates that the object at the pointed end of the arrow is a user-defined function of the object at the other end of the arrow.

At the beginning of a simulation, all ponds are empty, and they begin to fill sequentially. That is, the model behaves as if a spigot was turned on to begin filling the ponds. Fe(II) "leaves" a pond in two ways: (1) by flow ($TR_{\mathrm{Fe,out}}$), which is governed by concentration and flow rate, or (2) by oxidation to Fe(III) ($R_{\mathrm{Fe,ox}}$; governed by Eq. (6)). As the ponds fill, the Fe(II) concentrations decrease until the pond reaches hydrodynamic and chemical steady state. Once steady state is achieved, the ponds are modeled as ideal continuously-stirred tank reactors (Levenspeil, 1972), thus the model ignores complexities such incomplete mixing. The values reported for predicted Fe(II) concentrations in the ponds are these steady state values.

3. Results and discussion

3.1. Field data

Table 3 gives water quality parameters at various sites within the treatment systems, and Fig. 1 shows maps with sample locations. Conditions in the treatment systems used for model verification are given in Table 4, and Tables 5 and 6 give the measured and predicted Fe(II) concentrations. The ponds of the Morrison, Filson 5&6, Mead Run, and Argentine systems have pH values between 5.2 and 6.8. The Howe Bridge system is net acidic because the anoxic limestone drain does not add sufficient alkalinity; the pH values in these ponds ranged from 2.8 to 6.4. Volumetric flow rates for all systems ranged from 4.25×10^3 to 85.2×10^3 L hr^{-1}. Fe(II) concentrations in the influents ranged from 7.5 to 236 mg L^{-1}. Temperatures ranged from 9.8 to 30°C.

3.2. *T. ferrooxidans* concentrations

T. ferrooxidans concentrations in the treatment ponds were surprisingly low. Of the 17 samples analyzed, only 6 samples had concentrations greater than the detection limit of 5×10^{-7} mg L^{-1} (dry weight). Two of 6 microbiological samples collected at another treatment facility had measurable concentrations; these data are not presented because the system was not in hydrodynamic steady state and could not be modeled. Table 3 gives the measured bacteria concentrations for the Howe Bridge and Filson 1 facilities. The bacteria concentrations for input into the model are listed in Table 4, and the discrepancy between measured and input concentrations is discussed in a later section. There was no clear pattern between bacterial concentrations and pH, although no samples with pH greater than 6.2 contained measurable bacterial concentrations. The authors know of no enumeration of *T. ferrooxidans* from field studies in comparable systems and are, therefore, unable to compare the concentrations to other field data.

The accurate enumeration of viable Fe-oxidizing bacteria, especially *Thiobacillus ferrooxidans*, is essential for the study of Fe oxidation kinetics in natural environments. However, the growth of *thiobacilli* in an Fe-precipitating environment makes their study difficult. Several methods exist for studying cell populations (growth) in the laboratory, however, each method has limitations for the examination of natural samples.

With the use of abiotic controls, the measurement of Fe(II) oxidation (Ramsay et al., 1988; Suzuki et al., 1990) is a good technique to study bacterial metabolic

Table 6
Measured and predicted effluent Fe^{2+} concentrations (mg L^{-1}) and range of Fe^{2+} oxidation rates for systems in which all ponds had pH greater than 5

Facility	Pond 1		Pond 2		Pond 3		Pond 4		System-wide range of predicted rates (mol L^{-1} s^{-1})
	meas	pred	meas	pred	meas	pred	meas	pred	
No bacteria in model									
Morrison 6/12/97	98	65	86	61	64	41	–	–	0.03 to 8.3×10^{-8}
Filson 5 and 6 6/23/97	7.3	3.3	nd	18	22	21	3.0	0.05	0.04 to 2.0×10^{-8}
Mead Run	4.0	3.9	–	–	–	–	–	–	4.1 to 8.3×10^{-9}
Argentine (measured pH)	24	10	6.9	1.6	4.3	0.7	2.1	0.2	0.13 to 2.6×10^{-8}
Argentine (pH = 6.45)	24	24	6.9	5.8	4.3	3.7	2.1	2.5	0.42 to 4.1×10^{-8}

nd indicates not determined.

activity, but it cannot be used by itself to measure the bacterial contribution to Fe oxidation kinetics because it does not quantify the bacterial component in terms of viable cell counts or concentration. When combined with Fe(II) oxidation, protein assays (Ramsay et al., 1988) are limited in the study of Fe-oxidizing cell numbers because they measure Fe-oxidizing bacteria, non Fe-oxidizing bacteria, dead cells and natural organic material. Molecular methods can be used to quantify Fe-oxidizing bacteria in natural systems (Goebel and Stackebrandt, 1994; de Wulf-Durand et al., 1997). Using the polymerase chain reaction (PCR) and molecular probes as few as 50 cells mL^{-1} (1.4×10^{-5} mg L^{-1}, dry) can be detected. However, the detection of each genus of Fe-oxidizing bacteria requires a unique molecular probe and these probes detect DNA occurring in both viable and dead bacterial cells.

The Most Probable Number (MPN) technique combined with a suitable growth medium (above) provides a quantitative measure of viable acidophilic Fe-oxidizing bacteria (Southam and Beveridge, 1992). MPN analysis eliminates the problem of low plating efficiency making it the best available technique to estimate populations of *thiobacilli.* The growth of Fe-oxidizing bacteria as Fe-cemented aggregates results in an underestimate of the actual population of Fe-oxidizing bacteria (Southam and Beveridge, 1993).

It is possible for some bacteria (e.g., endospore formers) to be present in natural systems and not contribute to biogeochemical cycling. However, *T. ferrooxidans* does not possess a resting stage. Therefore, the concentration (mass) of viable *T. ferrooxidans* accurately reflects biological Fe oxidation activity. *T. ferrooxidans* must compete with the loss of available energy through chemical oxidation combined with the precipitation of Fe (chemical or biological) on *T. ferrooxidans* surfaces (Southam and Beveridge, 1992, 1993), which limits the diffusion of nutrients, slows biological oxidation, and eventually kills the organisms.

3.3. Theoretical effect of pH, T, DO, Fe(II) and T. ferrooxidans on Fe oxidation

Based on Eq. (4) and Eq. (5), Fig. 3 shows the modeled effects of abiotic and biological factors on Fe(II) oxidation rates at fixed Fe(II) and dissolved O_2 concentrations at varying pH values. Eq. (4) produces the abiotic pH-dependent part of Fig. 3, whereas different rate laws hold for pH less than 4 (Singer and Stumm, 1970) or greater than 7 (Millero, 1985). Eq. (4) predicts an increasing oxidation rate with increasing pH, whereas Eq. (5) predicts a decreasing oxidation rate with increasing pH.

Based on the combined abiotic/biological rate law given in Eq. (6), Fig. 4 shows the predicted effect of changes in pH, temperature, *T. ferrooxidans* concentration, Fe(II) concentration, and dissolved O_2 concentration on the Fe(II) oxidation rate. Increasing temperature, Fe(II) concentration, or dissolved O_2 causes an increase in the overall oxidation rate, affecting both abiotic and biological oxidation. Increasing the *T. ferrooxidans* concentration causes an increased oxidation rate only for a pH less than approximately 5. Fig. 3 and Fig. 4 suggest that at pH values greater than 5, the rate is primarily determined by abiotic processes, whereas below pH 5, the rate is also strongly influenced by microbial catalysis.

3.4. Choices and uncertainties of input values

The field setting causes increased uncertainties over more controlled laboratory conditions. The discussion below addresses sources of uncertainty inherent in the field data and the likely effect on modeling.

Iron(II) oxidation creates an O_2 demand within the ponds. The dissolved O_2 (DO) concentration is dependent upon several factors, including diffusion across the atmosphere-water interface, concentration of Fe(II), rate of Fe(II) oxidation, photosynthesis, aerobic respiration of organisms, water velocity and

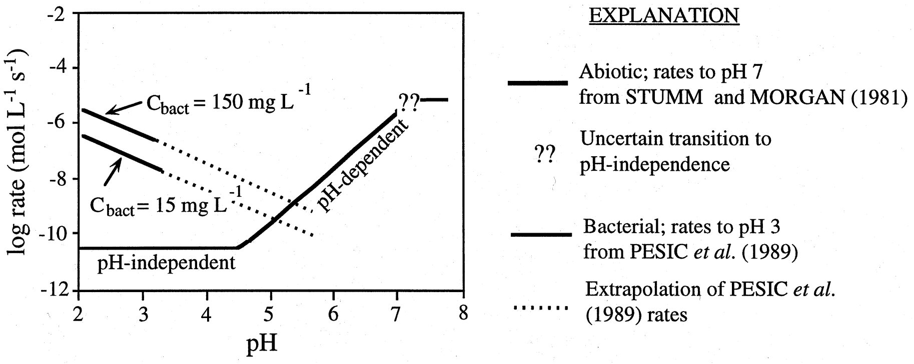

Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Equations 4 and 5).

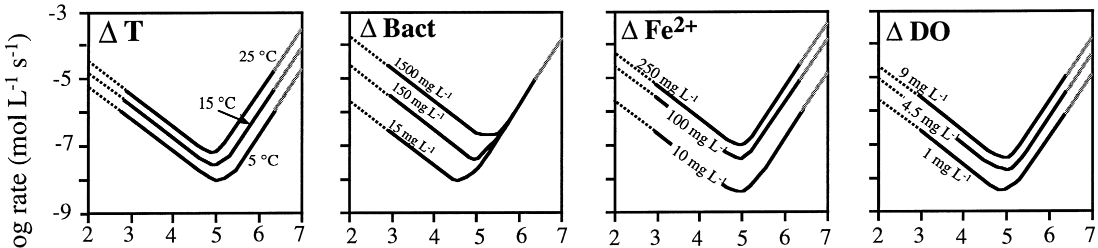

Fig. 4. Predicted effect of varying pH, temperature, *T. ferrooxidans*, Fe(II), and dissolved oxygen on the rate of Fe(II) oxidation. Unless otherwise specified, calculations are based on Fe(II) = 100 mg L^{-1}, C_{bact} = 150 mg L^{-1}, DO = 9 mg L^{-1}, and T = 20°C. Dashed lines indicate pH range over which the model has not been field-checked. Gray lines indicate pH range where oxidation appears to be slower than predicted by the abiotic rate law.

turbulence, and temperature. Selected water column DO concentrations in Pond 3 of the Howe Bridge system are shown in Fig. 5; these data were collected the day following the data in Table 3. This survey was conducted to help choose input values for DO in the models. As Fig. 5 demonstrates, the DO concentrations in this pond are far from uniform, and DO decreased with depth at most sites. There were 3 sites at which DO increased slightly near the sediment-water interface; none of these sites is displayed in Fig. 5. Because DO concentrations generally decrease from the surface to the sediment-water interface, the authors revised the DO values measured near the surface of ponds (Table 3) downward before entering them into the model (see Table 4). The input DO concentrations are necessarily approximations of the average DO in the ponds. However, improving the DO estimate would require much more extensive field measurements or a more sophisticated model of DO concentrations. Because, compared to pH, the model is relatively insensitive to DO, these approximate DO concentrations have been used as input values. DO concentrations for Howe Bridge sites 5 and 6 (Table 3) are higher than all DO concentrations found during the DO profiling. One possible explanation is that the DO measurements in Table 3 were made near the bank of the pond in shallow water, and there is more aquatic vegetation, which could contribute to elevated DO concentrations. DO concentrations used in the model for Pond 3 reflect the DO profiling data.

The volumetric flow rate estimates are subject to errors due to incomplete capture of water by temporary weirs. In a few cases, the treatment systems had known and suspected seeps of both mine drainage and uncontaminated water that could not be accounted for because some of the seeps enter the ponds underwater. This problem was significant in the Morrison system, in which the flow rate doubled from the influent to the effluent. In Pond 1 (actually a long ditch) of the Morrison system, the measured Fe(II) concentration in downstream locations was higher than immediately upstream, indicating an underground acidic mine drainage seep. Hedin et al. (1994a) show that Mg can be used as a conservative tracer to determine if treatment systems are diluted by rain water or if mine drainage enters the system by seepage. Mg concentration

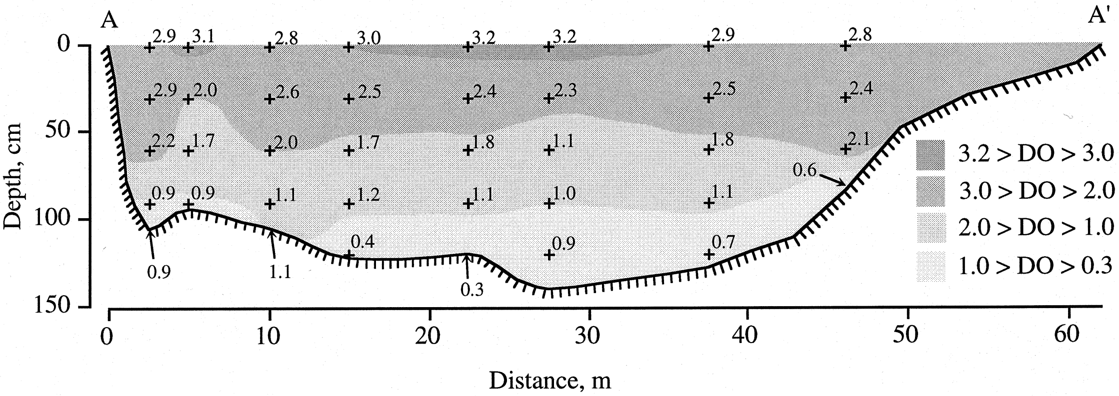

Fig. 5. Dissolved oxygen profile in the water column of Pond 3 of the Howe Bridge treatment system.

increases 33% from the influent to Pond 2, showing that additional acidic mine drainage with total dissolved solids higher than the sampled influent is entering the system. The predicted Fe(II) concentrations for this system are 40 to 50% higher than observed values, due at least in part, to the acidic seeps which could not be modeled because their Fe(II) concentrations could not be measured. The Filson 5&6 system also doubles in flow from influent to effluent; however, virtually all of the "extra" water enters the system downstream of Pond 4, thus Ponds 5 and 6 were not modeled. Only initial (influent) volumetric flow rates were used to model all of the systems, thus flow rates between all ponds are assumed to be equal.

Pond volumes used in modeling are based on estimates provided by consultants who designed the treatment systems. In some cases, these estimates assumed rectangular ponds with perpendicular side walls; however, the ponds all have sloping sides (gradient approximately 2:1 or 3:1). The volumes provided do not account for the accumulation of sediments since the systems began operation. The irregular shape of many ponds also contributes to the uncertainty of pond volumes. All pond volumes have been revised downwards (based on a small number of area and depth measurements) to reflect the differences between the estimates provided and the actual volumes. As with DO estimates, uncertainties could not be significantly lessened without extensive surveying, but the model is much less sensitive to volume than pH.

When *thiobacilli* concentrations measured by the MPN method were used in the Stella™ model, the predicted Fe(II) concentrations in the ponds were vastly overestimated. That is, the measured bacterial concentrations were orders of magnitude lower than those required to show any significant bacterial effect on the oxidation rate using the Pesic et al. (1989) rate law. Due to this behavior, bacterial concentrations for input into the model (see lower part of Table 4) ranged from 158 to 395 mg L^{-1}, whereas the highest measured concentration was 4×10^{-5} mg L^{-1}. [Before discovering the mistake in the Pesic et al. (1989) rate law, the estimated values entered for bacterial concentration were 1, 1.5 and 2.5 mg L^{-1}. The values in Table 4 are simply those original values multiplied by a factor of 158, the difference in the original and corrected frequency factor, to correct the mistake.] Possible reasons for the discrepancy between the entered and measured concentrations are discussed in a later section. Until this discrepancy is resolved (see "Remaining questions" below), the bacterial concentration in this model is necessarily treated as a fit parameter rather than a variable.

At the Filson 1 site, the initial influent entered the first pond below the water surface, thus this system was modeled downstream of the effluent of Pond 1. Average temperature, DO and pH values were entered into the model for each pond. Only influent Fe(II) concentrations were entered into the model, and predicted downstream Fe(II) concentrations were not adjusted to match observed concentrations in each pond.

This model only considers reactions that take place in the water column, not in the interstitial water within sediments below the water column. If a treatment system is not "leaky" or specifically designed to have water flow downward through the sediment package, the flux of water within the water column should be orders of magnitude faster than the flux within the sediments, thus the reactions within sediments can be ignored to a first approximation. Although it is clear that Fe reduction does occur within the sediments, these reduction reactions will have little impact on Fe(II) concentration or oxidation rates within the treatment ponds. SAPS systems (see Kepler and McCleary, 1994) would be an exception to this statement because Fe(III) is intentionally reduced by passing through organic matter in these downflow ponds. The only SAPS component that is modeled in this study is Pond 2 of the Morrison system. The residence time within the part of the Morrison system with reducing conditions is less than 10% of the total residence time within the system, thus these reducing conditions should affect the modeled Fe(II) concentrations by 10% or less.

3.5. Verification using field data

Table 5 and Table 6 gives measured and predicted Fe(II) concentrations for all facilities in this study. Four sites (Morrison, Filson 5&6, Mead Run, and Argentine) had pH greater than 5 throughout the facilities, thus no bacterial concentrations were entered into the model for these sites. Preliminary runs using bacterial concentrations of 158 mg L^{-1} indicated that biologically-catalyzed oxidation rates were negligible compared to abiotic rates.

The Mead Run system is the simplest site examined in this study, with only one pond. Until the pond fills up in modeling runs, there is no discharge from the pond, and Fe(II) only "leaves" the system by oxidation. The Fe(II) concentration reaches steady state (the predicted effluent concentration) some time after the pond fills, depending on flow conditions and the Fe(II) oxidation rate. The measured effluent Fe(II) concentration is 4.0 mg L^{-1}, in close agreement with the predicted effluent of 3.9 mg L^{-1}.

The flow path of the upper portion of the Howe Bridge system (Fig. 1a) exhibits a considerable deviation from ideal continuously-stirred tank reactor behavior because the inflow from the downstream anoxic limestone drain (ALD) enters Pond 1 approximately 5 m from either the inflows to Pond 1 or the outflow from Pond 1. Therefore, an unavoidable small systematic error is introduced no matter how the flow in this portion of the facility is modeled. The authors chose to model this downstream ALD as influent to Pond 2 rather than Pond 1. Pond 3 had pH less than 5 (Table 4), thus estimated bacterial concentrations were entered into the model. The measured Fe(II) concentrations and predicted Fe(II) concentrations and oxidation rates are shown in Table 5 and Table 6. Fig. 6 shows predicted changes in the Fe(II) concentrations at the Howe Bridge site versus time for the September date. The solid lines were produced assuming 158 mg bacteria L^{-1}. The predicted steady state Fe(II) concentrations (the straight line portion of each curve) match the measured values quite well. If the concentration of bacteria is chosen to be either zero or the highest measured value (dashed line), the Fe(II) concentration for Pond 3 (pH 3.32) is significantly overestimated, indicating that bacterial catalysis of Fe oxidation must be occurring in Pond 3, whereas predictions for Ponds 1 and 2 were unaffected by changing the bacterial concentration. Thus in the ponds with higher pH values, the oxidation rate is dominated by abiotic processes, and one can model these ponds without considering bacteria. In the low pH part of the system, the rate is dominated by *T. ferrooxidans* catalysis, and one must consider the bacteria in order to model the oxidation.

Bacterial concentrations of 395 mg L^{-1} were used for the Filson 1 site (Fig. 1b), at which pH values in the ponds were all less than 3.65. Table 5 and Table 6 shows that the predicted Fe(II) concentrations at the Filson 1 site matched measured concentrations well. If measured bacterial concentrations were used for the Filson 1 site, the model predicted virtually no Fe oxidation.

The model predicts oxidation rates that are close to field-measured rates. In the spring of 1996 under different field conditions, Kirby and Elder Brady (1998) measured the field rate of Fe(II) oxidation using a continuously-stirred tank reactor as $2.0 \pm 1.0 \times 10^{-8}$ mol L^{-1} s^{-1} for Howe Bridge Site 4. The current model predicted steady-state Fe(II) oxidation rates of 6.6×10^{-9} and 1.5×10^{-8} mol L^{-1} s^{-1} for the June and September dates, respectively. For Howe Bridge Site 6, Kirby and Elder Brady (1998) found that the rate was less than 1×10^{-9} mol L^{-1} s^{-1}, and the current model predicted 4.4×10^{-9} and 2.6×10^{-9} mol L^{-1} s^{-1} for the June and September dates, respectively (assuming 158 mg L^{-1} bacteria).

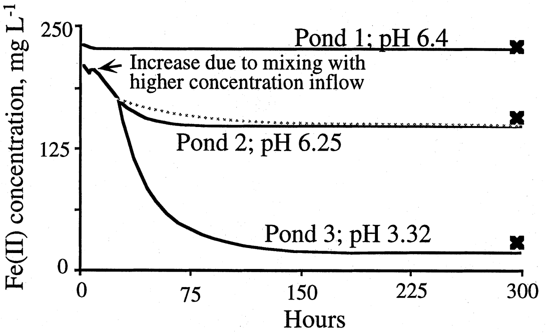

Fig. 6. Measured (x) and predicted Fe(II) concentrations in Howe Bridge ponds for 9/97 (assumes ponds are initially empty and bacteria concentration = 158 mg L^{-1}). The dotted line shows the prediction for Pond 3 assuming no bacteria are present.

The Morrison system (Fig. 1c) appears simpler than the Howe Bridge system because it has no intentional discharges in locations that cannot be modeled well. However, the effluent flow rate is approximately double the incoming flow rate, and acidic seeps actually cause increases in Fe(II) concentrations going downstream at two sites (see Choices and uncertainties of input values). Table 5 and Table 6 shows that although predicted Fe(II) concentrations decrease downstream, the model underpredicts the Fe(II) concentrations measured in the ponds, which should be expected due to the increased Fe loading from seeps.

The Filson 5 and 6 system (Fig. 1d) has a more complicated flow path than other systems in this study. Two small seeps are visible at this site. The final flow rate is approximately double the incoming flow rate, but the extra flow enters by groundwater recharge downstream of Pond 4; therefore only Ponds 1–4 were modeled. Table 5 and Table 6 shows that the measured and predicted concentrations are close in value, but the model slightly underestimates Fe(II) concentrations in Ponds 1 and 4.

The Argentine system contains 4 ponds, and the predicted Fe(II) concentrations are lower than measured Fe(II) (Tables 5 and 6), suggesting that Fe(II) oxidizes more slowly than the model predicts. This system has higher pH values (6.57 to 6.80) than other systems studied. If the pH is chosen as 6.45 for all ponds, the predicted Fe(II) concentrations closely match the measured concentrations (Tables 5 and 6). This behavior suggests that Eq. (5) begins to overestimate the Fe(II) oxidation rate at pH values above pH 6.4, and suggests that the laboratory kinetics (Stumm and Morgan, 1981) may not apply at higher pH values in the field. It is unclear which processes (e.g., photoreduction, complexation, presence of surfaces) influence Fe(II) oxidation in the field above pH 6.4, but it appears that oxidation is inhibited at circumneutral pH values.

3.6. *Effect of varying parameters—pH, T, DO, pond volume, initial Fe(II), and T. ferrooxidans*

In order to perform a sensitivity analysis and simulate the effect of changing parameters, input variables for the Mead Run system and Pond 3 of the Howe Bridge system were systematically varied from the actual conditions (Table 3 and Table 4). These two sites were chosen because the flow, temperature, and chemistry conditions within the systems were quite different. Table 7 shows the current conditions, modifications, and the predicted Fe(II) concentrations for the effluent of the Mead Run system. Fig. 7 graphically shows the effect of changing input variables on predicted Fe(II) concentrations for Mead Run and Pond 3 of Howe Bridge.

With use of the 20 g Fe m^{-2} day^{-1} criterion from Hedin et al. (1994a) for the Mead Run treatment system, the Fe loading of 15 kg/day would require a 750 m^2 pond for treatment, whereas an 1800 m^2 pond is actually in place. The influent Fe(II) concentration is 7.5 mg L^{-1}, and the effluent Fe(II) concentration is 4.0 mg L^{-1}, thus Fe is not oxidizing sufficiently rapidly at this site. This model predicts an effluent Fe(II) concentration of 3.9 mg L^{-1}, which is quite close to the actual effluent concentration. The watershed group administering this treatment system is considering increasing the size of the pond to increase Fe removal. Table 7 shows that below pH 6.4, changing pH has the most dramatic effect on predicted Fe(II) concentration, and pond volume has less effect. As discussed above, the model overestimates the Fe(II) oxidation rate at pH values above pH 6.4, thus the predicted Fe(II) concentration for pH 6.7 is likely an underestimate of the actual effluent concentration. The pond volume and dissolved O_2 have much less effect than pH for pH values below 6.4. Increasing the influent Fe(II) concentration predicts a more rapid Fe(II) oxidation rate than for current conditions. However, the effluent Fe(II) concentration is much higher than for current conditions, indicating that such a small

Table 7
Predicted effect of changing DO, pond size, pH, T, and influent Fe(II) concentration on predicted Fe(II) concentration for a single wetland cell system (Mead Run)

Actual conditions:

pH = 6.4 DO = 6 mg L^{-1}
Pond size = 36 000 L T = 20°C
Influent Fe(II) = 7.5 mg L^{-1}
Effluent Fe(II) = 4.0 mg L^{-1}

Parameter changed	predicted Fe(II) effluent (mg/L)
DO (mg L^{-1})	
4	4.5
6	**3.8**
8	3.2
9	3.0
pond size relative to current size	
0.5X	4.8
1X	**3.8**
2X	2.6
4X	1.6
pH	
5.8	7.1
6.1	6.0
6.4	**3.8**
6.7	1.5*
T (°C)	
10	6.0
20	**3.8**
25	2.6
influent Fe(II) (mg L^{-1})	
7.5	**3.8**
75	38
250	125

Actual DO, size, T, Fe(II), and pH are indicated in bold print. *Asterisk indicates that concentration is likely underestimated at pH values greater than 6.4.

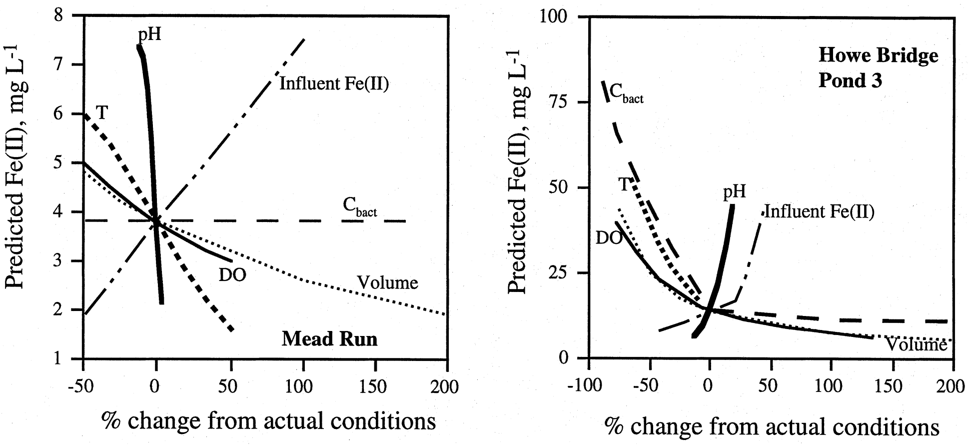

Fig. 7. Predicted Fe(II) concentrations obtained by varying input parameters values for the Mead Run system and Pond 3 of the Howe Bridge system.

system would be overloaded by high influent Fe concentrations.

Variables with steeper slopes in Fig. 7 indicate greater influence on the predicted Fe(II) oxidation rates and concentrations. For the circumneutral Mead Run site, pH has the greatest influence, followed by temperature and influent Fe(II) concentration, with DO and pond volume having less import. The bacterial concentration has no influence at pH values above 5. For the low-pH Howe Bridge Pond 3, pH again has the greatest influence, although in contrast to the Mead Run site, increasing pH decreases the oxidation rate. Other parameters display less influence, and the magnitude of the influence depends upon the magnitude of the change from actual conditions.

Although numerous other biological and abiotic factors can influence Fe(II) oxidation rates, using estimated *T. ferrooxidans* concentrations and knowledge of the influent Fe(II) concentration, temperature, volumetric flow rate, pH, DO concentration, and pond volume allows reasonably accurate prediction of Fe(II) concentrations in oxygenated ponds where pH is between 2.8 and 6.4 and the Fe(II) concentration is less than 240 mg L^{-1}. The model suggests that pH increases up to pH 6.4 may most dramatically increase system efficiency. This result does not necessarily imply that increasing pH is the most desirable change because system design is limited by each field setting and available funds. It may be difficult or impossible to increase pH further without active chemical addition because the pH increase and alkalinity added by anoxic limestone drains is limited (Hedin et al., 1994a). In addition, evidence from the Argentine system suggests that increasing pH above 6.4 may not result in significant increases in oxidation rate. The addition of DO in passive systems is usually limited by the elevation changes on site. The area available for ponds is limited by topography and land ownership. Increasing pond depth may not result in as significant an increase in efficiency as expected unless sufficient DO levels can be maintained at depth. Increasing temperature usually requires the addition of energy, and is thus not likely for passive systems. The present results suggest that systems are likely to be least effective in winter due to decreases in both abiotic and biological oxidation rates with decreasing temperature.

3.7. Other effects on Fe oxidation

In an experiment primarily designed to model Fe(II) oxidation in active treatment systems, Hustwit et al. (1992) used an in-line aeration and neutralization system on synthetic acid mine drainage to test the applicability of an "Fe-dependent model" (Eq. (3)) against an "O_2-dependent model" for Fe(II) oxidation. The rate law for the latter model was given as

$$\frac{d[Fe^{2+}]}{dt} = -7(k_{O_2})[O_2]_{sat} \tag{7}$$

where k_{O_2} is a rate constant for O_2 transfer, $[O_2]_{sat}$ is the O_2 concentration at saturation. They suggest that O_2 can be a limiting factor in Fe(II) oxidation in mine drainage. Their experiments involved Fe(II) concentrations between 783 and 2474 mg L^{-1}, circumneutral pH, and Fe(II) in large excess of supplied O_2. They found that the "O_2-dependent model" (Eq. (7)) fits the observed Fe(II) oxidation rates dramatically better than the "Fe-dependent model" (Eq. (3)). These findings do not conflict with the results of the present study because the highest influent Fe(II) concentration in this study was 236 mg L^{-1}. Hustwit et al. (1992) also mention an experiment with an initial Fe(II) concentration of 300 mg L^{-1} that did display Fe dependence. Oxygen limitation may play a role in circumneutral systems where Fe(II) concentrations are higher than those in the present study.

There have been contrasting results in previous studies on the role of photoreduction processes in Fe oxidation. McKnight et al. (1988) found approximately two-fold increases in the daytime Fe(II) concentration in an acidic stream which correlated with increases in solar radiation. Total Fe concentrations in this study were less than 2 mg L^{-1}. In contrast, Wieder (1994) found dramatic diel variations in mine drainage treatment systems containing up to 125 mg L^{-1} dissolved Fe, indicating that Fe(II) concentrations decreased during daylight hours. The significance of these documented diel variations on Fe(II) concentrations or oxidation rates in mine drainage is not yet clear.

Barry et al. (1994) examined Fe(II) oxidation kinetics in an acidic (pH 4 to 6) lake for Fe concentrations up to approximately 1 mg L^{-1}. They propose that a rate law applicable to field Fe oxidation should ideally include terms for three Fe(II) species, DO, OH^-, concentration of bacteria, surface area of reactive solids, and possibly other variables (such as H_2O_2). They demonstrate a strong correlation between particle surface area and Fe(II) oxidation rate. They also show that bacterial catalysis plays a role in Fe(II) oxidation in this pH range. In contrast to McKnight et al. (1988), they find an increasing oxidation rate with increasing incident sunlight, and they suggest that photochemical production of (possibly) H_2O_2 is responsible. Although the mechanisms and the form of the rate law suggested in the Barry et al. (1994) study may well be correct, the present results suggest that not all of these variables are necessary to predict Fe(II) oxidation rates over a wide pH range at higher Fe(II) concentrations. It is noteworthy that Barry et al. (1994) give a bacterial term in the rate law which predicts decreasing Fe(II) oxidation rate with decreasing pH, contrary to the Pesic et al. (1989) rate law used in this study. Tamura et al. (1976) and Barry et al. (1994) have shown that Fe hydroxide solids can catalyze Fe(II) oxidation. Sung and Morgan (1980) suggest that autocatalysis becomes important only at pH 7 or higher. Ponds in the present study were often quite turbid due to Fe hydroxide solids. However, oxidation rates were approximately equal to or slower than those predicted by homogeneous oxidation (Eq. (4)).

Theis and Singer (1974) demonstrated significant inhibition of Fe(II) oxidation by tannic acid, less extensive inhibition by glutamine and vanillic acid, and catalysis by citric acid. Miles and Brezonik (1981) demonstrated inhibition by tannic and humic acid, and catalysis by citric acid. The authors did not measure dissolved organic C (DOC) concentrations in the original study. It is possible that oxidation rates slower than those predicted by Eq. (4) could be due to the presence of organic C; however the ponds in this study were not colored dark (even where the water is relatively free of Fe hydroxide solids) by humic compounds as they are in many natural wetlands. Based on a reviewer suggestion, two samples (corresponding to samples 1 and 3; Fig. 1) from the Howe Bridge site were analyzed for unfiltered total organic C (TOC) in July 1998. TOC concentrations were 1.0 and 1.1 mg L^{-1} for samples 1 and 3, respectively. Two samples from a similar passive treatment system (not in this study) had TOC concentrations of less than 1.3 mg L^{-1}. Using data from Theis and Singer (1974) for a 28 mg L^{-1} Fe(II) and 170 mg L^{-1} tannic acid solution, 10% of the Fe(II) is complexed with tannic acid. The low concentrations of organic C observed at the Howe Bridge site suggest that complexation by organic compounds has little effect on the oxidation of Fe(II) in the ponds in this study.

3.8. Model limitations, application, and possible refinements

The model presented here does not predict metal removal, although metal removal is the basis for most regulatory oversight of active mine reclamation. It is unclear whether this model of Fe(II) oxidation is valid for mine drainage systems that are significantly different from the coal mine drainage systems studied, i.e., waters with pH 2.8 to 6.4 dominated by Fe, HCO_3^-, and SO_4^{2-}±H^+. For example, mine drainage from metal ore deposits, with high major and trace metal concentrations, may not behave according to this model. Variables that were not considered may become increasingly important at very high or low Fe(II) concentrations. This study does not examine the documented reduction of Fe(III) to Fe(II) as solutions flow through layers of organic matter in SAPS systems. It should be noted that there is an important gap in the present data base: due to the nature of passive treatment systems, the study has very few data at pH 3.5 to 5.2. Most ponds in the treatment systems had pH values below 3.5 or above 5.5 (the authors examined two ponds with pH 4.5, but the system was not in hydrodynamic steady state and could not be modeled).

This study suggests that while biological factors may have some influence on Fe(II) oxidation in passive pond coal mine drainage treatment systems with circumneutral pH, the biological effect is less than or on the same order of magnitude as abiotic factors. At the very least, it can be said that these systems can be modeled reasonably accurately without calling upon bacterially-mediated catalysis of Fe or upon abiotic factors other than flow rate, temperature, influent Fe(II) concentration, pH, pond volume, and dissolved O_2 concentration. However, for lower pH systems, bacterial catalysis by *T. ferrooxidans* appears to be necessary to explain observed Fe(II) oxidation rates and concentrations.

This model is not sufficiently accurate for prediction of effluent concentrations for compliance with regulations. However, it should prove to be valuable for semi-quantitatively comparing the impact that design parameters will have on pond performance before construction. As an example, numerous net alkaline discharges in the Pennsylvania Anthracite region appear to be candidates for passive pond treatment using the Hedin et al. (1994a) sizing criteria. However, the pH will drop to unknown levels due to the limited amount of alkalinity available and due to metal hydrolysis. When the pH and Fe(II) concentrations drop, this model predicts that Fe(II) will oxidize slowly. Ponds designed to treat such discharges may provide insufficient treatment, regardless of pond size, unless these factors are taken into consideration and sufficient alkalinity can be added to prevent a drop in pH.

One of the first steps in most passive treatment methods is to raise pH. An increase in pH could be accomplished by aeration to degas CO_2 (Langmuir, 1997). In some settings, raising pH causes difficulties due to Fe and Al hydroxide coating and/or armoring of limestone. In some situations where pH is 2 or lower, it may be possible to capitalize on very rapid Fe(II) oxidation rates in the design of treatment facilities. For example, under current conditions, the present model predicts that at pH 2.9, the Fe(II) concentration of Howe Bridge Pond 3 is 13 mg L^{-1}. If either pH 2.0 or pH 6.4 is used in the model, the predicted Fe(II) concentration is 2 mg L^{-1}. Allowing Fe(II) to oxidize before pH is raised might require more active methods than are currently in favor for abandoned mine lands. Some currently operating mines employ active methods in conjunction with pond systems. An upstream pond could be designed to allow Fe(II) oxidation to occur at low pH, and such a pond could be followed by downstream ponds in which the pH is raised by limestone diversion wells (Arnold, 1991) or by active addition of bases. Precipitation of metal hydroxides could then proceed after most of the Fe(II) has already been biologically oxidized. This approach might be favored in situations where construction of an anoxic limestone drain is precluded by high dissolved O_2, Fe(III) or Al concentrations.

3.9. Remaining questions about the use of the laboratory rate laws in the field

One major question that remains is whether the measured bacteria concentrations from this study are too low or whether the Pesic et al. (1989) rate law attributes too little catalytic effect to each bacterial cell. If the Pesic et al. (1989) rate law is correct, then the measured bacteria concentrations from this study are too low. If bacteria concentrations from this study are correct, then the biological rate constant, k_{bio}, is too low. Because of the large discrepancy between the two approaches, Pesic et al. may have underestimated and the authors are likely overestimating the bacterial contribution to Fe(II) oxidation rates. The rate law developed by Pesic et al. (1989) is important because it stresses the significance of Fe-oxidizing bacteria and the observed trend of decreasing rate with increasing pH (at low pH). Bacterial populations in both studies may have been affected by the following:

1. Growth of Fe-oxidizing bacteria results in the precipitation of ferric oxyhydroxides and jarosite (Ramsay et al., 1988). In Pesic et al. (1989), the Fe-oxidizing bacteria that possess the most active metabolism and presumably precipitating the most Fe were removed along with the Fe precipitates by filtration through Whatman No. 1 filter paper. The oxidation kinetics of potentially more active bacterial populations needs to be determined. Measured bacterial populations in the present study may have been underestimated (by approximately a factor of 10 to 100) due to incomplete dissolution of Fe hydroxides during the MPN enumeration procedure.
2. The presence of Fe(III) on the bacterial surfaces was not determined. If fine-grained Fe precipitates were present, the bacterial component used in their rate law may have been overestimated (bacteria plus precipitated Fe), resulting in an underestimate of the bacterial contribution to the rate constant.
3. Pesic et al. (1989) did not determine the proportion of viable to dead bacteria. Although bacterial cultures are assumed to be reasonably healthy, dead bacteria within their experimental system would further underestimate the bacterial role.

In addition to the above issue, the authors hope to address several uncertainties in a more comprehensive study. Issues to be addressed include: (1) the rates of oxidation above pH 6.4, (2) the effect of higher concentrations of Fe and trace metals (such as from metal ore mine drainage), (3) O_2 limitation at high Fe(II) concentrations, (4) direct comparison of predicted and field-measured oxidation rates, (5) prediction of pH and dissolved O_2 changes within ponds using a geochemical model such as PHREEQE (Parkhurst et al., 1982) rather than extensive field sampling, (6) reducing the uncertainty in volume and discharge estimates by more thorough surveying, and (7) the role of surfaces in both abiotic and biological Fe(II) oxidation.

The results presented suggest that by combining abiotic and biological laboratory rate laws with a differential equation solver, both the rate of Fe(II) oxidation and concentrations in coal mine drainage can be modeled successfully. The general trends predicted—increasing rate with increasing Fe(II), temperature, and dissolved O_2; variable rate with changing pH—match field observations. With increasing pH, abiotic oxidation proceeds more rapidly whereas biological oxidation proceeds more slowly. The model presented is applicable to coal mine drainage with Fe(II) concentrations up to approximately 240 mg L^{-1}, dissolved O_2 concentration greater than 2 mg L^{-1}, and pH values between 3 and 6.4 (less applicable to 6.8).

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