Ferrous oxidation chemistry in passive abiotic systems for the treatment of mine drainage

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ABSTRACT: The rates of chemical oxidation and gas transfer were determined for two passive abiotic systems for the treatment of mine drainage. One system (HB) is a series of ponds whose discharge was net acidic. The second treatment system (CK) has shallow channels and net alkaline discharge. The O_2 mass transfer coefficient was 2 cm h^{-1} for HB Pond #2 and ranged from 4 to 40 cm h^{-1} for the CK channels, depending on channel velocity and depth. The CO_2 mass transfer coefficient was 1.3 cm h^{-1} for HB Pond #2 and ranged from 1.4 to 15 cm h^{-1} for the CK channels. Oxygen transfer appeared to be the rate-limiting step for oxidation of Fe(II) at HB Pond #2. The oxidation rate for Fe(II) adsorbed to already-formed ferric oxides (heterogeneous oxidation) appeared to control the rate of oxidation of Fe(II) at the CK channels. Based on field data, the heterogeneous rate constant for oxidation of Fe(II) was 6.0×10^{-9} mg l^{-1} s^{-1} at 17°C or k_2 of 5.5×10^{-8} mg l^{-1} s^{-1} at 25°C. This value was consistent with previously reported values for k_2 based on laboratory experiments. The annual-averaged iron removal rates were 18 g d^{-1} m^{-2} for HB and 42 g d^{-1} m^{-2} for CK, compared to empirical design expectations of 10 to 20 g d^{-1} m^{-2}. Heterogeneous oxidation accounted for >80% of the oxidation of Fe(II) at HB and >90% of the oxidation of Fe(II) at CK.

INTRODUCTION

Treatment processes for acid mine drainage can be divided into active and passive systems. Active systems require continuous monitoring of chemicals and usually require dedicated pumps and other equipment. Passive systems require infrequent maintenance, and usually require neither pumps nor chemical additions. The design and performance of passive systems are described by Hedin & Nairn (1992, 1993), Hedin *et al.* (1994), Gazea *et al.* (1996) and others. Typically, discharge from an anoxic limestone drain (ALD) passes through ponds where abiotic processes dominate over microbial processes, followed by aerobic wetlands where microbial processes dominate (Kirby *et al.* 1999). Abiotic ponds in these systems usually remove between 10 and 20 g of Fe(II) per m^2 of pond surface area per day (Hedin & Nairn 1992). This has become an established design parameter for passive abiotic ponds, usually expressed as a designed iron removal rate (IRR) of 10 to 20 g m^{-2} d^{-1}. The surface area (SA) that would be required to treat a mine drainage discharge can be estimated given the required removal of Fe(II)

$$SA = \Delta[Fe(II)] \times Q/IRR \qquad (1)$$

where Δ[Fe(II)] is the desired removal of Fe(II) from inlet to outlet of the pond (g m^{-3}) and Q is the flow (m^3 d^{-1}). This paper has focussed on iron oxidation more than removal, but nevertheless the conventional parameter IRR has been used.

Oxidation of mine drainage requires transfer of O_2 into the water and subsequent oxidation of Fe(II). Hustwit *et al.* (1992) suggested that oxygen transfer is the rate-limiting step for passive treatment of mine drainage. Evaporation of CO_2 from mine drainage also helps to stabilize pH during passive treatment, counteracting the loss of alkalinity due to precipitation of ferric oxide. Rathbun (1998) and Schwarzenbach *et al.* (1992) have summarized empirical equations that can be used to estimate gas transfer in streams and in ponds. The O_2 transfer velocity at a stagnant air–water interface (e.g. the surface of a pond) is expected to be *c.* 2 cm h^{-1} (based on the water side) when the wind speed at 10 m is 1 m s^{-1} (Schwarzenbach *et al.* 1992). For an O_2 driving force of 3 to 6 mg l^{-1}, this transfer velocity would limit the oxidation of Fe(II) to 10 to 20 g m^{-2} d^{-1}. This illustrates the possibility that the oxidation of Fe(II) in abiotic ponds could be limited by transfer of O_2 from the atmosphere.

Alternatively, the oxidation of Fe(II) in abiotic ponds could be limited by the rate of the oxidation step. Stumm & Morgan (1996) reviewed mechanisms for the oxidation of Fe(II) by O_2. The rate determining step can involve oxidation of Fe^{2+}, $FeOH^+$, $Fe(OH)_2$, or sorbed Fe(II). Oxidation of the three dissolved species of Fe(II) is *homogeneous* oxidation, while oxidation of sorbed Fe(II) is *heterogeneous* oxidation. Among the homogeneous reactions, the oxidation of $Fe(OH)_2$ dominates when pH is >5 (e.g. Wehrli 1990). The rate equation for this homogeneous process is:

$$\text{Homogeneous rate} = (-d[Fe(II)]/dt)_{\text{batch}} = k_1[Fe^{2+}][O_2]\{H^+\}^{-2} \qquad (2)$$

Geochemistry: Exploration, Environment, Analysis, Vol. **1** 2001, pp. 81–88

where the formation constant for $Fe(OH)_2$ is included in the rate constant k_1. In some papers and texts, the homogeneous rate is expressed in terms of $\{OH^-\}^2$ rather than $\{H^+\}^{-2}$ so that the rate constant would differ from values reported in this paper by $(K_w)^2$. Sometimes the rate constant is expressed in terms of partial pressure of O_2 (p_{O2}) rather than $[O_2]$, so that the rate constant would differ from values reported in this paper by Henry's constant for O_2. Thus Stumm & Morgan (1996) reported a rate constant of 8.0×10^{13} l^2 min^{-1} atm^{-1} mol^{-2} at 20°C where the rate was expressed in terms of $\{OH^-\}^2$ and p_{O2}. Stumm & Morgan's rate constant corresponds to $k_1 = 9.3 \times 10^{-14}$ mol l^{-1} s^{-1} when the rate is expressed in terms of $\{H^+\}^{-2}$ and $[O_2]$. Millero *et al.* (1987) and Liang *et al.* (1993) summarized the literature regarding homogeneous oxidation. They reported k_1 values from 1.0×10^{-14} to 1.0×10^{-12} mol l^{-1} s^{-1}. At 25°C, Millero reported average k_1 of 2.7×10^{-14} mol l^{-1} s^{-1} (converted from their 1.6×10^{16} l^3 mol^{-3} min^{-1}).

At a $pH > 5$, the homogeneous rate increases one-hundred-fold with each unit increase in pH. The half-life of Fe(II) in an indifferent salt solution, p_{O2} of 0.2 atm, and pH of 7.0 is about 4 minutes. At $pH < 3.5$, the abiotic oxidation of Fe(II) is independent of pH because the oxidation of the Fe^{2+} species dominates. Under those conditions the half-life of Fe(II) due to abiotic reactions is *c.* 1000 days (Singer & Stumm 1970). However, *Thiobacillus ferrooxidans* and other bacteria catalyze the oxidation of ferrous iron at low pH values. Kirby *et al.* (1999) reported that abiotic oxidation processes dominate in passive treatment systems when $pH > 5$ and microbial oxidation dominates at $pH < 5$ for summer temperatures.

Sung & Morgan (1980) found that ferric oxy-hydroxide catalyzes the abiotic oxidation of Fe(II). This is a heterogeneous process since the mechanism involves interfacial (adsorbed) Fe(II). Accordingly, the rate of the heterogeneous reaction should be a function of the specific surface area and reactivity of the ferric oxide. Nonetheless, both Sung & Morgan (1980) and Tamura & Nagayama (1976) reported the rate constant in terms of the total concentration of Fe(III), usually expressed as mg l^{-1}. They also found that the concentration of sorbed Fe(II) was inversely proportional to $\{H^+\}$ over the pH range that they studied, leading to equation (3).

$$\text{Heterogeneous rate} = k_2[Fe(III)]\,[Fe^{2+}]\,[O_2]/\{H^+\} \qquad (3)$$

Tamura & Nagayama (1976) and Sung & Morgan (1980) both reported $k_2 = 2.6 \times 10^{-8}$ mg l^{-1} s^{-1} where the concentration of Fe(III) was expressed in mg l^{-1}. Ames (1998) measured $k_1 = 1.9 \times 10^{-13}$ mol l^{-1} s^{-1} and $k_2 = 3.6 \times 10^{-8}$ mg l^{-1} s^{-1} for 20 to 23°C, using synthetic mine drainage solutions with chemistry similar to our field sites. Since the heterogeneous mechanism dominated for most of the conditions that were tested by Ames, he expressed greater confidence in k_2 than in his k_1. The overall oxidation rate at $pH > 5$ is the sum of the homogeneous and the heterogeneous reactions, as described in equation (4).

$$\text{Overall abiotic rate for } pH > 5 = (k_1 + k_2[Fe^{3+}][H^+])\,[Fe^{2+}]\,[O_2]\,[H^+]^{-2} \qquad (4)$$

Millero *et al.* (1987) and Ames (1998) reported activation energy (E_{act}) for the homogenous oxidation reactions and Ames reported E_{act} for the heterogeneous reaction. Millero *et al.* (1987) found that E_{act} for the homogeneous reaction (units of l^3 mol^{-3} min^{-1}) was 125 kJ mol^{-1}, similar to the value they derived using data from Sung & Morgan (1980). Converting from k_1 dimensions of l^3 mol^{-3} min^{-1} to mol l^{-1} s^{-1} introduces an additional enthalpy of 112 kJ mol^{-1} (for $K_w{}^2$) and brings Millero's estimate for E_{act} to 237 kJ mol^{-1}. Ames estimated a higher E_{act} of 324 kJ mol^{-1} for k_1 (units of M s^{-1}). Ames estimated E_{act} of 179 kJ mol^{-1} for k_2.

Objectives

The purpose of this study was to quantify the gas transfer and Fe(II) oxidation processes for two passive abiotic systems for treatment of mine drainage. The two systems were significantly different in chemistry and in water velocity and depth. Specific objectives were: (1) determine and explain the mechanisms that determine iron removal rates at the two sites; (2) determine rate constants for the oxidation of Fe(II) at field sites; (3) determine gas transfer rates for O_2 and CO_2 at field sites; and (4) suggest ways to improve the design and the operation of passive abiotic systems for treatment of mine drainage.

MATERIALS AND METHODS

Samples for metals were collected in acid-cleaned 200 ml polyethylene bottles and H_2SO_4 was added to bring pH to <2. Samples for Fe(II) were placed on ice and analysed within 72 h using 1,10-phenanthroline (APHA 1989; Standard Methods 3500-Fe(D)). Samples for total inorganic carbon (TIC) were taken by syringe after several rinses, were placed on ice, and were analysed within 48 h using a Dohrmann 8000 Carbon Analyzer.

Temperature and pH were measured in the field using a VWR Scientific 2000 pH meter equipped with combination pH and temperature probes. The pH meter and electrodes were calibrated at each site using certified pH 4 and 7 buffers.

Dissolved oxygen (DO) was measured using a YSI model 54a meter. Meter and probe were calibrated at each site at the ambient water temperature and saturated humidity. Performance at low DO was verified by measuring DO in an excess sulphite plus Co(II) solution.

Flow was measured in 1 l increments using a 20 l plastic bucket and stopwatch. At least three flow measurements were made and averaged.

The transfer of O_2 from air into water is described by equation (5) for a batch or a completely mixed reactor without reactions:

$$d[O_2]/dt = K_{L,O2}a([O_2]_{sat} - [O_2]) \qquad (5)$$

where $[O_2]_{sat}$ is the saturation concentration, $[O_2]$ is the dissolved oxygen concentration and a is the ratio of interfacial area to water volume. For simplicity $[O_2]_{average}$ has been used to describe the dissolved oxygen concentration in the HB ponds and in the CK channel. The accumulation of O_2 equals the transfer from the air minus O_2 that has been used to oxidize Fe(II). This mass balance is described by equation (6):

$$([O_2]_{out} - [O_2]_{in})/\tau = K_{L,O2}a([O_2]_{sat} - [O_2]_{avg}) - \tfrac{1}{4}([Fe(II)]_{in} - [Fe(II)]_{out})/\tau \qquad (6)$$

where τ is the hydraulic residence time (volume divided by flow), and the factor ¼ represents the molar stoichiometry between O_2 and Fe(II) during oxidation of Fe(II). Mass transfer coefficients for CO_2 were calculated from the spatial changes in TIC and from the concentration gradient for $H_2CO_3^*$:

$$\Delta[TIC]/\tau = K_{L,O2}a([H_2CO_3^*]_{sat} - [H_2CO_3^*]_{avg}) \qquad (7)$$

where $[H_2CO_3{}^*]_{sat}$ was derived using $p_{CO2} = 10^{-3.5}$ atm and the Henry's Constant and enthalpy of reaction (Stumm & Morgan

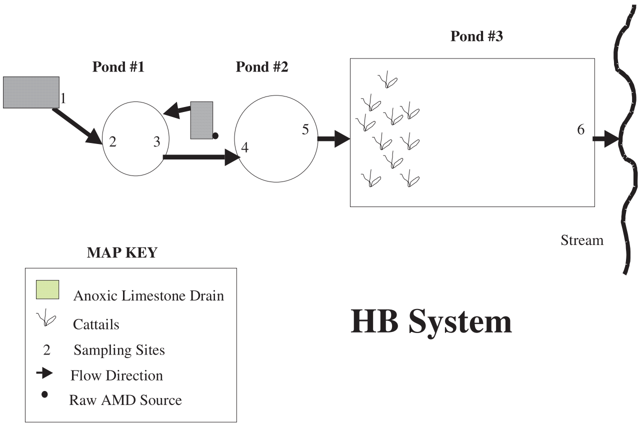

Fig. 1. HB site layout.

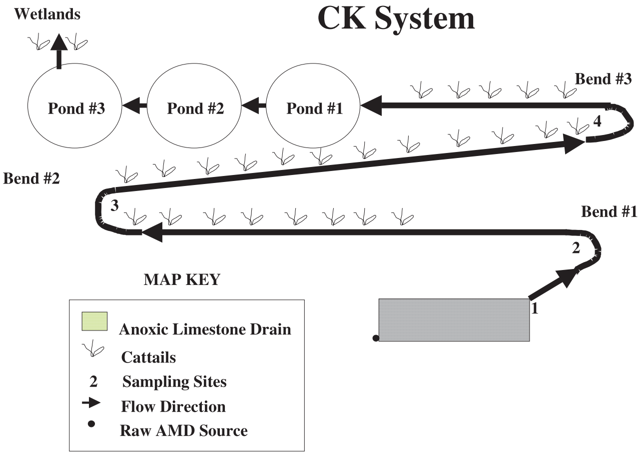

Fig. 2. Site layout of the CK system.

1996). The effects of temperature on $K_{L,O2}$ and $K_{L,CO2}$ were compensated using θ=1.0241 as suggested by Rathbun (1998).

The rate constants k_1 and k_2 were calculated using equation (8):

$$\{\Delta[\mathrm{Fe(II)}][\mathrm{H}^+]_{\mathrm{avg}}{}^2\}/\{\tau[\mathrm{Fe(II)}]_{\mathrm{avg}}[\mathrm{O}_2]_{\mathrm{avg}}\} = k_1 + k_2[\mathrm{H}^+]_{\mathrm{avg}}[\mathrm{Fe(III)}]_{\mathrm{avg}} \quad (8)$$

where all of the parameters were based on field samples and measurements. The homogeneous and heterogeneous rate constants k_1 and k_2 were obtained from least-squares linear regression of the left-hand side of equation (8) against $\{\mathrm{H}^+\}_{\mathrm{avg}}[\mathrm{Fe(III)}]_{\mathrm{avg}}$. For channels, the hydraulic retention time (τ) was calculated from flow, cross-sectional area, and distance.

Field sites

Both treatment systems are located in Jefferson County, PA. The Howe Bridge system (HB) is illustrated in Figure 1. Two ALD discharges enter Pond #1. Discharge from the first ALD (HB Site #1) passes through a shallow channel into Pond #1. One of the ALD discharges is submerged so that chemistry in Pond #1 could not be precisely determined without making assumptions about the chemistry of the second ALD discharge. Therefore the focus at HB was on Pond #2 (between HB Sites #4 and #5).

The CK system is illustrated in Figure 2. Discharge from the ALD (CK Site #1) passes over a small waterfall and race, and then passes through a channel from Site #2 past Site #4. Focus was placed on the first half of the race and channel system, up to CK Site #3.

Dimensions and hydraulic residence times (τ) for HB and CK are given in Table 1. The surface area for HB Pond #2 is 460 m^2 and cumulative surface area from CK Site #1 to Site #3 is 518 m^2. If iron removal were based solely on surface areas, then HB Pond #2 and CK to Site #3 should have similar IRR values. However, the average hydraulic retention times were quite different (54 h for HB Pond #2 v. 6 h for CK from Site #1 to Site #3). The average horizontal velocity was about 0.006 m min^{-1} in HB Pond #2, 0.6 m min^{-1} in the CK channel, and >6 m min^{-1} in the races. The transfer of heat was much greater for the CK channels compared to HB Pond #2. Figure 3 shows the heat transfer (W/m^2) for the CK channel v. the HB ponds. Calculation of the heat transfer was based on change in water temperature, flow, heat capacity of water, and surface area. Effects of evaporation were neglected since the two systems have similar surface areas. Kirby (pers. comm.) studied HB Pond #2 and discovered temperature and dissolved oxygen gradients, with higher values at the surface. Based on the large difference in heat transfer and Kirby's temperature and DO data, HB Pond #2 is sometimes stratified. Stratification often leads to short-circuiting, resulting in shorter than the theoretical value (volume/flow) and driving forces for transfer less than the difference between the saturation concentration and the depth-averaged concentration.

Table 1. *Physical descriptions of the abiotic portions of the HB and CK sites*

Location	Unit	Surface Area (m^2)	Volume (m^3)	Residence time (h)
HB Site #1 to #2	Race	7.1	0.54	0.070
HB Site #2 to #3	Pond #1	110	35	4.5
HB Site #3 to #4	Race	15	2.3	0.30
HB Site #4 to #5	Pond #2	460	420	54
CK Site #1 to #2	Race	28	4.2	0.16
CK Site 2 to #3	Channel	490	150	5.8
CK Site #3 to #4	Channel	620	94	3.7

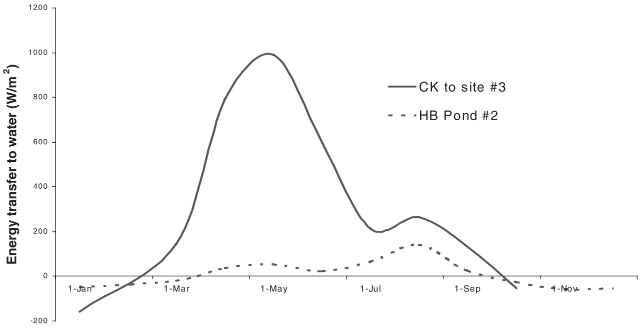

Fig. 3. Rate of heat transfer to the water at CK Sites #1 to #3 and at HB Pond #2.

RESULTS

Chemistry

Water samples were collected monthly during 1998 from HB Sites #1 through #6 and from CK Sites #1 through #4. Average annual results are shown in Table 2 for the HB sites and in Table 3 for the CK sites.

Table 2. *Average flow and concentrations at HB sites*

Parameter (units)	HB Site #1	HB Site #2	HB Site #3	HB Site #4	HB Site #5	HB Site #6
Flow (m^3 d^{-1})	130	185	ND‡	ND‡	ND‡	ND‡
pH	6.18	6.28	6.23	6.26	5.96	3.04
Total inorganic carbon (mmol l^{-1})	6.18	5.22	4.59	4.00	2.65	0.41
Fe(II) (mmol l^{-1})	4.38	4.21	3.89	3.77	3.04	0.95
Alkalinity (meq l^{-1})	2.93	2.96	2.28	2.18	0.91	−1.30
Dissolved oxygen (meq l^{-1})	0.05	0.43	0.58	0.75	0.76	1.01
Ca (mmol l^{-1})†	5.27	ND‡	ND‡	ND‡	4.94	4.79
Mg (mmol l^{-1})†	5.54	ND‡	ND‡	ND‡	5.16	4.69
Mn (mmol l^{-1})†	0.69	ND‡	0.69	ND‡	0.65	0.64
Sulphate (mmol l^{-1})†	12.5	ND‡	12.4	12.3	11.9	11.3

‡ND=not done. †Analyses were run three times for Ca and Mg, once for Mn and sulphate, and monthly for all other parameters.

Table 3. *Average flow and concentrations at CK sites*

Parameter (units)	CK Site #1	CK Site #2	CK Site #3	CK Site #4
Flow (m^3 d^{-1})	513	ND‡	ND‡	ND‡
pH	6.27	6.40	6.52	6.70
Total inorganic carbon (mmol l^{-1})	12.02	9.00	5.54	4.24
Fe(II) (mmol l^{-1})	1.68	1.52	0.81	0.38
Alkalinity (meq l^{-1})	6.57	5.79	3.92	3.40
Dissolved oxygen (meq l^{-1})	0.04	0.68	0.89	0.93
Ca (mmol l^{-1})	7.65	7.71	7.68	7.68
Mg (mmol l^{-1})	8.33	8.34	8.35	8.31
Mn (mmol l^{-1})	0.88	0.82	0.81	ND‡
Sulphate (mmol l^{-1})	13.5	ND‡	ND‡	10.4*

‡ND=not done. *Estimated based on the drop in sulphate through the entire CK system.

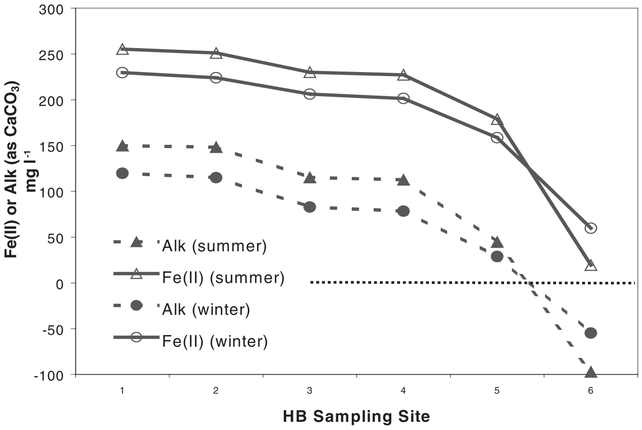

Fig. 4. Fall and summer Fe(II) (mg l^{-1}) and alkalinity (mg l^{-1} as CaCO$_3$) for HB Sites #1 to #6. Dotted line is 0 mg l^{-1}.

Table 4. $K_{L,O2}$ *in cm h*$^{-1}$ *for HB Pond #2, HB Race #2, and for Site #1 to Site #3 at CK*

Sampling date	HB Pond #2	HB Race #2	CK to Site #3
1 March	1.04	14.8	10.2
29 March	1.52	18.6	14.5
13 May 98	1.62	41.0	21.4
6 June 98	2.75	5.1	13.8
3 July 98	1.71	3.5	5.2
5 August 98	1.83	15.8	3.9
26 August 98	2.11	13.2	NA
26 September 98	1.29	9.9	NA
25 October 98	3.30	11.9	NA
22 November 98	2.43	18.4	NA
Mean	1.96	15.2	11.5

HB was net acidic, as illustrated in Figure 4. Since the post-ALD alkalinity at HB was less than required for the complete oxidation of Fe(II), the alkalinity was completely used up before the final discharge (HB Site #6) and the average final discharge had pH of 3. Figure 4 also shows that the decreases in alkalinity and in Fe(II) were independent of season except for a small change in the slope for Pond #2 (between HB Sites #4 and #5) and a large decrease in effectiveness of the HB wetland (between Sites #5 and #6) during the cold months. Table 3 shows that CK was net alkaline. The post-ALD discharge (Site #1) provided more than enough alkalinity for the complete conversion of Fe(II) to ferric oxide. The pH never dropped below 6 at any of the CK sample sites.

The evaporation of CO$_2$ is important for proper operation of passive abiotic treatment ponds and channels. Losses of CO$_2$ at HB and at CK are shown in Tables 2 and 3, as changes in the total inorganic carbon (TIC). The evaporation of CO$_2$ resulted in an increase in pH over the entire length of the CK channel (see Table 2) and provided pH buffering for the HB ponds at about 6.25, in spite of acidity that was generated by the oxidation and precipitation of iron.

Neither system removed very much Mn(II). There was some removal of sulphate at both HB and CK. Ca(II) and Mg(II) were decreased slightly at HB.

Monthly values for DO, flow, temperature, and Fe(II) at HB Site #5 are shown in Figure 5. The flow was consistent during the year. Dissolved oxygen decreased to about 3 mg l^{-1} during the summer. The concentration of Fe(II) at HB Site #5 was consistently between 150 and 180 mg l^{-1}, which represented removal of 30% of the influent Fe(II).

Table 5. *$K_{L,CO2}$ in cm h^{-1} for HB and CK*

Sampling date	HB Pond #2	HB Race #2	CK Site #1 to #3
6 June 98	NA	NA	7.53
3 July 98	1.25	12.63	3.57
5 August 98	1.25	5.60	2.41
26 August 98	0.78	6.26	2.33
26 September 98	1.02	8.20	1.42
25 October 98	2.08	15.03	NA
Mean	1.27	9.54	3.45

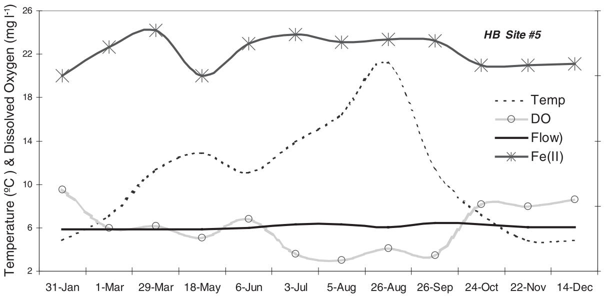

Fig. 5. Seasonal variations in temperature, dissolved oxygen, flow and [Fe(II)] at HB Site #5.

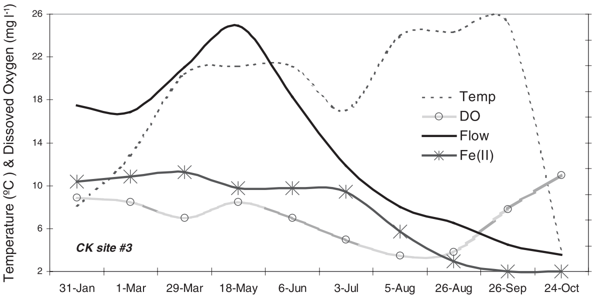

Fig. 6. Seasonal variations in temperature, dissolved oxygen, flow and [Fe(II)] at CK Site #3.

Chemistry and flow were more variable at CK, and this is illustrated in Figure 6 for CK Site #3. Flow decreased during late spring and all summer and there was no discharge after the end of October. The concentration of Fe(II) at CK Site #3 ranged from 70 mg l^{-1} during the high-flow cooler months to 0 mg l^{-1} during the low-flow, warmer months. On average 52% of Fe(II) was oxidized between the ALD discharge and Site #3 at CK.

Gas transfer coefficients

Equations 6 and 7 were used to calculate $K_{L,O2}$ and $K_{L,CO2}$ values for the HB and CK systems. $K_{L,O2}$ values are reported in Table 4 and $K_{L,CO2}$ values are reported in Table 5. The average $K_{L,O2}$ for HB Pond #2 was 1.96 cm h^{-1}, which is the O_2 transfer velocity that is expected for a pond when the wind speed at 10 m is *c.* 1 m s^{-1} (Schwarzenbach *et al.* 1992).

The $K_{L,O2}$ values for the races and channels were higher than for the pond, as shown in Figure 8. The HB race from Sites #3 to #4 had $K_{L,O2}$ of 15.2 cm h^{-1} and the CK channel to Site #3 had $K_{L,O2}$ of 11.5 cm h^{-1}. $K_{L,O2}$ increased with flow as shown in Figure 7 for CK from Site #2 to #3. Equations from Churchill *et al.*, O'Connor & Dobbins and Owens *et al.* are often used to estimate $K_{L,O2}$ for flowing water (cf. Rathbun 1998). The equation by Owens *et al.* has been calibrated to water velocity as low as 2.4 m min^{-1} and depth down to 0.12 m. The average water velocity in the CK channel (0.6 m min^{-1}) was too low, and the depth in the HB race (2 cm) was too shallow for application of these equations.

Some anomalies were observed in the transfer of gases in both the field and laboratory. The $K_{L,CO2}$:$K_{L,O2}$ ratio was 0.65 & 0.63 at HB Pond #2 & Race #2, respectively, and 0.30 at CK Site #3, compared to an expected ratio between 0.85 and 0.92 (Rathbun 1998). The poor transfer of CO_2 might be due to a reaction within the interfacial zone that decreased the driving force for evaporation of CO_2, such as conversion to HCO_3^- due to increased pH. Ames (1998) measured lower $K_{L,CO2}$ for the mine drainage samples than for a sulphite solution, and he suggested that the difference might be due to a floating layer of ferric oxide. A film of solids at the surface of the water was also observed at the HB and CK sites.

Oxidation rate constants

Oxidation rate constants were estimated using data for the CK channel to Site #3. The water velocity in the CK channels was an order of magnitude greater than the velocity in HB Pond #2 and there was no apparent stratification in the CK channels. Thus, the assumption of plug flow through the channels was more reasonable than any flow assumptions that could be made for HB Pond #2. Also, the consistent accumulation of O_2 through the CK system indicated that mass transfer exceeded reactive use of O_2, and therefore oxidation of Fe(II) was probably the rate limiting step for removal of Fe(II). HB was not used for this exercise due to the low horizontal velocity and possible short-circuiting. The concentration of O_2 did not change significantly across HB Pond #2 for most sample dates.

Data from mid-March to early-July were used to determine oxidation rate constants for the CK channel. During these sampling dates, the average water temperature in the channel was about 17°C and the flow was above 400 m^3 d^{-1}. Results

Table 6. *Oxidation rate constants from present work and from literature*

Researcher(s)	Temperature (°C)	k_1 (mol l^{-1} s^{-1})	k_2 (mg l^{-1} s^{-1})
CK average (this study)	17		6.0E-09
Ames (1998)	20–23	1.9E-13†	3.1E-08
Tamura *et al.* (1976)	25	2.0E-14	2.6E-08
Sung & Morgan (1980)	25	3.3E-14	2.6E-08
Stumm & Morgan (1996)	25	9.3E-14	
Millero *et al.* (1987); Liang *et al.* (1993)	25 (literature)	1E-14 to 1E-12	
Millero *et al.* (1987)	25 (average)	2.7E-14	

†Ames had less confidence in k_1 than in k_2 because heterogeneous oxidation dominated in his system.

Table 7. *Temperature, flow and iron removal rates for HB Pond #2 (Site #4 to Site #5)*

Sampling date	Temperature (°C)	Flow ($m^3\ d^{-1}$)	HB Pond #2 IRR ($g\ d^{-1}\ m^{-2}$)	Predicted IRR using k_1 and k_2†	Predicted IRR using $K_{L,O2}$‡
31 Jan 98	4.8	174	NA	NA	NA
1 Mar 98	7.1	174	11.6	73.9	9.3
29 Mar 98	11.3	174	12.0	81.0	11.6
13 May 98	12.9	174	16.9	73.1	11.7
6 June 98	11.1	180	20.1	87.7	22.2
3 July 98	13.9	196	20.7	96.6	18.0
5 Aug 98	16.5	196	22.0	94.7	19.0
26 Aug 98	21.2	185	18.0	88.8	20.1
26 Sept 98	11.3	201	18.2	86.4	14.5
25 Oct 98	7.3	196	22.0	70.5	36.9
22 Nov 98	4.8	185	18.8	70.5	18.7
14 Dec 98	4.8	185	12.0	50.2	NA
Mean	11.7	186	17.5	79.4	18.2

†The k_1 and k_2 values and activation energies were taken from Ames (1998). ‡$K_{L,O2}$ values were from Table 4.

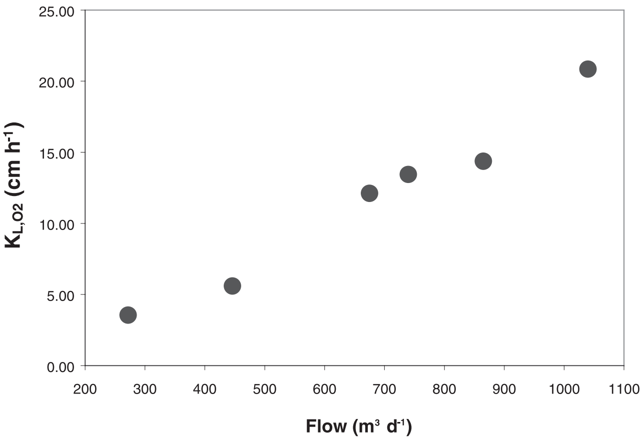

Fig. 7. Measured $K_{L,O2}$ v. flow for CK to Site #3.

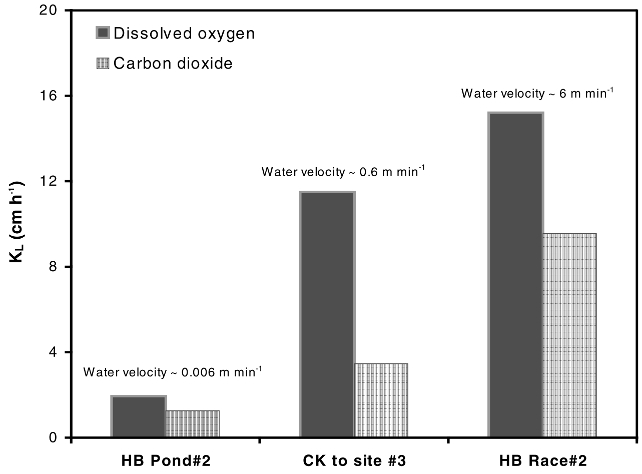

Fig. 8. Annual average $K_{L,O2}$ and $K_{L,CO2}$ for a pond, channel and race.

from field data are shown in Figure 9, where k_2 (the slope) was 6.0×10^{-9} mg l^{-1} s^{-1}. After compensating for temperature, this gave k_2 of 5.5×10^{-8} mg l^{-1} s^{-1} at 25°C. Roscoe (1999) also evaluated k_1 and k_2 values for each sampling trip, based on longitudinal changes in stream chemistry and removal of Fe(II). Roscoe calculated an average k_1 of 6.8×10^{-14} mol l^{-1} s^{-1} and k_2 of 2.2×10^{-8} mg l^{-1} s^{-1}.

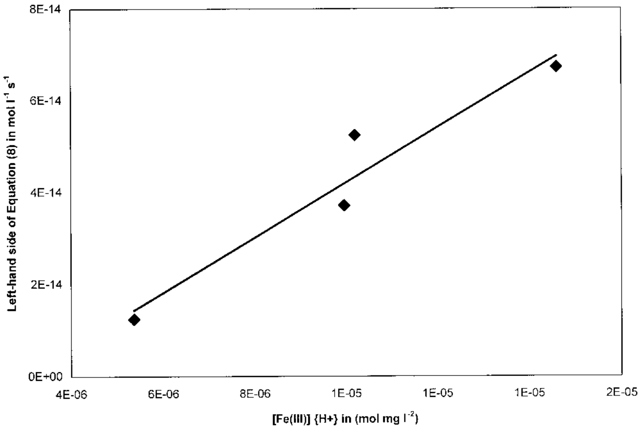

Fig. 9. Determination of k_2 from slope of $\{\Delta[\mathrm{Fe(II)}][\mathrm{H^+}]_{avg}^2\}/\{\tau[\mathrm{Fe(II)}]_{avg}[\mathrm{O_2}]_{avg}$ v. $[\mathrm{H^+}]_{avg}[\mathrm{Fe(III)}]_{avg}$ (equation 8).

These k_1 and k_2 values are compared to literature values in Table 6. The primary importance of these field-derived k_1 and k_2 values is that they are consistent with literature values that are based on laboratory experiments, usually with different temperature and different conditions for alkalinity, sulphate and ferric oxides. The heterogeneous oxidation of Fe(II) has not been previously invoked to explain the removal of Fe(II) in treatment of mine drainage. This validation of literature values for the heterogeneous process means that these parameters can be used to design passive abiotic treatment systems with slightly alkaline pH, in which heterogeneous oxidation might be enhanced by suspension or recirculation of ferric oxides.

Iron removal rates

Iron removal rates at HB Pond #2 ranged from 12 to 22 g m^{-2} d^{-1}, which is consistent with the design expectations for abiotic ponds (see Table 7). IRR for CK were approximately double the typical design rate, and averaged 42 g m^{-2} d^{-1} (see Table 8).

The actual and the predicted iron removal rates for HB Pond #2 are shown in Figure 10. The oxidation rate model (predicted from the k_1 and k_2 values) predicted a much higher IRR than was measured. This could be due to stratification and short-circuiting of the pond, which would decrease the hydraulic residence time (less time available for oxidation than presumed) and could result in lower concentration of dissolved oxygen in

Table 8. *Temperature, flow and iron removal rates through CK Site #3*

Sampling date	Temperature (°C)	Flow (m^3 d^{-1})	CK IRR (g d^{-1} m^{-2})	Predicted IRR using k_1 and k_2†	Predicted IRR using $K_{L,O2}$‡
31 Jan 98	8.0	702	38.7	44.0	122
1 March 98	12.8	675	31.3	39.8	166
29 March	20.4	865	56.5	48.8	202
13 May 98	21.1	1040	50.1	30.4	122
6 June 98	21.1	740	57.8	47.7	53
3 July 98	16.9	446	34.8	43.5	40
5 Aug 98	24.0	272	33.8	37.0	
26 Aug 98	24.3	205	34.4	27.3	
Mean	19.4	618	41.6	39.8	117

†The k_1 and k_2 values and activation energies were taken from Ames (1998). ‡$K_{L,O2}$ values were from Table 4.

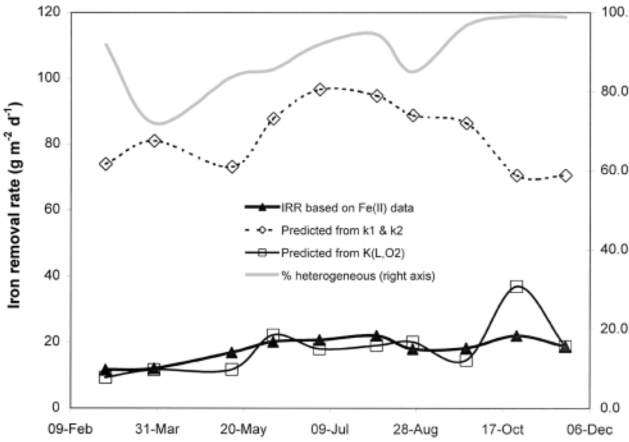

Fig. 10. Iron removal rates (g m^{-2} d^{-1}) for HB Pond #2 (left axis) and predicted percent heterogeneous reaction (right axis).

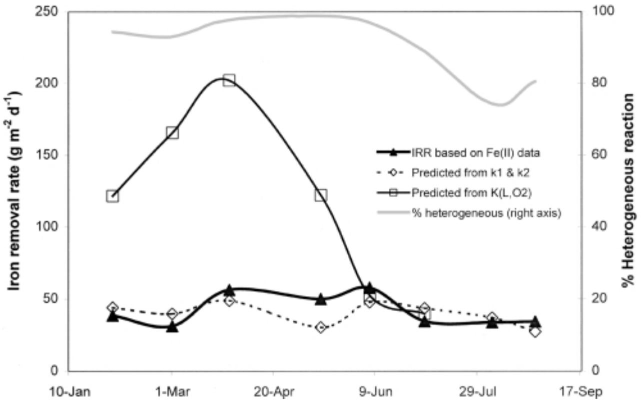

Fig. 11. Measured and predicted iron removal rates at CK to Site #3 (left axis) and predicted percent heterogeneous reaction (right axis).

the depths of the pond (thus decreasing the oxidation rate). Transfer of O_2 is a function of $K_{L,O2}$ and surface area, and is insensitive to the hydraulic retention time. At HB Pond #2, there could also be physical separation of zones with high dissolved oxygen (close to the surface) and zones with high ferric oxide (closer to the bottom due to longer settling times in ponds v. channels).

The actual and the predicted iron removal rates for the CK channel are shown in Figure 11. For CK, the oxidation rate model provided good predictions of the actual IRR. The O_2 transfer model (predicted using $K_{L,O2}$ and dissolved oxygen concentration) over-predicted IRR during the high-flow months. This result is consistent with the observed accumulation of dissolved oxygen in the channel.

The $K_{L,O2}$ value for HB Pond #2 and the CK channel were based on mass balances of Fe(II) and dissolved oxygen, but the derived $K_{L,O2}$ values for HB Pond #2 were consistent with established models for O_2 transfer in stagnant ponds (see *Gas Transfer Coefficients* section above). The model parameters k_1, k_2, and activation energy were taken from Ames (1998) and were independent of field observations.

Improved designs for treatment of mine drainage

This work has demonstrated the benefits of channel designs for passive abiotic treatment of mine drainage. Although channels provide less hydraulic retention time for equivalent surface areas (due to shallower depths), this was more than compensated by other benefits. Better gas transfer, improved heat transfer (beneficial in the summer) and increased suspension of ferric oxides were observed in channels compared to ponds. Improved gas transfer resulted in higher pH due to faster removal of CO_2 in addition to higher DO.

Passive systems are favourable due to low maintenance costs, simplicity of operation and quality of the sludge that is produced. Active systems allow faster oxidation and therefore less treatment area, but with higher costs for maintenance and operation. Most active systems involve addition of excess alkalinity and pH is >8, resulting in low-density sludge due to homogeneous precipitation mechanisms (Herman & Korb 1989; Dempsey 1993). Figures 10 and 11 show heterogeneous oxidation as a percentage of total removal of Fe(II). Jeon (1998) demonstrated that heterogeneous oxidation mechanisms result in denser solids that are easier to dewater. Active systems that operate at pH<6.8 are now being piloted in which heterogeneous oxidation of Fe(II) dominates. This can increase IRR without losing the beneficial characteristics of passive treatment, such as dense sludge and robust performance without daily maintenance and attention.

CONCLUSIONS

The Iron Removal Rate (IRR) for the HB oxidation pond treating alkaline mine water averaged 18 g d^{-1} m^{-2}, which is typical of performance for these systems. The CK channel system had a higher average IRR (42 g d^{-1} m^{-2}) and removal rate increased with flow.

The O_2 transfer coefficient ($K_{L,O2}$) for HB Pond #2 was 1.96 cm h^{-1}, which is consistent with an average wind velocity of 1 m s^{-1} at 10 m. The CO_2 transfer coefficient ($K_{L,CO2}$) for HB Pond #2 was 1.27 cm h^{-1}. $K_{L,O2}$ and $K_{L,CO2}$ were an order of magnitude higher for the CK channel running at design flow than for HB Pond #2. Both transfer coefficients increased with water velocity. The ratio of $K_{L,CO2}/K_{L,O2}$ was lower than predicted by stagnant film or surface renewal models.

Oxidation rate constants from field data averaged 6.0×10^{-9} mg l^{-1} s^{-1} for the heterogeneous rate constant k_2. The predicted heterogeneous rate constant was 5.5×10^{-8} mg l^{-1} s^{-1} at 25°C. These rate constants are consistent with values reported from various laboratory studies.

The heterogeneous oxidation process accounted for most of the oxidation of Fe(II) at HB Pond #2 and in the CK channels. The k_2 rate constant from field work was similar to values that have been reported in the literature.

Based on results from this paper, channels are better than ponds for passive abiotic treatment of net-alkaline mine drainage. Channels provided better O_2 and CO_2 transfer and higher heterogeneous oxidation rate due to higher pH and suspended Fe(II).

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