Aeration to degas CO\textsubscript{2}, increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage

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A B S T R A C T

Passive treatment systems for mine drainage use no energy other than gravity, but they require greater area than active treatment systems. Researchers are considering “hybrid” systems that have passive and active components for increased efficiency, especially where space limitations render passive-only technology ineffective. Flow-through reactor field experiments were conducted at two large net-alkaline anthracite mine discharges in central Pennsylvania. Assuming an Fe removal rate of 20 g m\textsuperscript{-2} day\textsuperscript{-1} and Fe loading from field data, 3.6 × 10\textsuperscript{3} and 3.0 × 10\textsuperscript{3} m\textsuperscript{-2} oxidation ponds would be required for the passive treatment of Site 21 and Packer 5 discharges, respectively. However, only a small area is available at each site. This paper demonstrates aeration to drive off CO\textsubscript{2}, increase pH, and increase Fe(II) oxidation rates, enabling treatment within a small area compared to passive treatment methods, and introduces a geochemical model to accurately predict these rates as well as semi-passive treatment system sizing parameters. Both net-alkaline discharges were suboxic with a pH of \approx 5.7, Fe(II) concentration of \approx 16 mg L\textsuperscript{-1}, and low Mn and Al concentrations. Flow rates were \approx 4000 L min\textsuperscript{-1} at Site 21 and 15,000 L min\textsuperscript{-1} at Packer 5. Three-h aeration experiments with flow rates scaled to a 14-L reactor resulted in pH increases from 5.7 to greater than 7, temperature increases from 12 to 22 °C, dissolved O\textsubscript{2} increases to saturation with respect to the atmosphere, and Fe(II) concentration decreases from 16 to \approx 0.05 mg L\textsuperscript{-1}. A 17,000-L pilot-scale reactor at Site 21 produced similar results although aeration was not as complete as in the smaller reactor. Two non-aerated experiments at Site 21 with 13 and 25-h run times resulted in pH changes of \approx 0.2 and Fe(II) concentration decreases of less than 3 mg L\textsuperscript{-1}.

An Fe(II) oxidation model written in a differential equation solver matched the field experiments very well using field-measured pH, temperature, dissolved O\textsubscript{2}, and initial Fe(II) concentration. The maximum oxidation rate was 1.3 × 10\textsuperscript{-4} mol L\textsuperscript{-1} s\textsuperscript{-1}. The model was modified to predict alkalinity, R\textsubscript{CO\textsubscript{2}}, dissolved O\textsubscript{2}, and pH changes based on initial conditions and aeration rate. This more complex model also fits the data well, is more predictive than the first model, and should serve as a tool for predicting pond size needed for aerated Fe(II) oxidation at the field scale without the need for field pilot studies. Iron(II) oxidation modeling of actively aerated systems predicted that a 1-m deep pond with 10 times less area than estimated for passive treatment would lower Fe(II) concentrations to less than 1 mg L\textsuperscript{-1} at summer and winter temperatures for both sites. The use of active aeration for treatment of CO\textsubscript{2}-rich, net-alkaline discharges (including partially treated effluent from anoxic limestone drains) can result in considerably reduced treatment area for oxidation and may lower treatment costs, but settling of Fe hydroxides was not considered in this study. The reduced capital cost for earthmoving will need to be compared to energy and maintenance costs for aeration.

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

and subsequent precipitation of Fe(III) solids

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

where Fe(OH)$_3$ could be one of several amorphous or crystalline solids. In the absence of sufficient alkalinity, acidic mine drainage will also dissolve metals other than Fe from surrounding rocks. Such a solution will be “net acidic” and will require alkalinity addition for successful treatment (Kirby and Cravotta, 2005a,b). However, if sufficient alkalinity is available, the resulting solution will be “net alkaline” and can “treat itself,” i.e., Fe and metals will be essentially removed, and the water will have pH $> 6.3$, given sufficient time in a treatment system (Kirby and Cravotta, 2005a, b).

Net-alkaline AMD would have a positive value for its net alkalinity. If negative values for Hot Acidity (APHA, 1998) are reported (not always common practice), Kirby and Cravotta (2005b) recommend the use of

\[ \text{net alkalinity} = -\text{measured Hot Acidity}_{(\text{APHA, 1998})} \]

or, not

\[ \text{net alkalinity} = \text{Alkalinity}_{\text{measured(APHA,1998)}} - \text{Acidity}_{\text{calculated}} \]

where Acidity is calculated as

\[ \text{Acidity}_{\text{calculated}} = \text{Acidity}_{\text{calculated}}(\text{mg} L^{-1} \text{as CaCO}_3) \]

\[ = 50 \cdot (10^{3-\text{pH}}) + 2 \cdot C_{\text{Fe}}/55.8 + 2 \cdot C_{\text{Mn}}/54.9 + 3 \cdot C_{\text{Al}}/27.0, \]

where $C$ is dissolved concentration in mg L$^{-1}$.

Ground water and coal mine drainage commonly contain elevated concentrations of dissolved CO$_2$ in association with elevated partial pressures of CO$_2$ (P$_{\text{CO}_2}$) of 10$^{-1.5}$ to 10$^{-4}$ atm/nat in the vadose zone and/or underlying saturated zone (Cravotta and Dietz, 2002; Budeit, 2007; Means, 2007; Schmidt, 2007). Cravotta (2007) also uses Eq. (6) with the computer code PHREEQC (Parkhurst and Appelo, 1999) to model the kinetics of the processes involved.

1.2. This study

Flow-through reactors were used in the field to determine how well the aeration of net-alkaline mine water drives off CO$_2$, increases pH, and therefore increases Fe(II) oxidation rates. Two Fe oxidation models were developed. Model 1 predicts only Fe(II) concentrations and requires knowledge of several other parameters throughout the experiment. In addition to Fe(II) concentration, Model 2 predicts pH changes, consumption of alkalinity, dissolved O$_2$ concentration, and degassing of CO$_2$ based on the initial solution composition, requiring only temperature data during the experiment. The models were applied to calculate the size of aerated ponds required for Fe oxidation; this size was more than 10 times smaller than the size required for completely passive non-aerated ponds for the two mine discharges studied.

2. Methods

Aeration has long been used in active treatment because it can (1) add O$_2$, (2) help with mixing, and (3) degas CO$_2$, although treatment practitioners commonly focus only on the addition of O$_2$. More recently, aeration has been considered or used as a supplement to passive treatment, and attention is being given to CO$_2$ removal as a way to increase pH and Fe oxidation rates (Cravotta, 2007; Budeit, 2007; Means, 2007; Schmidt, 2007). Cravotta (2007) discusses an aeration approach similar to that taken in the current study for accelerating Fe(II) oxidation in net-alkaline mine water. Cravotta (2007) also uses Eq. (6) with the computer code PHREEQC (Parkhurst and Appelo, 1999) to model the kinetics of the processes involved.

2.1. Site 21 discharge

The Operation Scarlett (Gannett Fleming Corddery and Carpenter, Inc., 1972) Site 21 discharge is located along Quaker Run in Rans-}
discharge, the Packer 5 discharge has a much higher flow rate of \( \approx 15,000 \text{ L min}^{-1} \) and higher alkalinity (Cravotta, 2005).

### 2.3. Field methods

Two aerated flow-through experiments using a 14-L Plexiglas tank (Fig. 1) were conducted at Site 21; one such experiment was conducted at Packer 5. One preliminary 13-h, non-aerated 14-L experiment, with limited data collected, was conducted at Site 21. Experiments were either naturally shaded or shaded by a canopy over the reactor to prevent direct sunlight exposure. At the start of each experiment, AMD was scooped from the source without stirring up sediment using a bucket and poured gently into the reactor tank with as little aeration as possible. Subsequently, a peristaltic pump introduced the AMD from the source into the upflow end of the reactor tank. Reactor volumes, flow conditions, average residence times \( (t_{\text{res}}) \), and experiment durations are listed in Table 1. An aquarium pump with four (eight for the second Site 21 experiment) diffuser stones was used to provide 4 L min\(^{-1} \) (8 L min\(^{-1} \) for the second Site 21 experiment) air in the upflow end of the reactor water.

A YSITM multiparameter XLM 600 sonde was placed in the reactor tank to measure water temperature \( (T) \), pH, and DO, which were logged to a YSI\textsuperscript{TM} 650 MDS. A sample for Fe(II) concentration was taken about every 10 min, filtered (0.45 \( \mu \text{m} \)), and acidified samples were conducted in the laboratory. The spectrophotometer was zeroed using distilled water/reactant sample. The experiment was run until the reactor was no longer detectable in the samples taken.

![Schematic diagram of 14-L flow-through reactor.](image)

**Fig. 1.** Schematic diagram of 14-L flow-through reactor.

For the non-aerated Site 21 experiment, a 400-L plastic swimming pool with a flow rate of 0.33 L min\(^{-1} \) was run for 25 h. These flow conditions are scaled down from a hypothetical full-scale 1-m deep pond based on a 20 g m\(^{-2} \) d\(^{-1} \) Fe removal rate for net-alkaline passive treatment ponds (Hedin et al., 1994; Watzlaf et al., 2004). Without aeration, CO2 degassing and therefore Fe oxidation and precipitation occur much slower, so parameters were measured less frequently than in other experiments.

For the second Site 21 14-L aeration experiment, alkalinity was measured as follows. Raw unpreserved (RU) reactor water samples (25 mL) for alkalinity were collected and titrated in the field with stirring using 0.16 N H\(_2\)SO\(_4\) solution delivered in 1/800 mL increments from a Hach\textsuperscript{TM} digital titrator to a measured pH 4.5 endpoint.

#### 2.3.1. Pilot-scale reactor

A 17,000-L (4500-gallon) inflatable swimming pool was used as a field pilot-scale reactor at Site 21. Sump pumps introduced water from the discharge into the pool on the inflow side at 193 L min\(^{-1} \) until the reactor was full (1.5 h); experimental flow conditions are given in Table 1. Once the reactor was full, a 0.67 hp electric blower provided ambient air at 6.8 kpa (1.1 psi) to a 15-m length of Aeration Solutions, Inc. diffuser membrane in the middle of the pool. In order to examine chemical processes affected by residence time, inflow was reduced 3 h before the 26-h experiment ended. Sampling was conducted as in the 14-L reactor except that Fe(II) concentrations were approximated by analyzing filtered acidified samples for total dissolved Fe, which should be practically all Fe(II) in the pH range of the experiment (6.1–6.9).

#### 2.4. Laboratory chemical analyses

For the second Site 21 14-L aeration experiment, Fe(II) analyses of filtered acidified samples were conducted in the laboratory using the same methods as those used in the field. Filtered acidified samples for other metals (inductively-coupled plasma-mass spectrometry) and filtered unpreserved samples for SO\(_4^{2-}\), Cl\(^{-}\), NO\(_3^{-}\), and PO\(_4^{3-}\) (colorimetric analyses) were sent to a commercial laboratory. Total dissolved and total Fe samples for the pilot-scale reactor were analyzed colorimetrically by a commercial laboratory.

#### 2.5. PHREEQCI simulations

PHREEQCI (Parkhurst and Appelo, 1999) was used to model speciation of the influent and steady-state effluent solutions for the second Site 21 aeration experiment. Table 2 lists the major input parameters (other major ions were input to allow for charge balance) used to speciate the original solution. Table 2 also lists the changes simulated when the original speciated solution was aerated and amorphous Fe(OH)\(_3\), s was allowed to precipitate. Simulated “aeration” was accomplished by allowing equilibrium with respect to atmospheric P\(_{O2}\) and P\(_{CO2}\) using values of 10\(^{-0.7}\) and 10\(^{-3.4}\) atm, respectively. The solution was allowed to reach equilibrium with

---

### Table 1

Reactor flow conditions. \( t_{\text{res}} \) = residence time.

<table>
<thead>
<tr>
<th>Location</th>
<th>Reactor volume, L</th>
<th>Aerated?</th>
<th>Flowrate, L min(^{-1} )</th>
<th>Average ( t_{\text{res}} ), h</th>
<th>Run time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 21</td>
<td>14, #1</td>
<td>Yes</td>
<td>0.028</td>
<td>8.3</td>
<td>3</td>
</tr>
<tr>
<td>Site 21*</td>
<td>14, #2</td>
<td>Yes</td>
<td>0.046 (0.023)</td>
<td>5.1 (10)*</td>
<td>3</td>
</tr>
<tr>
<td>Site 21</td>
<td>14, #3</td>
<td>No</td>
<td>0.028</td>
<td>8.3</td>
<td>13</td>
</tr>
<tr>
<td>Site 21</td>
<td>400</td>
<td>No</td>
<td>0.33</td>
<td>2.0</td>
<td>25</td>
</tr>
<tr>
<td>Site 21</td>
<td>17,000</td>
<td>Yes</td>
<td>72 (36)</td>
<td>3.9 (7.9)*</td>
<td>26</td>
</tr>
<tr>
<td>Packer 5</td>
<td>14</td>
<td>Yes</td>
<td>0.028</td>
<td>8.3</td>
<td>3</td>
</tr>
</tbody>
</table>

* Indicates flowrate reduced after 2 h.

* Indicates flowrate reduced after 23 h.
respect to amorphous Fe(OH)$_3$, s. An additional simulation also used a final $P_{CO_2} = 10^{-2.42}$ atm, reflective of steady-state, non-equilibrium conditions (see Section 3.2).

### 2.6. Iron oxidation models

Using Stella$^\text{TM}$, a graphical interface differential equation solver, the model of Kirby et al. (1999) was modified to model abiotic Fe(II) oxidation. Iron(II) oxidation in the model is governed by a temperature-dependent version of Eq. (6) (see Fig. 2). The sensitivity of Fe oxidation for this is pH $>$ T $>$ influent Fe(II) concentration $>$ DO $>$ reactor volume (Kirby et al., 1999).

Model 1 is a subset (lacks the lower 3 fluxes in Fig. 2: HCO$_3^-$, H$_2$CO$_3^*$, and O$_2$) of Model 2. Model 1 was used for early experiments for which alkalinity was not measured. Input includes initial conditions for Site 21 PHREEQCI modeling. The concentrations for other major species are not shown but were included as input.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Run conditions for Site 21 PHREEQCI modeling. The concentrations for other major species are not shown but were included as input.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td>Value</td>
</tr>
<tr>
<td>Solve initial solution</td>
<td>$T, ^\circ C$</td>
</tr>
<tr>
<td>pH</td>
<td>$5.77$</td>
</tr>
<tr>
<td>Alkalinity, mg L$^{-1}$ (HCO$_3^-$)</td>
<td>117</td>
</tr>
<tr>
<td>Fe(II), mg L$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>$P_{CO_2}$, atm</td>
<td>$10^{-3.4}$, $10^{-2.42}$</td>
</tr>
<tr>
<td>$P_{CO_2}$, atm</td>
<td>$10^{-1.9}$</td>
</tr>
<tr>
<td>Amorphous Fe(OH)$_3$, s</td>
<td>Saturation</td>
</tr>
</tbody>
</table>

**GOVERNING EQUATIONS**

\[
\frac{d[Fe(II)]}{dt} = -k[Fe(II)][O_2]^{2}_aH_+^{2}
\]

where

\[
k = Ae^{-(E_a/RT)}
\]

$A =$ Arrhenius frequency factor $= 4 \times 10^5$

$E_a =$ activation energy $= 96 \text{ kJ mol}^{-1}$

$R =$ gas constant $= 8.314 \times 10^{-3} \text{ kJ mol}^{-1} K^{-1}$

$T =$ temperature in Kelvin

$[ ] =$ mol L$^{-1}$

$a =$ activity

If reactor not full, then no flow, else inflow = outflow

\[
\frac{d[HCO_3^-]}{dt} = -2(\text{Fe(II) oxidation rate})
\]

\[
P_{CO_2} = [H_2CO_3^*]/K_{H_2}
\]

\[
\frac{d[CO_2]}{dt} = -k_1(\text{aeration rate})
\]

where

$k_1 =$ mass transfer coefficient

$A =$ surface area of aeration bubbles

\[
\frac{d[O_2]}{dt} = k_2(\text{aeration rate}) - 0.25(\text{Fe(II) oxidation rate})
\]

where

$k_2 =$ mass transfer coefficient

$A =$ surface area of aeration bubbles

---

**EXPLANATION**

Fe = Fe(II)

infl = mass or volume flowing in

out = mass or volume flowing out

init = initial influent concentration

= flux

= reservoir

= variable or parameter

Fig. 2. Schematic diagram representing the mathematical relationships in Model 2. Arrowheads point to parameter that is a function of the parameter at the initial end.
measured Fe(II) concentration and time-variant measured values for pH, DO, T, and solution flow rate. Output is the predicted Fe(II) concentration with time, which was compared to the measured Fe(II) field concentrations.

Model 2 was developed to be more widely predictive. Despite using field data for alkalinity and pH changes, Model 2 uses only the initial field data for alkalinity, DO, pH, and calculated initial CO₂ concentration, and it then predicts alkalinity, pH, P_CO₂ and CO₂, O₂, and Fe(II) concentrations with time, using governing equations (see also Fig. 2) as follows below.

P_CO₂ during the simulations was calculated from [H₂CO₃*] and the Henry’s law constant, Kₕ (Table 3). The initial value of P_CO₂ was calculated by PHREEQC speciation of field pH, alkalinity (HCO₃⁻ concentration), and major cations and anions. The rate of CO₂ loss was calculated by mass transfer (see Fig. 2). Because an attempt to calculate kₐ_air for the Aeration Solutions, Inc. diffuser/blower setup based on data from the manufacturer was not successful, kₐ_air and k₁ were lumped together (kₐ_air and used as a fit parameter. This fit was accomplished by iteratively changing kₐ_air until Fe(II) concentrations computed closely matched experimental values with time. The rate of O₂ gain was calculated by mass transfer (see Fig. 2). The same values for kₐ_air were used for CO₂ loss and O₂ gain.

Temperature-dependent equilibrium constant values from the PHREEQC database were combined to calculate pH in Model 2, giving pH as

\[
pH = -\log\left(\frac{K_1kₐP_CO₂/(0.92[HCO₃^-])}{0.92}\right)
\] (7)

where 0.92 is the value of the activity coefficient (calculated in PHREEQC) for HCO₃⁻ for solutions in this study. Over the course of a PHREEQC aeration simulation of field solution changes in this study, the ionic strength changes only approximately 10%, thus a constant value for the activity coefficient is a reasonable approximation. The log K values (Table 3) were added to logKₕ plotted in a spreadsheet and fitted to the simpler expression

\[
\log(K/Kₕ) = -4.233e - 05(T^2) + 1.887 \times 10^{-2}(T) - 9.682
\] (8)

where T is in Kelvin.

Loss of CO₂ does not affect alkalinity directly (Stumm and Morgan, 1996; Kirby and Cravotta, 2005a), but the alkalinity decreases as Fe oxidation and hydrolysis reactions proceed:

Fe²⁺ + 2HCO₃⁻ + 1/4O₂ + 1/2H₂O = Fe(OH)₃(s) + 2CO₂⁺.

By the stoichiometry of Eq. (9), Model 2 assumed that 2 mol HCO₃⁻ were consumed by oxidation of 1 mol Fe²⁺.

3. Results and discussion

3.1. Site 21 and packer 5 experiments and Model 1

Without aeration, chemical changes were minor because reaction rates were slow. During the preliminary 13-h, 14-L non-aerated Site 21 experiment, pH increased from 6.1 to 6.3, and the Fe(II) concentration only decreased from 16.3 to 13.8 mg L⁻¹. Despite the decrease in dissolved Fe(II) concentration, there was little visible turbidity or surface coating caused by Fe(III) precipitation.

The 400-L non-aerated Site 21 experiment ran for 25 h (Fig. 3). The pH remained constant (within analytical uncertainty). The DO apparently decreased from ≈68% to ≈40% saturation. The initial high DO may be an artifact due to introduction of mine water by pumping. The DO decrease observed cannot all be accounted for by the small amount of Fe(II) oxidation. The Fe(II) concentration only decreased from 15.2 to 12.5 mg L⁻¹. There was virtually no visible precipitate in the water or on the surface of the reactor. These results were most likely due to the very limited amount of gas exchange that occurred without aeration, thus the dissolved CO₂ and pH were maintained near initial values, and Fe(II) oxidation was much slower than aerated reactors.

Aeration produced rapid changes in solution chemistry compared to the non-aerated experiments. During the 3-h Site 21 aeration experiment, the water temperature rose from 12.2 to 19.1 °C, the pH increased from 5.7 to 7.6, the DO increased from 1.5 mg L⁻¹ to 8.9 mg L⁻¹ (∼100% saturation), and the Fe(II) concentration decreased from 15.8 mg L⁻¹ to below the 0.03 mg L⁻¹ detection limit (Fig. 4). The initial clear water in the reactor became visibly cloudy with orange precipitate within 0.5 h. The water temperature increased because it approached thermal equilibrium with ambient air. The DO increased rapidly to saturation with respect to the atmosphere, then decreased to remain in equilibrium as the water temperature increased. There were three major influences on pH change. Iron(III) oxidation (Eq. (1)) and CO₂ degassing cause pH to increase, while Fe(OH)₃ precipitation (Eq. (2)) causes pH to decrease. The net pH increase occurred because there was sufficient alkalinity to outweigh the effect of Fe(OH)₃ precipitation. Iron(III) oxidation decreased the Fe(II) concentration slowly until the pH rose; Fe(II) then decreased rapidly until the Fe(II) oxidation rate reached steady-state. Model 1 results (Fig. 4) matched the Fe(II) concentrations very well in both trend and actual values. The measured Fe(II) concentrations at steady-state were below detection limit (0.03 mg L⁻¹); model Fe(II) steady-state concentration was 0.01 mg L⁻¹ (99.5% oxidation).
For an ideally-mixed flow-through reactor, the reaction rate is calculated as

\[
\text{rate} = \frac{\text{concentration}_{\text{in}} - \text{concentration}_{\text{out}}}{\text{volumetric flow rate}}.
\]

The aerated reactor was not stirred and may not have been completely mixed, but the aeration did provide some mixing. Eq. (10) thus likely provides a reasonable estimate of the reaction rate. The maximum oxidation rate occurred at steady-state and was 1.3 \times 10^{-2} \text{mol L}^{-1} \text{s}^{-1}.

The 3-h Packer 5 aeration experiment yielded results similar to Site 21. The water temperature rose from 13.9 to 24.1 °C, the pH increased from 6.1 to 7.3, the DO increased from 3.7 to 7.4 (90% saturation) mg L\(^{-1}\), and the Fe(II) concentration decreased from 16.5 to 0.07 mg L\(^{-1}\) (Fig. 4). The maximum oxidation rate was the same as the Site 21 rate. Model 1 results (Fig. 4) again matched the Fe(II) concentrations very well.

The results presented above and in Fig. 4 show that the aeration and the consequent removal of dissolved CO\(_2\) in a net-alkaline water will increase pH and promote rapid Fe oxidation. Thus, the aeration of a pond treatment system would be an extremely effective method of Fe oxidation for either site studied or any other site with similar chemistry. The data show that as the aeration drove off the dissolved CO\(_2\), the pH increased, the Fe(II) oxidized more readily, and Fe(OH)\(_3\) formed rapidly compared to a non-aerated system.

### 3.2. Second site 21, 14-L aeration experiment and Model 2

Model 1 effectively reproduced field results, but it lacks predictive power because the changes in pH with time must be determined experimentally. Model 2 overcomes this problem by accounting for \(P_{\text{CO}_2}\) and alkalinity changes in order to predict pH values. Model 2 required input values for the initial \(P_{\text{CO}_2}\) and HCO\(_3\)\(^-\) concentration. The initial \(P_{\text{CO}_2}\) value of 10^{-2.66} atm was obtained by running PHREEQC. The initial HCO\(_3\) concentration was assumed to be equal to the measured 117 mg L\(^{-1}\) alkalinity as HCO\(_3\)\(^-\).

The second Site 21 aeration experiment (Fig. 5) used an initial solution flow rate of 46 mL min\(^{-1}\); this rate was decreased to 23 mL min\(^{-1}\) after 2 h. The steady-state pH values (1.25–2 h and 2.5–3 h) matched the measured pH well. Why the early transient-state Model 2 pH predictions are higher than the measured pH cannot be explained. Iron(II) concentration decreased slowly initially, decreased rapidly as pH increased, then decreased slowly as Fe(II) neared steady-state concentration. The Model 2 Fe(II) concentrations matched the field Fe(II) concentrations very well before and during steady-state conditions. The DO quickly rose, reaching saturation with respect to atmospheric O\(_2\), then fell as temperature rose, maintaining this equilibrium; measured DO values slightly greater than atmospheric saturation are thought to be due to imperfect calibration. Model 2 alkalinity value trends matched measured alkalinity trends well. However, except for the initial value, measured alkalinity values were higher than predicted values (see Section 3.4 for discussion). Temperature increased throughout the experiment as the deep mine water began to equilibrate with atmospheric temperature.

It had initially been assumed that the aerated system would reach equilibrium with atmospheric \(P_{\text{CO}_2}\) (10^{-3.4} atm). However, Model 2 \(P_{\text{CO}_2}\) values (Fig. 5: necessarily calculated rather than measured) decreased to steady-states (at different flow rates) that were...
supersaturated. Cravotta (2007) also observed elevated steady-state \( P_{\text{CO}_2} \) after prolonged aeration. Model 2 \( P_{\text{CO}_2} \) concentrations dropped from 192 to 5 \( \text{mg L}^{-1} \) (\( P_{\text{CO}_2} = 10^{1.00} \) to \( 10^{2.66} \) atm) as field and Model 2 pH increased. Model 2 pH and \( \text{CO}_2 \) concentration as well as field pH had reached a steady-state before the flow rate was decreased. However, when the field flow rate was decreased (Fig. 5), field and Model 2 pH increased to a new steady-state, and Model 2 \( P_{\text{CO}_2} \) concentration decreased to a new steady-state. This evidence strongly suggests that the system did not reach equilibrium with atmospheric \( P_{\text{CO}_2} \).

Table 4 compares field and modeled results for 7 parameters at either steady-state (experimental data and Model 2) or equilibrium (PHREEQC) for the second Site 21 14-L aeration experiment. The Model 2 final \( P_{\text{CO}_2} \) value of \( 10^{2.66} \) atm is higher than atmospheric \( P_{\text{CO}_2} \). Slowing the flow rate in Model 2 from field conditions (2 mL min\(^{-1}\)) resulted in a pH of 8.38 and equilibrium with atmospheric \( P_{\text{CO}_2} \) (10\(^{-1.4}\) atm); these Model 2 results closely agree with PHREEQC modeling. Fig. 5 and Table 4 support the conclusion that the system has not reached equilibrium with atmospheric \( P_{\text{CO}_2} \). However, atmospheric equilibrium is not required for adequate treatment as long as the pH increases sufficiently to promote rapid Fe(II) oxidation, as it did in all of the 14-L aeration experiments.

3.3. Site 21 pilot-scale aeration experiment and model 2

Fig. 6 shows experimental and model results from the 17,000-L pilot-scale experiment. Aeration stopped from 14.25 to 17.5 run h (8.5–5 am) due to equipment malfunction. Model 2-predicted pH values matched the measured pH very well both in trends and actual values; in particular the Model 2 response was convincing when the aeration failed, when aeration was restored, and when flow rate was reduced (\( \approx 14, 17, \) and 23 h, respectively. Temperature remained nearly constant (12.1 to 13.7°C) because of the large volume of the reactor. Iron(II) concentration initially decreased slowly, decreased rapidly as pH increased, then reached a steady-state value (interrupted by aeration failure and flow rate reduction) that indicated 79% oxidation. Predicted alkalinity values matched measured alkalinity values well. Dissolved O\(_2\) quickly rose, but apparently reached only 80%, falling to 40%, saturation with respect to atmospheric O\(_2\). The apparent decrease in DO as the experiment continued represents a systematic error: the DO membrane was discovered to be fouled by Fe hydroxides – it recorded values well below saturation in air-saturated water after the experiment was over. Model 2 predicted slight undersaturation (\( \approx 10% \)) with DO. End-of-experiment predicted \( \text{CO}_2 \) concentrations (\( P_{\text{CO}_2} = 10^{-2.0} \)) never reached atmospheric equilibrium (\( P_{\text{CO}_2} = 10^{-3.4} \)). As with the Model 1 results (Fig. 5), upward inflections in Model 2 predictions for pH, Fe(II), alkalinity, DO and \( \text{CO}_2 \) (Fig. 6) occur due to the decreased flow rate (increased \( t_{\text{loc}} \)). Because \( \text{CO}_2 \) degassing was less effective than in the 14-L experiment, pH and DO were lower, and Fe(II) and \( \text{CO}_2 \) were higher in the pilot-scale experiment.

Table 4 comparison of steady-state (or equilibrium for PHREEQC model) values for the second Site 21 14-L end-of-experiment parameters. See Section 3.4 for discussion of alkalinity values. * indicates that the average of the last nine alkalinity measurements was used to calculate the steady-state value. NC indicates not calculated because of measure alkalinity error, nd indicates no analysis was performed for this parameter.

<table>
<thead>
<tr>
<th>Field</th>
<th>Model 2</th>
<th>PHREEQC</th>
<th>Model 2</th>
<th>PHREEQC</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.43</td>
<td>7.32</td>
<td>7.3</td>
<td>8.38</td>
</tr>
<tr>
<td>( \text{H}_2\text{CO}_3 ), mg L(^{-1})</td>
<td>NC</td>
<td>9</td>
<td>10 (^{2.66})</td>
<td>1</td>
</tr>
<tr>
<td>( \text{P}_{\text{CO}_2} ), atm</td>
<td>NC</td>
<td>10 (^{2.66})</td>
<td>10 (^{-1.4})</td>
<td>1</td>
</tr>
<tr>
<td>( \text{HCO}_3^- ), mg L(^{-1})</td>
<td>nd</td>
<td>83</td>
<td>83</td>
<td>82</td>
</tr>
<tr>
<td>Alk, mg L(^{-1}) ( \text{HCO}_3^- )</td>
<td>93</td>
<td>83</td>
<td>83</td>
<td>82</td>
</tr>
<tr>
<td>Diss. Fe(II), mg L(^{-1})</td>
<td>( &lt;0.03 )</td>
<td>0.01</td>
<td>( 3 \times 10^{-11} )</td>
<td>( &lt;0.01 )</td>
</tr>
<tr>
<td>Diss. Fe(III), mg L(^{-1})</td>
<td>nd</td>
<td>nd</td>
<td>( 10^{-3} )</td>
<td>nd</td>
</tr>
</tbody>
</table>

Dempsey et al. (2001) attribute much of the Fe oxidation in some passive treatment systems to heterogeneous Fe(II) oxidation, i.e., catalysis by Fe hydroxide solids, and Dietz and Dempsey (2002) have shown that heterogeneous Fe(II) oxidation can be significantly more rapid than homogeneous Fe(II) oxidation at pH values in the range of the experiments. However, the Dietz and Dempsey (2002) experiments required considerable amounts of Fe hydroxide solid to be present before the catalysis was evident. Total (unfiltered) Fe in the reactor was measured at the end of the pilot-scale experiment, and it was found to be 16 \( \text{mg L}^{-1} \) as Fe, which is only 2–4 \( \text{mg L}^{-1} \) higher than the two “no-recycle” (their no-added-Fe-solids control) experiments of Dietz and Dempsey (2002). The close match in this study and in Cravotta (2007) between measured and modeled Fe(II) concentrations and oxidation rates suggest that homogeneous Fe(II) oxidation (Eq. (6)) adequately models the results in these two studies. It is likely that systems with higher Fe hydroxide solid concentrations will exhibit faster Fe(II) oxidation than the present experiments.

3.4. Alkalinity measurements and modeling

Because degassing of \( \text{CO}_2 \), oxidation of Fe(II), and alkalinity consumption can take place during sample storage (Eq. (9)), mine water charged with \( \text{CO}_2 \) presents a particular problem for alkalinity measurement, making sharp endpoints difficult to obtain. Due to this difficulty, the absolute values of the Model 2 alkalinities do not match field alkalinities well. The Model 2 results, because they are based on stoichiometric relationships (Eq. (9)) probably give a better value for the overall change in alkalinity than the measured alkalinities. Results from PHREEQC simulations returned the same change in alkalinities as Model 2.

3.5. Simple test for applicability of aeration

If a mine discharge is thought to be net alkaline and the major goal is to remove Fe (rather than Mn, which is more challenging to treat passively; e.g., Jacobson et al., 1999), a simple experiment can be performed to predict whether \( \text{CO}_2 \) degassing will yield a pH high enough for rapid Fe(II) oxidation. A sample of mine water can be aerated vigorously in a beaker containing a pH probe. Iron hydroxide should precipitate, and the pH should rise to a steady-state value in \( \approx 30 \) min. It should be noted that neither adding H\(_2\)O\(_2\) nor brief agitation are likely to degas \( \text{CO}_2 \) effectively (Cravotta and Kirby, 2004b). If the resulting pH is \( >6.3 \), the water is net alkaline. At higher pH values, Fe(II) oxidation will be more rapid, and the effectiveness of aeration for treatment will increase.

3.6. Implications for treatment

Model 1 was used to predict steady-state (effluent) Fe(II) concentrations (Table 5) for hypothetical non-aerated and aerated
ponds of different sizes for the Site 21 and Packer 5 discharges (Table 5). The larger pond size for non-aerated conditions was based on a widely used Fe removal rate of 20 g m$^{-2}$ d$^{-1}$ (Hedin et al., 1994; Watzlaf et al., 2004), assuming that each pond was 1-m deep, and using Fe(II) loading from field data. For the same discharge, the smaller pond size for aerated conditions was one-tenth of the non-aerated size; this approach assumes that aeration is as effective as in the 14-L reactor. Note that the Hedin et al. (1994) approach predicts total Fe removal, whereas the model predicts Fe(II) oxidation without addressing Fe solid removal. Summer and winter conditions were modeled because gas equilibria, pH, and Fe(II) oxidation kinetics are all affected by temperature. For both discharges under all conditions in Table 5, predicted Fe(II) concentrations are 6.50 mg L$^{-1}$, indicating that oxidation should be adequate even if treatment ponds are 10 times smaller than computed using the 20 g m$^{-2}$ d$^{-1}$ Fe removal rate.

**Fig. 6.** Measured data (symbols) and Model 2 results (solid curves) for pilot-scale Site 21 aeration experiment.

**Table 5**
Model 1 predicted steady-state treatment system effluent Fe(II) concentration for aerated ponds for summer and winter conditions and a 10-fold difference in pond size. The larger pond areas are equivalent to those required using a 20 g m$^{-2}$ d$^{-1}$ removal rate (Hedin et al., 1994; Watzlaf et al., 2004) for passive treatment.

<table>
<thead>
<tr>
<th>Site</th>
<th>pH</th>
<th>DO, mg L$^{-1}$</th>
<th>Flowrate, L h$^{-1}$</th>
<th>Pond area, m$^2$</th>
<th>Predicted Fe(II), mg L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 21</td>
<td>7.5</td>
<td>8</td>
<td>1.9 × 10$^3$</td>
<td>3.6 × 10$^3$</td>
<td>0.06</td>
</tr>
<tr>
<td>Site 21</td>
<td>7.5</td>
<td>8</td>
<td>1.9 × 10$^3$</td>
<td>3.6 × 10$^3$</td>
<td>0.08</td>
</tr>
<tr>
<td>Winter, 5°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 21</td>
<td>7.5</td>
<td>12</td>
<td>1.9 × 10$^3$</td>
<td>3.6 × 10$^3$</td>
<td>0.6</td>
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<tr>
<td>Site 21</td>
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<td>1.9 × 10$^3$</td>
<td>3.6 × 10$^3$</td>
<td>0.8</td>
</tr>
<tr>
<td>Summer, 25°C</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Packer 5</td>
<td>7.4</td>
<td>8</td>
<td>1.0 × 10$^6$</td>
<td>3 × 10$^4$</td>
<td>0.01</td>
</tr>
<tr>
<td>Packer 5</td>
<td>7.4</td>
<td>8</td>
<td>1.0 × 10$^6$</td>
<td>3 × 10$^4$</td>
<td>0.1</td>
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<tr>
<td>Winter, 5°C</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packer 5</td>
<td>7.4</td>
<td>12</td>
<td>1.0 × 10$^6$</td>
<td>3 × 10$^4$</td>
<td>0.1</td>
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<tr>
<td>Packer 5</td>
<td>7.4</td>
<td>12</td>
<td>1.0 × 10$^6$</td>
<td>3 × 10$^4$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The published Fe removal rate of 20 g m\(^{-2}\) d\(^{-1}\) (Hedin et al., 1994; Watzlaf et al., 2004) has proved useful for sizing successful passive treatment systems for net-alkaline water at numerous field sites. However, the Site 21 14-L and 400-L non-aerated reactors and their flows were scaled to ponds suggested to be adequately sized using 20 g m\(^{-2}\) d\(^{-1}\), but these experiments did not adequately oxidize Fe, showing only 16% and 22% oxidation, respectively, compared to nearly 100% oxidation from the well-aerated 14-L Site 21, Packer 5, and some other net-alkaline waters would be much slower than net-acidic discharges, many large, high-metal loading AMD sources in the anthracite and bituminous coal regions of Pennsylvania are net alkaline (e.g., Cravotta and Kirby, 2004a; Cravotta, 2005, 2008). For net-acidic AMD, anoxic limestone drains (ALD) or other limestone based systems are commonly used as the first stage of passive treatment of acidic mine drainage and, if effective, will produce net-alkaline CO\(_2\)-rich water that requires oxidation to complete its treatment. Therefore this research should prove valuable for the evaluation of treatment strategies for net-alkaline or net-acidic discharges.

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References