Effects of CO₂ Degassing on pH and Fe(II) Oxidation Rates in Coal Mine Effluents

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Abstract Elevated concentrations of dissolved CO₂ in groundwater from underground coal mines can depress pH and decrease the rate of removal of dissolved Fe(II) and associated metals within aerobic treatment ponds and wetlands. Mechanical aeration of the water can accelerate CO₂ removal (degassing), with consequent increases in pH and the rates of Fe(II) oxidation and Fe(III) precipitation. This paper uses kinetics modeling with the geochemical program, PHREEQC, to simulate interdependent changes in CO₂ degassing, pH, and Fe(II) oxidation rates that occur during aeration of waters discharged from abandoned coal mines.

Keywords abandoned mines; coal mine drainage; iron oxidation rate CO₂ degassing rate

Methods

Empirical time-series data on pH, temperature, dissolved oxygen (DO), and initial and final Fe(II) and alkalinity values during mechanical aeration experiments reported by Geroni et al. (2012) were used to estimate rates of Fe(II) oxidation and CO₂ degassing. Because the values for these unstable constituents changed rapidly, the mechanical aeration experiments were conducted for 2 hours or less. As previously described by Kirby et al. (2009), alkalinity was assumed to be consumed by the combined oxidation and hydrolysis of dissolved iron according to the stoichiometry:

\[ \text{Fe}^{2+} + 2 \text{HCO}_3^- + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 \rightarrow \text{Fe(OH)}_3 + 2 \text{CO}_2 \]  

Rates of Fe(II) oxidation were estimated to follow the abiotic homogeneous oxidation rate model presented by Stumm and Morgan (1996, 683–685):

\[-d[\text{Fe(II)}]/dt = k_1[\text{O}_2][\text{OH}^-]^2[\text{Fe(II)}] \]  

where at pH > 5 and 20 °C, \(k_1 = 8 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} \) (1.33 \times 10^{12} \text{ M}^{-2} \text{ atm}^{-1} \text{ s}^{-1}). The second-order dependence on [OH⁻] indicates a
change in pH of 1 unit results in a 100-fold change in the oxidation rate. At a given pH, the rate increases by a factor of 10 for a 15 °C increase. By using the activation energy of 23 kcal/mol reported by Stumm and Morgan (1996, p. 684) with the Arrhenius equation (Langmuir 1997, p. 62), the rate can be adjusted to different temperatures.

A spreadsheet based 4th order Runge-Kutta (RK4) model was used to compute the concentration of residual Fe(II) with elapsed time based on Eq. (4). Values input into the model were initial Fe(II) concentration, along with the pH, temperature, and DO for each 10-second interval logged throughout the experiments. The apparent value for the homogeneous Fe(II) oxidation rate constant \( k_1 = 1.33 \times 10^{12} \) to \( 1.33 \times 10^{14} \) M\(^{-2}\)atm\(^{-1}\) s\(^{-1}\) was chosen to yield the residual Fe(II) at the end of the experiment. These apparent rate constants were a factor of 1 to 100 times the reference value of \( 1.33 \times 10^{12} \) M\(^{-2}\)atm\(^{-1}\) s\(^{-1}\) at 20 °C (Stumm and Morgan 1996, p. 683).

To facilitate the evaluation of the interactions among the initial alkalinity, pH, and Fe(II) oxidation rate, the major carbonate speciation equations and thermodynamic constants from the PHREEQC data base (Parkhurst and Appelo 1999) were added to the spreadsheet RK4 model. The measured pH and temperature plus computed alkalinity (Eq. 3) were then used to estimate partial pressure of CO\(_2\) (\( p_{\text{CO}_2} \)) and the rate of CO\(_2\) degassing during the aeration experiments considering asymptotic exponential models (Langmuir 1997; Geroni et al. 2012). The integrated form of the 2\(^{nd}\) order asymptotic rate equation for CO\(_2\) degassing is shown as Eq. (5),

\[
t \cdot k_L a = \left[ \frac{1}{C_s-C_t} + 1 / (C_s-C_o) \right]
\]

where \( C_s \) is the steady state (equilibrium) value, \( C_o \) is the initial value and \( C_t \) is the value at time \( t \) for the negative logarithm of \( p_{\text{CO}_2} \) in atmospheres (\( p_{\text{CO}_2} \)). Values for \(-k_L a\) (the mass transfer coefficient) were calculated from the linear slope estimate of \( [1/(C_s-C_t)+1/(C_s-C_o)] \) vs. \( t \) over the first 10 to 25 minutes of the experiments. The value of \( C_s \) was varied to yield \( k_L a \) that approximated the trend for \( p_{\text{CO}_2} (C_t) \) during each experiment. The modeled values of \( C_s \) (\( p_{\text{CO}_2} = 10^{-34} \) to \( 10^{-17} \) atm) and \( k_L a \) for the batch aeration experiments were consistent with previous studies indicating initially rapid CO\(_2\) degassing and approach to a steady state that can be at disequilibrium with atmospheric CO\(_2\) (\( 10^{-34} \) atm; Cravotta 2007; Kirby et al. 2009).

The PHREEQC aqueous speciation model (Parkhurst and Appelo 1999) was used to couple the rate equations for CO\(_2\) degassing and Fe(II) oxidation and calculate the corresponding changes in pH and concentrations of Fe(II), dissolved CO\(_2\) species, and other aqueous ions, assuming spontaneous equilibrium with atmospheric O\(_2\) and considering thermodynamic feasibility for precipitation of Fe(OH)\(_3\). Initial values for pH, alkalinity, DO, and Fe(II) concentration and the average temperature during each CO\(_2\) stripping experiment were input along with estimated \( k_L a \) (calculated for the 2\(^{nd}\) order rate equation) and apparent \( k_1 \) values (as used in the RK4 model) estimated by multiplying the reference \( k_1 \) value of \( 1.33 \times 10^{12} \) M\(^{-2}\)atm\(^{-1}\) s\(^{-1}\) at 20 °C (Stumm and Morgan 1996, p. 683) by a factor ranging from 0.1 to 100. Model calibration was conducted by adjusting the apparent \( k_L a \) and \( k_1 \) values to obtain the best fit of measured data for logged pH (paired values) and measured alkalinity and Fe(II) at the beginning and end of each experiment.

Results and Discussion

Initial pH of discharges at all four sites before aeration was circumneutral (5.6 to 6.7); however, the effluents were either net-acidic, with positive hot acidity (Blenkinsopp, Tan-y-Garn, and Ynysarwed; Table 1), or net-alkaline, with negative hot acidity (Six Bells). After 2 hours of aeration and CO\(_2\) stripping from the net acidic waters, the Fe(II) concentration decreased from greater than 40 mg/L to less than 6 mg/L, while pH remained within 0.1 unit of the initial
In contrast, after only 30 minutes of aeration of the net-alkaline water, Fe(II) decreased from 19 mg/L to less than 0.1 mg/L and pH increased by almost 2 units (Table 1). The pH of net acidic waters increased initially because of rapid CO₂ degassing and then decreased because of protons released by Fe(III) hydrolysis (Figs. 1a – 1c), whereas the pH of the net alkaline water increased progressively during aeration (Fig. 1d). The rapid increase in pH during early stages of aeration of all the waters coincided with an asymptotic decrease in the dissolved CO₂ from initial \( p_{\text{CO}_2} \) values of \( 10^{-0.4} \) to \( 10^{-0.8} \) atm to estimated steady-state values ranging from \( 10^{-1.7} \) to \( 10^{-3.4} \) atm (Figs. 1 and 2).

Figs. 1 and 2 show the measured pH, Fe(II), alkalinity, and \( p_{\text{CO}_2} \) and the PHREEQC simulated values produced by coupling the rate equations for CO₂ degassing and Fe(II) oxidation. Fig. 1 shows the paired values of measured pH as subparallel dotted curves and corresponding estimates of the pH by selected rate models as additional curves. The apparent Fe(II) oxidation rate corrected to 20 °C for the net acidic waters were 47 to 107 times the reference \( k_1 \) value at 20 °C, whereas that for the net alkaline water was 1.5 times the reference value (Table 2).

Table 1. Comparison of measured hot acidity, cold acidity, alkalinity, pH, Fe(II) content, and temperature of water at the beginning and end of the batch-wise CO₂ stripping experiments

<table>
<thead>
<tr>
<th>Site</th>
<th>Time elapsed (min)</th>
<th>Cold Acidity (mg L⁻¹ CaCO₃)</th>
<th>Alkalinity (mg L⁻¹ CaCO₃)</th>
<th>pH</th>
<th>Fe(II) (mg L⁻¹)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tan-y-Garn</td>
<td>115</td>
<td>21 to 23</td>
<td>34 to 38</td>
<td>5.5 to 5.9</td>
<td>5.75</td>
<td>17.75</td>
</tr>
<tr>
<td>Ynasarved</td>
<td>127</td>
<td>45 to 51</td>
<td>5 to 7</td>
<td>5.7 to 5.8</td>
<td>2.79</td>
<td>18.3</td>
</tr>
<tr>
<td>Six Bells</td>
<td>28</td>
<td>0</td>
<td>618 to 631</td>
<td>8.4</td>
<td>0.05</td>
<td>20.0</td>
</tr>
</tbody>
</table>

For PHREEQC models, initial pH, Fe(II), and alkalinity values and average temperature for batch aeration tests defined the starting solution. Apparent oxidation rate constant, \( k_1^* \), for Eq. (4) indicated by \( k_1 \) factor multiplied by \( 1.33 \times 10^{12} \) M⁻² atm⁻¹ s⁻¹. Apparent rate constant corrected to 20 °C using Arhenius equation (Langmuir 1997, p. 62), with activation energy of 23 kcal/mol (Stumm and Morgan 1996). Exchange with atmospheric oxygen (\( \text{PO}_2 = 10^{-0.27} \) atm) and precipitation of Fe(OH)₃ to SI < 0 were specified to maintain equilibrium. For calibrated Six Bells models, precipitation of calcite after supersaturation was considered to maintain SI< 1.0.

Table 2. Values of constants and associated variables used in RK4 model of Fe(II) oxidation and calibrated PHREEQC kinetics models of CO₂ degassing and Fe(II) oxidation
tion rate equations (e.g. Dempsey et al. 2001) as an alternative model for the PHREEQC simulations. However, the inclusion of heterogeneous oxidation did not improve our ability to simulate the empirical results. By adjusting only the apparent rate constants for homogeneous Fe(II) oxidation and CO₂ degassing, the observed pH, Fe(II), and alkalinity data could be simulated. For refinement of the Tan-y-Garn and Ynysarwed models, the starting alkalinity values were increased from 58 to 70 mg/L and 148 to 165 mg/L, respectively, and for the Six Bells model, precipitation of calcite was simulated upon reaching supersaturation ($\text{SI}_{\text{CALCITE}} < 1.0$). After calibration, simulated values for pH were within the range of measured values, and simulated values for Fe(II) and alkalinity were comparable to those at the beginning and end of the experiments (Figs. 1 and 2).

**Conclusions**

Elevated concentrations of dissolved CO₂ in effluent from underground coal mines can depress pH and decrease the rate of removal of dissolved Fe(II) within aerobic treatment ponds and wetlands. Aeration of the effluent can accelerate CO₂ removal (degassing) and increase pH, with a consequent increase in the rate of Fe(II) oxidation and Fe(III) precipitation.

**Fig. 1** Comparison of measured pH and estimated Fe(II) concentrations from spreadsheet based RK4 model to simulated pH and Fe(II) from PHREEQC models (after Geroni et al. 2012): (a) Ynysarwed (ynys), (b) Tan-y-Garn (tan), (c) Blenkinsopp (blen), (d) Six Bells (6bells). Values for initial alkalinity and rate constants used for RK4 and PHREEQC models are summarized in Table 2. In legend, Alk₀ (58 to 749 mg/L CaCO₃ equivalent), steady-state $p_{\text{CO}_2}$ (2.0 to 3.4) and $k₁$ multiplication factor (1× to 90×) are given for each simulation. The unbroken red curve indicates the reference simulation for values of $k₁ = 1.33 \times 10^{12}$ M⁻²atm⁻¹s⁻¹ and steady-state $p_{\text{CO}_2} = 2.8$. Dashed curves show results for calibrated models; for Six Bells, calcite precipitation maintained $\text{SI}_{\text{CALCITE}} < 1$ (cci).
The rate of CO₂ degassing during mechanical aeration experiments was successfully described using a 2nd order asymptotic exponential model and that for Fe(II) oxidation was described using a 1st order exponential rate model for homogeneous oxidation. Because the homogeneous rate model for Fe(II) oxidation is strongly dependent on the pH, the rate of CO₂ degassing was a major factor affecting the rate of Fe(II) oxidation. With the PHREEQC modeling approach, the pH was permitted to change with reaction progress and was controlled primarily by the rate of CO₂ degassing and secondarily by the extent of Fe(III) hydrolysis and the available alkalinity. The empirical data and associated simulations indicated that hydrolysis of Fe(III) depressed the pH of net acidic water to a greater extent than that of net alkaline water. Although the rates of Fe(II) oxidation for the net acidic effluents were 47 to 107 times the reference $k_1$ value at 20 °C, the Fe(II) oxidation and removal rates were slower for net acidic effluents than for the net alkaline effluent.

The measured trends in pH and Fe(II) concentrations during aeration experiments demonstrated potential for pH to affect Fe(II) oxidation rate in accordance with the homogeneous oxidation rate model. Despite limited availability and quality of the time-series data,
kinetics modeling using the geochemical speciation program, PHREEQC, provided insight into the interactions among chemical processes and the relative importance of specific reactions, such as CO₂ degassing, Fe(III) hydrolysis, and calcite precipitation, on the pH of poorly buffered water. Empirical data on temperature, DO, pH, alkalinity, Fe(II) concentration, and associated solutes and solids generally are needed to estimate the kinetics of CO₂ degassing and Fe(II) oxidation during aeration tests or within treatment systems. With this information, treatment strategies can be evaluated to optimize the removal of Fe(II) while minimizing the use of chemicals for pH adjustment.

References