

# AERATION TO DEGAS CO<sub>2</sub>, INCREASE PH AND IRON OXIDATION RATES, AND DECREASE TREATMENT POND SIZE IN TREATMENT OF NET ALKALINE MINE DRAINAGE<sup>1</sup>

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**Abstract.** Flow-through reactor field experiments were conducted at two large net alkaline mine discharges in central Pennsylvania. The goal was to drive off CO<sub>2</sub>, increase pH, and document increased Fe(II) oxidation rates compared to passive treatment methods.

Both discharges were low Mn, low Al, net alkaline discharges with pH of  $\approx 5.7$  and Fe(II) concentration of  $\approx 16$  mg/L. Flow rates were  $\approx 3000$  and  $15000$  L/min. Three-hour 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 oxygen increases to saturation with respect to the atmosphere, and Fe(II) concentration decreases to less than 0.05 mg/L. The same experiment at one of the sites with a 13-hour run time and no active aeration had a pH change from 6.1 to 6.3 and decrease in Fe(II) concentration from 16.3 to 13.8 mg L<sup>-1</sup>.

Results from an Fe(II) oxidation model, using field-measured pH, temperature, dissolved oxygen, and initial Fe(II) concentration and written in a differential equation solver, were the same as the field experiments within analytical uncertainty. The maximum oxidation rate was  $1.3 \times 10^{-4}$  mol L<sup>-1</sup> sec<sup>-1</sup>. The model was also modified to predict alkalinity, P<sub>CO<sub>2</sub></sub>, and pH changes based on initial conditions and aeration rate. This modified model also matched the data within analytical uncertainty, 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.

Using a published Fe removal rate of 20 g m<sup>-2</sup> day<sup>-1</sup> and Fe loading from field data,  $3.6 \times 10^3$  and a  $3.0 \times 10^4$  m<sup>2</sup> passive oxidation treatment ponds would be required for Site 21 and Packer 5 discharges, respectively. Fe(II) oxidation modeling of actively aerated systems predicted that a 1 m deep pond with 10 times less area would be adequate to lower Fe(II) concentrations to less than 1 mg L<sup>-1</sup> at summer and winter temperatures for both sites. The use of active aeration for net alkaline discharges with high CO<sub>2</sub> concentrations can result in considerably reduced treatment area for oxidation and may lower treatment costs, but settling of iron 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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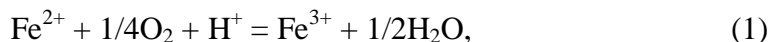
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## Introduction

Passive or semi-passive treatment systems usually receive waters in which pyrite (FeS<sub>2</sub>) has already oxidized and dissolved. The primary reactions to remove Fe are oxidation of ferrous iron



and precipitation of ferric iron solids



where Fe(OH)<sub>3,s</sub> could actually be one of several amorphous or crystalline solids. If sufficient alkalinity and time are available, the resulting solution will be “net alkaline,” and iron will oxidize and precipitate without alkaline addition.

Elevated concentrations of dissolved CO<sub>2</sub> in coal- mine drainage temporarily contribute to acidity and depresses the pH (Kirby and Cravotta, 2005a, b). Upon reaching the surface, CO<sub>2</sub> will degas to equilibrate with atmospheric Pco<sub>2</sub>. Degassing of CO<sub>2</sub> from AMD can be accelerated by aggressive aeration (Jageman *et al.*, 1988).

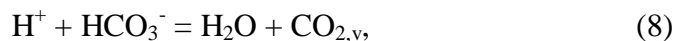
Most alkalinity in AMD is from the species HCO<sub>3</sub><sup>-</sup> (Kirby and Cravotta, 2005a, b), which reacts with H<sup>+</sup> to form carbonic acid:



where \* indicates the sum of the species H<sub>2</sub>CO<sub>3</sub><sup>0</sup>,<sub>aq</sub> and CO<sub>2</sub>,<sub>aq</sub>. When exposed to the air, dissolved CO<sub>2</sub> will degas to reach equilibrium with the atmosphere:



Equation 8 more clearly shows that H<sup>+</sup> consumption causes a rise in pH and CO<sub>2</sub> loss:



where “v” indicates vapor phase. The rise in pH is critical to the treatment of net alkaline mine drainage: it causes the Fe(II) oxidation rate to increase with a decrease in concentration of H<sup>+</sup>:

$$\frac{d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{O}_2][\text{H}^+]^2 \quad (9)$$

(Stumm and Morgan, 1996; Kirby *et al.*, 1999). As long as pH remains high enough, the rate of formation of iron hydroxide solid (Eqn. 2) increases as the oxidation rate is increased. Dempsey *et al.* (2001) showed that catalysis of Fe(II) oxidation by iron hydroxide solids can be important, although considerable amounts of iron hydroxide solids may be required for catalysis to be evident.

In this study, we used a flow-through reactor in the field to determine how well the aeration of net alkaline mine water drives off CO<sub>2</sub>, increases pH, therefore increasing Fe(II) oxidation rates. The overall objective was to scale up experimental results and predict the required aerated treatment pond size of net alkaline high-CO<sub>2</sub> mine drainage. We modeled the results and used the model compare the size of aerated treatment ponds needed to the size of passive treatment ponds without aeration. We also developed a model to predict pH changes, consumption of alkalinity, and degassing of CO<sub>2</sub> based on the initial solution composition; this latter model does not require field data for pH changes. The model was applied to calculate the size of aerated

ponds required for treatment; this size was then compared to the size required for completely passive ponds.

### Methods

The Operation Scarlift (Gannet *et al.*, 1972) Site 21 discharge, located in Ranshaw, PA, has net alkaline water, high dissolved CO<sub>2</sub>, low concentrations of dissolved oxygen (DO), Al and Mn, and approximately 16 mg L<sup>-1</sup> Fe(II) (Cravotta and Kirby, 2004). The combined (borehole + breach) Packer 5 mine discharges in Girardville, PA have water chemistry very similar to the Site 21 discharge (Cravotta, 2004).

14-L aerated Plexiglas tank flow-through experiments were conducted at both field sites. One non-aerated experiment was conducted at Site 21. After filling with a bucket, a pump introduced water into the reactor tank. An aquarium pump with diffuser stones provided air to the reactor.

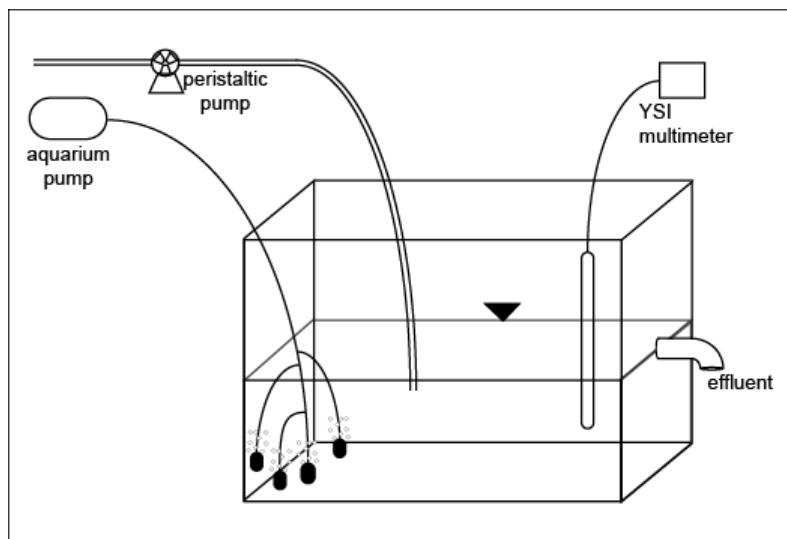


Figure 1. Schematic diagram of flow-through reactor.

A YSI™ multiparameter sonde measured water temperature, pH, and dissolved oxygen (DO). Samples for Fe(II) concentration were filtered and acidified. A Hach™ 1,10 phenanthroline reagent and spectrophotometer were used to measure Fe(II). Alkalinity was field-measured on raw unpreserved samples using a Hach™ digital titrator, 25 mL of reactor water, and sulfuric acid solution to a pH 4.5 endpoint (by pH meter).

PHREEQCI (Parkhurst and Appelo, 1999) was used to model speciation of the influent and steady state effluent solutions. Table 1 lists the changes modeled when the original speciated solution was aerated and amorphous Fe(OH)<sub>3, s</sub> was allowed to precipitate. Aeration was modeled by allowing equilibrium with respect to atmospheric P<sub>O<sub>2</sub></sub> and P<sub>CO<sub>2</sub></sub> using values of 10<sup>-0.7</sup> and 10<sup>-3.4</sup> atm, respectively. The solution was allowed to reach equilibrium with respect to amorphous Fe(OH)<sub>3, s</sub>. An additional simulation used a final P<sub>CO<sub>2</sub></sub> = 10<sup>-2.42</sup> atm, reflective of steady state, non-equilibrium conditions.

Table 1. Run conditions for PHREEQCI modeling. The concentrations for other major species are not shown but were included as input.

Input	Value		Value
<b>Solve initial solution</b>		<b>Equilibrate with</b>	
T, °C	12	T, °C	22
pH	5.77	P <sub>O2</sub> , atm	10 <sup>-0.7</sup>
Alkalinity, mg L <sup>-1</sup> (HCO <sub>3</sub> <sup>-</sup> )	117	P <sub>CO2</sub> , atm	10 <sup>-3.4</sup> ; 10 <sup>-2.42</sup>
pe	4	amorphous Fe(OH) <sub>3, s</sub>	Saturatio n
Fe(II), mg L <sup>-1</sup>	16		
Charge balance on:	SO <sub>4</sub> <sup>2-</sup>		

Using Stella™ 8.1.4, a graphical interface differential equation solver, the model of Kirby *et al.* (1999) was modified to model abiotic Fe(II) oxidation. For our initial experiments and Model 1, the measured values from the field for pH, DO, temperature (T), initial Fe(II) concentration, and solution and air flow rate were entered. Figure 1 is a schematic of Model 2; Model 1 differs from Model 2 in that it lacks the lower two fluxes in Fig. 1 (HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub>\*), and Model 1 uses field values for pH. Because pH, DO, and T changed with time, these measured values were entered as functions equivalent to the field changes. The Fe(II) concentration at other than the initial time was calculated by the model and compared to the measured field data.

Model 2 is more widely predictive. Model 2 uses only the initial field data for alkalinity and pH, and it then predicts alkalinity, pH, P<sub>CO2</sub>, and CO<sub>2</sub> and Fe(II) concentrations with time during an experiment as follows: Ingassing/degassing of CO<sub>2</sub> is governed by Equation 7, and the Henry's law equilibrium constant, K<sub>H</sub>, and is related to the partial pressure of CO<sub>2</sub> by

$$P_{CO_2} = [H_2CO_3^*]/K_H \quad (10)$$

The initial value of P<sub>CO2</sub> was calculated by PHREEQCI speciation of field pH, alkalinity (HCO<sub>3</sub><sup>-</sup> concentration), and major cations and anions. The rate of CO<sub>2</sub> loss was assumed to be governed by

$$d[H_2CO_3^*]/dt = -k_{degas}SA_{air}[H_2CO_3^*]^n \quad (11)$$

where SA<sub>air</sub> is the surface area of air bubbles, k<sub>degas</sub> is a rate constant for CO<sub>2</sub> degassing, and n is the reaction order (assumed = 1) with respect to H<sub>2</sub>CO<sub>3</sub>\*. SA<sub>air</sub> and k<sub>degas</sub> were not quantified: the measured air flow rate (L hr<sup>-1</sup>) served as a proxy value for SA<sub>air</sub>, and k<sub>degas</sub> was treated as a fit parameter with the value 10 mol<sup>-2</sup> hr<sup>-1</sup>.

Temperature-dependent equilibrium constant values from the PHREEQCI database were used in Model 2 to calculate pH as

$$pH = -\log \{ K_1 K_H P_{CO_2} / (0.92[HCO_3^-]) \}, \quad (15)$$

where 0.92 is the value of the activity coefficient HCO<sub>3</sub><sup>-</sup>. The rate of HCO<sub>3</sub><sup>-</sup> loss is given by

$$d[HCO_3^-]/dt = 2(\text{Fe(II) oxidation rate}) \text{ in mol L}^{-1} \text{ hr}^{-1}. \quad (17)$$

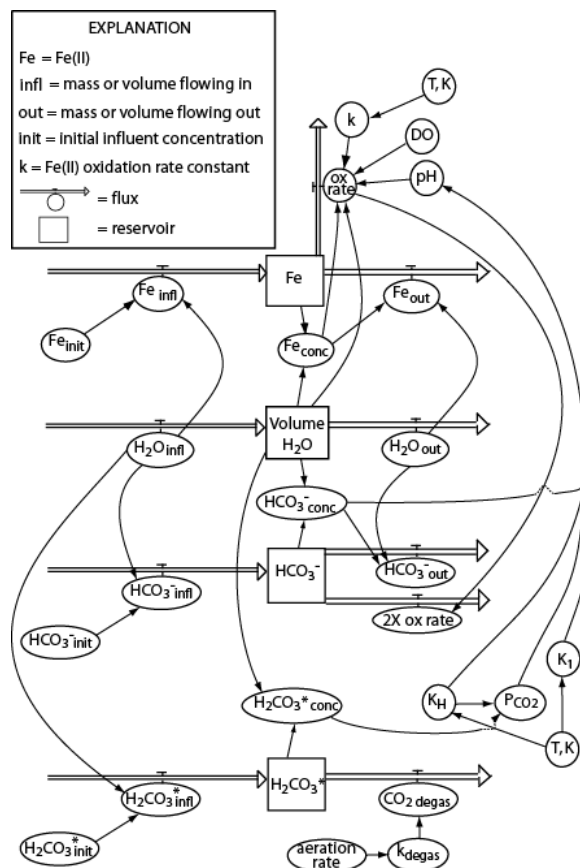


Figure 1. Schematic diagram representing the mathematical relationships in Model 2. Fluxes are differential equations governing the mass or volume in a reservoir. Arrows show mathematical links with the parameter at the arrowhead end a function of the parameter at the initial end; *e.g.*,  $k$  is  $f(T, K)$  at the top of the model.

## Results and Discussion

A 13-hr nonaerated Site 21 experiment yielded a pH change from 6.1 to 6.3, and the Fe(II) concentration only decreased from 16.3 to 13.8 mg L<sup>-1</sup>. After 13 hours, water in the reactor contained little visible precipitate. Very limited gas exchange occurred without aeration, thus much of the dissolved CO<sub>2</sub> remained in solution, pH remained low, and Fe(II) oxidation was slow.

Results of the Site 21 aeration experiment are shown in Fig. 2a. The initially clear water in the reactor became visibly cloudy with orange precipitate within 30 minutes. DO increased rapidly to saturation with respect to the atmosphere, then decreased to remain in equilibrium as the water temperature increased. The net pH increase occurred because there was sufficient alkalinity to outweigh the effect of Fe(OH)<sub>3,s</sub> precipitation. Fe(II) oxidation decreased the Fe(II) concentration slowly until the pH rose, Fe(II) then decreased rapidly until the rate slowed as Fe(II) was beginning to be exhausted. Model 1 results (Fig. 2a) matched the measured Fe(II) concentrations very well.

The Packer 5 aeration experiment yielded results very similar to Site 21 (Fig. 3a). Model 1

results (Fig. 3a) again matched the Fe(II) concentrations very well: the rate of oxidation and steady state concentrations in the field data and Model 1 results are the same within analytical uncertainty.

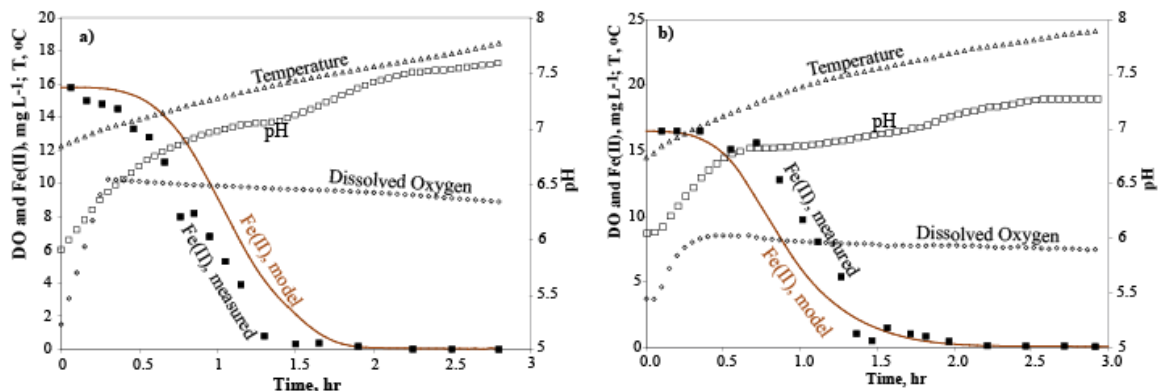


Figure 2. Data and Model 1 ( $P_{CO_2}$ , alkalinity, and pH measured, not predicted) results for a) first Site 21 aeration experiment, and b) Packer 5 aeration experiment.

The results presented above show that the removal of dissolved  $CO_2$  in a net alkaline water will increase pH and promote rapid iron oxidation. Thus, the aeration of a pond treatment system would be an extremely effective method of iron oxidation for either site studied or any other site with similar chemistry. Our data show, and modeling supports the contention, that as the aeration drove off the dissolved  $CO_2$ , the pH increased, the Fe(II) oxidized more readily, and  $Fe(OH)_{3,s}$  formed rapidly compared to a non-aerated system.

#### Comparison of field-scale treatment pond sizes

Using an Fe removal rate of  $20 \text{ g m}^{-2} \text{ day}^{-1}$  (Hedin *et al.*, 1994; Watzlaf *et al.*, 2004) and Fe loading from field data, a  $3.6 \times 10^3 \text{ m}^2$  passive treatment pond was required for Site 21. For the combined Packer 5 discharges, Cravotta (2004) suggested the need for a  $3 \times 10^4 \text{ m}^2$  pond based on Fe removal rate of  $20 \text{ g m}^{-2} \text{ day}^{-1}$ . Fe(II) oxidation Model 1 predicted that a 1 m deep pond with 10 times less area would be adequate to lower Fe(II) concentrations to less than 1 mg/L at summer and winter temperatures for both sites. Note that the Hedin *et al.* (1994) approach predicts total Fe removal, whereas our model predicts Fe(II) oxidation without addressing Fe solid removal.

#### Site 21 Aeration Experiment and Model 2

Model 1 effectively reproduced field results but lacks predictive power because the change of pH with time must be determined experimentally. Model 2 overcomes this problem by accounting for  $P_{CO_2}$  and alkalinity changes in order to predict pH values. The initial  $P_{CO_2}$  value of  $10^{-0.80} \text{ atm}$  was obtained by running the geochemical speciation model PHREEQCI. The initial  $HCO_3^-$  concentration was assumed to be equal to the measured  $117 \text{ mg L}^{-1}$  alkalinity as  $HCO_3^-$ .

The flow rate for the second Site 21 experiment was reduced in half after 2 hours. Figure 3 shows experimental and Model 2 results from this second experiment. DO quickly rose, reaching saturation with respect to atmospheric oxygen, then fell as temperature rose, maintaining this equilibrium. Fe(II) concentration decreased slowly initially, decreased rapidly

as pH increased, then decreased slowly as Fe(II) neared exhaustion. The Model 2 steady state Fe(II) oxidation rate and concentrations are the same as the field data same within analytical uncertainty.

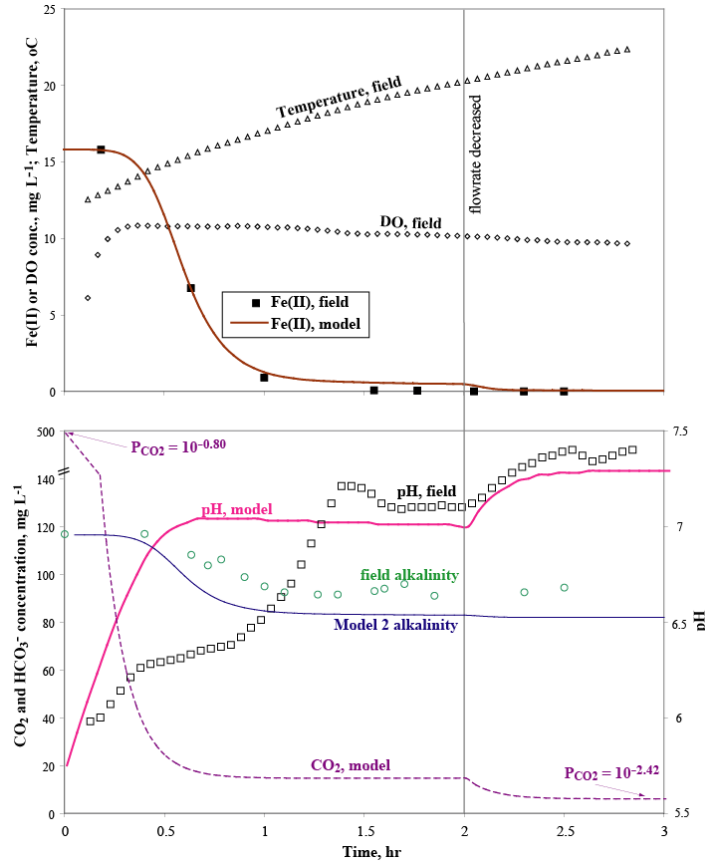


Figure 3. Data and Fe(II) Model 2 ( $P_{CO_2}$ ,  $HCO_3^-$ , and pH predicted) results for second Site 21 aeration experiment.

### Simple test for applicability of aeration

If a mine discharge is known to be net alkaline and the major goal is to remove iron (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  $CO_2$  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 a matter of minutes. If the resulting pH is greater than approximately 7, the expense of aeration may be justified by the increased Fe(II) oxidation rate.

### Implications for treatment

Although addition of oxygen without considerable  $CO_2$  removal can increase Fe(II) oxidation rates, Kirby *et al.* (1999) showed that the Fe(II) oxidation rate is much more sensitive to pH than to oxygen concentration as long as oxygen is present in measurable concentration. It is possible for oxygen to become rate-limiting, especially in cases where the Fe(II) concentration is high.

Therefore, aeration at the upflow end of a pond may successfully drive off CO<sub>2</sub> and increase pH, but iron oxidation may not be complete without placement of additional aeration devices downflow to ensure that oxygen is not rate-limiting.

The semi-passive treatment of net alkaline, CO<sub>2</sub>-rich mine drainage by aeration can be an extremely effective method to oxidize Fe(II) rapidly and in smaller areas than completely passive treatment. Aeration can allow the treatment pond size to be as much as ten times smaller than a passive treatment pond. A settling pond of undetermined size would be needed downflow of the oxidation pond. There is also a power requirement for the aeration that will be dependent upon the flow rate, Fe(II) concentration, and method of air introduction. Smaller air bubbles will provide more efficient air transfer and CO<sub>2</sub> degassing due to higher surface area.

Although net alkaline discharges are likely not as common as net acidic discharges, several very high-flow, high-metal loading discharges in both the anthracite and bituminous coal regions of Pennsylvania are net alkaline (e.g. Cravotta, 2004; Cravotta and Kirby, 2004). This research should prove valuable to anyone planning treatment of such discharges.

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