IRON OXIDATION IN NET ALKALINE CO_2-RICH MINE WATERS[1]

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Abstract: Iron oxidation and hydrolysis were examined in net alkaline mine waters exiting abandoned underground lead and zinc mines. It was hypothesized that degassing of excess CO_2 would result in increased pH, and thus positively influence rates of iron oxidation, despite subsequent proton production during hydrolysis. It was also hypothesized that the addition of iron oxide solids would positively influence iron removal rates. The relative roles of CO_2 degassing and iron solids additions were evaluated in a field microcosm experiment in June 2001. Five treatments were established in triplicate (closed, open, open + Fe, open + aeration, open + aeration + Fe). After 36 hours, greatest water quality changes were found in the open + aeration + Fe treatment. Dissolved oxygen was greater than 7.5 mg/L and pH was greater than 7.7, while alkalinity and Fe decreased to 52 and 0.81 mg/L, respectively. In non-aerated treatments, dissolved oxygen was less than 1.6 mg/L and pH was less than 6.2. Alkalinity decreased in all aerated treatments to less than 70 mg/L, but remained greater than 200 mg/L in all other treatments. Iron concentrations remained greater than 70 mg/L in non-aerated treatments. Aeration and the active degassing of excess CO_2, coupled with the presence of iron oxide solids, resulted in the greatest changes in water quality.

Key Words: carbonate equilibria, iron removal, wetlands, water quality

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Introduction

In net alkaline mine waters, degassing of excess CO_2 may result in increased pH by shifting carbonate equlibria (equation 1) and thus positively influencing rates of iron oxidation (equation 2) despite subsequent proton production during hydrolysis (equation 3). Presence of iron oxide solids has also demonstrated a positive influence on iron removal (Dempsey et al., 2001).

$$HCO_3^- + H^+ \rightarrow H_2CO_3^* \rightarrow CO_2(g) + H_2O \qquad (1)$$

$$Fe^{+2} + 0.25O_2 + H^+ \rightarrow Fe^{+3} + 0.5H_2O \qquad (2)$$

$$Fe^{+3} + 2H_2O \rightarrow FeOOH(s) + 3H^+ \qquad (3)$$

Methods

The relative roles of these processes were evaluated in a field microcosm experiment in June 2001 at the Tar Creek Superfund Site in northeastern Oklahoma. Polluted mine water (pH 5.9, alkalinity 414 mg/L as $CaCO_3$, 172 mg Fe/L, 11 mg Zn/L, 0.01 mg Cd/L and 0.02 mg Pb/L) discharging from an abandoned lead and zinc mine was collected in 19-L plastic microcosms. The mine drainage discharge effervesced with dissolved gasses upon exposure to the atmosphere. Five microcosm treatments were established in triplicate: 1) closed (sealed with low permeability plastic cover); 2) open (uncovered); 3) open + Fe (uncovered and with addition of iron oxide precipitates collected from the discharge point), 4) open + aeration (uncovered and aerated with standard aquarium pumps) and 5) open + aeration + Fe (uncovered, aerated with standard aquarium pumps and with addition of iron oxide precipitates). *In situ* measurements of dissolved oxygen, pH, temperature, specific conductance and alkalinity were collected over a 36-hour period. At the end of the experiment, samples were collected from each microcosm for total iron analysis (APHA 1995). Statistical comparisons were conducted using paired Student's t-tests.

Results and Discussion

After 36 hours, pH was greater than 7.7 and dissolved oxygen was greater than 7.5 mg/L for aerated treatments (Figs. 1a and 1b). In non-aerated treatments, pH was less than 6.2 and dissolved oxygen was less than 1.6 mg/L. Alkalinity decreased in aerated treatments to less than

70 mg/L, but remained greater than 200 mg/L in all other treatments (Fig. 1c). Greatest pH and dissolved oxygen increases and alkalinity decreases were found in the open + aeration + Fe treatment and aerated treatments without iron were not significantly different. All other treatments were significantly different from each other. Active degassing of CO_2 resulted in the greatest water quality changes. Net pH increases indicated that CO_2 degassing compensated for any pH decreases due to iron oxidation and hydrolysis. Iron concentrations were significantly decreased in all treatments compared to the untreated waters ($p<0.05$; Figure 1d).

Conclusions

Simple aeration, perhaps coupled with addition of iron solids to the water to encourage heterogenous oxidation, promoted efficient iron removal from net alkaline mine waters by degassing CO_2. The resulting increase in pH likely increased iron oxidation rates. Passive treatment systems that promote efficient aeration and suspension of iron solids, e.g., open channels as opposed to settling ponds, may improve iron retention capabilities.

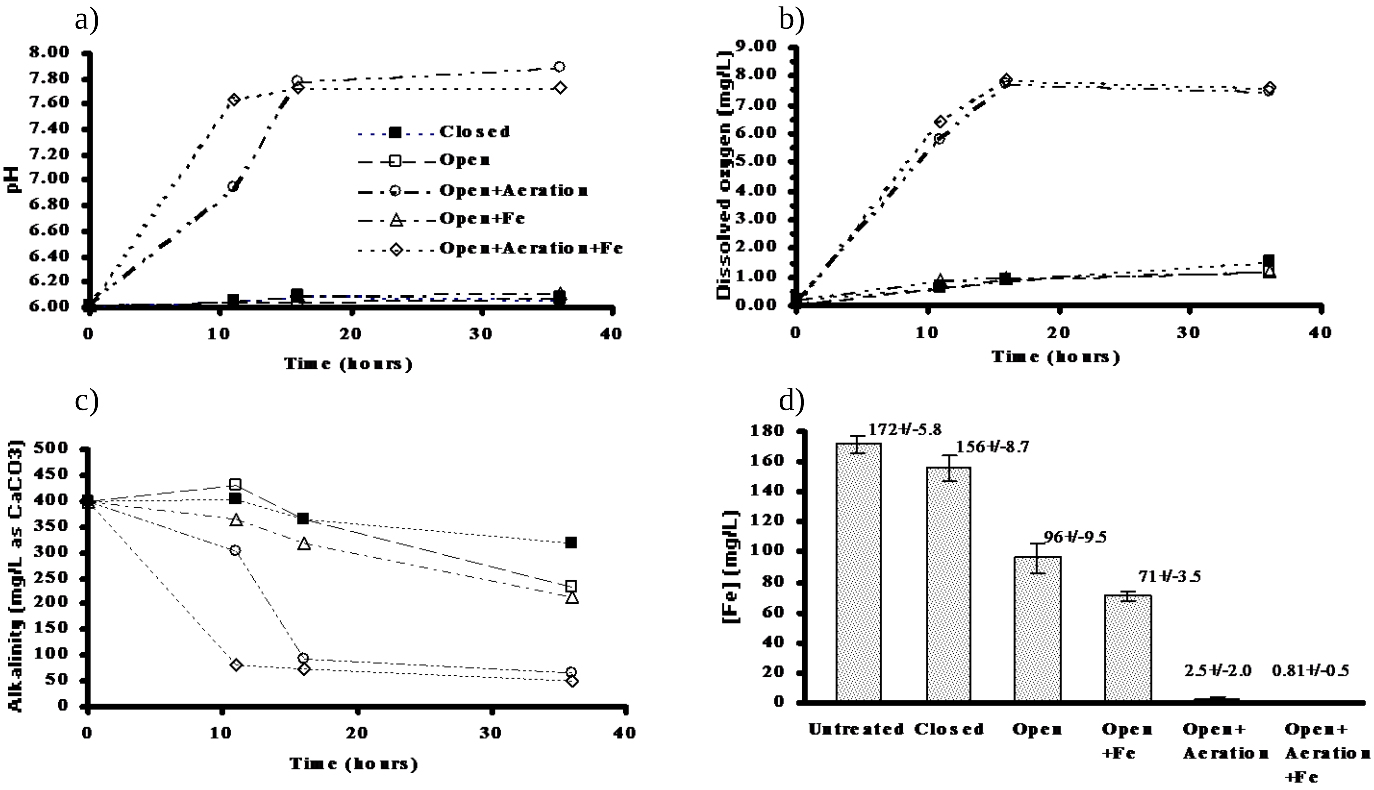

Figure 1. Changes in water chemistry in the microcosms during the 36- hr experiment for a) pH, b) dissolved oxygen, c) alkalinity and d) iron concentrations (at 36 hrs.)

Literature Cited

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