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Iron oxyhydroxide coating of pyrite for acid mine drainage control

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ABSTRACT

When pyrite oxidizes at near neutral pH in the presence of sufficient alkalinity, Fe oxyhydroxide coatings develop on the surface. As these coatings grow thicker and denser they block oxidant transport from the solution to the pyrite surface and reduce the rate of pyrite oxidation. The authors' measurements of pyrite oxidation rates in a $NaHCO_3$ solution show that the coating grows in two stages. In the first stage Fe oxyhydroxide colloids form and then attach to the pyrite surface to produce a slight reduction in oxidant transport. In the second stage interstitial precipitation of Fe oxyhydroxide material between the colloidal particles reduces the oxidant's diffusion coefficient by more than five orders of magnitude. This causes the pyrite oxidation rate to decline as the square root of time. The kinetic predominance diagram, which compares the rates of Fe transformation reactions, shows that when pyrite oxidation releases Fe quickly enough for the total Fe concentration to rise to about 10^{-8} m, ferrihydrite forms but lower rates of Fe release will not produce coatings. Extrapolation of the results to longer times predicts that pyrite-bearing materials need to be treated with an extra source of alkalinity for several decades to produce coatings that are thick enough to be sustained by alkalinity levels typical of groundwater. However, once the coatings develop no additional treatment is needed and further pyrite oxidation simply causes the coating to grow thicker and denser until the entire pyrite grain is pseudomorphically replaced by goethite.

1. Introduction

Although acid mine drainage (AMD) is a widespread and intensely studied environmental problem, there is a continuous struggle to find scientifically sound and economically viable strategies to mitigate it. Current AMD management practices often treat the symptom, which is the acidic effluent, but not the source, which is the oxidizing pyrite. *AMD develops when acid is generated by sulfide mineral oxidation faster than it is neutralized by alkalinity from the surroundings* so an important strategy for long-term remediation programs is to supply alkalinity to the mine wastes faster than their rate of acid production. Acid base accounting in mine wastes is a well-established tool for predicting whether there is a sufficient amount of alkalinity generating minerals already in the mine wastes (White et al., 1999) and when a sufficient alkalinity supply does not exist, various alkalinity-generating materials can be incorporated into the wastes (Smith and Brady, 1998). However, having a favorable acid base accounting is not always sufficient to mitigate AMD. In order to be effective, the alkalinity-generating materials must dissolve and supply alkalinity as fast, or faster than acidity is generated by pyrite oxidation. In order to treat the wastes in the most economic way it is necessary to determine just how fast alkalinity must be supplied immediately after the wastes are disposed, when pyrite oxidation rates are fastest, and then later on after the oxidation rates have declined. In most cases a decline in acid generation is simply due to the consumption of pyrite but both field and experimental evidence suggests that a more rapid decrease in acid generation occurs if the waste disposal is designed to encourage the growth of a layer of Fe oxyhydroxides on the pyrite surface. As this Fe oxyhydroxide coating grows thicker and denser over time, it becomes an increasingly effective barrier to oxidant transport to the pyrite surface thereby slowing the oxidation rate and the rate of acid generation. Eventually the coating becomes so effective that the rate of acid generation falls below the rate of alkalinity delivery by groundwater and AMD generation stops. This could occur even if the acid base accounting is unfavorable but it does require very rapid alkalinity addition soon after disposal.

Because of its abundance, pyrite is commonly the main source of acid production in mine wastes. The pH of freshly exposed pyrite bearing rocks is usually greater than four so that dissolved O_2 (DO) is the principal pyrite oxidant and the rate of acid production is relatively low (Fig. 1, py–DO reaction in Table 1) (Williamson and Rimstidt, 1994). However, if this acid is not neutralized as quickly as it is produced the pH drifts downward until it drops below four where dissolved Fe(III) becomes the principal oxidant. A further decrease in pH causes a large increase in Fe(III) concentration leading to even faster pyrite oxidation (Fig. 1, py–Fe(III) reaction in Table 1). This creates a runaway condition where fast pyrite oxidation continually lowers pH and raises the Fe(III) concentration causing the oxidation rate to accelerate. Because microbial activity

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Notation

A	surface area (m^2)
A_{sp}	specific surface area (m^2/g)
b	surface area constant (unitless)
C_i	concentration of species i (mol/m^3)
D	diffusion coefficient (m^2/s)
D_c and D_p	diameter of calcite and pyrite particles
I_r	groundwater infiltration rate (m/s)
J_i	flux (mol/m^2 s)
k_i	rate constant
m_i	concentration of species i (mol/kg)
M_i	concentration of species i (mol/L)
M_c and M_p	mass of calcite and pyrite
n_i	amount of species i (mol)
r_f	flow rate (kg/s) (1 kg $H_2O \sim 0.001\ m^3$)
r_i	specific rate of reaction of species i (mol/m^2 s)
r'_i	apparent rate of reaction of species i (mol/s)
t	time (s)
t_R	response time (s)
V_R	volume of reactor (m^3)
V_m	molar volume (m^3/mol)
x	thickness of coating (m)
φ	porosity, unitless ratio from 0 to 1

quickly regenerates Fe(III) from the Fe(II) released by the pyrite (Williamson et al., 2006), there is always sufficient Fe(III) to sustain the runaway AMD condition. Avoiding or recovering from runaway AMD requires that the acid from the py–DO or py–Fe(III) reaction be neutralized by the addition of alkalinity faster than it is produced. When the rate of alkalinity addition meets or exceeds this rate, the Fe released from the pyrite rapidly oxidizes to Fe(III) and precipitates as an Fe oxyhydroxide coating on the pyrite surface.

Coating pyrite grains with a substance that blocks oxidant transport from solution to the surface may be a practical way to reduce the oxidation rate. Several types of pyrite coatings have been proposed including ferric phosphate (Evangelou, 1995), phosphosilicates (Fytas and Bousquet, 2002; Fytas et al., 1999; Fytas and Evangelou, 1998), ferric hydroxide–silica (Zhang and Evangelou, 1998), phospholipids (Kargbo et al., 2004), and iron-8 hydroxyquinoline (Lan et al., 2002). These coatings have been shown to reduce oxidation rates in the laboratory but they require relatively expensive reagents, which do not specifically target the pyrite so that a large excess may be required to insure an effective coating. In addition, because they are not self-healing and permanent they require a long-term commitment to site management. In comparison, Fe oxyhydroxide coatings form naturally in high alkalinity environments, they are self-healing and they become more and more effective with time so that the demand for alkalinity addition declines. Nicholson et al. (1990) showed experimentally that the addition of relatively inexpensive bicarbonate alkalinity to oxidizing pyrite produces Fe oxyhydroxide coatings that slow oxidant transport from solution to the pyrite and thus slow pyrite oxidation rates. The effectiveness of this strategy is supported by more recent laboratory studies (Homstrom et al., 1999; Pérez-López et al., 2005, 2007b; Zhang and Evangelou, 1996).

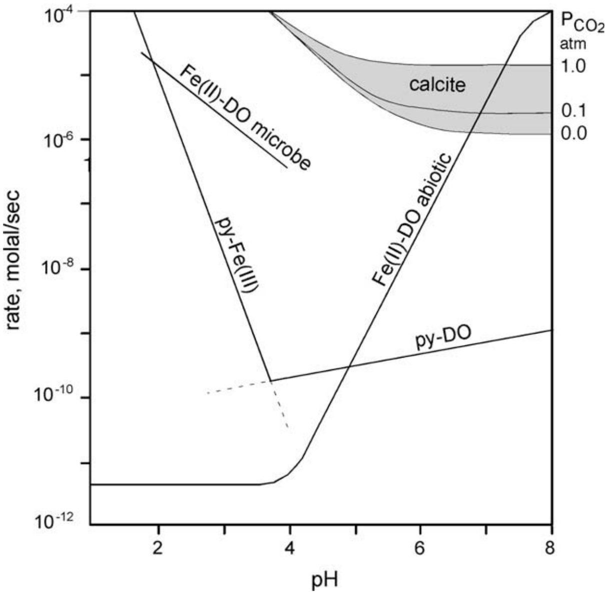

Fig. 1. Comparison of the rates of generation and consumption of Fe(II) in AMD solutions using the rate laws and assumptions described in Williamson et al. (2006). At pH > 4, the py–DO reaction rate is faster than the py–Fe(III) rate and the Fe(II) released from the pyrite is abiotically oxidized. The resulting Fe(III) rapidly precipitates from solution. At pH < 4, the py–Fe(III) reaction is fastest and the Fe(II) released from the pyrite is microbally oxidized. The resulting Fe(III) is very soluble and available to react with more pyrite. The grey zone in the upper right corner shows the range of rates for H^+ consumption by dissolving calcite (Plummer et al. 1978). All rates are for 1 m^2 of mineral surface area per 1 kg of solution.

We can predict the long-term behavior of Fe oxyhydroxide coatings by considering a natural analogue, limonite pseudomorphs after pyrite (Fig. 2). Limonite pseudomorphs form where pyrite has oxidized under high alkalinity conditions. They are often found in limestone where large amounts of HCO_3^- ions are available to neutralize the acid from pyrite oxidation. Under high pH conditions, abiotic oxidation of Fe(II) (Stumm and Lee, 1961) is much faster than pyrite oxidation by dissolved O_2 (Fig. 1) so that Fe(II) released from the pyrite quickly oxidizes to Fe(III). Because Fe(III) is very insoluble at near neutral pH, it quickly hydrolyzes and precipitates. Initially formed, metastable $Fe(OH)_3$ and/or ferrihydrite eventually converts to goethite. These coupled reactions produce an approximately 1 for 1 volume replacement of pyrite (23.94 cm^3/mol) by goethite (20.82 cm^3/mol) creating a pseudomorph with only about 13% porosity. Additional pore filling by the oxidation and precipitation of outward diffusing Fe(II) fills the pores near the outer edge of the pseudomorph to create a dense outer rim. Fig. 2 shows that a typical limonite pseudomorph has a relatively porous interior, often with some remaining pyrite, surrounded by a relatively dense outer rim. Limonite pseudomorphs after pyrite are compelling evidence that Fe oxyhydroxide coatings can be stable and grow to great thickness on pyrite grains.

The objective of this paper is to present a conceptual and quantitative model of declining pyrite oxidation rate caused by the formation of a Fe oxyhydroxide coating under high alkalinity conditions. Experiments were performed that bridge the time in the coating process between the initial attachment of $Fe(OH)_3$ colloids and the infilling between the colloids to form a more dense coating. Data from the authors' and previous experiments (Nicholson et al., 1990; Zhang and Evangelou, 1996) were analyzed to determine the effective diffusion coefficients of oxidants through